Vestnik Otdelenia nauk o Zemle RAN, VOL. 3, NZ6043, doi:10.2205/2011NZ000173, 2011

Comparison of data on the solubility of columbite, pyrochlore and oxides of Ta and Nb in alkaline aqueous solutions at T=550°C, P=1000 bar (Co-CoO buffer)

V. S. Korzhinskaya, N. P. Kotova
Institute of Experimental Mineralogy RAS, Chernogolovka
vkor@iem.ac.ru, fax: 8 (496 52) 44425, phone: 8 (496) 5225861
kotova@iem.ac.ru, fax: 8 (496 52) 44425, phone: 8 (496) 5225861

Key words: experiment, pyrochlore, columbite,Ta and Nb oxides, solubility, sodium alkaline solutions

Citation: Korzhinskaya, V. S., N. P. Kotova (2011), Comparison of data on the solubility of columbite, pyrochlore and oxides of Ta and Nb in alkaline aqueous solutions at T=550°C, P=1000 bar (Co-CoO buffer), *Vestn. Otd. nauk Zemle, 3*, NZ6043, doi:10.2205/2011NZ000173.

The data on behavior of Ta and Nb in alkaline aqueous solutions available in literature are not enough to understand the role of hydrothermal-metasomatic processes in genesis of Ta-Nb deposits. So we carry out systematic experimental studies on the solubility of tantalo-niobates mineral phases of complex composition (columbite, pyrochlore etc.) stable under natural conditions as well as simple oxides of Ta and Nb [*Korzhinskaya and Zaraisky,* 2009*; Kotova and Zaraisky,* 2009].

We studied concentration dependence of solubility of natural columbite, pyrochlore and Ta_2O_5 and Nb_2O_5 in carbonate (Na_2CO_3) and alkaline (NaOH) solutions with concentrations from 0.01 to 2 m at T = 550° C, P = 1000 bar and under Co-CoO oxidizing conditions. The performed runs allow us to compare solubilities of natural minerals with niobium and tantalum oxides and thus, to expend the investigating the behavior of these metals in alkaline solutions what is actual for the deposits of Ta and Nb, genetically connected with alkaline granites.

According to our experimental data over all investigated of concentrations in Na_2CO_3 and NaOH solutions columbite, pyrochlore and simple Ta and Nb oxides dissolve incongruently with the formation of new phases. At columbite dissolution in Na_2CO_3 solutions sodium niobate (structural type of perovskite – ABO_3, where A is Na; B is Nb, there is a bit of Ta, Mn and Fe) is formed as a new phase. At pyrochlore dissolution in sodium carbonate solutions on the initial crystal new little crystals of a cubic shape of about 30 mkm in size precipitated from the solution are formed. They represent pyrochlores precipitated from the solution but practically purely sodium ones of the following composition: Na_2O-18%; CaO-3,12%; Nb_2O_5-71,17%; TiO_2-1,17%; SrO-2,87%; FeO-0,60%; MgO-0,85% as well as other phases - $CaNb_2O_6$, CaF_2, NaF. In NaOH solutions columbite dissolves with the formation of microlyte, but the presence of the impurities of phosphorus, calcium and silicon in natural columbite is favourable to form tephroite (Mn_2SiO4) with the impurity of Ca and partially apathite - $Ca_5(PO_4)_3(OH)$. Pyrochlore dissolves in NaOH solutions with the formation of Na niobate $NaNbO_3$, needle-like crystals of a complex composition (Na_2O-1,58%; CaO-43,97%; SrO-1,39%; Nb_2O_5-21,08%; Ta_2O_5-3,15%; SiO_2-25,82%; F-2,52%; MgO-0,24%) and crystals $CaMgSiO_4$. In all investigated alkaline and carbonate solutions oxides of Ta and Nb dissolve with the formation of new phases: $Na_2Ta_4O_{11}$, $Na_2Nb_4O_{11}$, $NaTaO_3$ и $NaNbO_3$.

The results of the runs are shown in Figs.1-4. During the runs we determined that Nb oxide solubility does not practically change with the rise of Na_2CO_3 concentration and it is within the limits of 10^{-6} – 10^{-5}m (Fig. 1). For columbite and pyrochlore concentration dependence of solubility has minimum of 0.1m Na_2CO_3 and is $n*10^{-7.5}$m for columbite and $n*10^{-6.5}$m for pyrochlore. At the increase of Na_2CO_3 concentration the content of Nb grows and reaches the value 10-5m for columbite and 10-4m for pyrochlore what is an order of magnitude higher than columbite solubility. A comparison of data on solubility of pyrochlore, columbite and Nb oxide has shown that in the region of low concentrations of Na_2CO_3 (0.01 and 0.1m) the content of Nb in the solution is maximum for Nb_2O_5, but in the region of high concentrations Na_2CO_3 (1 and 2m) it is maximum for pyrochlore.

It was found that the Ta_2O_5 solubility isotherms have a negative trend in all studied carbonate solutions (Fig.2). The tantalum content is in the limits $n*10^{-5}$m for 0.1m Na_2CO_3 and $n*10^{-7}$m for 1m $_{Na2CO3.}$ For columbite and pyrochlore concentration dependence of solubility has minimum of 0.1m Na_2CO_3 and is $n*10^{-7.5}$m for columbite and $n*10^{-6.5}$m for pyrochlore. The tantalum content in the solution Na_2CO_3 is also an order of magnitude higher for pyrochlore than that of columbite. The

content of Ta in carbonate solution has the highest value for tantalum oxide up to 1m Na_2CO_3. At greater concentrations of Na_2CO_3 the tantalum content remains the same for all three minerals.

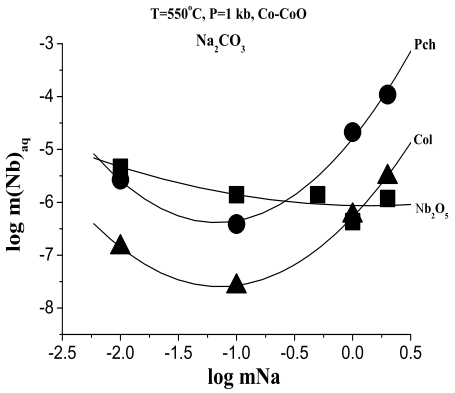

Fig. 1 Concentration dependence of Nb content at solubility of pyrochlore, columbite and Nb_2O_5 in Na_2CO_3 solutions at T=550°C, P=1000 bar (buffer Co-CoO).

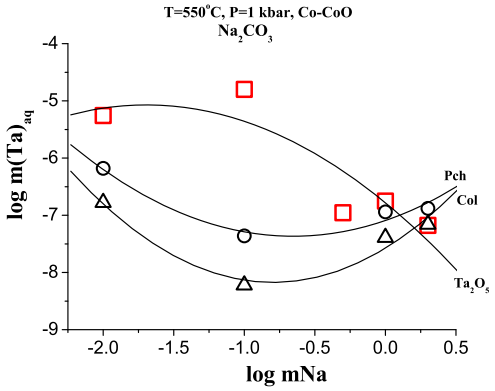

Fig. 2 Concentration dependence of Ta content at solubility of pyrochlore, columbite and Ta_2O_5 in Na_2CO_3 solutions at T=550°C, P=1000 bar (buffer Co-CoO).

The data represented in Fig.3 show that solubility of Nb oxide in the region of low concentrations NaOH (to 0.1m) is $n*10^{-4}$m. At higher concentrations of NaOH the niobium content in the solution for Nb_2O_5 drops sharply down to the value of magnitude 10^{-7}m. For pyrochlore the niobium content in the solution with increasing of NaOH concentration decreases: in 0.01m solution Nb concentration has a maximum value and is $6.6*10^{-4}$m, but in 2m solution NaOH it is $4.37*10^{-7}$m. For columbite the niobium content in the solution with increasing of NaOH concentration remains practically the same and for 0.01m NaOH it is $7.21*10^{-7}$ m, but for 1m NaOH it is $1.51*10^{-6}$m.

It was found (Fig. 4) that concentration dependence of Ta_2O_3 solubility is similar to that in the Na_2CO_3 solutions. Tantalum content is within the limits $n*10^{-5}$m for 0.01m NaOH and $n*10^{-8}$m for 2m NaOH solution. The content of Ta in NaOH solutions at pyrochlore solubility is low, does not pratically depend on NaOH concentration and is at the level of the value $n*10^{-8}$m, but for columbite it is lower than the detection limit ($\leq 10^{-8}$m).

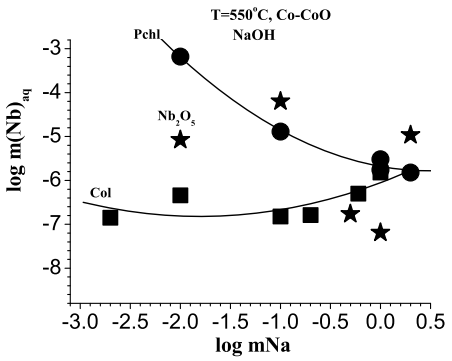

Fig. 3 Concentration dependence of Nb content at solubility of pyrochlore, columbite and Nb_2O_5 in NaOH solutions at T=550°C, P=1000 bar (buffer Co-CoO).

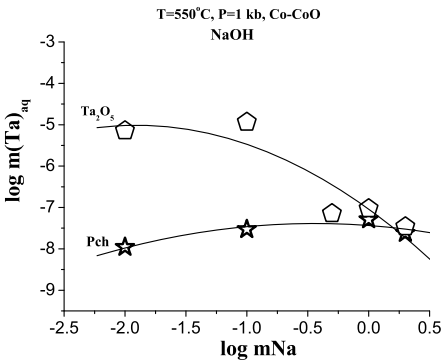

Fig. 4 Concentration dependence of Ta content at solubility of pyrochlore and Ta_2O_5 in NaOH solutions at T=550°C, P=1000 bar (buffer Co-CoO).

From the obtained experimental data on solubility of natural columbite, pyrochlore and simple Nb and Ta oxides in alkaline aqueous solutions at T = 550°C, P = 1000 bar we can conclude that pyrochlore dissolves much better than columbite in both carbonate and alkaline sodium solutions. Nb solubility in the whole studied range of concentrations is higher (approximately by an order of one and

a half) as compared to Ta solubility. Thus, the obtained data allow us to consider that Nb is more capable to form complexes in alkaline solutions, whereas Ta complex formation is mainly supressed. It is principally important to understand the genesis of rare metal deposits of Nb and Ta connected with alkaline granites, sienites and carbonatites for which pyrochlore is the main ore mineral.

Financial support by RFBR, projects 08-05-00835, 10-05-00292

References

Korzhinskaya V. S., G. P Zaraisky, (2009), Experimental study of concentration dependence of pyrochlore and columbite solubility in NaOH solutions at T = 550°C P = 1000 bar, Vestn. Otd. Nauk Zemle RAN, № 1(27), 2009, Moscow, IPE RAS.
URL:http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/hydroterm-15.pdf.
http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/hydroterm-15e.pdf

Kotova N. P., G. P. Zaraisky, (2009), Experimental study of concentration dependence of Ta_2O_5 solubility in the alkaline solutions at T=550°C, P=1000 bar and low oxygen fugacity (Co-CoO buffer), Vestn. Otd. Nauk Zemle RAN, № 1(27), 2009, Moscow. IPE RAS.
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/hydroterm-21e.pdf