

MINERAL COMPOSITION OF RARE ELEMENT ENRICHED ROCK BODIES FROM THE BÜKK MTS., NE HUNGARY

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Abstract: A rare earth (REE) and further rare element (Zr, Nb, Th, Ta) enrichment was found recently within the CriticEl project in 2016. Due to continuing studies, now we know about several enriched rock bodies from the SE and NE part of the Bükk Mts. The enrichment was caused by metasomatic processes, during which fluids penetrated through the rock bodies, causing chemical and mineralogical changes. The enriched rock bodies are Triassic metavolcanics and siliciclastic metasedimentary rocks. The protoliths consist of quartz, feldspars (albite and potassic feldspars), phyllosilicates (various micas and chlorites) and calcite, and in minor quantities Fe- and Ti-oxides, fluorapatite and titanite. The characteristic metasomatic minerals are monazite-(Ce), zircon and Nb-bearing Ti-oxide. Based on our data, micas and potassic feldspars were generated at least partly during the rare element mineralization process, while titanite, chlorite and albite were consumed. Apatite and Ti-oxides were decomposed and formed. The original mineral composition had a strong influence on the rate and mode of alteration.

Keywords: *Rare earth elements (REE), High Field Strength Elements (HFSE), metasomatism, alteration processes, phyllosilicates, feldspars, Bükk Mts.*

1. INTRODUCTION

As part of the CriticEl project and subsequent research programs, a previously unknown high field strength elements (HFSE) enrichment was found in the Bükk Mts [1]. The highest enrichment ratios compared to the upper crust average [2] reach 18 for Zr, 16 for Nb, 30 for Th, and 13 for Ce. The alteration was caused by metasomatic processes, which is proved by the presence of grain replacing aggregates, pseudomorphs and the small grain size (maximum a few tens of micrometers) of the HFSE-bearing minerals: monazite-(Ce), zircon, niobian Ti-oxides, and rare REE carbonates. In addition to the formation of new minerals, the process led to the alteration of the earlier rock-forming minerals. However, it was not the only alteration process to take place in the Bükk, so determining the exact origin of the minerals is often difficult.

Primary deposits of high field strength elements are rare and mainly connected to carbonatites and other alkaline bodies. High-field strength elements can be considered immobile in most geological environments. However, experience has shown that they can be transported by magmatic, metamorphic, and ocean-bottom

hydrothermal solutions. Their mobility is affected by the p-T conditions, pH, and the dissolved ions [3].

Fenitisation is a process which can be compared to what occurred in the Bükk Mts. This is a rock alteration associated with metasomatic enrichment of alkaline elements and HFSEs. The process takes place on a stable continental plate around carbonatites and other alkaline complexes [4]. During the process, the wallrock of the intrusion (which may also be sedimentary layer) is penetrated by volatile elements from an alkaline magma source [5]. According to IUGS, fenites are metasomatic rocks formed at high temperatures. The typical mineral association consist of potassic feldspar and albite, nepheline, alkaline pyroxenes, and amphiboles, as well as smaller amounts of biotite-phlogopite mica, magnetite, ilmenite, titanite and apatite, sometimes calcite [6]. The composition of the resulting fenitic rock depends on the original rock material and the composition of the source magmatic body. Minerals with HFSE content often form polycrystalline aggregates, sometimes with vesicular filling. The typical temperature range can vary from 450 to 700 °C, with a pressure range between 100 bar and 5 kbar. Areas affected by fenitisation can be found to a distance up to 4 km from the source intrusion [4]. In the Bükk Mts. we do not know the source body; probably, it is deeply buried and tectonically disconnected from the altered rocks.

2. GEOLOGICAL SETTING

The age of the outcropping rocks of the Bükk Mts. extends from late Carboniferous to Jurassic, covered with thick Cenozoic sediment. In the area of “Bükk Parautochthonous” (i.e., Pre-Cenozoic Bükk without the Szarvaskő unit), the Permian-Triassic sedimentation is characterized by marine succession: continuous formation of carbonate platforms from the Late Permian to the Early Triassic, carbonate platforms in the Middle Triassic, and then basin facies sediment formation in the Late Triassic. After a sedimentary gap, they are overlain by deep-sea siliciclastic-carbonate sediment formation in the Jurassic.

The Middle-Upper Triassic of Bükk is characterized by metamorphosed volcanics and deformed sedimentary layers. Metavolcanics are classified into three formations [7]. Major occurrences of Szentistvánhegy Metaandesite and Bagolyhegy Metarhyolite are located on the north side of the Great Plateau and to the east from it, separated from the small bodies of Szinva Metabasalt by a regional shear zone [1]. These small bodies are usually interbedded into carbonates and can even be peperitic.

In Cretaceous, the Paleozoic-Mesozoic rocks of the Bükk underwent dynamothermal anchizonal regional metamorphism. The degree of metamorphism is not uniform. [8]. Based on the different deformation styles three main tectofacies group can be specified: the North Eastern, Central, and South Eastern Units; among them the Central Unit is the most deformed. The units are divided from each other by fault zones which contain the HFSE-mineralized rock bodies. Mineralized bodies occur in two groups: at the boundary of the North Eastern and Central Units in Lillafüred,

NE Bükk Mts, and at the boundary of the Central and South Eastern Units in the SE Bükk Mts. Sampling localities are shown in *Figure 1*.

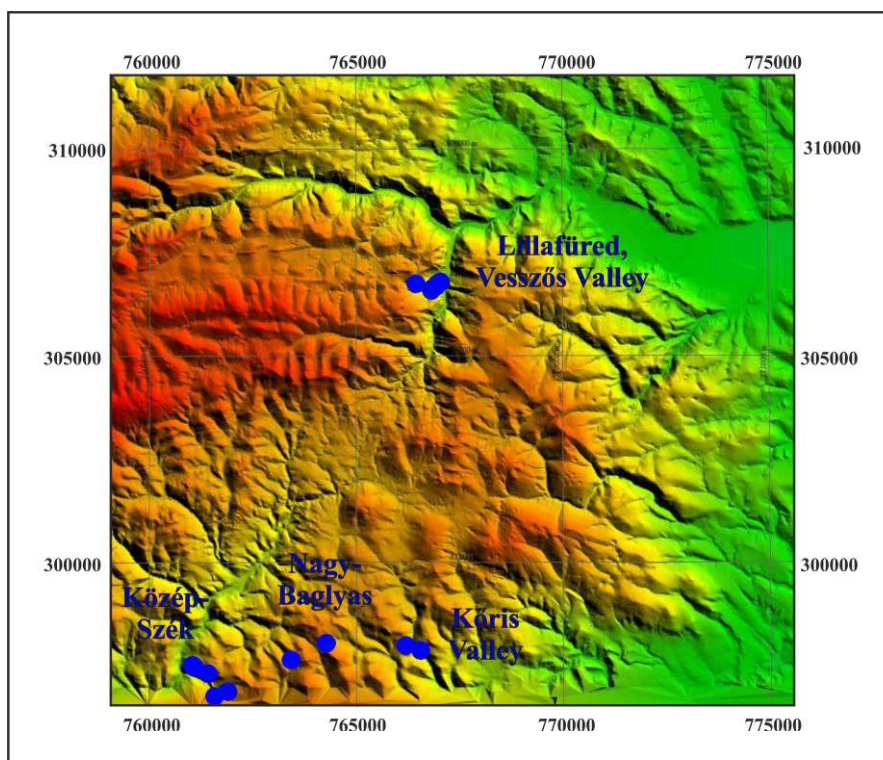


Figure 1

Schematic map showing the localities of the sampled rock bodies (Digital Elevation Model created by Global Mapper)

3. APPLIED METHODS

The qualitative and quantitative mineral composition of the studied samples was determined by X-ray powder diffraction (XRD). For the measurement, a Bruker D8 Advance (40 kV, 40 mA Cu K- α radiation) machine with a Vantec-1 position sensitive detector was used. The instrument produces parallel beam geometry using a Göbel mirror. The qualitative evaluation was carried out using DiffracPlus EVA software, based on the ICDD PDF2 2005 database, while the quantitative evaluation was carried out with Diffrac.suite Topas software based on the Rietveld method.

Electron-microprobe studies were used to identify the chemical composition of the individual grains (energy dispersive X-ray spectrometry, EDX point measurement) and to detect the presence of the different minerals on back scatter electron (BSE) images. This method has particular significance because no other method was suitable to detect the HFSE-bearing minerals due to their small grain size and low

amount. For the electron microprobe studies we used a SamX-controlled JEOL JXA 8600 Superprobe electron beam microprobe (15–20 kV accelerator voltage, 20 nA sample current), equipped with an SDD-EDX detector.

Because of the micrometric or submicrometric grain size of the alteration minerals, optical microscopy played a subordinate role, but rock-forming minerals and rock textures were thoroughly examined with it. Both examination methods described above were performed at the Institute of Mineralogy and Geology, University of Miskolc.

4. RESULTS

4.1. Mineral composition of the rock bodies, NE Bükk

In the NE Bükk enriched rock bodies were found at Vesszős Valley, Lillafüred. These rock bodies are siliciclastic sedimentary layers a few decimeters thick, embedded into carbonates of the Hegyestető Formation. Enriched and non-enriched beds with probably similar original composition and environment were also sampled. *Table 1* summarizes the mineral composition of the samples.

Table 1
Mineral composition of rock samples from NE Bükk, based on XRD analyses

Phase Name	enriched metasedimentary rocks				non-enriched metasedimentary rock	mineralized marly layers		wall rock limestone		
	V18	KMA-1	KMA-2	KMA-3	V36	V181	V182	V183	V18Ma	V18Mb
quartz	0.14	23.81	2.51	21.22	25.87	1.40	1.48	14.58	0.23	
microcline			1.50							
orthoclase				5.00						
albite					4.97		0.29	0.35		
talc										0.50
chlorite					3.43	2.11	1.08			
illite		9.13	14.06	17.45	10.64	4.39	4.20			
smectite					0.65					
biotite										2.02
muscovite	15.51	56.37	59.31	39.24	0	70.44	17.29	1.21	0.27	0
phengite	66.15	0	0	0	31.05	8.56	0.49	0	0	0
goethite	6.29				0.84		0.28			0.73
anatase					1.08	0.28	0.40			
rutile	0.55									
calcite			5.35		6.27		74.50	80.87	66.91	67.72
dolomite			0.67						26.53	16.50
amorphous	11.36	10.70	16.60	17.10	15.00	12.50		3.00	6.00	7.00

The main rock forming minerals are phengitic dioctahedral micas, but in some less enriched rocks the amount of quartz also can be significant (up to about 25 wt%). Calcite is also a rock forming component of marly beds. Feldspars are minor

components only. In only two samples was the feldspar content detectable with XRD: an enriched layer has about 5 wt% K-feldspar, while the non-enriched sample contains albite in the same amount. The most enriched sample consists almost completely of micas, with a significant amount of goethite (6 wt%) causing its reddish color. Based on the EDX measurements smectite is also an important phase in this rock.

In addition to siliciclastic sedimentary rocks, marly layers and wall rock limestones were also examined. The marly layers also have a slightly raised HFSE-content compared to the wall rocks. These layers contain lower amount of quartz or mica, and 1-2 wt% chlorite. The wall rock of the most enriched bed consists of calcite and dolomite (whereas the marly layers do not contain any dolomite). Other important minerals could be chlorites, phlogopite, and iron-oxides, and based on optical microscopy potassic feldspar is also present as vein and void filling phase.

Minor and accessory phases present in the Vesszős Valley samples are apatite, detrital zircon, and rare monazite, which can be distinguished from their metasomatic counterparts by their larger size (some tens of micrometers). Probably Ti-oxide minerals occurred also as detrital grains, replaced and transformed into niobian Ti-oxides and sometimes into REE-Nb-Ti oxides. The wall rock limestone also contains HFSE minerals.

4.2. Mineral composition of the rock bodies, SE Bükk

The studied rocks from SE Bükk are partly metavolcanics (Nagy-Baglyas, Kőrös Valley), partly siliciclastic sedimentary beds (Közép-szék), although these latter beds may represent redeposited volcanoclastics as well. Mineralized metavolcanics most probably belong to the Szinva Metabasalt Formation, and could be divided into two groups, “pure” metavolcanics and peperites. Peperite is defined as tuff or breccia material, which is formed by pushing magma into wet sediment [9]. The mineral composition of the samples is summarized in *Table 2*. Metavolcanics usually contain micas and feldspars in similar quantities. Feldspars are albite and potassic feldspars (Ca-plagioclase is absent). In most of the cases chlorite is not detectable by XRD, only by electron-microprobe analyses. The quantity of quartz is highly variable, ranging from 5 to 40 wt%. The calcite is often significant as a peperitic constituent, but usually rock bodies with higher calcite content have lower HFSE values. Non-mineralized rocks from Szinva Metabasalt contain significantly more albite, chlorite and titanite, and only minor quartz.

The composition of the siliciclastic sediments from the area is variable, but most often they contain less feldspars than metavolcanics, and these feldspars are mainly albites. Dioctahedral micas and quartz are general constituents, but their quantity varies. Certain layers can contain calcite and/or chlorite.

In both rock types, iron- and titanium-oxides, apatite and dioctahedral micas are important minor constituents. The metasomatic mineral phases are niobian Ti-oxides, zircon, monazite, and in one sedimentary rock REE-carbonates.

Table 2
Mineral composition of rock samples from SE Bükk, based on XRD analyses

Phase Name	mineralized metavolcanics			slightly affected metavolcanics	chert	peperitic metavolcanics				
	1167	HOR 12	HOR 31	HÓR 25	783/2	783/1	783/3	783/4	783/5	783/6
quartz	34.0	14.6	12.8	19.51	36.41	30.62	41.32	18.85	23.20	6.23
tridymite								0.20		
microcline			13.2					6.62		3.61
albite	6.3	10.2	17.0	29.19	0.53	7.29	1.32	9.83	7.64	11.75
sanidine		25.1		0.91						
orthoclase	8.0	5.6			2.10	3.85	2.33	1.29	1.18	
kaolinite					2.14					
chlorite IIb			8.8	7.08						
smectite				0.85						
celadonite				13.73						
biotite 1M		0.5			6.25	1.54				
muscovite	1.9	5.7	26.2	7.69	7.01	3.61	4.1	1.51	1.36	1.9
illite	25.5	29.2	6.8	11.82	7.47	0	9.69	10.84	0	25.5
goethite					0.60	1.07	0.93	1.21		0.78
titanite			2.5							
anatase			1.0	2.22	0.52		0.29	0.09	0.16	0.32
rutile										0.13
calcite	17.0				18.09	23.05	17.47	19.93	19.05	28.10
calcite (Mg)					15.18	21.03	11.84	12.56	41.81	31.89
ankerite								0.48		
amorphous	7.3	9.1	8.4	7.00	3.70	7.95	10.70	16.60	5.60	17.20

Phase Name	peperitic metavolcanics			wall rock carbonate	siliciclastic sedimentary rocks?				
	783/7	783/8	783/9	783/10	HOR 41	HOR 42	HOR 38	HOR 39	HOR 40
quartz	5.55	7.92	6.62	14.63	7.71	15.4	52.09	24.20	63.96
microcline	2.01	2.30	3.37	0.66					
albite	10.51	8.26	11.85	10.47		14.1	5.85	0.69	0.26
sanidine					7.93	22.3			
orthoclase	2.29	3.24	4.56			4.9			
kaolinite			1.20						
chlorite							5.59	0.54	6.47
biotite		1.11	0.84			3.1	0.67	0.73	0.62
muscovite	0	0	0	0	1.56	0	20.78	50.63	17.38
illite	2.9	3.91	5.17	0	6.74	20.8	5.62	10.58	5.02
goethite	1.42	0.48	0.39	0.17		1.1			
titanite					0.72				
anatase	0.13	0.32	0.45	0.11		0.5	0.48	0.51	0.28
rutile	0.16	0.04	0.05	0.09					

	peperitic metavolcanics			wall rock carbonate	siliciclastic sedimentary rocks?				
calcite	28.82	33.58	29.15	36.19	26.57	13.5	3.90	0.12	
calcite (Mg)	39.41	30.83	28.44	30.39	43.81				
ankerite					1.96				
amorphous	6.80	8.00	7.90	7.30	3.00	4.2	5.00	12.00	6.00

4.3. Characteristics of the minerals

The identified mineral phases are partly inherited from the protolith, which itself is a metamorphic rock, or can be formed during metasomatism. Most of the mineral groups could be the product of different processes, e.g. micas could form during sericitization or other alteration processes, but sometimes original, deformed magmatic mica plates are observable as well. In the following we summarize the distinguishing characteristics of the most important mineral groups.

Feldspars

Except for some siliciclastic and marly layers from Vesszős Valley, all studied rock bodies contain alkaline feldspars. The higher the K-concentration in a rock body, the higher the rate of potassic feldspars to albite in general, but rocks with low feldspar and high mica content often have albite dominance. Potassic feldspars have the highest share of total feldspars in metasomatised metavolcanics, while other, non-mineralized metavolcanics from the Bükk Mts. usually contain albite. Based on our observations, metavolcanics with higher albite contents usually have lower HFSE-concentrations. There are albite phenocrysts which are relict and/or dissolved, and fine-grained albite occurs replacing other phenocrysts (with potassic feldspars, calcite and mica) and in the matrix. Potassic feldspars are either replacement phases or fine-grained matrix constituents, often associated with metasomatic monazite.

Micas

The micas in the rock bodies are predominantly dioctahedral with phengitic composition. According to XRD, they can have both illite and muscovite structure. The peperitic and carbonate samples with low HFSE concentrations contain very low amounts of mica. In other cases, micas dominate the oriented matrix, but also occur as replacement phases (in plagioclase and other pseudomorphs) and as vein fillings. The chemical composition measured by EDX are diverse (*Figure 22*), with K-content ranges between 2.5–4.5 atomic%, Fe between 0.05–3 atomic%, Mg between 1–4 atomic%. These differences may indicate more than one generation of micas, but this could not be verified. Because of the small grain size of the mica in the matrix, neighbouring minerals often influence our measurements, or we measure a group of grains instead of an individual plate; therefore, chemistry data

based on EDX are not always absolutely accurate. Phengites from the most enriched layer usually lack Fe in their composition, and often have a low F-content (about 1 atomic %). Biotite may occur in metavolcanics as a rock forming mineral: these are mainly large, deformed plates, i.e., inherited crystals, which are clearly observed with an optical microscope. Sometimes secondary biotites could be present. They occur in vein filling and grain replacing position, in some cases together with metasomatic HFSE-minerals, like zircon. The wallrock carbonates from Vesszős Valley do not contain any dioctahedral micas, but the phlogopites are also iron-poor and have F-content up to 3.6 atomic %.

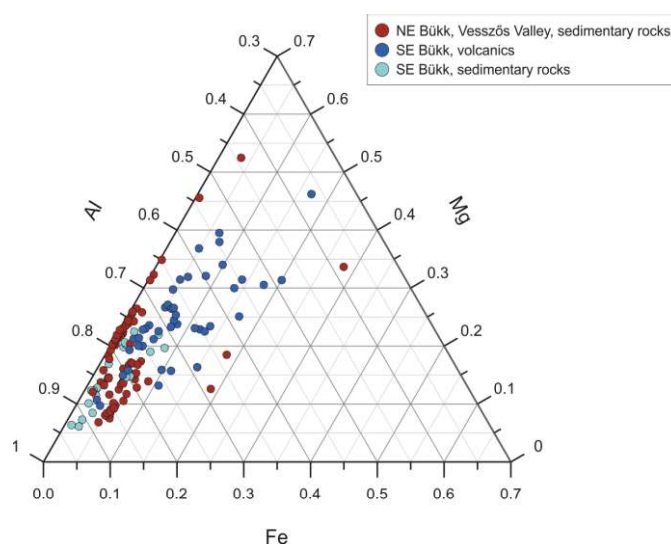


Figure 2
Crystal chemistry of dioctahedral micas, based on EDX data

Chlorites

Chlorite is a major rock forming mineral both in metavolcanics and shale formations of the Bükk Mts. In our sample set, it was detected with XRD in marly and carbonate samples and in non-mineralized rocks only, but it was often observed with electron microprobe at several points, mainly in less enriched samples. These are the samples that contain the most albites. Chlorite compositions might be diverse like in the case of micas, but some samples display specific compositions: the chlorites of the carbonate wall rock of the most enriched sample from Vesszős Valley do not contain any iron, similarly to the phlogopites of this layer.

Ti-oxides

Ti-oxides are common accessory minerals in all of the studied rock bodies. Based on XRD, Ti-oxide can be both rutile and anatase. Ti-oxides are very often present as decomposed, relict grains or as concretions on grain edges. Ti-oxides of the most

enriched rock body usually are disseminated micrometric, euhedral–rhombohedral grains, but in several cases, these form veinlets and nests associated with zircon of similar size. In other cases, Ti-oxides are associated with apatite, either in nests or on edges of relict grains. However, in samples from Szinva Metabasalt which are not affected by the alteration, electron microprobe studies showed that the characteristic Ti-containing accessory mineral is titanite [1]. Based on data in the literature, hydrothermal alteration of titanite can create titanium oxide [10].

Based on electron microprobe analysis, Ti-oxides of the mineralized rock bodies contain Nb. Typical Nb₂O₅ content ranges from 0.5% to 8% and can vary widely within a given sample. In the Vesszős Valley samples a REE-Nb-Ti-oxide mineral was also detected: according to its composition it is aeschynite or euxenite.

Other accessory minerals

Apatites can form small-grained assemblages associated with titanium-oxides, as nests of dissolved grains or with Ti-concretions on their boundary. Apatite phenocrysts are in several cases fragmented or zoned. Based on these types of appearance, it is possible that more than one generation is present. The occurring apatites are always F-apatites, with low Cl-content occasionally (0.1 to 0.2 atomic %). They could contain REEs, but according to EDX measurements always less than 1 atomic % (including Y). These grains occur next to HFSE minerals. Apatite grains with Ti-oxide on the edges rarely contain REEs.

Monazites of the studied samples are always Ce-dominant. Monazites are usually present as μm sized disseminated grains, but often form band-like concretions and linear arrays along grain boundaries or fractures. They could be associated to Fe-oxides. Sometimes monazites form 100 μm large aggregates, but it is a rare phenomenon. Although non-mineralised siliciclastic layer from Vesszős Valley also contains monazites, they are different in chemical composition and size from the others, which refers to their detrital origin.

Other REE minerals are rare, restricted to certain localities. HREE-bearing xenotimes were detected in two measuring points from siliciclastic sedimentary rock, SE Bükk only. REE carbonates (bastnäsite and parisite) were also found in metasediments of the SE Bükk.

Zircon is observed as idiomorphic phenocrysts or fragments in 100 μm magnitude, but also could be a metasomatic product. In this case it is micrometric, occurring in veinlets in the micaceous matrix or as replacement, associated with Nb-bearing Ti-oxides.

4.4. Possible alteration processes

Based on the results of chemical analyses HFSE-enriched rock bodies are usually characterized by an increased K-content compared to non-mineralized bodies. This suggests that fluids carried the HFSEs were originally K-rich, so the process that occurred was similar to the potassic case of fenitisation. This type is characteristic for shallower depths because K is more mobile than Na at low temperatures. The

potassic type fenite can contain up to 90% potassic feldspar and may include albite, apatite, pyroxene, and rutile. If Mg is added to the system, potassic feldspar may be transformed to phlogopite [11]. Although the typical mineral association is not totally the same as in the Bükk, here there are also signs that new potassic feldspars were generated, while the albites usually occur as partially transformed relict grains. In rare cases, slightly elevated HFSE-content without potassic metasomatism was also observed, but these anomalous samples belong to formations which had a relatively high HFSE content primarily. Based on the XRD data the potassic feldspars can be orthoclase, microcline and sanidine alike. Metavolcanics of the Bükk Mts. contain microcline and, in minor amount, orthoclase, but do not contain sanidine as a rock forming mineral in general, so sanidine also can be assumed to be the product of the metasomatism.

Metasomatized siliciclastic metasedimentary rocks with low total feldspar and high mica content often have more albite than K-feldspars, or albite is the only feldspar. The low rate of potassic feldspars does not mean the lack of K enrichment, but here micas incorporated the excess potassium. As chlorites occur in low abundance in the mineralized rocks, these were probably decomposed during the alteration process and altered to phengitic mica due to potassium gain. This is indicated by the similar Mg/(Mg+Fe) ratios of coexisting mica and chlorite phases, while an earlier generation of mica of the same rock has different ratios (*Figure 33*). Mica and chlorite in these samples also display transitional compositions, and similar textural occurrence. Micas, both phengitic dioctahedral micas and biotite, are generally associated with HFSE-bearing minerals, which further supports their relationship with the mineralization. The differences in the chemical composition and appearance of the relict and metasomatic biotites are shown in *Figure 4*.

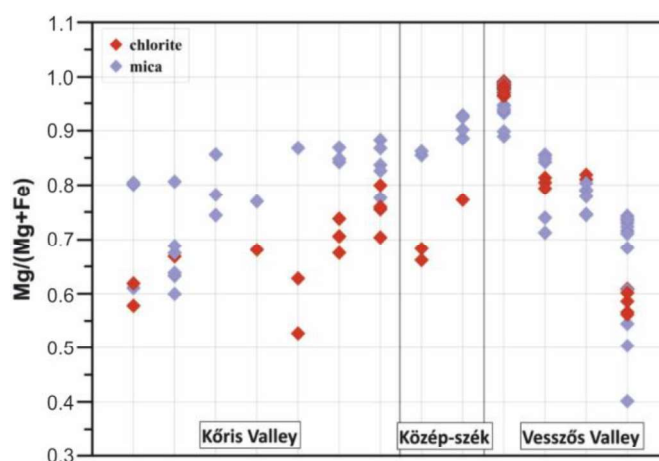


Figure 3

Crystal chemistry of micas and chlorites. Points below each other belong to the same samples.

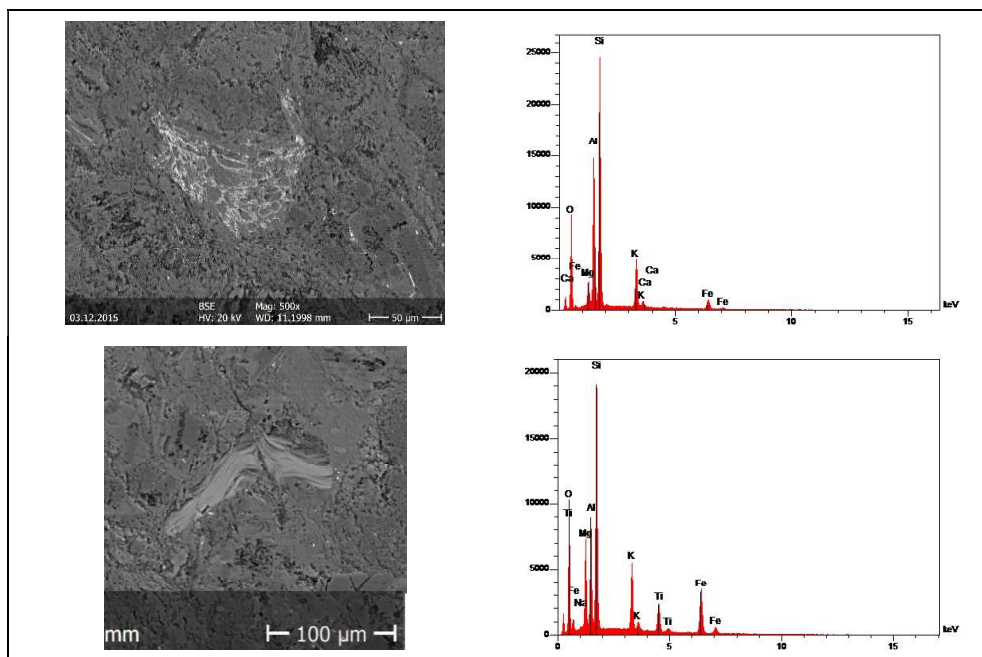


Figure 4

Newly formed biotite with zircon (upper image) and a bent, relict plate (lower image) (BSE images and EDX spectra). Ti is detected in the relict grain only.

The role of other rock-forming minerals during the mineralization is less clear. Some highly enriched rock bodies contain significant amount of quartz, while in others it is lacking almost completely. According to the classical definition of fenitisation, during the process the amount of quartz usually decreases, but depending on the initial composition the reverse situation also could occur [11–14]. Mineralized rocks in the Bükk Mts. also can display either a high abundance or a complete lack of quartz, although this may depend on the initial composition. The non-enriched, non-peperitic metavolcanics of the Szinva Metabasalt Formation usually have 1–3 wt% quartz, while the enriched ones 5–40 wt%, so it seems that here the enrichment causes quartz gain. However, it is not the most enriched samples that contain the most quartz, so the role of other circumstances should be considered. In the peperitic metavolcanics the amount of quartz of sedimentary origin is likely to be significant, just like in cherty limestone. In metasedimentary rocks there are enriched rocks without quartz (Vesszős Valley) or with quartz content up to 50 wt%. Here the initial composition was the main controlling factor. Examples from the literature prove that quartz could be consumed during the genesis of potassic feldspars [15]. Mica could be also generated from quartz and feldspars [16], while in other cases micas and quartz are the consuming phases and potassic feldspars are generated [15].

Accessory minerals also could play an important role during mineralization. Preexisting apatite can serve as a trap for REEs, or the P content may contribute to monazite formation [17,18]. Apatite may be the product of fenitisation [19] and we cannot exclude the possibility that newly formed apatites are also present. Based on our observations, apatite belongs to the group of consumed phases, as mineralized rocks are P-depleted. Several grains are remnants of partly dissolved phenocrysts. REE content is rarely detectable by EDX; therefore, it is not a significant host of the HFSE enrichment.

Ti is another depleted element in the mineralization, and titanite, an accessory phase of the precursor rocks, is lacking. Titanite, also a potential host of HFSE, can be replaced by aggregates of fine-grained minerals such as monazite, rutile, apatite, quartz, calcite, chlorite, due to hydrothermal processes [20]. Although no altered titanite was identified, similar alteration is also likely to occur in our case, producing fine-grained Ti-oxides and other minerals. Relict anatase grains are mostly replaced by fine-grained aggregates of Ti-oxides, zircon, and apatite. Ti-oxides can also be altered by a combined dissolution and deposition process, generating high-porosity trace-element-rich grains and newly formed Ti-oxide elsewhere at the same time [21]. In our case, the fine-grained assemblages on the grain edges, in veinlets and in replaced grains may be the newly formed phases. The most important role of Ti-oxides is to incorporate Nb into their structure, so the released Ti of preexisting minerals can serve as a significant contribution to the Nb enrichment. In the enriched Veszőz Valley rocks, the Nb-carrier phase is aeschynite, which probably also occurs as replacement of earlier Ti-oxides.

5. CONCLUSIONS

Metasomatic HFSE-enrichment in the rocks of the Bükk Mts. caused changes in the mineral composition, which depend highly on the preexisting mineral association. Silicate minerals – mainly feldspars and phyllosilicates – played the most important role in the alteration process. Consumed mineral phases are albite (mainly in feldspar-rich metavolcanics), chlorite, apatite and Ti minerals, but most probably the last two are also present as newly precipitated grains in decreased quantities. Minerals which are partly formed due to the alteration process are micas (mainly dioctahedral phengite-like micas, but also trioctahedral biotites), potassic feldspars, and HFSE-bearing minerals. The probable alterations are chlorite → mica, titanite → Ti-oxide and albite → potassic feldspars. If the quantity of feldspars is low in the original rock, micas incorporate the excess K. The alterations above correspond well with the general K-gain observed in HFSE-enriched rock bodies, although it is quite probable that other mineral phases (e.g., quartz, calcite) also took place in different reactions. The exact processes depend highly on the original composition of the protolith, so different parageneses were produced in rock bodies of different mineralogical composition.

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REFERENCES

- [1] Németh N., Baracza M. K., Kristály F., Móricz F., Pethő G., Zajzon N. (2016). Ritkaföldfém- és ritkaelem-dúsulás a Bükk hegység délkeleti részének vulkáni eredetű kőzetesteiben. *Földtani Közöny*, 146 (1), pp. 11–26.
- [2] Rudnick, R., Gao, S. (2013). Composition of the Continental Crust. *Treatise on Geochemistry*, 4, <https://doi.org/10.1016/B978-0-08-095975-7.00301-6>.
- [3] Jiang, S.-Y., Wang, R.-C., Xu, X.-S., Zhao, K. (2005). Mobility of high field strength elements (HFSE) in magmatic-, metamorphic-, and submarine-hydrothermal systems. *Physics and Chemistry of the Earth Parts A/B/C*, pp. 1020–1029, <https://doi.org/10.1016/j.pce.2004.11.004>.
- [4] Pirajno, F. (2013). *Effects of Metasomatism on Mineral Systems and Their Host Rocks: Alkali Metasomatism, Skarns, Greisens, Tourmalinites, Rodingites, Black-Wall Alteration and Listvenites*. https://doi.org/10.1007/978-3-642-28394-9_7
- [5] Rock, N. M. S. (1976). Fenitisation around the Monchique alkaline complex, Portugal. *Lithos*, 9, pp. 263–279, [https://doi.org/10.1016/0024-4937\(76\)90018-9](https://doi.org/10.1016/0024-4937(76)90018-9).
- [6] Zharikov, V. A., Pertsev, S. S., Rusinov, V. L., Callegari, E., Fettes, D. J. (2007). Metasomatism and metasomatic rocks. In *Recommendations by the IUGS Subcommission of the Systematics of Metamorphic Rocks*. British Geological Survey, <https://silos.tips/download/9-metasomatism-and-metasomatic-rocksf>.
- [7] Less G., Kovács S., Pelikán P., Pentelényi L., Sásdi L. (2005). *A Bükk hegység földtana: Magyarázó a Bükk-hegység földtani térképéhez (1:50 000)*. Magyar Állami Földtani Intézet, Budapest.
- [8] Árkai, P. (1983). Very low- and low-grade Alpine regional metamorphism of the Paleozoic and Mesozoic formations of the Bukkium, NE-Hungary. *Acta Geologica Hungarica*, 26, pp. 83–101.

- [9] Maitre, R., Streckeisen, A., Zanettin, B., Le Bas, M., Bonin, B., Bateman, P. (2004). *Igneous Rocks: A Classification and Glossary of Terms*. Cambridge, UK: Cambridge University Press.
- [10] Morad, S., El-Ghali, M., Caja, M. Á., Sirat, M., Al-Ramadan, K., Mansurbeg, H. (2010). Hydrothermal alteration of plagioclase in granitic rocks from Proterozoic basement of SE Sweden. *Geological Journal*, 45, 105–116. <https://doi.org/10.1002/gj.1178>
- [11] Elliott, H. A. L., Wall, F., Chakhmouradian, A. R., Siegfried, P. R., Dahlgren, S., Weatherley, S., Finch, A. A., Marks, M. a. W., Dowman, E., Dedy, E. (2018). *Fenites associated with carbonatite complexes: A review*. <https://doi.org/10.1016/j.oregeorev.2017.12.003>
- [12] Currie, K. L. (1971). A Study of Potash Fenitization around the Brent Crater, Ontario,—A Paleozoic Alkaline Complex. *Canadian Journal of Earth Sciences*, 8 (5), pp. 481–497, <https://doi.org/10.1139/e71-052>.
- [13] Morogan, V., Woolley, A. R. (1988). Fenitization at the Alnö carbonatite complex, Sweden; distribution, mineralogy and genesis. *Contributions to Mineralogy and Petrology*, 100 (2), pp. 169–182. <https://doi.org/10.1007/BF00373583>
- [14] Dowman, E., Wall, F., Treloar, P. J., Rankin, A. H. (2017). Rare-earth mobility as a result of multiple phases of fluid activity in fenite around the Chilwa Island Carbonatite, Malawi. *Mineralogical Magazine*, 81 (6), pp. 1367–1395, <https://doi.org/10.1180/minmag.2017.081.007>.
- [15] Mian, I., Bas, M. J. L. (1987). The biotite-phlogopite series in fenites from the Loe Shilman carbonatite complex, NW Pakistan. *Mineralogical Magazine*, 51 (361), pp. 397–408. <https://doi.org/10.1180/minmag.1987.051.361.06>
- [16] Ferguson, J., McIver, J. R., Danchin, R. V. (2010). Fenitisation associated with the alkaline-carbonatite complex of Epembe, South West Africa. *Trans. Geol. Soc. S. Afr.*, 78, pp. 111–121.
- [17] Chen, W., Honghui, H., Bai, T., Jiang, S. (2017). Geochemistry of Monazite within Carbonatite Related REE Deposits. *Resources*, 6 (4), p. 51. <https://doi.org/10.3390/resources6040051>
- [18] Migdisov, A., Williams-Jones, A. E., Brugger, J., Caporuscio, F. A. (2016). Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. *Chemical Geology*, 439(C), Article LA-UR-16-21989, <https://doi.org/10.1016/j.chemgeo.2016.06.005>.

- [19] Dumanska-Slowik, M., Heflik, W., Kromska, A., Sikorska, M. (2015). Sodic fenites of the Oktiabrski Complex exposed in the Khibodarivka quarry (East Azov, SE Ukraine): Reconstruction of their growth history. *Neues Jahrbuch für Geologie und Paläontologie – Abhandlungen*, 275.
<https://doi.org/10.1127/njgpa/2015/0471>
- [20] Pan, Y., Fleet, M. E., MacRae, N. D. (1993). Late alteration in titanite (CaTiSiO₅): Redistribution and remobilization of rare earth elements and implications for U/Pb and Th/Pb geochronology and nuclear waste disposal. *Geochimica et Cosmochimica Acta*, 57 (2), pp. 355–367.
[https://doi.org/10.1016/0016-7037\(93\)90437-2](https://doi.org/10.1016/0016-7037(93)90437-2)
- [21] Zeh, A., Cabral, A. R., Koglin, N., Decker, M. (2018). Rutile alteration and authigenic growth in metasediments of the Moeda Formation, Minas Gerais, Brazil – A result of Transamazonian fluid–rock interaction. *Chemical Geology*, 483, pp. 397–409, <https://doi.org/10.1016/j.chemgeo.2018.03.007>.