

Interaction in the systems of fluid–melt–crystal

Kotelnikov¹ A.R., Chevychelov¹ V.Y., Suk¹ N.I., Korzhinskaya¹ V. S., Kotelnikova^{1,2} Z.A. Model for formation of tantalate-niobate ores in deposits of Transbaikalia according to experimental investigations. UDC: 550.42

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Abstract. To assess the conditions and mechanism of the formation processes of tantalate-niobate ores, the solubility of Ta-Nb minerals in granitoid melts was studied depending on the composition and TP-parameters. The possibility of accumulation of Ta and Nb due to the processes of magmatic differentiation and the formation of specific lithium-fluorine granites is shown. The phase relationships in the systems of tantalate – niobate – quartz – potassium fluoride solution were experimentally studied in a wide range of TP-parameters. The concentrations of Ta and Nb in the liquid phases of the studied system are shown. At natural conditions, when Li-F granites are treated with alkaline fluorine- and silicate-containing fluids (system H₂O – KF – SiO₂) at 750-650°C and pressure of 2-3 kbar, specific alkali-silicate solution-melts with high fluorine content are formed, which can contain up to ~1 wt. % Nb. Thus, the formation possibility of tantalate-niobate deposits according to the two-stage model of the ore genesis process, theoretically predicted in the works of G.P. Zaraisky and F.G. Reyf, is experimentally shown.

Keywords: *lithium-fluoride granites; tantalate-niobates; fluid; ore genesis*

The development of new criteria for forecasting and searching for rare metal deposits requires a clearer understanding of the conditions for their formation than is currently the case. In the work of G.P. Zaraisky et al. (2009) it is shown that in the series granodiorite - biotite granite - leucogranite - lithium-fluorine granite - ore in accordance with the degree of their differentiation the residual melts are enriched in rare metals (Ta, Nb, Sn, W, Mo, Be). For example, the content of Ta in the series biotite granite - leucogranite - metasomatically unchanged Li-F granite increases by almost an order of magnitude.

As reference deposits, we consider the detailed studied tantalum deposits of Eastern Transbaikalia (Orlovskoye and Etykinskoye), located in albitized and greisenized Li-F granites (“apogranites” according to A.A. Beus et al., 1962). Their discovery in the mid-1950s stimulated the search and discovery of similar deposits in other parts of the world. So far,

few such deposits are known. Among them are Voznesenskoye, Pogranichnoye, Snezhnoye in Russia, Yichong, Geyang, Nanping, Limu in China, Abu Dabbab and Nuweibi in Egypt, Echassières (Beauvoir) in France, Fouquet in Thailand. Li-F granites themselves and their subvolcanic analogues, ongonites, are much more widely distributed throughout the world, always bearing elevated concentrations of Ta, Nb, Li, Rb, Cs, Be, Sn, W and other rare metals. In many cases, tantalum ore occurrences and signs of non-industrial mineralization are associated with Li-F granites. It can be assumed that the prospects for discovering new deposits of this type of tantalum in the world are quite high. But for this it is necessary to have a clear idea of the conditions of their formation.

Ore-bearing Li-F granites belong to the granitoids of the alkaline earth series. According to morphology, they are small dome-shaped bodies 0.5-2 km in diameter (“stocks”), composed of approximately equal proportions of quartz, albite and microcline (often amazonite), with a small amount of lithium micas (lepidolite, zinnwaldite) and topaz. Industrial mineralization extends to a depth of no more than 100 m from the contact with the roof and is represented by small scattered dissemination of columbite-tantalite, less often microlite in albitized and greisenized granites. Thus, the ores are the mineralized granites themselves in the upper part of the domes. The ores are poor (0.010 -0.034%), the deposits are small and medium in terms of reserves - from the first thousand to 10 -15 thousand tons, but their morphology is favorable for open pit mining, shallow quarries. In addition, the ores are characterized by an increased Ta/Nb ratio (1.2 -1.5).

The most generally accepted are the genetic representations of V.I. Kovalenko (1977), according to which, rare-metal Li-F granites hosting tantalum ores are formed as a result of the most advanced crystallization fractionation of ordinary granite magma under specific conditions that ensure the gradual accumulation of F, Li, Ta, Nb and other rare metals in the residual granite melt. A convincing confirmation of this hypothesis is the distinct inheritance of geochemical, petrochemical and mineralogical specifics in the differentiation series: biotite granite → leucogranite → lithium-fluorine granite. An alternative hypothesis is the representation of A.A. Beus et al. (1962) on the hydrothermal supply of F, Li, Ta, Nb, etc. from a magma chamber by an ascending aqueous fluid flow with the deposition of rare metals in the domes of ordinary biotite granites, transformed as a result of metasomatic processing into albitized and

greisenized rocks (“apogranites”) with lithium micas and topaz. The main argument of this hypothesis is the close connection of tantalum ores with albitization and greisenization of granites. There is also a hypothesis of an autonomous magmatic origin of Li-F granites from a lower crustal or mantle source, which is based on an anomalously high content of rare metals in Li-F granites, their specific appearance, the presence of lithium micas, topaz, and the discovery of individual “mantle marks” in them. Experimental studies may provide new criteria for the selection and development of a genetic model.

To evaluate the most probable hypothesis of ore genesis at the magmatic stage, we carried out experimental studies. The maximum contents (solubilities) of Ta and Nb in water-saturated acid melts were determined, the diffusion coefficients of these elements in the melt were estimated, and their partitioning between the aqueous fluoride fluid and the melt was studied (Chevychelov et al., 2010). Both remelted Li-F granites of the Orlovskoye deposit (mol. $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO}+\text{MnO}+\text{FeO}) = 1.3$) and model acid glasses with mol. $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O}) = \text{A/NK} = 1.7, 1.1$ and 0.64 , with SiO_2 concentration $\sim 73-75$ wt.%, $\text{Na}_2\text{O}/\text{K}_2\text{O} \sim 1.55$ and additions of ~ 2.5 wt.% LiF, of ~ 0.5 wt.% MnO, and of ~ 0.5 wt.% FeO were used in the experiments. Natural columbite $(\text{Mn,Fe})(\text{Nb,Ta,Ti})_2\text{O}_6$ was used as the dissolved mineral. The experiments were

conducted in internally heated pressure vessel pressurized with pure Ar gas, designed by IEM RAS, in a wide temperature and pressure range ($T = 650-980^\circ\text{C}$, $P = 0.3-4$ kbar). The run duration of the experiments was 3-7 days. The solid products of the experiments were studied by electron probe microanalysis.

As a result of experimental studies, it was found that the composition (alumina-alkalinity) of the melt has the strongest effect on the solubility of columbite. In the alkaline melt ($\text{A/NK} = 0.64$), the solubility reaches 5 wt.% Nb concentration and more than 2 wt.% Ta. In the subaluminous haplogranite melt ($\text{A/NK} = 1.1$), the solubility of columbite is 10 times lower, and it decreases by another 2 times in the peraluminous melt ($\text{A/NK} = 1.7$). On the whole, this solubility decreases by ~ 1 order of magnitude for Ta and by almost ~ 2 orders of magnitude for Nb; in the alkaline melt, the Nb concentration is higher, and in the peraluminous melt, Ta is higher (Fig. 1). The temperature dependence of solubility is positive, but less pronounced than the compositional one. In the subaluminous melt, as the temperature decreases from 850 to 650°C , the concentrations of Ta and Nb decrease from $0.6-0.8$ to $0.15-0.05$ wt.%. In this case, the Ta/Nb weight ratio increases from $0.7-0.6$ to 2.8 . The effect of pressure on solubilities of Ta and Nb in the studied range ($0.3-4$ kbar) is insignificant.

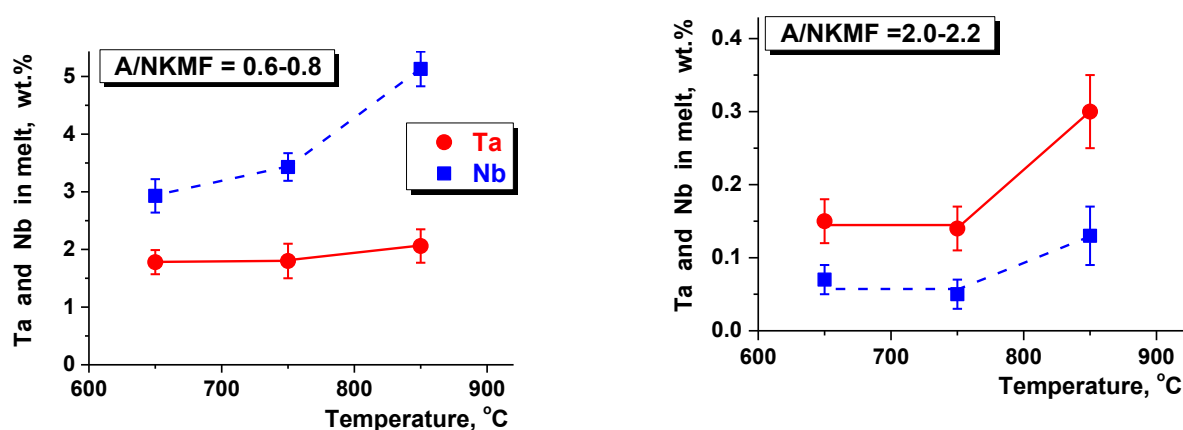


Fig. 1. Influence of composition and temperature on the contents of Ta and Nb in granitoid melt in experiments on the dissolution of columbite ($T=650-850^\circ\text{C}$, $P=1$ kbar, A/NKMF – mol. $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO} + \text{FeO})$ in the melt).

It is shown that the partitioning of Ta and Nb between the aqueous-fluoride fluid and granitoid melts is sharply shifted in favor of the melt ($D_{\text{Nb,Ta}}^{\text{fluid/melt}} = 0.001-0.022$). The partition coefficients of Ta and Nb increase with decrease in the alkalinity of the melt and increase in temperature; moreover for Nb they are 2–3 times higher than for Ta.

It has been established that at liquidus and above solidus conditions, Ta and Nb are concentrated in the residual melt of rare-metal Li-F granites, without

passing into fluid and without dissipating in other minerals. With decreasing temperature the concentration of Ta in the alumina-enriched Li-F granite melt becomes higher than that of Nb. This is the reason for the formation of tantalum deposits proper, in which the Ta/Nb ratio is higher than 1. Due to the high content of F and H_2O , the solidus temperature of such granite melts can decrease to $570-630^\circ\text{C}$ and lower. At near-solidus conditions, when the melt is saturated with tantalum, Ta-bearing columbite can crystallize directly from the magmatic

melt. The final formation of tantalum ores in the apical endocontact parts of the massif occurred at metasomatic conditions through the mobilization and redeposition of Ta by aqueous-fluoride solution-melts and fluids.

In metasomatically unaltered Li-F granites of the Orlovskoye and Etykinskoye deposits, the content of Ta_2O_5 is 30-50 ppm, and further concentration of Ta to an industrial level of 100-350 ppm occurred in postmagmatic conditions. To study these conditions, we carried out experimental studies in the system Tnt (tantalite, $Mn(Ta_{0.65}Nb_{0.35})_2O_6$) \pm Pchl (pyrochlore) \pm Qz (quartz) \pm granite in the presence of 0.5 -1M KF solution at temperature of 550-850°C and pressure 1 and 5 kbar. The experiments were carried out in Pt capsules in internally heated pressure vessel. The run duration of the experiments was 5-10 days. The products of the experiments were studied by following methods: solution by ICP-MS and AAS; solid products by electron probe microanalysis. To assess the phase composition of the fluid, the method of synthetic fluid inclusions in quartz was used.

It was shown that at 550°C and pressure of 1 kbar, at initial solution concentration of 0.5 M, the fluid is homogeneous: only G+L inclusions were encountered. If, at the same TP conditions, the concentration of the initial solution is increased to 1 M, then the fluid is heterogenized, as evidenced by the formation of heterogeneous inclusions. The H_2O - KF - SiO_2 system belongs to the systems of type II, which are characterized by the presence of an immiscibility region of the $L_1 + L_2$ type. When immiscible phases $L_1 + L_2$ coexist due to the hydrolysis reaction with separation of components: $KF + H_2O = HF\uparrow + KOH\downarrow$, the denser phase is enriched in alkaline components, and the less dense phase is enriched in acidic ones. In this case, by reaction with Qz, alkali metal silicates are formed: $2KOH + SiO_2 = K_2SiO_3 + H_2O$. With decrease in temperature, glasses of potassium silicates are observed in the products of the experiments. Thus, in the Pchl + Qz system, in the presence of 1M KF, silicate solution-melts are formed. These are potassium silicate melts containing a lot of water (>15 wt.%) and fluorine (from 1 to 3 wt.%). It is shown that the silicate phase contains relatively high amounts of Nb_2O_5 , up to 6 -8 wt.%. In the Tnt + Qz system in the presence of 1M KF, alkaline silicate solution-melts are also formed containing fluorine in the amount of a few wt.%. At $P = 1$ kbar, glasses contain up to 3 wt.% Nb_2O_5 and 4-6 wt.% Ta_2O_5 . As the pressure increases, the contents of Ta and Nb somewhat decrease. Thus, we can conclude that alkaline silicate melts with high contents of H_2O and F can concentrate significant amounts of Ta and Nb.

These solution-melts can be formed at the final stages of the evolution of magmatic melts in the

presence of fluoride fluid (Na,K)F. These solution-melts are very mobile and can be squeezed out of the crystallizing Li-F granite massifs into their apical, colder parts. To test the possibility of transport of silicate and Ta-Nb material at hydrothermal conditions, we carried out special experiments at conditions of temperature gradient at $P = 3.5$ kbar. The starting materials were a model mixture of feldspar, tantalite, and quartz. A solution of salts KF (NaF) + KCl (NaCl) + K_2CO_3 (Na_2CO_3) + NH_4Cl with a total salt concentration of 25-30 wt.% was used as a transport medium. The compositions of ore-generating fluids were selected based on numerous data from the study of fluid inclusions in minerals and experimental data on phase equilibria (Reif, 1990; Damdinov et al., 2019). Experiments were carried out in sealed Pt capsules at the gradient of ~7-10 deg/cm. The temperature at the bottom of the capsule is 700°C, at the top of the capsule is 650°C. These parameters of the formation of Orlovskoye apogranites were estimated from the structural state of feldspars and from the study of the densities of carbon dioxide fluid inclusions. During the experiment (14 days), the substance was completely transferred (weight ~1.5 g) to the upper part of the capsule (Fig. 2). Thus, the possibility of simultaneous transfer of silicate and Ta-Nb substances at gradient conditions has been shown.

Our experimental data unambiguously confirm the leading role of crystallization fractionation of granitic magma in ensuring the stepwise concentration of Ta in the melt during the formation of tantalum deposits associated with Li-F granites. This provides increase in Ta concentration from ~5 to ~30-50 ppm in Li-F granites. Further concentration of tantalum to industrial level of 100-350 ppm, apparently, occurs by hydrothermal-metasomatic way in the process of greisenization and albitization of Li-F granites by postmagmatic fluids with redeposition of previously crystallized accessory tantalate-niobates in the upper part of granite domes under the screen of hornfelsed shale roof. It has been experimentally shown that aqueous alkaline silicate solution-melts enriched in salt components (fluorides, chlorides, carbonates) are formed under the influence of a salt heterophase fluoride fluid in the silicate system at 650-550°C. The total salinity of such solution-melts reaches 20-30 wt.%. These solution-melts can concentrate Ta and Nb up to the first wt.%. Sedimentation of silicate and ore matter (formation of parageneses $Fsp + Qz + Tnt$) is carried out at the contact of upwardly moving solution-melts with host rocks. Crystallization of solution-melts occurs due to decrease in pressure, temperature and water discharge.

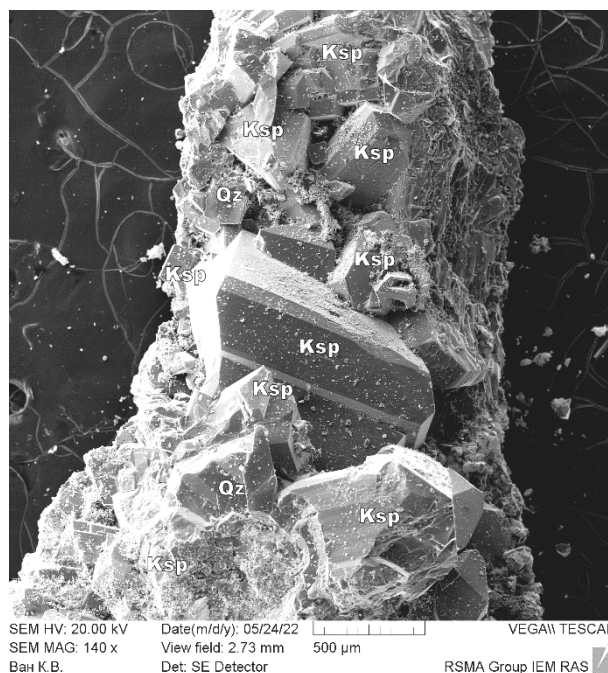
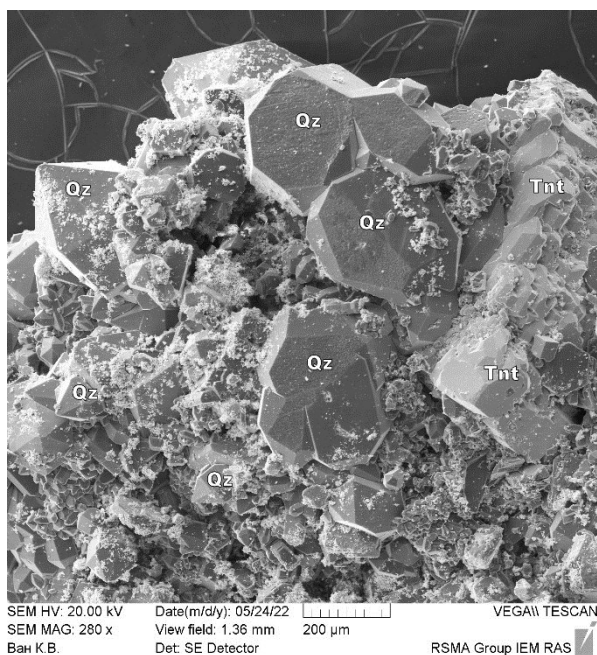


Fig. 2. Crystals formed as a result of the transfer of a substance to the upper part of the capsule. Qz is quartz, Ksp is potassium feldspar, Tnt is tantalite.

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Khodorevskaya L.I., Varlamov D.A. Experimental study of the interaction of granite with H₂O-1M HCl fluid under the conditions of a gradient of P-T parameters. UDC: 123.456

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Abstract. Experiments on the removal of Si, Al, K and Na from granitic glass *G*₁ and their reprecipitation on amphibolite, which provoked the formation of granitic glass *G*₂, were reconstructed at T=750°C and P=500 MPa at a temperature and pressure gradient inside an capsule. Part of dissolved constituents remained in solution and precipitated upon quenching as fine globules of quenching melt *G*₂. The fluids involved in oxide transport consisted of H₂O and 1m HCl. It has been shown that upon granite - H₂O fluid interaction under gradient conditions more Si than Al and more sodium than potassium is removed from granite. As a result, the algaipitic crystallization series of granitic melts increases. Elements removed from granite can form syngenetic plagiogranite or quartz veins. Upon interaction of granite with acidified solutions (1 m HCl) under T-P gradient conditions the edge parts of the granite will shift towards the leucogranite due to the removal of alkaline elements. Syngenetic metasomatic changes will be expressed in the formation of potassium-containing minerals, such as potassium feldspar, biotite, muscovite.

Keywords: granites; H₂O; HCl, fluid; metasomatism; T-P gradients

Contact zones, formed upon the intrusion of granitic magma into host rocks, are believed to be due not only to a purely diffusion mechanism but

also a simultaneous effect exerted on the rocks by infiltration fluids separating from intrusive granitic units. On removal of alkalis and silica from granites, such fluids provoke metasomatic host rock reworking. In addition, the removal of elements from granite by a fluid phase results in changes in the chemical composition of the original granite.

The goal of the present study was to assess changes in granite composition triggered by the removal of petrogenetic constituents under P – T gradient conditions. Our experiments reflect the simplest model showing the intrusion of granites into host rocks.

To simulate the removal of petrogenetic elements from granite in experiments conducted at the external parameters $T=750^{\circ}\text{C}$ and $P=500\text{ MPa}$, variations in pressure along the capsule were provoked by placing a thick-walled microchamber in the upper part of the capsule (Khodorevskaya, 2004). As a result of these variations in pressure, a minor uncontrolled temperature gradient arose along the capsule and temperature in its upper portion declined due to the abrupt expansion of fluid volume in the decreased pressure range (throttling). P-T gradient along the capsule triggered the directed movement of solutions with dissolved Si, Al, K and Na from granitic glass Gl located in the lower portion of the capsule and their redeposition on the surface, consisting of *Bt-Grt* metapelite (experiment K-3) or amphibolites (experiments A-4, L-6, L-8). Granite and the surface were not in contact, the distance between them was 15–20 mm. The formation of the Gl_1 rim occurred only due to the transfer of granite components by fluid (fig. 1).

The bulk composition of rim Gl_1 in each experiment was identical to that of granitic glass Gl . This shows that equilibrium between the elements removed from the lower portion of the capsule and those redeposited in the surface rim can be achieved. In addition, in some experiments, the appearance of small, ≤ 1 microns, spherules, also representing tempered glass Gl_2 , was observed. Similar spherules were located on granite samples and along the edges of the substrate. The compositions of such spherical shapes were mostly close to $Gl - Gl_1$, but the smallest of them were distinguished by a high content of SiO_2 and K_2O . Apparently, these tiny spherules represented the most recent portions of the deposited elements from the fluid.

All the experiments were conducted in gold capsules 5 mm in diameter. The original composition of pre-synthesized glass Gl was: $\text{SiO}_2 - 79.80$, $\text{Al}_2\text{O}_3 - 12.39$, $\text{Na}_2\text{O} - 3.86$, $\text{K}_2\text{O} - 3.95$ mas. %. The original solutions consisted of H_2O or 1m HCl (0.05–0.07 ml). Oxygen volatility in the experiments was not controlled because the capsules were hard to fill. The experiments lasted 20 to 450 hours.

After the experiments the capsules were opened, hardened granitic glass was taken out from the

capsule, placed into a container, which was filled with epoxy glue. The sample was then polished and analyzed. The compositions of hardening melts were studied by local X-ray spectrographic microanalysis using a Tescan VEGA-II XMU scanning electron microscope with an INCA Energy 450 energy dispersion spectrometer. Photomicrography was done in a back-scattered electron (BSE) substance contrast regime at 8.5 to 4000-fold magnification and the working resolution of photographs of 1280x1280 pixels.

Quenching granite glass were subjected to microprobe analysis using basic standard samples for comparison: SiO_2 (Si), albite (Na), Al_2O_3 (Al), orthoclase (K) and NaCl synth. (Cl). Oxygen was calculated stoichiometrically. Petrogenetic oxides in the quenching melt totalled 89–91 rather than 100 mas. %, To see if the sums of analyses are correct, comparative analyses of anhydrous native quartz and albite were constantly performed. The sums of oxides were underestimated primarily because water was part of the melts. Because all the experiments were carried out with an excess of a fluid phase, the melt formed was water-saturated. At experimental parameters, the water content of felsic to intermediate melts was about 10 mas. % (McMillan, 1994), contributing basically to the underestimated sum of oxides in analysis. The underestimation of the relative amount of sodium due to its migration from an electron beam excitation zone was also taken into account. To avoid this, we decreased absorbed electron current to 100–180 nA (which corresponds to beam currents of 0.5–1 nA) and defocused the beam in a scanning regime at sites varying in size from 10x10 to 50x50 μm to neutralize Na scattering during analysis. Under these conditions, the effect of alkaline element migration is practically indicated by measurement errors of about 0.5–0.6 mas. % for Na_2O with a probability of 95.45%.

The results of the study of the interaction of granite with H_2O (experiments K-3, A-4) and 1m HCl (experiments L-6, L-8) are reported below.

After experiment the granite surface displays irregularly distributed cavities up to 200 μm in size. It is shown in fig. 1 that most cavities are concentrated near the granite-fluid contact. It is in such regions that the most considerable variations in oxides, which are part of granite, occur. Cavities in the central portion of granite are either much less abundant or do not occur at all.

It is clear from fig. 2a that the $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{SiO}_2)$ ratio increases from the centre of granite to the contact with the fluid (H_2O) in experiments K-3 and A-4. This indicates that Si and Al were poorly removed by solution in these experiments; hence, equilibrium was achieved only on granite margins. Equilibrium is indicated by the

$Al_2O_3/(Al_2O_3+SiO_2)$ ratio on the margin of granite Gl and on the margin of surface Gl_1 . However, more Si than Al is removed Al, as indicated by changes in the $Al_2O_3/(Al_2O_3+SiO_2)$ ratio towards granite margins in comparison with the original ratio (5 in Fig. 2a). The increase in the $Al_2O_3/(Al_2O_3+SiO_2)$ ratio to the edges of granite is explained by the fact that the Si distribution coefficient between the fluid and the melt ($D_{Si}^{fluid/melt}$) is higher than that of Al distribution coefficient between the fluid and the melt ($D_{Al}^{fluid/melt}$). Indeed, as shown in studies (Chevychev, 2013), in granitoid melts at $T = 750^\circ C$, $P = 100$ MPa in neutral-slightly acidic (H_2O) media $D_{Si}^{fluid/melt} > D_{Al}^{fluid/melt}$ by approximately an order of magnitude. Thus, the separation of H_2O from granite at a gradient of P-T conditions, for example, when granite is introduced into the upper horizons, leads to an increase in agpaitness in the marginal zones of the massif.

The $K_2O/(K_2O+Na_2O)$ ratio in the A-4 experiment along the center-edge sections of granite almost does not change and remains close to the initial one (4 end in Fig. 2b). This indicates the practical identical removal of Na and K by water from granite.

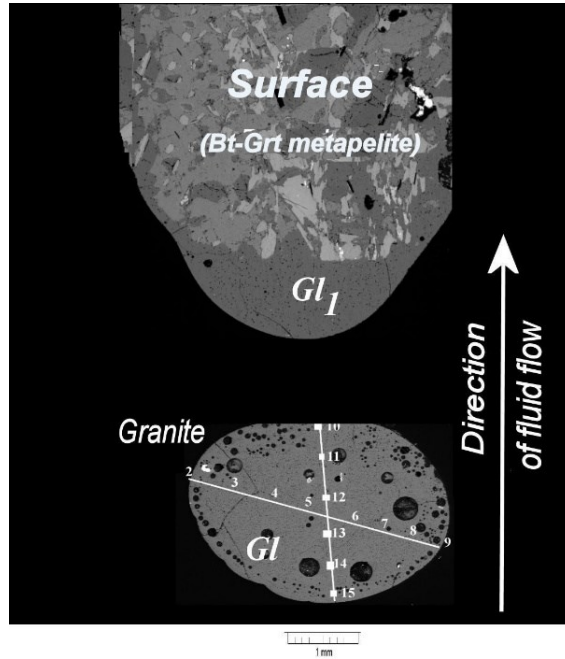


Fig. 1. Scheme of the experiments (experiment K-3).

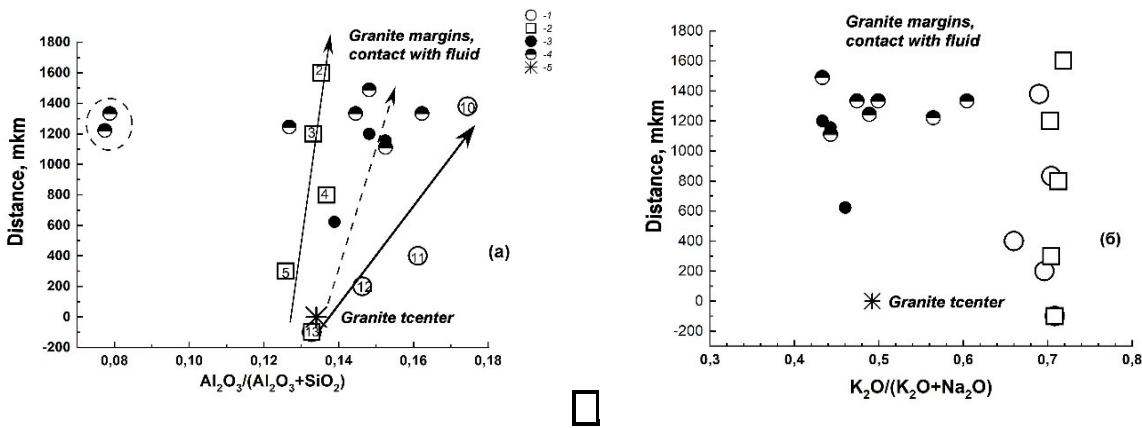


Fig. 2. $Al_2O_3/(Al_2O_3+SiO_2)$ (a) and $K_2O/(K_2O+Na_2O)$ (b) ratios (mas. %) in granite, depending on distance from the granite centre (dashed line) towards the granite margins, which are in contact with fluid. 1-2-3 – cross-sections 13-10, 13-2, 13-9 (sample K-3, Fig.1); 4 – sample A-4; 5 – original granite.

The compositions of the smallest spherical forms of Gl_2 are characterized by a decrease in the ratio of $Al_2O_3/(Al_2O_3+SiO_2)$ in granite and an increase in the ratio of $K_2O/(K_2O+Na_2O)$ (the bordered area in Fig. 2a, b). This indicates that the last portions of the fluid were enriched with silicium and potassium relative to sodium.

The $K_2O/(K_2O+Na_2O)$ ratio in experiment K-3 along the cross-sections discussed and in experiment A-4 (Fig. 2b) remains almost unchanged. In other words, in this experiment there is a more noticeable removal of Na relative to K compared to the A-4 experiment. Accordingly, the marginal zones of

granite are enriched with potassium. The higher values of this ratio in the K-3 experiment are obviously explained by the longer conditions of the experiment (72 hours) compared to the A-4 experiment (35 hours), since in long-term experiments a larger amount of solution seeped through granite and, accordingly, a more noticeable removal of elements. The predominant removal of sodium indicates that in these experiments $D_{Na}^{fluid/melt} > D_{K}^{fluid/melt}$. According to the data (Chevychev, 2013) $D_{Na}^{fluid/melt}$ there can be both larger and smaller values of $D_{K}^{fluid/melt}$.

Experiments L-8 and L-6 were carried out to study the interaction of granite with the fluid of 1m HCl. Fig. 3a shows that the $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{SiO}_2)$ ratio in experiments L-8 and L-6 remains practically unchanged from the centre of samples towards their

margins in both experiments. This indicates that equally small amounts of Al and Si are removed from granite, which indicates that $D_{\text{Si}}^{\text{fluid/melt}} \approx D_{\text{Al}}^{\text{fluid/melt}}$.

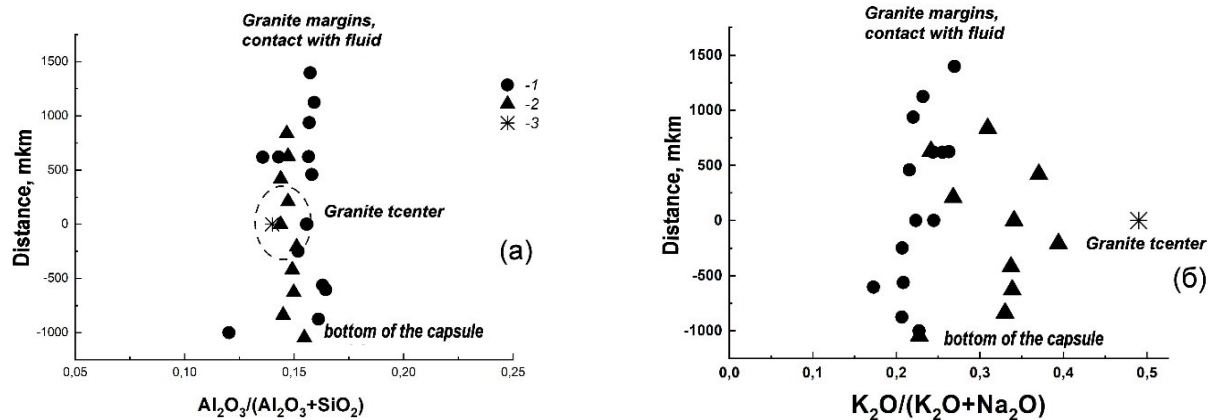


Fig. 3. $\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3+\text{SiO}_2)$ (a) and $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$ (b) ratios, (mas. %) in granite (samples L-8, L-6), depending on distance from the granite centre (dashed line) to the margins, which are in contact with fluid. 1-2 – experiments L-8 and L-6, respectively, 3 – original granite.

The $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$ also remained constant along each of the samples. It is clear from Fig. 3b that the above ratios are lower than those of the original granite, i.e. both Na and K are removed by HCl solutions upon interaction with granite. In experiment L-6, the $\text{K}_2\text{O}/(\text{K}_2\text{O}+\text{Na}_2\text{O})$ ratio is lower than that in experiment L-8. This is due to the fact that the duration of experiments L-8 and L6 was 140 and 450 hours, respectively. This is due to the fact that the duration of experiments L-8 and L6 was 140 and 450 hours, respectively. Accordingly, in longer experiments, the removal of elements is more noticeable.

Thus, as experiments have shown, water fluids separating from granite carry Si and Na to a greater extent compared to Al, K (Fig. 4). As a result, there is an increase in the alpaicity of granite melts and an increase in the potassium content relative to sodium, possibly up to the formation of marginal charnokite zones of the massif. Syngenetic metasomatites will be determined by the formation of plagiogranite or quartz veins.

In cases where the exhumation of the boundary takes place in permeable media with the participation of external HCl-containing fluids, the edge parts of the granite will shift towards the leucogranite due to the removal of alkaline elements. The predominant removal of potassium relative to sodium will lead to the formation of marginal plagiogranite zones (Fig. 4). Concomitant metasomatic changes will be expressed in the formation of potassium-containing minerals, such as potassium feldspar, biotite, muscovite.

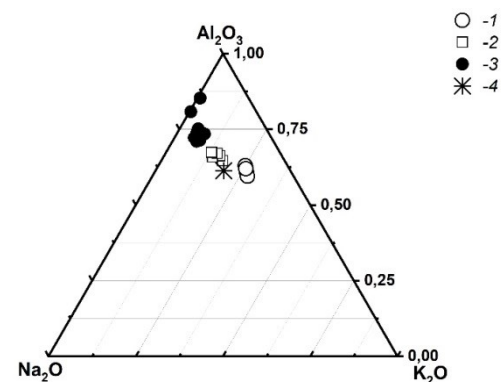


Fig. 4. $\text{Al}_2\text{O}_3\text{-Na}_2\text{O-K}_2\text{O}$ ratio in granite upon its interaction with H_2O and $\text{H}_2\text{O-HCl}$ solutions. 1-2-3 – experiments K-3, A-4 and L-8, respectively, 4 – original granite.

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Kotelnikov A.R.¹, Korzhinskaya V.S.¹, Suk N.I.¹, Kotelnikova Z.A.^{1,2}, Akhmedzhanova G.M.¹, Van K.V.¹ Experimental study of the phase relations of pyrochlore and tantalite in the system H₂O – KF ± NAF ± Qz at temperature 650 – 850°C and pressure 1 – 5 kbar. UDC: 550.8.014

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Abstract. To assess the phase relationships of minerals – concentrators of Nb, Ta – pyrochlore and tantalite in the range of TP-parameters corresponding to the final stages of magmatic and the beginning of hydrothermal processes, experiments were carried out on the interaction of these minerals with a 1 M solution of KF (NaF) with the addition of a silicate substance (SiO₂) in system. The experiments were carried out on high gas pressure vessel. The formation of new phases – tantalum-containing rippite and silicate glass enriched in fluorine, containing significant amounts of Nb, Ta – is shown. The application of the obtained experimental data to the processes of formation of tantalum-niobate ore deposits is discussed.

Keywords: experiment, phase relations, pyrochlore, tantalite, magmatic and hydrothermal processes

Pyrochlore – (Na,Ca)₂(Nb,Ti,Ta)₂O₆[F,OH] and tantalite – (Mn, Fe)(Nb,Ta)₂O₆ are ores of very important elements for industry, such as niobium and tantalum. Therefore, the study of their phase equilibria with a fluorine-containing fluid in the presence of a silicate substance is interesting for studying the genesis of tantalum-niobate deposits.

Experiments on the study of the phase relationships of pyrochlore and tantalite were carried out at a temperature of 550–850°C, a pressure of 1 and 5 kbar using the ampoule method in Pt ampoules. Pchl±Qz and Tnt±Qz mixtures were used as starting materials. In the original pyrochlore, tantalum was practically absent, while tantalite had the following composition: Mn(Nb_{0.35}Ta_{0.65})₂O₆. The experiments were carried out on UVD-10000 hydrothermal high-pressure units and a high gas pressure vessel designed by IEM RAS. The duration of the experiments was 5–20 days, depending on the TP-parameters of the experiment. The products of the experiments were analyzed by various methods: solids – by microanalyzer, solutions after the experiments – by ICP-MS and AAS methods. The results of the experiments are presented in Tables 1 and 2.

Based on the experimental results, the following conclusions can be done about the phase equilibrium of pyrochlore.

1. Pyrochlore is stable in 1M KF solutions over the entire temperature range (550 ÷ 850°C) and pressures of our experiments.

2. The composition of pyrochlore (Na_{0.900}Ca_{1.038}K_{0.014})_{1.952}Nb_{1.999}O₆[F_{0.952}(OH)_{0.233}]_{1.185} does not change in experiments in the presence of 1M KF at a temperature of 550–650°C. However, at temperatures of 750 and 850°C, ion exchange with the solution begins and the content of K₂O in pyrochlore reaches 2–3.5 wt%.

3. At P=1 kbar in the experiments in the presence of quartz at T ≥ 650°C, silicate glass was found in the products of the experiments. The appearance of the glassy phase is accompanied by a decrease in the pH of the solution due to the distribution of alkaline elements in the silicate melt relative to the fluid. This is clearly observed at a pressure of 1 kbar. With an increase in pressure, a distinct decrease in pH values with the appearance of a glassy phase is not observed.

4. The content of niobium in silicate glasses is from 3 to 8 wt% (Nb₂O₅). At P=5 kbar, the niobium concentration in glass increases (from 3.3 to 8.3 wt.% Nb₂O₅) with increasing temperature, and at P=1 kbar, an inverse relationship is observed (Fig. 1).

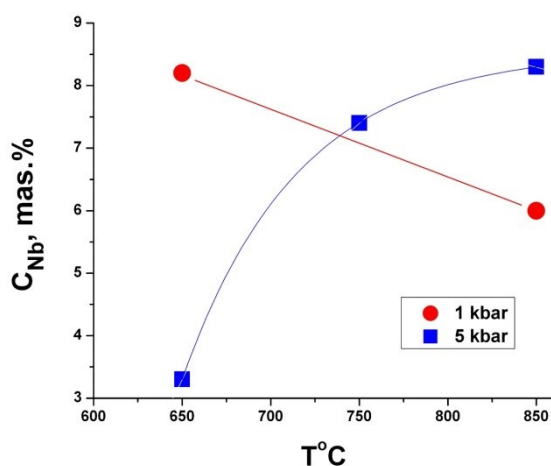


Fig. 1. Nb concentration in silicate melts in equilibrium with pyrochlore at 650–850°C and pressures of 1 and 5 kbar.

5. The rippite phase (KNbSi₂O₇) at P=1 kbar is formed at 850°C. With an increase in pressure up to 5 kbar, rippite crystals are found even at T=650°C. Thus, rippite can be considered an indicator of increased pressure during mineralogenesis.

Based on experimental data on the stability of tantalite in fluoride solutions at high parameters, the following conclusions can be drawn:

1. Tantalite is stable in 1M KF(NaF) solutions over the entire temperature and pressure range of our experiments. At P=1 kbar in the experiments in the presence of quartz at $T \geq 650^\circ\text{C}$, silicate glass was found in the products of the experiments. Glasses are quite heterogeneous in composition. The rippite phase (KNbSi_2O_7) at P=1 kbar is formed only at 650°C . In experiments at $\geq 650^\circ\text{C}$, a pyrochlore phase

is formed. At a pressure of 5 kbar, rippite is synthesized in experiments in the presence of quartz at temperatures from 550 to 750°C . At 850°C , rippite formation is not observed.

2. Rippite in experiments with tantalite, contains a significant amount of tantalum (up to 65-70 mol.% of the KTaSi_2O_7 mineral).

3. At 750°C and P=1 kbar, hieratite (K_2SiF_6) was found in the experimental products.

Table 1. Phase relations in the Pchl+Qz system in the presence of 1M KF (NaF) fluid at a temperature of $550\text{--}850^\circ\text{C}$ and a pressure of 1 and 5 kbar.

№ samples	Initial weight	Solution	T°C	pH b/e ¹⁾	pH a/e ¹⁾	Products	Nb ²⁾ gl.%	Ta ²⁾ gl.%
P = 1 kbar								
Px-1	Pchl + Qz ³⁾	1M KF	550	7.3	8.2	Pchl + Qz	-	-
Px-2	Pchl + Qz	1M NaF	550	6.7	7.5	Pchl + Qz	-	-
Px-3	Pchl	1M KF	550	7.3	-	Pchl	-	-
Px-4	Pchl + Qz	1M KF	650	7.4	6.9	Pchl + Qz + gl	8.2	-
Px-5	Pchl + Qz	1M KF	850	7.3	1.9	Pchl + gl + Rip	-	-
Px-6	Pchl + Qz + rpan	1M KF	850	7.3	6.0	Pchl + gl	6.0	-
P = 5 kbar								
Px277-1	Pchl	1M KF	650	7.3	7.5	Pchl + Rip	-	-
Px277-2	Pchl + Qz	1M KF	650	7.3	8.2	Pchl + Qz + Rip + gl	3.3	-
Px276-1	Pchl	1M KF	750	7.3	7.5	Pchl	-	-
Px276-2	Pchl + Qz	1M KF	750	7.3	6.6	Pchl + Qz + Rip + gl	7.4	-
Px278-1	Pchl	1M KF	850	7.3	10	Pchl	-	-
Px278-2	Pchl + Qz	1M KF	850	7.3	7.9	Pchl + gl1 + gl2	8.3	-
							3.6	

1) b/e – before experiment, a/e – after experiment; 2) content of Nb_2O_5 (Ta_2O_5) in glass (wt.%);

3) gl – glass, Pchl – pyrochlore, Qz – quartz, Rip – rippite.

Table 2. Phase relationships of tantalite in 1M KF (NaF) in the presence and absence of quartz (P=1.5 kbar).

№ samples	Initial weight	Solution	T°C	pH b/e ¹⁾	pH a/e ¹⁾	Products	Nb ²⁾ gl.%	Ta ²⁾ gl.%
P = 1 kbar								
KT104-1	Tnt ³⁾	1M KF	550	7.3	10.5	Tnt	-	-
KT104-2	Tnt + Qz	1M KF	550	7.3	8.5	Tnt + Qz	-	-
KT105-1	Tnt	1M NaF	550	6.3	-	Tnt	-	-
KT105-2	Tnt + Qz	1M NaF	550	6.3	-	Tnt + Qz	-	-
KT109-1	Tnt	1M KF	650	7.3	10.3	Tnt	-	-
KT109-2	Tnt + Qz	1M KF	650	7.3	7.0	Tnt + Pchl + gl + Rip	1.3	4.7
KT111-1	Tnt	1M NaF	650	6.3	8.5	Tnt	-	-
KT111-2	Tnt + Qz	1M NaF	650	6.3	7.0	Tnt + Pchl + gl	-	-
263-2	Tnt + Qz	1M KF	750	7.3	6.0	Tnt + Qz + gl1 + gl2 + hier	2.6	5.8
265-1	Tnt	1M NaF	750	6.3	-	Tnt	-	-
265-2	Tnt + Qz	1M NaF	750			Tnt + Qz + gl	-	-
KT107-1	Tnt	1M KF	850	7.3	7.0	Tnt	-	-
KT108-2	Tnt + Qz + gran	1M KF	850	7.3	5.5	Tnt + Mcl + gl	3.2	6.4
P = 5 kbar								
KT114-1	Tnt	1M KF	550	-	-	Tnt + Pchl + Cry + gl	0.3	1.2
KT114-2	Tnt + Qz	1M KF	550	-	-	Tnt + Rip + gl	0.3	1.4
KT113-1	Tnt	1M KF	650	7.3	9.5	Tnt + Pchl	-	-
KT113-2	Tnt + Qz	1M KF	650	7.3	8.0	Tnt + Rip + gl	1.0	1.5
KT112-1	Tnt	1M KF	750	7.3	9.5	Tnt + Pchl	-	-

No samples	Initial weight	Solution	T°C	pH b/e ¹⁾	pH a/e ¹⁾	Products	Nb ²⁾ gl.%	Ta ²⁾ gl.%
KT112-2	Tnt+Qz	1M KF	750	7.3	6.0	Tnt+Rip+gl1+gl2	1.0	5.3
KT115-1	Tnt	1M KF	850	-	-	Tnt+Pchl+gl+Cry	8.6	5.7
KT115-2	Tnt+Qz	1M KF	850	-	-	Tnt+gl1+gl2	3.4	10.4

1) b/e – before experiment, a/e – after experiment; 2) content of Nb₂O₅ (Ta₂O₅) in glass (wt.%);

3) – minerals: Cry – cryolite, gl – glass, Mcl – microlite, Pchl – pyrochlore, Qz – quartz, Rip – rippite, Tnt – tantalite, hier – hieratite, gran – granite.

4. The concentration of niobium in glasses obtained in experiments on the stability of the Tnt + Qz ± granite association (in the presence of 1 M KF) at a pressure of 1 kbar decreases with decreasing temperature from 3.2 wt.% Nb₂O₅ (850°C) to 1.3 wt.% Nb₂O₅ (650°C). A similar dependence of the solubility of niobium in a silicate melt is also observed for experiments at 5 kbar (Fig. 2): niobium concentration decreases from ~6.9 wt.% Nb₂O₅ (850°C) to 0.3 wt.% Nb₂O₅ (550°C).

5. The content of tantalum in silicate melts in equilibrium with tantalite (in the presence of quartz (or granite)) is shown in Fig. 3. It can be seen that the

concentration of tantalum in silicate melts decreases with decreasing temperature: at a pressure of 1 kbar, from 6.4 wt.% Ta₂O₅ (850°C) to 4.7 wt.% Ta₂O₅ (650°C); at a pressure of 5 kbar, from 5.6 wt.% Ta₂O₅ (850°C) to 1.4 wt.% Ta₂O₅ (550°C). In one experiment (KT-115-2), a Ta₂O₅ concentration of up to 10.4 wt % is observed.

6. The concentration of fluorine in silicate melts at a pressure of 5 kbar is practically independent of temperature and amounts to ~0.9 wt.%; when the pressure is reduced to 1 kbar, the fluorine content increases to ~4.8 wt.%.

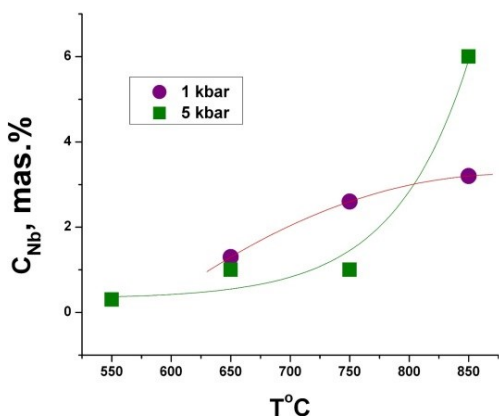


Fig. 2. Nb concentration in silicate melts in equilibrium with tantalite at 550-850°C and pressures of 1 and 5 kbar.

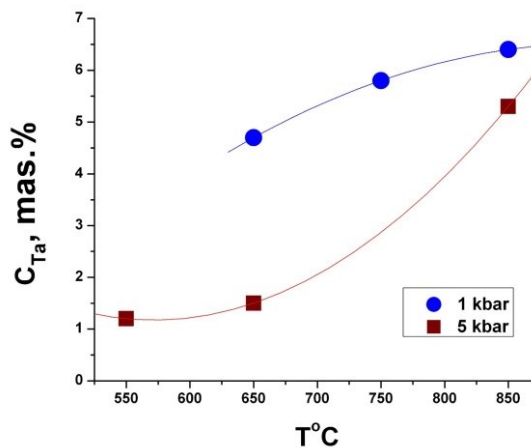


Fig. 3. Ta concentration in silicate melts in equilibrium with tantalite at 650-850 °C and pressures of 1 and 5 kbar.

In general, it follows from the experimental results that the resulting silicate melts can serve as a phase – a concentrator of niobium and tantalum. Moreover, the content of tantalum in glasses generally increases with a decrease in pressure and an increase in the concentration of fluorine. Thus, under the conditions of crystallization of residual melts of lithium-fluorine granites, with a decrease in pressure and the presence of a fluid containing potassium and sodium fluorides, residual alkaline silicate melts containing water and fluorine will form. They can serve as a phase – concentrator of tantalum, which, when crystallized, will give rocks similar to ore apogranites.

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