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KAINOSITE-(Y) IN VEINED SYENITES OF THE PENYZEVYCHI QUARRY (KOROSTEN PLUTON, UKRAINE)

Rare-earth minerals represented by Y-REE-silicocarbonate, xenotime-(Y), bastnaesite-(Ce), allanite-(Ce), unidentified Y- and Y-Ti-Ca-silicates have been discovered in veined syenites among ilmenite norites in the Penzyevychi quarry (Malyn district, Zhytomyr region). The Y-REE-silicocarbonate kainosite-(Y) $\text{Ca}_2(\text{Y,Ce})_2\text{Si}_4\text{O}_{12}(\text{CO}_3)\cdot\text{H}_2\text{O}$ – a rather rare mineral – has been diagnosed in crystalline rocks of Ukraine for the first time. Kainosite-(Y) from Penzyevychi quarry differs from typical mineral from the other massifs by exceptionally increased FeO content. Increased or high FeO content is due to a thin (dispersed) micro-nanosize Fe-phase ($< 1 \mu\text{m}$). Decreasing of Si, Ca, Y and REE in mineral composition in comparison with the typical kainosite-(Y) is due to increased FeO content. This makes it difficult to diagnose.

Key words: kainosite-(Y), yttrium minerals, syenite, Korosten pluton, Ukrainian shield.

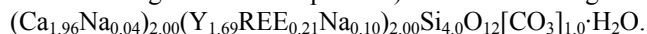
Abundant accessory mineralization represented by Y-REE-silicate-carbonate, xenotime-(Y), bastnaesite-(Ce), allanite-(Ce), Zr, Th and U minerals, unidentified Y- and Y-Ti-Ca-silicates has been found in the veined syenites of the Penzyevychi quarry (Malyn district, Zhytomyr region).

Y-REE-silicate-carbonate is the most interesting among these accessory minerals.

The first identification attempt of this mineral has been described in [2]. Based on the features of chemical composition and XRD-results, this mineral was previously identified as kainosite-(Y) $\text{Ca}_2(\text{Y,Ce})_2\text{Si}_4\text{O}_{12}(\text{CO}_3)\cdot\text{H}_2\text{O}$.

To do more precise determination of chemical composition of this mineral, the microprobe studies of individual grains (from 50 to 400 μm) have been carried out additionally (see Table). According to obtained results, quite wide variations in the content of the main elements are established, mass %: SiO_2 – 18.42–34.53; FeO – 0–43.84; MgO – 0.76–0.93; CaO –

5.71–15.41; UO_2 – 0.10–0.62; PbO – 0.29–0.52; Na_2O – 0.23–1.29; Y_2O_3 – 10.05–28.08; REE_2O_3 – 4.40–12.46; F – 0–2.14; Cl – 0–0.28 (Fig. 1). However, the most representative analyzes (with low FeO and high total of components) show such averaged empirical formula:



Composition of kainosite-(Y) from the Penzyevychi quarry, mass %

Components	1	2	3	4	5
SiO_2	33.97	34.53	34.40	33.52	33.69
FeO	2.30	0.93	3.82		0.77
CaO	13.80	15.41	14.92	13.99	14.20
Na_2O	0.50	0.23	0.34	0.94	0.71
Y_2O_3	22.45	26.06	24.94	26.63	25.53
La_2O_3	0.50			0.42	
Ce_2O_3	1.15			0.50	
Nd_2O_3	0.82			0.47	
Sm_2O_3	0.68				0.44
Gd_2O_3	1.27	1.51	1.20	1.11	0.98
Tb_2O_3				1.85	2.31
Dy_2O_3	2.01	2.48	2.51		
Ho_2O_3	0.78				
Er_2O_3	1.65	2.18	2.05	1.84	1.70
Yb_2O_3	2.65	2.80	2.28	1.87	2.41
$\Sigma\text{REE}_2\text{O}_3$	11.51	8.97	8.04	8.06	7.84
F	1.79		0.81		
Cl				0.28	0.26
$[\text{H}_2\text{O}]_{\text{calc}}$	2.22	2.42	2.34	2.43	2.36
$[\text{CO}_2]_{\text{calc}}$	5.43	5.90	5.71	5.93	5.75
$[\text{FeOOH}]_{\text{calc}}$	2.84	1.15	4.72		0.95
Total	99.29	97.00	98.47	93.28	93.10
Formula based on 4 Si atoms per formula unit					
Si	4.00	4.00	4.00	4.00	4.00
Ca	1.99	2.05	2.05	1.85	1.94
Y	1.61	1.72	1.70	1.75	1.73
REE	0.27	0.18	0.16	0.17	0.16
Na	0.13	0.06	0.08	0.23	0.18

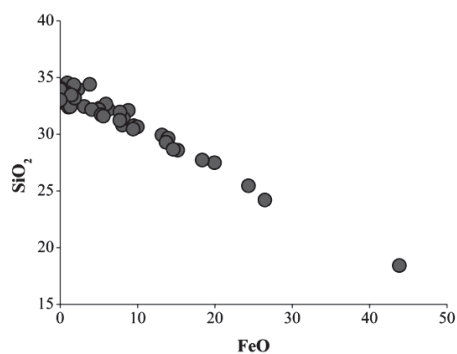


Fig. 1. Correlation of FeO vs SiO_2 for kainosite-(Y) and its alteration products, mass %.

In comparison with the previously published data [2], the FeO content is even more significant and varies greatly even within individual grains. The presence of increased or significant Fe content is caused parallel decreasing of the Si, Ca, Y, and REE contents (see Fig. 1). According to our results, high admixture of FeO is due to the appearance of intergranular skins or scattered inclusions of iron oxides or hydroxides (goethite, hydrogoethite?). The presence of these inclusions was resulted to dark brown or brown colour (under the binocular) that is untypical for this mineral (common colour of kainosite-(Y) is colourless to yellowish-brown, greenish-yellow, yellow) and some complication in recalculation obtained analyzes also. It was impossible to select a sample of kainosite-(Y) completely free in Fe.

Some crystals show presence of distinct zoned structure (Fig. 2). Light parts of these grains have generally lower FeO content and, correspondingly, higher contents of SiO_2 , CaO, Y_2O_3 and REE_2O_3 . Sometime zoned grains contain isometric or irregular small (10–20 μm) inclusions of REE-F-carbonates (probably, bastnaesite-(Ce)) in outer part. Obviously partial capture of these inclusions by microprobe beam might caused an increased F established in some analyzes. Even homogeneous kainosite-(Y) grains are characterized by significant variations in FeO detected in different sites of these grains. Study of these sites under higher magnification has also revealed rather inhomogeneous structures caused by the presence of micro-nanosized inclusions of Fe-rich phases and their heterogeneous distribution (Fig. 3).

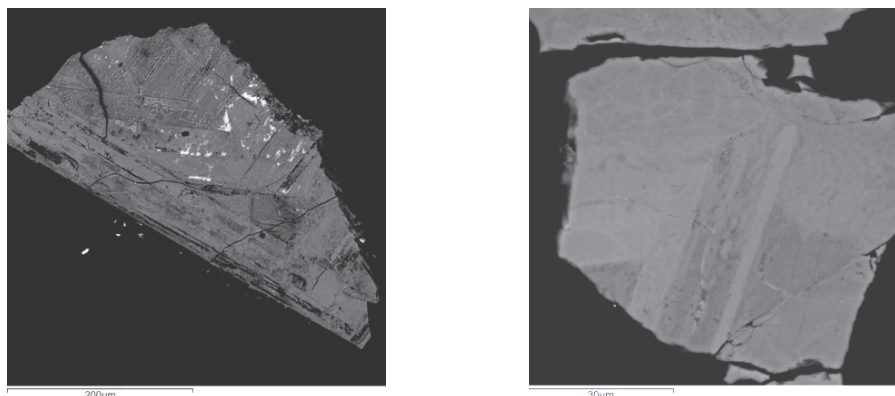


Fig. 2. The zoned grain of kainosite-(Y) from the veined syenites of the Penzyevychi quarry, BSE-photo.

Zoning is caused by alternation of sites enriched (dark) and depleted (light gray) in FeO. Light inclusions found in the central part of the crystal are represented by bastnaesite-(Ce).

In most cases, in calculated formulas the $(\text{Ca} + \text{REE} + \text{Y})/\text{Si}$ ratio is more than 1 (more than 4 Si atoms per formula unit), which could be explained by the decreasing of REE and Y contents due to the excess of iron. But in most analyzes the $(\text{Ca} + \text{REE} + \text{Y})/\text{Si}$ ratio is approaches to 1, which, together with previous results of X-ray diffraction analysis, makes it possible to suggest that this mineral is really related to kainosite-(Y).

Kainosite-(Y) is typical for rocks of various composition, but it is usually localized into fractures and vugs of uraniferous, rare earth pegmatite or granites of alkaline complexes enriched in REE and Y. Commonly kainosite-(Y) in these rocks is considered as secondary mineral, which is formed by replacing the primary Y- and REE-enriched minerals (hellandite-(Y), gadolinite-(Y), yttrialite-(Y), xenotime-(Y), etc.) [1]. Kainosite-(Y) is believed to be formed at postmagmatic stages and through alteration by solutions enriched in CO_3^{2-} .

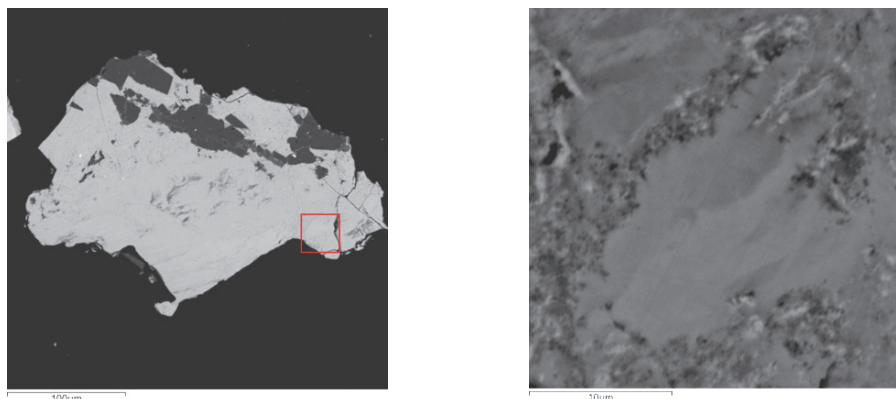


Fig. 3. The grain of kainosite-(Y) and its enlarged fragment, BSE-photo.

The heterogeneity of this grain is well visible due to fine-dispersed impregnations of phases enriched in FeO (dark sites).

The relationship between xenotime-(Y) and the above mentioned Y-minerals in the investigated syenite is not completely established. Intergrowths of kainosite-(Y) and xenotime-(Y) might be treated as replacement of xenotime-(Y) by kainosite-(Y) as well as. Individual xenotime-(Y) grains altered by churchite-(Y) (without visible development of secondary kainosite-(Y)) are found in nature.

In our opinion, Y and REE minerals found in the veined syenites of the Penzyevychi quarry taken together with petrographic and mineralogical peculiarities of these rocks could indicate their genetic relationship with intrusion of alkali syenites. Increased alkalinity promotes accumulation by Y and REE, partly U, Th, Zr, in the residual melts. Further crystallization of the melts as veins caused the various accessory mineralization (kainosite-(Y), the first finding in Ukraine, xenotime-(Y), churchite-(Y), bastnaesite-(Ce), uraninite, thorite) in the investigated syenites. Based on our results, the studied rocks could also include such minerals as keiviite-(Y) $Y_2Si_2O_7$ and Y-REE-Ti-Ca-silicate (yttrian titanite).

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КАЙНОЗИТ ІЗ ЖИЛЬНИХ СІЄНІТІВ ПЕНИЗЕВИЦЬКОГО КАР'ЄРУ (КОРОСТЕНСЬКИЙ ПЛУТОН, УКРАЇНА)

У жильних сієнітах серед ільменітових норитів Пенizeвицького кар'єру (Малинський р-н, Житомирська обл.) діагностовано серію мінералів-концентраторів рідкісних земель, представлених Y-REE-силікокарбонатом, ксенотимом-(Y), бастнезитом-(Ce), аланітом-(Ce), недиагностованими Y- та Y-Ti-Ca-силікатами. За особливостями хімічного складу виявлений Y-REE-силікокарбонат діагностовано як досить рідкісний мінерал – кайнозит-(Y) $\text{Ca}_2(\text{Y,Ce})_2\text{Si}_4\text{O}_{12}(\text{CO}_3)\cdot\text{H}_2\text{O}$, який у кристалічних породах України визначено вперше.

Кайнозит-(Y) Пенizeвицького кар'єру відрізняється від типового мінералу з інших масивів підвищеним умістом домішки FeO. Підвищений або високий вміст FeO пов'язаний з тонким (дисперсним) вкрапленням залізистої фази (< 1 мкм). Її наявність зумовлює зменшення вмісту Si, Ca, Y та REE у складі мінералу, порівняно з типовим кайнозитом-(Y), і утруднює його діагностику.

Ключові слова: кайнозит-(Y), мінерали ітрію, сієніт, Коростенський плутон, Український щит.