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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 the 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*.

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

Thus, in a system with $H_2C_2O_4$ a separation of mobilized from eudialyte *REE* from other cations in the *solid crystalline (oxalate) phase* happens. These oxalates 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 their further extraction because we see a relatively easy way to convert *REE* 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 an agent 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.