Chapter 3
Influence of Silicate Substance on Pyrochlore and Tantalite Solubility in Fluoride Aqueous Solutions (Experimental Studies)

A. R. Kotelnikov, V. S. Korzhinskaya, Z. A. Kotelnikova, and N. I. Suk

Abstract Experimental results of behavior of natural minerals of pyrochlore and tantalite in solutions KF, NaF and LiF in the presence of quartz (granite) at T = 550°–850 °C, P = 1 kbar are presented. The considerable influence of silicate substance presence on mineral solubility in water solutions of alkali metal fluorides in hydrothermal conditions is shown. The study of fluid inclusions in quartz showed that under experimental conditions (heterogeneous state of the fluid) the reactions of high-temperature hydrolysis KF: $KF + H_2O = KOH + HF$, with the separation of acid and alkaline components between the immiscible phases of the fluid are intensive. In this case, the interaction of alkaline components with quartz occurs: $SiO_2 + 2KOH = K_2SiO_3 + H_2O$, with the formation of a phase of silicate glass (aqueous solution-melt). This phase of silicate alkaline melt enriched with fluorine concentrates tantalum and niobium (up to 8% of Ta_2O_5 and 16% of Nb_2O_5) and can serve as a phase—a concentrator of ore elements in the formation of tantalum-niobate deposits at the last low-temperature stages of crystallization of rare-metal granites.

Keywords Niobium-tantalum deposits · Experimental modeling · Hydrothermal fluoride fluid · Pyrochlore solubility · Tantalite solubility · Alcaline-silicate melt-concentrator

3.1 Introduction

In the 50s of the last century in our country a new type of rare-metal deposits of Ta, Nb, Be, W, Sn, timed to the domes of albitized and greisenized granite was discovered and studied in detail (Beus et al. 1962). Typical representatives of such fields are

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Orlovskoye and Etykinskoye fields of Ta, Nb, which are located in the Eastern Transbaikalia. The development of the zones of albitization and greisenization, containing own ore minerals, took place on specific lithium-fluorine granites. This term for lithium and fluorine enriched granite rocks was first introduced by Kovalenko (1977). These rocks contain initially magmatic lithium- and fluorine-containing minerals—lithium mica and topaz. Discovery of this type of deposits activated the search for similar objects in other parts of our planet. These include Voznesenskoye, Pogranichnoye, Snezhnoye fields in Russia and a number of similar fields in China, South-East Asia, Egypt and France. Lithium-fluorine granites and their subvolcanic analogues—ongonites—are more frequent. As a rule, all ongonites are enriched with Ta, Nb, Li, Rb, Cs, Be, Sn, W. Almost all lithium-fluorine granites produce tantalum and tantalum mineralization ore manifestations. Lithium-fluorine ore-bearing granites belong to the alkaline earth granitoid series. According to morphology, they are small dome-shaped bodies of 0.5–2 km in diameter (“stems”), formed in approximately equal proportions of quartz, albite and microcline (often amazonite), with a small number of lithium mica (lepidolite, tsinnvaldite) and topaz. Ore bodies are located in the upper parts of granite domes, usually covered by keratinized crystalline shale. The industrial mineralization is concentrated in the albitized and greisenized granites. The ores are relatively poor (100–350 g/t), and Ta_2O_5 reserves usually do not exceed 10–15 thousand tons (Zarayskiy 2004).

3.1.1 Magmatic Stage of Formation of Rare-Metal Deposits

All deposits of tantalum-niobium ores in lithium-fluorine granites are located near large biotite and leucocratic massifs and have a genetic connection with them. The initial melt of initially granite composition usually appeared under post-threshold activation conditions of stretching. Deep troughs were laid at the periphery of the previously consolidated collision areas. The source of such granite melts could be the anatectic or paling melting of the granitogneissic continental crust near the Conrad boundary. That is, the upper crust in the path structures was lowered to the area of high temperatures (up to the depth of 15–20 km), where the rocks were heated up. Additional heating occurred due to mantle fluids coming from deep faults in zones of tectonic-magmatic activation (Zarayskiy 2004). The granite melt rose along the deep faults and was introduced in the form of laccolithic intrusions. Laccolite and lenticular bodies of granites are located in a subhorizontal orientation on the boundary of the crystalline rocks of the pre-Cambrian basement and the Phanerozoic cover. Their sizes reach 20–30 km with a capacity of up to 5–8 km in their central parts (Zarayskiy 2004, 2009). Further evolution of melts at their crystallization differentiation resulted in formation of residual melts. These melts corresponded to the compositions of lithium-fluorine granites and were separated from the mother granites in their upper part, squeezing out the cracks. Lithium-fluorine granites represent the latest portions of melt introduction and form small bodies of 0.5–2 km in size and thickness up to 0.5 km. Mass ratios of mother and lithium—fluorine granite are about $500 \div 100$:

1. According to experimental data (Chevychelov et al. 2005; Borodulin et al. 2009) partition coefficients in the system of lithium-fluorine granite melt—fluid is about 150 ÷ 350 in favor of the melt (at 800–650 °C). Therefore, tantalum and niobium remain in the melt and crystallize in the form of micron inclusions of tantalum-niobates along the grain boundaries of rock-forming minerals when separating the fluid. Calculations of the model of crystallization of the ancestral Hangilaisky pluton (Zaraiskiy 2004) show that to enrich lithium-fluorine granites with tantalum up to 30–50 g/t it is necessary to crystallize 95% of the initial granite melt. It is difficult to expect complete compression and crack segregation of the entire volume of Li-F granites with a high degree of crystallization. Therefore, it is practically impossible to achieve ore concentrations of tantalum by direct crystallization fractionation.

3.1.2 Hydrothermal-Metasomatic Stage of Formation of Rare-Metal Deposits

Accumulation of such rare metals as Be, Sn, W, Mo in granite melts at fractional differentiation is much lower than their saturation concentrations. Therefore, they also cannot crystallize in the form of independent mineral isolations and dissipate in large volumes of crystallizing granites. However, unlike tantalum and niobium, they have significantly lower melt/fluid partition coefficients and can be converted into a separating fluid in significant amounts. According to a number of researchers (Chevychelov 1998; Rjabchikov 1975; Gramenitskiy et al. 2005), these coefficients are ~2 ÷ 5, and for molybdenum and tungsten up to 1. Therefore, the formation of deposits of these metals can occur hydrothermally-metasomatically.

For tantalum and niobium there is no possibility of extraction by the separating fluid because of the high affinity of Nb and Ta to melts. Therefore, the question of concentration and re-deposition of the scattered ore substance of tantalum-niobates at the hydrothermal stage of evolution is acute. It is known (Rub and Rub 2006; Aksyuk 2002, 2009) that lithium-fluorine granites producing tantalum-niobium ore deposits have potassium specifics. According to the data (Aksyuk 2002) obtained on the basis of the experimentally developed mica geofluorometer, at the transient magmatic-hydrothermal stage of evolution of ore-magmatic systems the concentration of HF in water fluids separating from the granite melt is about 0.01 mol/kg H_2O for copper-molybdenum porphyry deposits. It is an order of magnitude higher at Greisen deposits of W, Mo, Sn, Be, Bi of Akchatau type (0.1 mol/kg H_2O) and reaches the maximum values of 1.0 mol/kg H_2O at rare-metal deposits of tantalum in lithium-fluorine "apogranites" of the Orlovsky and Etykinsky rare-metal massifs. Thus, fluorine content in hydrothermal solutions can reach 1 mol/kg. It is clear that fluorine is contained in a postmagmatic fluid in the form of fluoride salts (LiF, NaF, KF). Moreover, taking into account the potassium specificity of rare-metal lithium-fluorine granites, potassium fluoride (KF) solutions will dominate. This fact is confirmed by the study of water extracts from lithium-fluorine granite rocks (Aksyuk 2009), which showed high content of potassium fluoride. In addition, the paper (Badanina et al. 2010) suggested that the final concentration of tantalum and niobium is carried out at the postmagmatic stage by a high concentration salt solution containing significant amounts of fluorine. Earlier it was shown that fluorine-containing salt fluid actively interacts with silicate substance (quartz), forming a phase of silicate glass (Kotelnikova and Kotelnikov 2002, 2008). Therefore, it was interesting to study the transport of tantalum and niobium in saline fluoride solutions in the presence of silicate substance.

We have carried out experiments on the solubility of minerals containing niobium and tantalum (pyrochlore and tantalite) in hydrothermal solutions of LiF, NaF, KF in the temperature range of 550–850 °C and pressures of 0.5–1 kbar. To study the influence of the presence of silicate substance (quartz or granite melt) on the solubility of pyrochlore and tantalite in fluoride solutions, experiments were carried out with the addition of quartz (granite) and without silicate substance.

3.2 Experimental Method

3.2.1 Starting Materials

As initial materials we used quartz (Perekatnoye deposit, Aldan), amorphous SiO_2; pyrochlore $(Ca, Na)_2(Nb, Ta)_2O_6(O, OH, F)$ from weathering zone of carbonatite deposit of Tatarka of following composition (wt%): Na_2O—7.61; CaO—14.28; Nb_2O_5—71.61; F—5.18; TiO_2—0.83; $Ta_2O_5 \leq 1$ (conversion to 4 cations including charge balance): $(Na_{0.92}Ca_{0.95}Sr_{0.06})_{1.93}(Ti_{0.04}Nb_{2.02})_{2.06}O_6[F_{1.02}(OH)_{0.18}]_{1.20}$ and tantalite $(Mn, Fe)(Ta, Nb)_2O_6$ from the Vishnyakovsky tantalum deposit in the rare-metal pegmatites of the East Sayan belt, which has a composition (wt%): Ta_2O_5—57.98; Nb_2O_5—21.93; MnO—15.59; WO_3—4.16. Recalculation of composition (by 6 atoms O) has shown the following formula: $Mn_{0.984}(Nb_{0.738}Ta_{1.172}W_{0.08})_{1.990}O_6$. For experiments with the presence of silicate substance we used leukocrat granite of Orlovka deposit of following composition (wt%): SiO_2—72.10; TiO_2—0.01; Al_2O_3—16.14; Fe_2O_3—0.68; MnO—0.09; CaO—0.30; MgO—0.01; Na_2O—5.17; K_2O—4.28; P_2O_5—0.02; F—0.32; H_2O—0.18.

The investigated area of physico-chemical parameters to study the solubility of these minerals was 550–850 °C at a pressure of 1 kbar. Concentrations of initial fluoride solutions of KF, NaF and LiF ranged from 0.08 to 1M, which were prepared from the corresponding high purity reagents on the basis of bidistilled water. It should be noted that the selected range corresponds to the real range of fluoride concentrations in natural postmagmatic fluids in deposits associated with granites.

In order to study the influence of the presence of silicate substance (quartz or granite melt) on the solubility of pyrochlore and tantalite in fluoride solutions, the composition of fluids was determined by solutions with concentrations: LiF (0.08M); NaF (1M); KF (0.5 and 1M).

The experiments were carried out on a high gas pressure vessel (HGPV-10000) of IEM design (at T > 650 °C). HGPV is characterized by high accuracy of setting and determination of temperature and pressure, high working volume, high productivity and the possibility of long-term experiments, which makes it indispensable in the study of magmatic processes. The heater with tungsten-rhenium or molybdenum wire as a heating element allows to conduct experiments at temperatures up to 1400 °C. Temperature was regulated and controlled by Pt-PtRh10 thermocouples with accuracy of ±2 °C, pressure up to 6 kbar was measured by a spring pressure gauge with an error of ±1%. The heater was calibrated by the melting point of gold. The gradient-free zone is 50 mm, the operating diameter of the furnace is 15 mm. Part of the experiments in the temperature range of 550–650 °C was conducted on a hydrothermal plant with a cold gate and external heating (IEM RAS design). Temperature control accuracy was ±5 °C, pressure ±50 bar.

3.2.2 Methodology of Experiments

Experiments were conducted using the ampoule method. The solubility of pyrochlore and tantalite was estimated by the composition of quenching solutions. Quantitative analysis of the solution required a sufficiently large amount of fluid, so the experiments were carried out in platinum ampoules with a diameter of 7 mm and a volume of about 2 mL. Ampoules were loaded with the pyrochlore or tantalite crystals and the solution was poured. For experiments with silicate matter, a quartz crystal or granite powder was added, as well as amorphous silica. The method of synthetic fluid inclusions was used to estimate the phase state of the fluid. For the synthesis of fluid inclusions (by healing cracks) we used prisms sawn from natural quartz crystals (Perekatnoye deposit, Aldan). Quartz prisms were subjected to a thermal shock by heating them up to 250–300 °C, and then discharging them into alcohol, thus forming a network of cracks in them. After drying in a drying closet and ignition at 1100 °C in a muffle furnace, a quartz crystal was placed in a platinum ampoule. In addition, amorphous silica was added for better healing of cracks in quartz and poured with the selected fluoride solution. Then the ampoule was hermetically sealed and weighed. After run (time of quenching was 2–5 min) the ampoules were weighed to check the tightness. Experiments on healing cracks in quartz were carried out both in the presence of ore minerals (pyrochlore and tantalite) and without them.

3.2.3 Methods of Analysis

After the experiment, the hardening solution was analyzed by ICP/MS and ICP/AES (mass spectra and atomic emission) methods on a number of elements (Nb, Ta, Na, Ca, Mn, Fe, Ti, W, etc.). For the analysis of solutions experimentally obtained, 0.2 mL of concentrated HCl (37% GR, ISO, Merck) and an internal standard (Cs) were added to the original aliquot. The solution was then diluted to 10 mL with water. This method was described in a previous article (Zarayskiy et al. 2010). No precipitation was observed in the solutions. This is due to the fact that transition metals such as Ta and Nb are not deposited at low pH values. The time between solution preparation and measurement did not exceed 4-8 h. The concentrations of elements in the solutions were determined by the quantitative method using standard solutions containing 1–500 μg/L of Nb, Ta, Mn, Ti, W and Sn and 100–10 000 μg/L of Mn, Fe and Ti. Error in element concentration depends on the setting spectrometer, purity of input system, conical state of mass spectrometer, etc. The content of elements was determined by atomic emission analysis (AES) for rock-forming elements (Mn, Fe) and mass spectral (MS) for impurity elements (Nb, Na). For standard solutions, the error of element concentration according to Mn (MS; AES) was 0.7 μg/L; Fe (AES)—9 μg/L; Nb (MC)—0.4 μg/L; and Ta (MC)—0.02 μg/L. After experience, the pH value of the quenching solution was measured.

Compositions of solid products after experiments were determined by the method of electron-probe X-ray spectra analysis using scanning electron microscope Tescan Vega II XMU (Tescan, Czech Republic), equipped with INCA Energy 450 X-ray microanalysis system with energy dispersive (INCAx-sight) and crystal diffraction (INCA wave 700) X-ray spectrometers (Oxford Instruments, England) and INCA Energy + software platform. The analysis conditions when using only the energy dispersive spectrometer were as follows: accelerating the voltage of 20 kV, the current of absorbed electrons at Co 0.3 nA, the analysis time at 70 s. When using the crystal diffraction spectrometer together with the energy dispersive conditions of the analysis were different: accelerating the voltage of 20 kV, the current of absorbed electrons at Co 20 nA, the total time of analysis at 170 s. The accuracy of quantitative X-ray analysis using an energy dispersive spectrometer is comparable to that of a crystal diffraction spectrometer with elemental content above 1 wt% (Reed 2005). The content of the elements to be determined in the samples under study in most cases exceeded 1 wt%. When using an energy dispersive detector to record X-ray radiation, the detection limits of the detectable elements are in the range of 0.1–1 wt%; when detecting elements with a crystal diffraction spectrometer, the detection limits of the elements are in the range of 0.02–0.7 wt%. The accuracy of the determination is 0.2 wt% of the element when using an energy dispersive spectrometer and 0.05 wt% of the element when using a crystal diffraction spectrometer. To prevent sodium losses (especially from water-bearing phases), the scanning mode was used: the analysis was performed from the area of 10 × 10 μ and more.

The samples were polished and sprayed with a thin conductive layer of carbon. Shooting of microphotographs was carried out in back-scattered electron mode with real contrast (BSE—back-scattered electrons) with magnifications from 8.5 to 2500 times.

3.3 The Results of the Experiments

3.3.1 Fluid Phase State

Data on the phase state of the fluid were obtained by studying synthetic fluid inclusions in quartz. If the fluid was homogeneous at the experimental parameters, all inclusions had the same phase composition and the same values at thermo- and cryometry. In the case of heterogeneous fluid, different inclusions capture portions of immiscible phases or mechanical mixtures of these phases, as a result of which two or more types of inclusions with different thermobarogeochemical characteristics are formed.

In experiments with LiF solution (concentration 0.08M) at the pressure of 1 kbar and temperatures of 550, 650 °C the fluid existed in heterogeneous state: two-phase gas + liquid (G + L) and three-phase gas + liquid + crystal (G + L+S) inclusions were found in the samples.

In experiments with NaF solution (concentration of 1M), unlike LiF solutions, at pressures of 0.5, 1 kbar and temperature of 550 °C there was a homogeneous fluid: only two-phase inclusions of G + L were found. With increasing temperature up to 650 °C, the interaction of the fluid with solid phases resulted in the deposition of a small number of solid phases. The course of homogenization of two-phase inclusions is near-critical, which testifies to the proximity of TPX parameters of the experiment to the critical point of the system.

In experiments with KF solution (concentrations of 0.5M and 1M) for 550 °C and 1 kbar at the starting solution concentration of 2.9 wt% (0.5M) the fluid is homogeneous: only G + L inclusions were found. If under the same PT conditions the concentration of the initial solution is increased up to 1M (5.8 wt%), the fluid is heterogenized and different types of inclusions are formed. By results of study of fluid inclusions in quartz it is possible to conclude that at parameters of experiments (550, 650, 750 and 850 °C and pressure of 1 kbar) 1M (5.8 wt%) solutions of potassium fluoride stratified on vapor (low concentrated) phase and a phase of a salt fluid (highly concentrated phase). At the temperature of 650 °C and higher (at P = 1 kbar) the phase of silicate glass is found in inclusions.

3.3.2 Solubility of Pyrochlore and Tantalite

Data on the solubility of natural minerals of pyrochlore and tantalite in the presence of quartz (granite) and without it are presented in Tables 3.1, 3.2 and Figs. 3.1, 3.2, 3.3, 3.4.

It has been experimentally established that at T = 550 °C and P = 1 kbar the presence of quartz at dissolution of pyrochlore mineral significantly reduces the content of Nb in KF solutions by more than 3 orders of magnitude; in 1M NaF—by half an order and in 0.08M LiF—quite insignificantly (Fig. 3.1) (Kotelnikov et al.

Table 3.1 Conditions and results of experiments on the solubility of pyrochlore in alkali metal fluoride solutions (T = 550–850 °C, P = 1 kbar)

Sample No.	Hitch	Initial solution	pH before run	pH after run	Phases	Composition of solution after run		
						Nb, mg/L	Na, mg/L	Ca, mg/L
550 °C								
Px239-1	46 mg *Pchl*	1745 mcl 0.5M KF	6.72	7.54	*Pchl*	17.5	112	2.3
Px239-2	62 mg *Pchl* + 367 mg *Qtz* + 92 mg amf. SiO_2	1777 mcl 0.5M KF	6.72	7.48	*Pchl* + *Qtz*	0.042	151	1.9
Px240-1	145 mg *Pchl*	1953 mcl 1M KF	7.32	8.42	*Pchl*	45.4	252	2.2
Px240-2	31 mg *Pchl* + 499 mg *Qtz* + 102 mg amf. SiO_2	1805 mcl 1M KF	7.32	8.10	*Pchl* + *Qtz*	0.045	290	2.4
Px232-1	32 mg *Pchl*	1983 mcl 0.08M LiF	6.31	6.25	*Pchl*	0.10	22.8	<DL
Px232-2	27 mg *Pchl* + 121 mg *Qtz* + 31 mg amf. SiO_2	1942 mcl 0.08M LiF	6.31	5.22	*Pchl* + *Qtz* + *Sil-gl*	0.16	15.9	<DL
Px231-1	49 mg *Pchl*	2088 mcl 1M NaF	6.33	7.21	*Pchl*	0.3	14,944	1.2
Px231-2	39 mg *Pchl* + 255 mg *Qtz* + 62 mg amf. SiO_2	1804 mcl 1M NaF	6.33	7.27	*Pchl* + *Qtz*	0.12	15,857	<DL
650 °C								
Px251-1	259 mg *Pchl*	693 mcl 1M KF	7.32	9.93	*Pchl*	2.7	1754	1
Px251-2	275 mg *Pchl* + 163 mg *Qtz* + 15 mg amf. SiO_2	699 mcl 1M KF	7.32	6.97	*Pchl* + *Qtz* + *Sil-gl*	14.8	2080	1.1
Px252-2	238 mg *Pchl* + 365 mg *Qtz* + 21 mg amf. SiO_2	543 mcl 1M NaF	6.33	8.25	*Pchl* + *Qtz* + *Sil-gl*	2.6	10,955	9.3
Px253-2	247 mg *Pchl* + 235 mg *Qtz* + 15 mg amf. SiO_2	601 mcl 0.08M LiF	6.31	–	*Pchl* + *Qtz*	1.5	907	7.9

(continued)

Table 3.1 (continued)

Sample No.	Hitch	Initial solution	pH before run	pH after run	Phases	Composition of solution after run		
						Nb, mg/L	Na, mg/L	Ca, mg/L
850 °C								
Px250-1	129 mg *Pchl*	638 mcl 1M KF	7.32	10.2	*Pchl*	22	3068	<DL
Px250-2	74 mg *Pchl* + 157 mg *Qtz* + 25 mg amf. SiO_2	601 mcl 1M KF	7.32	1.90	*Pchl* + *Qtz* + *Sil-gl*	222	189	22
Px255-2	75 mg *Pchl* + 157 mg granite + 22 mg amf. SiO_2	423 mcl 1M KF	7.45	6.23	*Pchl* + *Qtz* + *AlSil-gl*	166.8	442	54.2
Px256-2	119 mg *Pchl* + 167 mg *Qtz* + 17 mg amf. SiO_2	734 mcl 1M NaF	6.33	1.80	*Pchl* + *Qtz* + *Sil-gl*	175	1801	4

<DL—less than detection limit

2018a, b). At the same time pyrochlore solubility in KF solutions increases at the increase of concentration from 0.5 to 1M by 0.6 order of magnitude, in similar experiments in the presence of quartz this effect is not observed.

For temperatures of 650° and 850 °C, the presence of quartz in the system increases the equilibrium content of Nb in the solution by an order of magnitude: at 650 °C, the niobium content in 1M KF solution is without quartz—2.91 * 10^{-5}, and in the presence of quartz—1.59 * 10^{-4} mol/kg H_2O; at 850 °C the content of Nb is without quartz—2.38 * 10^{-4}, and with quartz (or with granite melt)—2.39 * 10^{-3} mol/kg H_2O (Fig. 3.2). Measurement of pH of solutions (Tables 3.1 and 3.2) before and after the experiments showed that for 550 °C the initial solution of 1M KF after the experiment is alkalized, which reduces the solubility of pyrochlore; for 650 °C—pH is shifted to the acidic area, but only by half an order; for 850 °C—pH after the experiment is shifted to the acidic area significantly: (before the experiment pH = 7.32 and after experiment pH = 1.901). It can be assumed that due to the acid-base interaction at $T \geq 650$ °C, and especially at 850 °C, the concentration of HF in the fluid increases significantly. Note that at a temperature of ≥650 °C and P = 1 kbar the fluid is heterogenized to the high-salt and vapor phases. The effect of acidification of solutions, apparently, is associated with the formation of glass phase during the experiments and significant redistribution of potassium into the glass and high-salt phases. On the Fig. 3.3 the temperature dependence of equilibrium content of tantalum (Fig. 3.3a) and niobium (Fig. 3.3b) at dissolution of tantalum in 1M KF and 1M NaF depending on presence of quartz (granite melt) is presented.

Study of fluid inclusions in quartz, study of phase composition of experiments on pyrochlore and tantalite solubility showed that under the conditions of experiments

Table 3.2 Conditions and results of experiments on the solubility of tantalite in solutions of alkali metal fluorides (T = 550–850 °C, P = 1 kbar)

Sample No.	Hitch	Initial solution	pH before run	pH after run	Phases	Nb, mg/L	Ta, mg/L	Mn, mg/L	W, mg/L
550 °C									
KT104-1	34 mg *Tnt*	789 mcl 1M KF	7.32	10.5	*Tnt*	4.0	0.8	0.47	9.7
KT104-2	28 mg *Tnt* + 406 mg *Qtz* + 40 mg amf. SiO_2	789 mcl 1M KF	7.32	8.5	*Tnt* + *Qtz*	0.2	0.022	1.7	19.4
KT105-1	20 mg *Tnt*	518 mcl 1M NaF	6.33	–	*Tnt*	0.23	0.18	0.10	1.8
KT105-2	33 mg *Tnt* + 366 mg *Qtz* + 35 mg amf. SiO_2	544 mcl 1M NaF	6.33	8.0	*Tnt* + *Qtz*	0.89	0.29	4.3	1.6
650 °C									
KT109-1	22 mg *Tnt*	627 mcl 1M KF	7.32	10.3	*Tnt*	9	1.7	32.4	14.8
KT109-2	31 mg *Tnt* + 67 mg *Qtz* + 21 mg amf. SiO_2	645 mcl 1M KF	7.32	7	*Tnt* + *Qtz* + *Sil.gl*	4.4	0.04	9.3	16.9
KT111-1	32 mg *Tnt*	508 mcl 1M NaF	6.33	8.5	*Tnt*	0.54	0.042	6.8	1.3
KT111-2	58 mg *Tnt* + 117 mg *Qtz* + 12 mg amf. SiO_2	522 mcl 1M NaF	6.33	7	*Tnt* + *Qtz* + *Sil.gl*	2.0	0.018	6	0.72

(continued)

Table 3.2 (continued)

Sample No.	Hitch	Initial solution	pH before run	pH after run	Phases	Nb, mg/L	Ta, mg/L	Mn, mg/L	W, mg/L
750 °C									
263-2	86 mg *Tnt* + 350 mg *Qtz* + 88 mg amf. SiO_2	769mcl 1M KF	7.32	6	*Tnt* + *Qtz* + *Sil.gl*	55.6	0.16	66.5	42.5
265-1	146 mg *Tnt*	523 mcl 1M NaF	6.33	≤10	*Tnt*	0.63	0.96	2.1	8.3
265-2	97 mg *Tnt* + 148 mg *Qtz* + 14 mg amf. SiO_2	501 mcl 1M NaF	6.33	≈5	*Tnt* + *Qtz* + *Sil.gl*	82.7	0.038	7.1	23.7
850 °C									
KT107-1	59 mg *Tnt*	648 mcl 1M KF	7.32	7	*Tnt*	35.8	4.7	15.5	82.1
KT108-2	71 mg *Tnt* + 152 mg granite + 24 mg amf. SiO_2	538 mcl 1M KF	7.32	5.5	*Tnt* + *Qtz* + *Sil.gl*	53.0	0.93	21.5	4.2

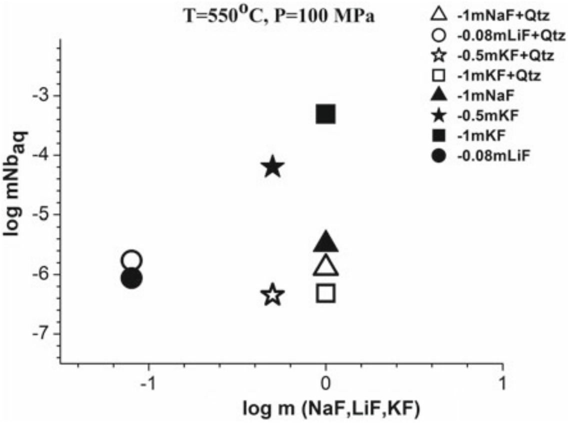


Fig. 3.1 The concentration dependence of the equilibrium content of niobium when pyrochlore dissolves in solutions of 0.08M LiF; 0.5 and 1M NaF; 0.5 and 1M KF at 550 °C and P = 1 kbar (in the presence of quartz and without it)

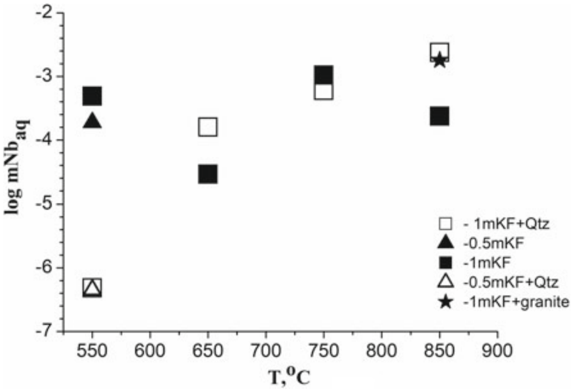


Fig. 3.2 Temperature dependence of the equilibrium niobium content when pyrochlore dissolves in 0.5 and 1M KF solutions at 550, 650, and 850 °C and P = 1 kbar (in the presence of quartz and without it)

the reactions of high-temperature hydrolysis of KF occur: $KF + H_2O = KOH\downarrow + HF\uparrow$, the interaction with quartz occurs: $SiO_2 + 2KOH = K_2SiO_3 + H_2O$, with the formation of a silicate glass phase (aqueous melt-solution) at T ≥ 650 °C and P = 1 kbar. This phase of alkaline glass is a concentrator of Ta and Nb (Table 3.3). Contents of tantalum and niobium (Ta_2O_5 and Nb_2O_5) in the granite melt reach 6 wt% (850 °C). When dissolving pyrochlore in 1M KF (T ≥ 650 °C) in the presence of quartz, a silicate melt with a content of Nb_2O_5 up to 8 wt% is formed.

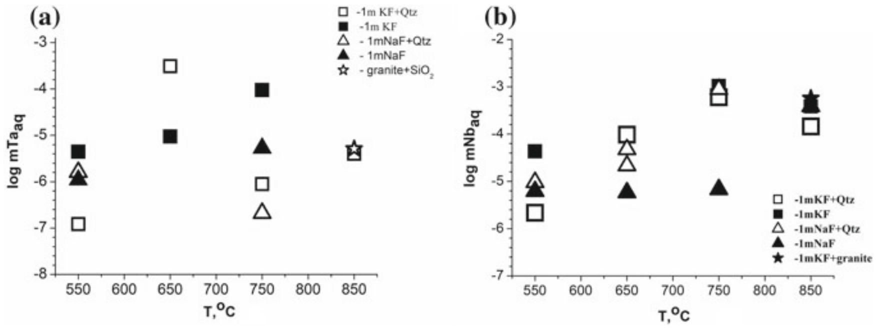
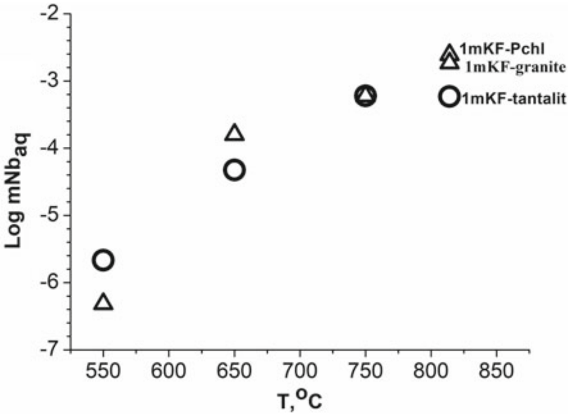


Fig. 3.3 Temperature dependence of the equilibrium content of tantalum (**a**) and niobium (**b**) when tantalite is dissolved in 1M KF and 1M NaF solutions, depending on the presence of quartz (granite). Filled shapes—without quartz; not shaded—with quartz; asterisk—1M KF + granite + SiO_2 amorphous

Fig. 3.4 Comparison of data on the content of niobium in solution in the presence of quartz by dissolving natural pyrochlore minerals (triangles) and tantalite (circles) in 1M KF solution



On the Fig. 3.4 the data of niobium content in solution in the presence of quartz at dissolution of natural minerals of pyrochlore and tantalite in 1M KF are compared. As can be seen, the dependences of the niobium content in the solution for both minerals are of the same type.

3.4 Discussion of Results

3.4.1 Pyrochlore Solubility

It is shown that pyrochlore solubility in KF solutions at 550 °C and P = 1 kbar depends on their concentration (Fig. 3.1). Thus, when the solution concentration

Table 3.3 The compositions of the products of experiments (wt%) on the solubility of pyrochlore in solutions of alkali metal fluorides

	650 °C, 1 kbar, 1M KF		750 °C, 1 kbar, 1M KF		
Sample No.	Px-251-2		Px-257-2		
Phases	*Pchl* + *Qtz* + *Sil* (melt)		*Pchl* + *Qtz* + *Sil* (melt)		
Oxide	*Pchl*	*Gl*	*Pchl*	*Rip**	*Gl*
F	4.82	0.98	4.92	–	2.70
Na_2O	7.55	0.36	7.11	–	0.72
Al_2O_3	–	–	–	–	–
SiO_2	–	71.35	–	37.67	56.51
K_2O	1.20	10.69	0.25	16.13	18.57
CaO	15.28	–	15.14	–	0.23
MnO	0.40	0.26	–	–	–
Nb_2O_5	72.11	8.16	70.06	44.19	12.44
Ta_2O_5	–	–	–	–	–
Sum	101.36	91.80	97.48	97.99	88.47

*Rip**—$K_{1.023}Nb_{1.023}Si_{1.967}O_7$ (the crystal-chemical formula may be correspond to the mineral rippite: $K_2(Nb,Ti)_2Si_4O_{12}O(O,F)$ (Doroshkevich et al. 2016)

changes from 0.5 to 1M, pyrochlore solubility [lg(mNb)aq] increases by an order of magnitude (−4.3 to −3.3). The temperature dependence of pyrochlore solubility is insignificant; it can be described by the linear regression equation: [lg(mNb)aq] = −3.745 + 0.0001*(T°C); (Sx = 0.71, Ex = 1.1). Based on this dependence at T = 550 °C and P = 1 kbar lg(mNb)aq = –3.70, and at T = 850 °C and P = 1 kbar it will be equal to −3.66. The presence of silicate substance in experiments at T = 550 °C and P = 1 kbar reduces solubility [lg(mNb)aq] to −6.3 (i.e. by about 3 orders of magnitude). In the presence of silicate substance (quartz or granite) there is a clear dependence of Nb solubility on temperature: [lg(mNb)aq] = −12.44 + 0.0122 * (T°C); (Sx = 0.52, Ex = 0.8). According to this equation, the solubility of Nb increases from −5.8 to −2.1 with an increase in the temperature of experiments from 550 to 850 °C. The solubility of pyrochlore at T = 550 °C and P = 1 kbar in 1M KF solutions is almost two orders of magnitude higher than in 1M NaF (lg(mNb)aq values are −3.3 and −5.5, respectively).

3.4.2 *Tantalite Solubility*

Solubility of tantalite in relation to tantalum [lg(mTa)aq] differs from pyrochlore solubility (by niobium). Tantalite solubility experiments were carried out at P = 1 kbar in the temperature range from 550 to 850 °C in 1M NaF and 1M KF solutions. Presence of a silicate phase at T = 550 °C reduces solubility of tantalite in 1M

KF from −5.4 to −6.9 (by one and a half orders of magnitude). At the same time, at 650 °C, the presence of quartz increases the solubility of tantalite. However, in the temperature range from 550 to 850 °C the dependence of tantalite solubility on the temperature in the presence of silicate matter is small, the regression equation calculated from the data for temperatures of 550, 650, 750 and 850 °C as follows: [lg(mTa)aq] = −6.69 + 0.0017 * (T°C); (Sx = 1.1, Ex = 1.4). The calculated values of lg(mTa)aq are −5.7 (550 °C) and −5.2 (850 °C). Without silicate substance dependence of tantalite solubility in 1M KF on temperature is described by the following linear equation [lg(mTa)aq] = −9.35 + 0.0070 *(T°C); (Sx = 0.14, Ex = 0.4). The calculated solubility values are as follows: −5.5 (550 °C) and −3.4 (850 °C). In 1M NaF solutions, the solubility of tantalite at 550 °C is practically independent of the presence of quartz: −5.9 (without quartz) and −5.7 (with quartz). With increasing temperature, the solubility in the system without quartz increases to −5.2 (750 °C). In the presence of silicate substance in the system solubility of tantalite with increasing temperature decreases to −6.6 (750 °C). In the tantalite used by us there is a lot of niobium (up to 21.93 wt% Nb_2O_5), that is why solubility of tantalite in relation to niobium has also been studied. In silicate-containing systems, the solubility of tantalite with respect to Nb is similar to that of pyrochlore (Fig. 3.4). Solubility of Nb [lg(mNb)aq] for pyrochlore and tantalite depending on temperature was studied in 1M KF at a pressure of 1 kbar in the presence of silicate substance (quartz or granite). The temperature dependences of solubility [lg(mNb)aq] are described by polynomials of the 2nd degree: for pyrochlore:

$$\left[\mathrm{lg(mNb)aq}\right] = -33.904 + 0.0751 * (\mathrm{T^\circ C}) - 0.0000451 * (\mathrm{T^\circ C})^2$$
$$(\mathrm{Sx} = 0.22;\ \mathrm{Ex} = 0.35);$$

for tantalite:

$$\left[\mathrm{lg(mNb)aq}\right] = -25.904 + 0.0548 * (\mathrm{T^\circ C}) - 0.0000330 * (\mathrm{T^\circ C})^2$$
$$(\mathrm{Sx} = 0.13;\ \mathrm{Ex} = 0.21).$$

In general, we can conclude that the niobium component of the solid solutions of pyrochlore and tantalite in fluoride aqueous solutions is significantly more soluble than that of tantalum.

3.4.3 Silicate Melt Phase

As it was mentioned earlier, in experiments in the presence of silicate substance (quartz or granite) in the conditions of heterophase fluid silicate (aluminosilicate) melt was formed, which dissolved significant amounts of niobium and tantalum oxides. This melt can be considered to be saturated with respect to Nb_2O_5 and Ta_2O_5, because in the experiments in equilibrium with silicate melt there were pyrochlore or tantalite (“saturation phases”). The formation of silicate melt enriched with niobium and tantalum is observed both in experiments with 1M NaF fluid and for experiments with 1M KF fluid. Most of the experiments were performed with 1M KF solution (Tables 3.3 and 3.4). In experiments with pyrochlore the content of Nb_2O_5 in silicate glass varies from 8.16 wt% (650 °C) to 12.44 wt% (750 °C). In experiments with tantalite in silicate glass the concentration of Nb_2O_5 changed from 1.38 wt% (650 °C) to 1.9–3.2 wt% (850 °C). The content of Ta_2O_5 in the melt varied from 5.3 (650 °C) to 8.50 wt% (850 °C). In experiments with pyrochlore one can draw a conclusion about the incongruent dissolution of pyrochlore, while a significant share of such elements as Na, Ca, Mn was redistributed into the fluid phase, while the main part of niobium was distributed into the silicate melt phase. In experiments with tantalite, the picture is different. From the content of MnO, Nb_2O_5, Ta_2O_5 oxides in silicate melts it is possible to calculate the formula of hypothetical dissolved tantalite. On the average, the following formula (conversion to 6 atoms O) was obtained for experiments with fluid 1M KF: $Mn_{1.06}(Nb_{0.72}Ta_{1.26})_{1.98}O_6$. The original tantalite has a formula: $Mn_{0.98}(Nb_{0.74}Ta_{1.17}W_{0.08})_{1.99}O_6$. Within the error of analysis, these formulas are similar. One can note a relative increase in the tantalum content in the melt with a decrease in temperature. The molar fraction of tantalum $X_{Ta}^{Liq} = Ta/(Nb + Ta)$ depending on temperature is described by the following equation:

$$X_{Ta}^{Liq} = 0.945 - 0.000414 * (T°C);\ \ S_x = 0.05.$$

Thus, according to this equation at 850 °C, the value of $X_{Ta}^{Liq} = 0.59$; with a decrease in temperature to 650 °C, $X_{Ta}^{Liq} = 0.68$.

In some experiments on solubility of tantalite in the presence of silicate melt small amounts of microlite—tantalum member of pyrochlore—microlite solid solution were formed (Fig. 3.5). Tantalites (saturation phase) and silicate melts are completely free of tungsten. According to the analysis of compositions of solutions coexisting with the melt, tungsten is redistributed into the fluid phase. This is consistent with the data (Marakushev and Shapovalov 1994; Shapovalov et al. 2019) on the predominant enrichment of tungsten salt phase. In experiments with pyrochlore (in the presence of 1M KF solution), rippite crystals ($KNbSi_2O_7$), an ore mineral from a number of niobium deposits, were found in the silicate glass phase (Doroshkevich et al. 2016). This phase is also a niobium concentrator. The pyrochlore itself is almost identical in composition to the original one, except for a small amount of potassium, apparently added from potassium-fluoride fluid.

Based on the experimental data obtained by us it is possible to conclude that a low-temperature high-alkaline melt is formed under heterogeneous fluid conditions at a pressure of 1 kbar. Thus, for aluminosilicate melt (experience of KT-108) the agpaitic coefficient is 2.5 ± 0.2. The formation of such an ultra-alkali melt is connected with the fluid-magmatic interaction of the high-temperature fluid under conditions of its heterogenization. You can write the following reaction equation: $KF + H_2O = KOH\downarrow + HF\uparrow$ (arrows indicate that HF enriches the vapor phase of the stratified fluid and KOH—the liquid phase). This saline alkaline phase reacts with the silicate phase

Table 3.4 The compositions of the products of experiments (wt%) on the solubility of tantalite in solutions of alkali metal fluorides

	650 °C, 1 kbar, 1M KF		750 °C, 1 kbar, 1M KF			850 °C, 1 kbar, 1M KF			850 °C, 1 kbar, 1M KF		750 °C, 1 kbar, 1M NaF		
Sample No.	KT-109-2		Px-263-2			KT-108-2			KT-103-2		Px-265-2		
Phases	*Tnt* + *Qtz* + *Sil* (melt)		*Tnt* + *Qtz* + *Sil* (melt)			*Tnt* + *Mcl* + granite (melt)			*Tnt* + *Qtz* + *Sil* (melt)		*Tnt* + *Qtz* + *Sil* (melt)		
Oxide	*Gl*	*Tnt*	*Tnt*	*Gl1*	*Gl2*	*Mcl*	*Tnt*	*Gl*	*Tnt*	*Gl*	*Tnt*	*Mcl*	*Gl*
F	2.80	–	–	1.15	2.24	4.21	–	5.53	–	1.10	–	4.91	3.92
Na_2O	–	–	–	–	–	5.66	–	2.62	–	0.40	–	7.42	9.63
Al_2O_3	0.46	–	–	–	–	–	–	8.83	–	–	–	–	3.58
SiO_2	69.15	–	–	63.84	60.62	–	–	49.74	–	63.53	–	–	60.49
K_2O	16.06	–	–	9.42	6.63	0.83	–	16.61	–	15.67	–	–	1.44
CaO	0.15	–	–	–	–	9.22	–	0.20	–	–	–	4.73	–
MnO	1.52	16.38	15.84	3.85	2.90	1.42	16.92	2.21	16.54	1.14	17.06	4.50	4.77
Nb_2O_5	1.38	25.49	20.45	3.99	4.23	10.54	25.27	3.24	23.54	1.88	24.97	20.82	3.30
Ta_2O_5	5.30	58.66	63.21	7.50	14.50	68.33	58.12	6.31	59.92	8.50	57.96	54.76	7.90
Sum	96.82	100.53	99.50	89.75	91.12	100.21	100.31	95.29	100.00	92.22	99.99	97.14	95.03

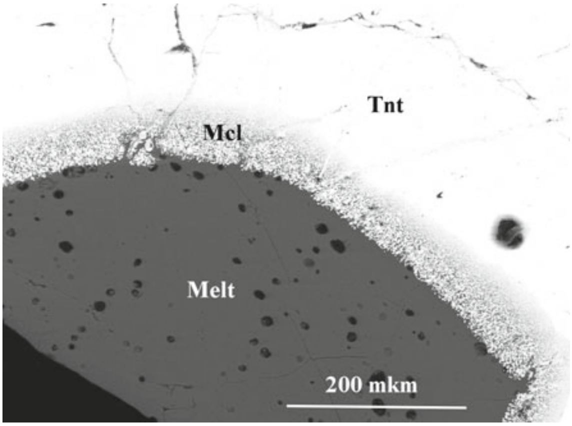


Fig. 3.5 Products of experiments on the solubility of tantalite in a solution of 1M KF in the presence of quartz at 850 °C, 1 kbar. Tnt—tantalite, Mcl—microlite

to form aqueous melt KSi_2O_5, with an excessive SiO_2 content. This is consistent with the stoichiometry of silicate melts from our experiments with quartz (Tables 3.3 and 3.4). This alkaline melt in experiments with granite dissolves in itself aluminum oxide, forming aluminosilicate melt. Such alkaline phase is a concentrator of tantalum and niobium—at a temperature of 650–850 °C the total content ($Nb_2O_5 + Ta_2O_5$) reaches from ~7.5 (650 °C) to ~10.5 (850 °C) wt%.

This alkaline low-temperature melt contains up to ~10 wt% volatile ($F + H_2O$) and can serve as a phase—concentrator of rare-metal elements (Ta, Nb) at the latest stages of crystallization of lithium-fluorine granites of potassium specialization. Due to the concentration of rare metals in this phase, there are ore accumulations of tantalum and niobium minerals in the upper parts of lithium-fluorine granite massifs—the so-called apogranites (Beus et al. 1962). Apogranites are formed during hydrothermal processing of ultra-alkali low-temperature melts. The fluids carry easily soluble alkaline components, and ore metals are concentrated in the form of iron and manganese tantalum-niobates.

3.5 Conclusions

1. The boundaries of heterogenization fields of fluoride fluids in the temperature range of 550–850 °C and pressure of 1 kbar were determined by the method of synthetic fluid inclusions.
2. The influence of silicate substance on pyrochlore and tantalite solubility in alkali metal fluoride solutions (LiF, NaF, KF) was studied. It is shown that the solubility of the above minerals is significantly affected by the presence of silicate (quartz) or aluminosilicate (granite) material in the experiments.

3. The temperature dependences of pyrochlore and tantalite solubility in aqueous solutions of alkali metal fluorides for the systems (H_2O ± LiF ± NaF ± KF ± Pchl ± Tnt) in the range of 550–850 °C and pressure of 1 kbar are determined.
4. It is established that in the presence of fluoride heterophase fluid in silicate systems with ore minerals (pyrochlore, tantalite) for concentrations of solutions of 0.5 and 1M at temperatures of 650–850 °C and pressure of 1 kbar the formation of alkaline silicate melt, which is a concentrator of Nb and Ta, occurs.
5. This phase of highly alkaline silicate melt can serve as a phase that concentrates significant amounts of ore elements. This phase, when treated with low concentrated aqueous solutions, forms ore apogranites.

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