Shapovalov Yu.B. Distribution of petro- and orogenic metals between granite and halide melt phases.

A wide scattering of experimental data on the distribution of ore metals between phases in magmatic and postmagmatic systems is mainly due to the different methods and experimental parameters. The most reliable values of distribution coefficients Kp = concentration of Me in a solution/ concentration of Me in a melt fall into the region from n•0.01 to n 1.0 (Malinin, Khitarov, 1984), i.e. ore metals for the most part remain in the melts and only partly migrate into the equilibrium with them solution. Therefore, simple separation of hydrothermal solutions from crystallizing magmas is not sufficient for ore formation. However, the process of crystallization is accompanied by the accumulation of ore metals in the residual melts and further scattering in ore forming and accessory minerals. For the mineralization to develop liquid layering of residual melts is necessary, which can be realized in closed magmatic systems providing accumulation of salt components in the course of magmas crystallization.

The experiments were run on the high gas pressure apparatuses with inner heating in sealed gold capsules at T=960°C, P=1 kbar. Starting material was normal biotite granite of the following composition (at% metals): Si=69.83, Al=15.67, Fe=1.55, Mn=0.05, Mg=0.79, Ca=1.74, Na=5.10 (P_{H2O}=5 kbar). The experiments yielded water-enriched glass. Oxides of ore metals were added to the glass and the obtained mixture was used in experiments in combination with fluorides of various compositions (from 20 to 30 wt% of the total weight of the 100-150 mg sample). The duration of experiments was from 72 to 240 hours. After the quick quenching silicate glasses in association with salt phase separated as drop-like thin crystalline isolations in silicate matrix with silicate glass prevailing in the upper part of the column.

The major task was the investigation of interphase distribution of ore metals in granite-fluoride systems. For this purpose the distribution coefficients of petrogenic elements were preliminarily determined. The content of the latters in a silicate phase decreases in the following sequence: Si, Al, K, Na, Fe, whereas in the salt phase the sequence is as follows: Na, Ca, Mg, Si, Al. Average values of distribution coefficients of the major granitic elements between fluoride and silicate phases are: Si (0.06), Al (0.15), K (0.27), Fe (0.27) i.e. they are preferentially distributed in the silicate glass whereas Mg (341), Ca (192), and Na (3.18) - in favor of fluoride (Fig.1).

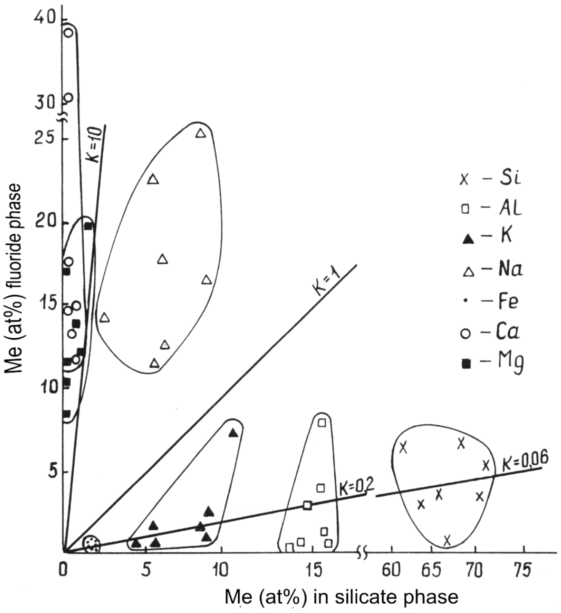

Fig.1.

The experiments with chlorides where elements distribution between phases is somewhat different from that in fluoride systems were carried out for comparison. Distribution coefficients for Si (0.09) and Al (0.27) are close, for Mg (6.65) and Ca (1.84) are also lower than unit and for Na (11.21) – higher than unit. The distribution of K (80) and Fe (1.06) is quite different. Thus, in the chloride system the distribution coefficients of Si and Al only are lower than unit, the other major granite metals are preferentially distributed in chlorides.

Phase distribution of tungsten, tantalum, niobium and tin in fluoride granite systems has been studied. While studying the systems with the additions of W, Sn, Nb and those with W, Sn, Ta we found out the systems with tungsten to differ essentially from those with tantalum, niobium and tin. The systems with tungsten, tin, and niobium are subdivided into sodium-potassium and sodium ones. The salt component of the sodium-potassium systems was hieratite (K_2SiFe_6). Its excess melt turned to be extremely effective extracting agent of tungsten whereas tin and niobium showed their indifference to the above extractant and after its separation remained in silicate phases (table 1). After an additional introduction of lithium fluoride into the system the extraction of tungsten by the salt melt phase increased whereas tin and niobium were very slightly effected by this additional component. Their concentration in the salt and silicate phases remained the same as in the starting composition. The main regularity of this layering is high concentration of tungsten in salt phases especially in phase V, which has the following composition of metals (without lithium) (at%): Al=12.26; Fe=1.02; Mg=7.02; Ca=15.51; Na=24.61; K=24.43; W=15.13. whereas the concentration of silicon, tin and niobium is practically equal to zero.

The concentration of tungsten at the salt extraction of this type becomes comparable with the concentration of petrogenic metals.

Table 1. Starting (I) and average compositions (at% of metals) of silicate (II) and salt (III-IV) phases of fluoride granite systems with different salt additions.

Comp.		*Si*	*Al*	*Fe*	*Mg*	*Ca*	*Na*	*K*	*Ta*	*Nb*	*Sn*	*W*
K_2SiF_6	I	57.55	11.33	1.15	0.76	1.27	4.33	21.07		0.64	0.95	0.95
	II	63.09	11.68	1.37	0.48	0.12	3.38	17.65		0.51	1.18	0.54
	III	1.42	11.08	0.44	8.27	17.24	21.16	33.59		0.37	0.53	5.90
	IV	0.59	14.18	0.25	6.29	14.68	23.39	36.83		0.54	0.31	2.94
	V	13.26	10.55	0.77	4.13	10.93	20.05	30.46		0.57	0.74	8.54
LiF	I	66.11	15.33	1.55	1.07	1.71	5.89	5.03		0.81	1.25	1.25
	II	70.28	15.72	1.75	0.16	0.27	5.24	5.45		0.67	0.42	0.04
	III	3.69	7.77	0.32	16.82	30.51	22.60	1.36		0.08	0.06	16.79
	IV	0.90	17.86	0,00	18.40	11.89	40.95	3.19		0.01	0.14	6.66
	V	2.91	3.76	0.29	9.03	38.23	14.56	0.90		0.47	0.16	29.69
LiF	I	63.18	14.64	1.49	1.04	1.62	5.64	4.80	2.53		2.53	2.53
	II	70.36	15.36	1.80	0.02	0.10	5.36	4.81	1.55		0.48	0.16
	III	14.36	16.56	0.82	9.61	11.39	25.48	2.15	0.74		0.15	18.74
	IV	13.86	15.41	0.92	16.33	6.12	33.56	2.75	1.04		0.18	9.83
	V	10.56	6.22	1.64	7.06	25.78	13.31	0.84	0.77		0.16	33.66
LiF+Na	I	49.82	11.52	1.17	0.80	1.31	13.13	16.34	1.97		1.97	1.97
+KF	II	56.40	14.10	1.74	0.11	0.10	6.50	17.56	1.59		1.58	0.32
	III	13.47	12.44	0.68	2.18	11.97	23.01	23,00	0.02		0.62	12.61
	IV	1.14	8.08	1.12	6.14	24.6	28.28	24.27	0.32		0,00	6.05
	V	14.09	10.66	1.52	0.04	5.58	21.65	19.80	0.76		0.08	25.82

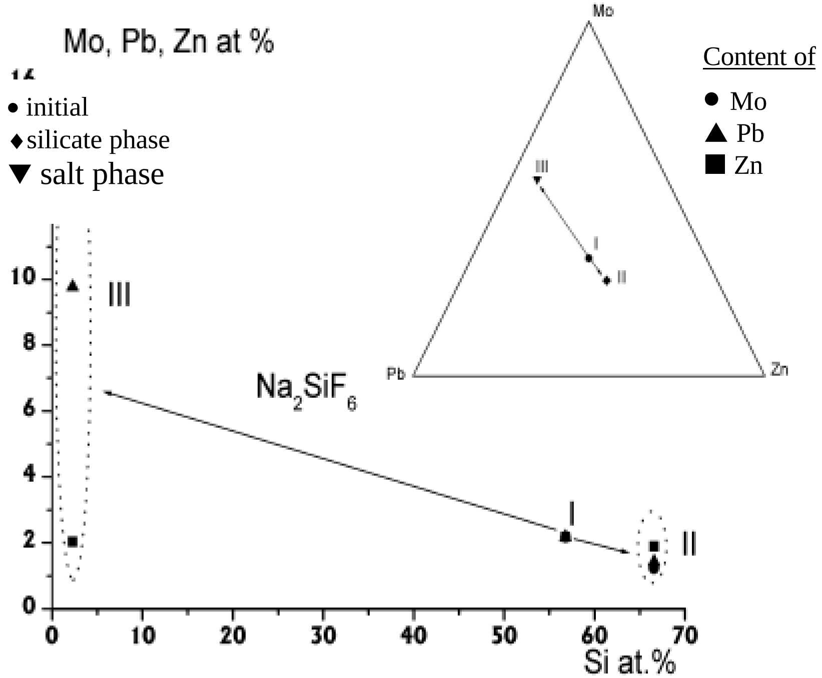

Fig.2.

This fact clearly demonstrates the efficiency of the method which may play an important role in the technology of tungsten extraction from ores and ore wastes.

Lithium and sodium aluminate when added to hieratite fluoride practically do not change the relationships in the fluoride granite system: the effective extraction of tungsten is observed, tin and niobium being indifferent to this process. Silicon almost utterly remains in the silicate melt, sodium, calcium, magnesium are effectively extracted by the salt phases.

The same regularities are observed in fluoride systems (without an addition of potassium fluorides to granite): highly effective extraction of tungsten, whereas niobium and tin at the separation of the salt melt do not concentrate in fluoride melts but remain in the silicate phase. The diagrams given in fig.2 and table 1 elucidate the characteristic phase ratios for the system granite + lithium fluoride.

When lithium in granite systems is substituted by sodium tungsten extraction is essentially reduced. Its content decreases from 15-35 to 6-10 at% of metals (without lithium). The extraction of niobium and tin, herewith, does not increase, because they remain in the silicate melt and do not transfer into the salt phases. The similar ratios have been obtained for some other systems (with additions of LiF +Na_2SiF_6 etc.).

Let us consider fluoride granite systems containing tantalum instead of niobium. As an example presented in table 1 are the results of the study on tantalum-bearing systems of lithium fluoride and with a complex fluoride composition (Li, Na, K). An effective salt extraction of tungsten is evident whereas tin and tantalum are not practically involved in this process and their content in salt phases is decimal and centesimal fractions of an at% of metals. Calcium, sodium, and magnesium are effectively extracted. Not entering the salt phases tantalum and tin remain in the silicate phase which is highly exhausted in tungsten. The content of the latter in the salt phases varies within a wide range (2-40 at%).

Analogous results have been obtained in experiments with niobium, whose behavior in the above processes of phase partitioning resembles that of tantalum.

Using chlorides of different composition: NaCl, KCl, LiCl, $AlCl_3$, NH_4Cl the distribution of tungsten, tin, and tantalum in the systems silicate melt – chloride melt has been studied at T=960°C and P=1 kbar. The compositions of the melt phases are given in table 1.

Table 2. Compositions of the melt phases in silicate-chloride systems (at%) at 850°C and P=1 kbar (I- silicate phases, II- chloride phase).

1		Si	Al	Fe	Mg	Ca	Na	K	Sn	Ta	W
1	I	70.38	20.62	0.00	0.00	0.22	0.84	6.91	0.00	0.53	0.50
	II	12.12	22.71	0.80	0.96	1.83	0.00	8.67	5.54	0.07	47.30
2	I	78.60	15.80	0.41	0.09	0.50	2.77	0.87	0.67	0.23	0.06
	II	17.43	37.92	0.52	2.46	2.01	19.01	2.92	4.63	0.08	13.02
3	I	80.40	14.89	0.26	0.09	0.06	0.70	0.67	0.70	1.82	0.41
	II	11.58	19.26	0.76	2.63	0.60	7.84	9.77	5.33	0.19	42.04
4	I	68.20	29.67	0.37	0.17	0.00	0.49	0.32	0.21	0.40	0.17
	II	30.80	31.81	2.13	14.97	0.54	0.77	0.57	1.05	1.90	15.46

Tungsten and tin are seen to concentrate in the chloride melt whereas tantalum for the most part remains in the silicate phase. Comparing these results with the results obtained on fluoride extraction we can state with assurance that tungsten is intensively extracted by fluoride and chloride melts alike, tin concentrates in the chloride phase and is indifferent to the fluoride one, and tantalum under the above experimental conditions cannot be extracted by both phases.

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