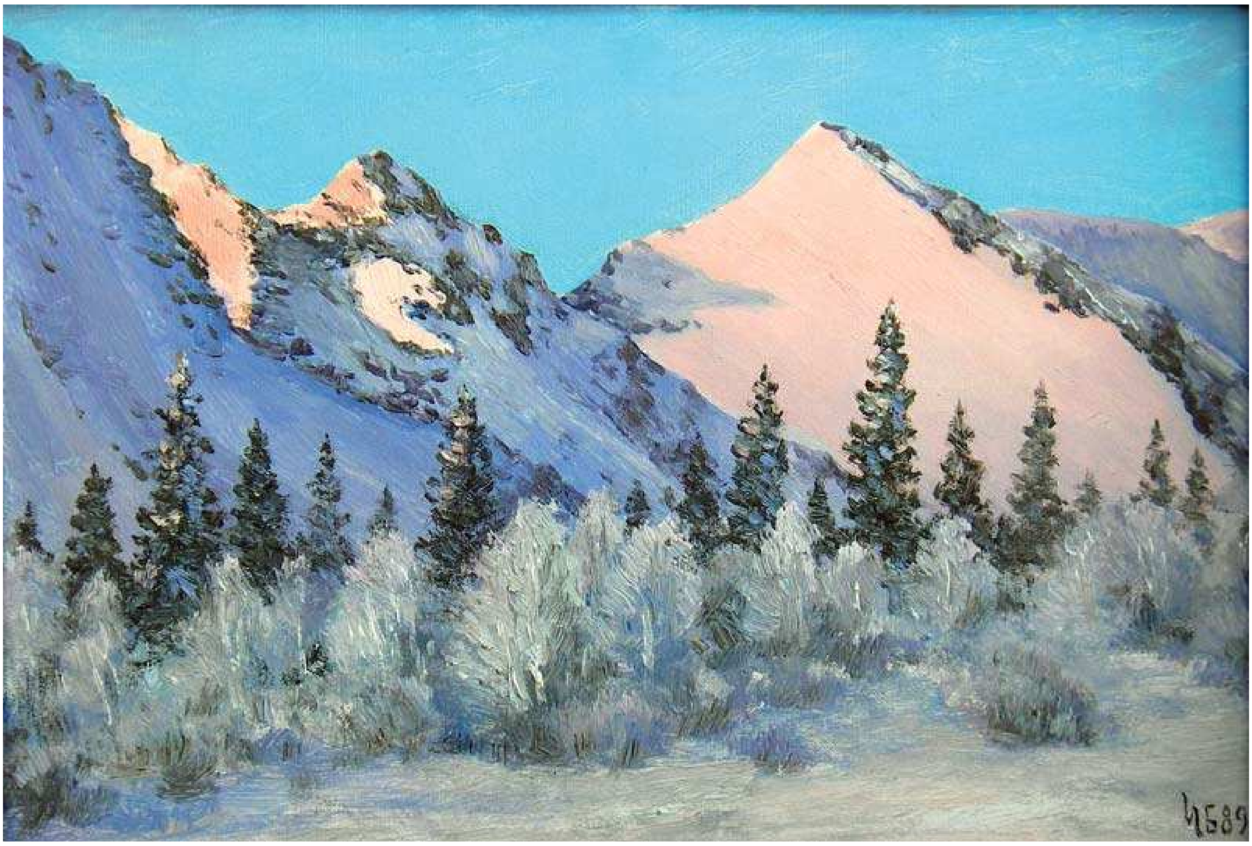
Alkaline Magmatism of the Earth and related strategic metal deposits



Proceedings of XXXII International Conference

7-14 August 2015

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The present volume was prepared for the XXXII international conference Alkaline Magmatism of the Earth and Related Strategic Metal Deposits. It contains short papers representing the frontier of geological, geochemical, petrologic, mineralogical and isotopic research on alkaline rocks, carbonatites and their associated deposits of critical (strategic) metals. The contributions assembled here address key problems of igneous petrology and metallogeny, including lithospheric and sublitospheric mantle processes, evolution of magmas from their mantle sources to highly differentiated systems, and behavior of critical metals in igneous and supergene environments. Some of the contributions discuss current issues facing critical metal exploration and extraction technology.

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The cover picture of "Pink mountains" (Khibiny, oil on canvas, 1989) was painted by artist Belkov I.V.

Belkov Igor Vladimirovich was doctor of geology-mineralogy sciences, director of the Geological Institute KFAN the USSR from 1961 to 1985. He was greatest scientist in the field of geology, geochronology, petrology, mineralogy and metallogeny of granites and genesis of metamorphic rocks. Together with Batyeva I. D., he discovered the Sakharyok and Kulyok alkaline massifs in the Kola Peninsula.

Lumpkin G.R., Smith K.L., Blackford M.G., Gieré R. and Williams C.T. The Crystalline-Amorphous Transformation in Natural Zirconolite: Evidence for Long-Term Annealing. In: McKinley, I. G – McCombie, C. (eds.): MRS Proceedings. (1997b), 506, *215-222.*

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Specific features of eudialyte decomposition in oxalic acid

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One of the main aspects of a possible practical use of eudialyte today is extracting of Zr, Hf, *REE* (especially *HREE*) and U. Numerous attempts to solve this problem using full decomposition of eudialyte by strong inorganic acids were not successful in technological aspect: silicon converts into solution forming a filterable gel which strongly hampers any processes of isolation and purification of valuable components.

We have studied the processes and products of eudialyte decomposition in dilute oxalic acid, $H_2C_2O_4$, and for comparison in HCl at t <100°C. For the experiments, two eudialyte varieties were used: (1) from rischorritic pegmatite, the Oleniy Ruchey apatite deposit (sample OLE-9), Khibiny, and (2) from naujaitic pegmatite, Mt. Alluaiv (sample UMB-2), Lovozero (both Kola peninsula, Russia). The Lovozero eudialyte is enriched with *REE* and Zr and has, according to our data, more defective crystal structure in comparison with the Khibiny sample.

Experiments with 1 and 3% $H_2C_2O_4$ gave similar results for the Khibiny eudialyte: it alters only from the surface to opal-like phase with overgrowing crystals (Fig. 1). Using the EMPA and IR spectroscopy data, we undoubtedly identified these crystals as Ca-Zr oxalates. In experiments with 7% $H_2C_2O_4$ the Khibiny eudialyte completely decomposes with the formation of a gel-like opal phase closely associated with crystalline oxalates of Ca and Zr with admixed *REE*.

The Lovozero eudialyte fully decomposes in 3, 5 and 7% $H_2C_2O_4$. On the surface of the formed opal phase, crystals (up to 40 µm) of both Ca-Zr and *REE* oxalates (Fig. 2) are abundant. Two types of *REE* oxalates occur: (1) with essentially yttrium cationic composition (enriched also with *HREE*) and (2) *LREE*–rich.

Thus, after the decomposition of eudialyte in $H_2C_2O_4$ *REE* separate from other cations fotming the *solid crystalline phases, oxalates*. They are almost insoluble in water and oxalic acid, and release of *REE* into the solution is minor, unlike a system with HCl. It seems very important for further extraction of *REE* because we see a relatively easy way to convert them into the molecular (rather than colloid!) solution using a complexing agent without any reaction with opal, a dried silica gel. It seems also important that a dilute solution of $H_2C_2O_4$ is used: oxalic acid is a chemical which, unlike corrosive and volatile mineral acids, may be easily transported and stored in an environmentally safe solid form.

Extraction of Zr (and Hf) into solution in experiments with $H_2C_2O_4$ is reduced as compared to HCl, but still significant. Also note the solubility of eudialyte significantly depends on the perfection of its structure (Ca-Fe-Zr-Si heteropolyhedral framework): the Khibiny sample is considerably more resistant to acid degradation than the Lovozero mineral.

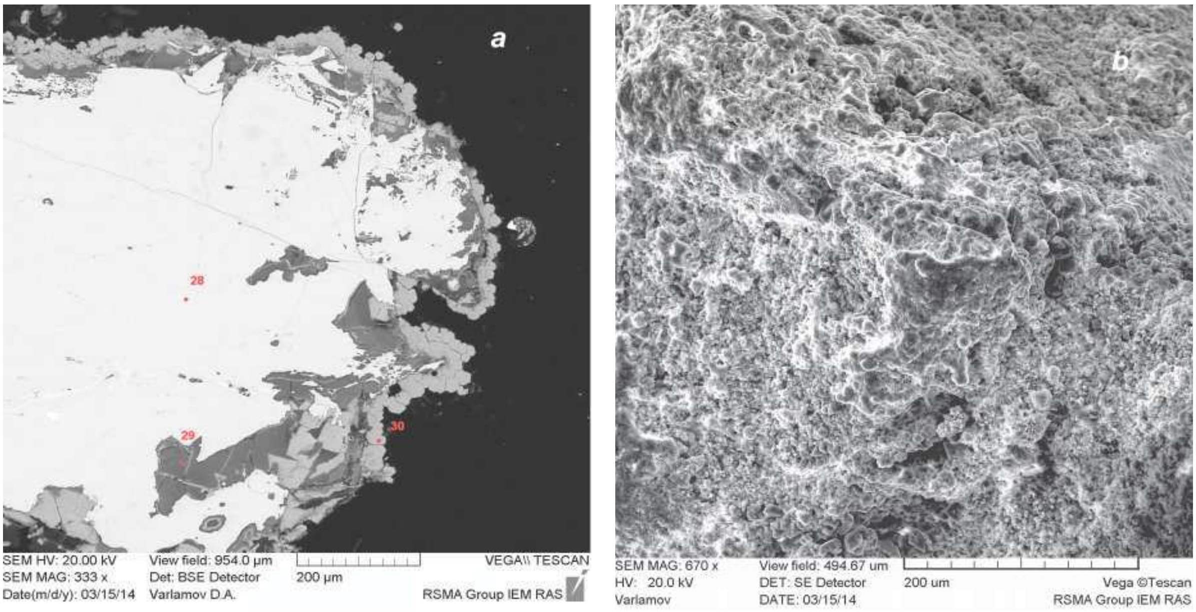

Fig. 1. The Khibiny eudialyte after the experiment with 1% $H_2C_2O_4$. On section (a), an opal-like phase (p.29) and Ca-Zr oxalate crusts (30) overgrowing unaltered eudialyte (28) are observed. On the rough surface (b), Ca-Zr oxalate crystals are abundant. SEM image: (a) BSE, (b) SE.

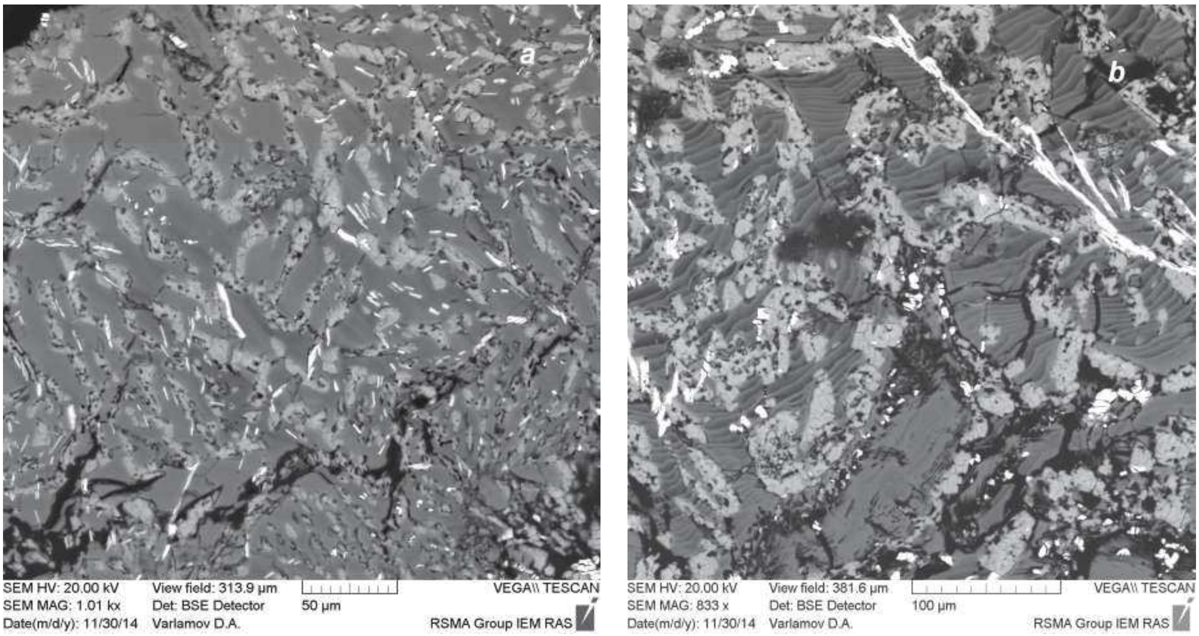

Fig. 2. Surface of the opal-like product formed as a result of full decomposition of eudialyte in 7% (a) and 5% (b) $H_2C_2O_4$ [SEM (BSE) image]. White zones correspond to *REE* oxalates and light gray zones to Ca-Zr-oxalates.

Table. Contents of rare elements and Ti (ppm) in thousandfold diluted solutions after the experiments with HCl and $H_2C_2O_4$ of different concentrations and eudialyte from Khibiny (OLE-9) and Lovozero (UMB-2). ICP MS data; bdl – below detection limit; dash – not analysed.

	HCl						**$H_2C_2O_4$**						
	OLE-9			**UMB-2**			**OLE-9**				**UMB-2**		
	10%	**7%**	**2%**	**10%**	**7%**	**2%**	**7%**	**5%**	**3%**	**1%**	**7%**	**5%**	**3%**
Zr	2486	1671	135	1600	1528	390	306	260	477	122	1100	1739	1311
Hf	36	20	1.2	28	26	5	-	bdl	-	1.8	22	35	28
Ti	93	91	-	79	72	41	-	-	-	-	-	85	57
Ta	bdl	0.1	bdl	bdl	0.3	0.6	-	-	-	0.7	4	5	0.7
Th	0.8	0.8	0.3	0.8	1.1	0.4	bdl	bdl	bdl	bdl	0.2	0.6	0.3
U	1.5	1.6	0.5	0.5	0.7	0.3	0.4	0.3	0.5	0.3	0.2	0.6	0.5
Sr	176	182	56	210	157	94	5	4	4	3	5	5.5	5.5
Ba	44	45	13	2	1.8	2	10	7	6	4	0.8	0.6	0.1
Y	43	44	12	107	86	53	0.4	0.2	bdl	bdl	0.9	1.1	0.9
La	25	26	7	49	5	24	0.7	0.3	bdl	bdl	1	1.8	0.1
Ce	32	31	14	101	87	50	1	0.4	bdl	0.1	0.9	1.2	0.2
Pr	5.5	5.5	1.5	13	18	6	bdl	bdl	bdl	bdl	bdl	0.1	bdl
Nd	22	23	6	58	79	28	0.3	0.15	bdl	bdl	bdl	0.1	bdl
Sm	5	5	1.5	17	24	9	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Eu	2	2	0.5	6	8	2.9	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Gd	6.5	6.5	1.5	18	27	8.5	0.1	bdl	bdl	bdl	bdl	bdl	bdl
Tb	1.2	1.2	0.3	3.8	5	2	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Dy	8	8	2	24	32	12	bdl	bdl	bdl	bdl	bdl	bdl	0.1
Ho	1.8	1.8	0.5	4.6	6.5	2	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Er	5.5	6	1.5	14	20	7	bdl	bdl	bdl	bdl	bdl	0.1	0.1
Tm	0.8	0.9	0.2	2	2.8	1	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Yb	5	5	1.5	12	17	6	bdl	bdl	bdl	bdl	0.2	0.4	0.3
Lu	12	8	0.2	1.7	17	0.8	bdl	bdl	bdl	bdl	bdl	8.5	7

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Thermal analysis of carbonaceous shales as a way to forecasting of gold mineralization (at the example of Beloretsk metamorphic dome, Southern Urals)

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The Beloretsk zonal methamorphic complex is situated in the eastern part of the Bashkirian meganticlinorium in the limits of Mayardak anticlinorium. It bends in a horseshoe way around the northern periclinal end of the Zilair synclinorium and stretches in the northeastern direction at a distance of about 120 km, being 20 to 40 km wide. The complex is composed of the Lower- to Upper Riphean deposits, with a thickness of 4 – 5 km (Alexeev et al, 1984).

The initial rocks of the complex are mainly sandy-argillaceous, carbonate and carbonaceous terrigenous deposits, and much less often - intrusive bodies and effusions of basic composition. In the Late Vendian (?) time the rocks have been exposed to a metamorphism exerted by a deep-seated large granite or granite-migmatite intrusive body, reliably fixed by geophysical methods. Therefore a zonal metamorphic complex was formed, with a core (diameter of 7-8 km) composed of rocks of eclogite facies; the intermediate zone (width of 2-10 km) belongs to amphibolitic and external (width of 15-20 km) – to greenschist facies (Alexeev & al., 2009). The carbonaceous deposits are developed in the Yusha, Mashak, Zigalga and Zigazino-Komarovo Formations. Their position in sections and lithological character are described in detail in a monograph (Snachev et al. 2012) and are not considered here. The most widely developed are the carbonaceous schists in the Zigazino-Komarovo Formation (RF_2zk). They are combined in various proportions with chlorite-sericite-quartz, micaceous-quartz, micaceous-fieldspar-quartz schists, quartz siltstones and sandstones, enriched with carbonaceous substance; by their petrochemical features they can be attributed to a terrigenous-carbonaceous