

SOME REE-BEARING ACCESSORY MINERALS IN TWO TYPES OF VARISCAN GRANITOIDS, HUNGARY

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Abstract: The two main types of Hungarian Variscan granitoids are different in many respects. The older one, occurring in South Hungary (Mecsek Mts.), is syncollision S-, I-type, migmatitic with a monzonitic suite. The rocks are enriched in REE with abundant REE-bearing accessory minerals such as allanite, zircon, apatite, thorite, monazite, titanite and secondary rare earth fluorcarbonates. The REE distribution pattern of the whole rock is strongly influenced by the composition of allanite which is the most common REE-rich mineral. Later hydrothermal alteration caused depletion of Ce, Th etc., from allanite and resulted in crystallization of secondary rare earth fluorcarbonates and thorite. The different REE contents of zircon and apatite crystal cores suggest variable source rocks.

The younger postcollision Variscan granitoids (along the Velence-Balaton tectonic line) are intrusive S- or A-type with a granodioritic suite. The granitoids as well as their allanites are relatively enriched in HREE+Y, due to flux of a volatile enriched solution at the end of crystallization but the Σ REE content is low.

Key words: Hungary, Variscan granitoids, REE distribution, allanite, zircon, apatite, RE-fluorcarbonates.

Introduction

Two main types of Variscan granitoids were identified in Hungary. The older type (360 Ma, Balogh et al. 1983) occurs in the southern part of Hungary forming a NE-SW narrow belt between the Mecsek Mts. and Danube-Tisza Interfluve; it outcrops only in the Mecsek Mts. (Mórág, Erdősmecke etc.; Fig. 1). This granitoid is mainly S-mixed with I-type (Buda 1985), a typical "in situ" migmatite, crystallized from a water-saturated melt. It has a very heterogeneous composition about 60 % peraluminous and 40 % metaluminous chemical characters, slightly al-

kaline showing a monzonitic suite, while only the aplitic variety has granitic composition. The independent distribution of K versus Si and the texture of rocks suggest K-metasomatism. The biotite is Mg-rich with low oxidation ratio. This, together with rather high NH_4 -content, suggests a low-temperature, low oxygen fugacity, sedimentary protolith (S-type components). The amphibole-rich restite, "floating" in the microcline megacryst bearing granitoid, was most probably basic igneous rock, as concluded from the high Cr-content and from small chromite inclusions in biotite (I-type components). The K-feldspars are medium-ordered in the groundmass ($\Delta = 0.50$) and the megacrysts

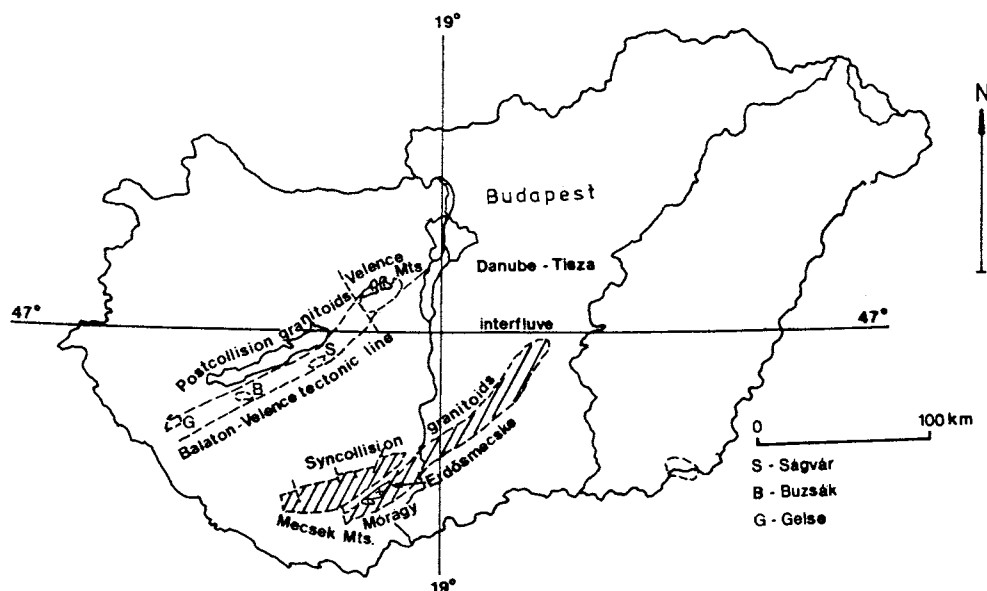


Fig. 1. Geological sketch map of Hungarian granitoids (continuous line = surface, dotted line = subsurface occurrences).

Table 1: Trace element content of megacryst bearing microcline granitoid and separated minerals measured by INAA (Mecsek Mts., Mórággy).

g/t	1.	2.	3.	4.	5.	6.
La	61.8	13.3	8.4	670	710.5	338
Ce	119.3	27.9	12.3	3480	763.5	916
Nd	42.8	9.7	2.8	2211	431.0	213
Sm	11.4	3.0	0.73	1143	179.0	193
Eu	1.27	0.48	0.99	75.1	22.5	11.5
Tb	1.01	0.32	0.10	130.0	102.8	9.4
Tm	0.47	0.18	0.05	58.0	42.3	4.6
Yb	2.37	1.34	0.24	565.0	458.0	34.9
Lu	0.36	0.12	0.03	42.7	87.6	4.67
ΣREEM	240.78	56.34	25.64	8374.8	2797.2	1725.07
ΣREEC	270.6	64.9	29.61	11093.7	4370.0	1985.7
ΣLREE	247.6	56.98	26.12	8004.7	2196.1	1738.7
ΣHREE	23.00	7.91	3.49	3089.0	2174.7	246.97
$\Sigma\text{L}/\Sigma\text{H}$	10.8	7.20	7.48	2.59	1.01	7.04
Eu/Eu*	0.40	0.58	4.5	0.23	0.25	0.28
Sc	9.5	29.8	0.42	37.2	210	0.8
Cr	49.6	337.0	4.17	542.0	1.0	-
Co	18.4	37.9	2.47	3.5	5.3	1.10
Rb	239.6	718.0	252.0	30.0	30.0	580.0
Cs	11.6	59.0	3.3	5.2	0.2	-
Hf	7.8	3.3	0.45	44.8	1.24	0.9
Ta	3.2	2.8	0.18	550.0	7.1	-
Th	38.3	13.2	2.83	367.0	1627	50.2
U	10.6	5.2	1.60	241.0	1283	34.3

1. Rock (average of 13 samples); 2. Biotite (average of 5 samples); 3. Microcline (average of 5 samples); 4. Titanite* rich in allanite; 5. Zircon* rich; 6. Apatite* rich
* separated by heavy liquid.

(M = measured, C = calculated, L = light, H = heavy)

are highly ordered ($\Delta = 0.85-0.90$, Buda 1974). The former crystallized rapidly from a water-saturated anatectic melt at slightly higher temperature, while the latter formed from a K-rich fluid at lower temperature. These granitoids are classified as the syncollisional type (Pearce et al. 1984).

The younger type is (280 Ma, op. cit) postcollisional, peraluminous S- (Buda 1985) or A-type (Uher & Broska 1994) and occurs as small intrusive bodies along the tectonic line of Velence-Balaton, outcropping only in the Velence Mts. Other granitoids were found by drilling and only core samples are available for study (Ságvár, Buzsák, Gelse; Fig. 1). These intrusive granitoids have a thermal contact aureole. It is suggested that the initial water-saturated melt in the crust became water-undersaturated, due to the heat-flux caused by upwelling of upper mantle. This high temperature melt intruded into the higher level of the continental crust as a hypabyssal pluton. As a result of crystal fractionation, a water-saturated eutectic melt formed. These granitoids show calc-alkaline granodioritic differentiation trend. Orthoclase crystallized at about 680 °C. Slightly ordered K-feldspar formed only locally in water-saturated pegmatitic "pods" at about 550 °C (Buda 1993).

The accessory minerals of the two occurrences were investigated by Pantó (1975, 1977), Gbelský & Határ (1982), Pantó et al. (1988), Dani & Buda (1994). According to Pantó (1975)

xenotime occurs in the Velence Mts. and is absent in the Mecsek Mts. Monazite is abundant in the Mecsek Mts. and subordinate in Velence Mts. The bastnäsite-group minerals are widespread in the Mecsek Mts. and was not found in Velence Mts. Fluorapatite is common in both occurrences, containing Y in the Velence Mts., and Ce, Y enriched in the Mecsek Mts. (Pantó 1977). Allanite can be identified in both occurrences, but according to Pantó (1975) its quantity proved to be subordinate and consequently it does not play an important role in the REE accumulation.

The results of the typology of the zircon population also confirm the genetic differences of the Velence and Mecsek Mts. (Gbelský & Határ 1982; Dani & Buda 1994). Zircon shows alkaline or subalkaline characters in the biotite-granite and old granite-porphry of Velence whereas in the younger granite porphry of Velence and granitoids in Mecsek zircon has a K-calc-alkaline character (Pupin 1985).

Analytical procedure

Microprobe analyses were performed by WDS analysis using a EPMA type JCSA-733 (JEOL) instrument, operating at an accelerating potential of 20 kV and sample current of 40-60 nA

Table 2: Allanite and epidote from granitoids and restite (Mecsek Mts.).

wt. %	1.	2.	3.	4.	5.
SiO ₂	32.03	30.60	32.65	38.05	32.08
Al ₂ O ₃	13.42	15.12	12.57	23.53	15.02
FeO	11.87	11.05	13.44	11.08	12.75
MgO	0.68	1.47	0.72	0.00	1.31
CaO	11.20	10.06	12.79	23.23	10.12
MnO	1.46	0.31	0.92	0.01	0.15
TiO ₂	1.48	1.47	1.52	0.02	1.21
Y ₂ O ₃	0.04	0.09	0.02	n.d.	0.32
La ₂ O ₃	4.71	6.63	5.32	n.d.	5.46
Ce ₂ O ₃	12.78	11.72	10.45	0.29	11.67
Pr ₂ O ₃	0.86	0.98	1.03	n.d.	1.09
Nd ₂ O ₃	3.11	3.30	2.93	n.d.	3.69
Sm ₂ O ₃	0.31	0.36	0.28	n.d.	0.58
Eu ₂ O ₃	0.03	0.02	0.03	n.d.	0.01
Gd ₂ O ₃	0.14	0.24	0.20	n.d.	0.45
Dy ₂ O ₃	0.00	0.00	0.37	n.d.	0.19
Er ₂ O ₃	0.00	0.00	0.03	n.d.	0.04
ThO ₂	0.81	1.50	0.65	0.01	1.25
UO ₂	0.09	0.13	0.09	0.01	0.09
Σ	95.02	95.05	96.01	96.23	97.48
Numbers of ions on the basis of 12.5 oxygens					
Si	3.161	3.032	3.183	3.128	3.093
Al	-	-	-	-	-
Al	1.561	1.767	1.445	2.280	1.708
Fe	0.980	0.916	1.095	0.761	1.029
Mg	0.100	0.217	0.104	0.000	0.188
Ca	1.185	1.068	1.337	2.046	1.045
Mn	0.122	0.026	0.076	0.001	0.012
Ti	0.110	0.109	0.112	0.001	0.088
Y	0.002	0.005	0.001	0.000	0.016
La	0.172	0.243	0.191	0.009	0.194
Ce	0.462	0.425	0.373	0.000	0.412
Pr	0.031	0.036	0.036	0.000	0.038
Nd	0.110	0.117	0.102	0.000	0.127
Sm	0.010	0.012	0.010	0.000	0.019
Eu	0.001	0.001	0.001	0.000	0.001
Gd	0.005	0.008	0.006	0.000	0.014
Dy	0.000	0.000	0.012	0.000	0.006
Er	0.000	0.000	0.001	0.000	0.001
Th	0.018	0.034	0.014	0.000	0.027
U	0.002	0.003	0.002	0.000	0.002
ΣREE+Y	0.79	0.85	0.73	0.009	0.83
Sm/Nd	0.09	0.10	0.10	-	0.15
Ce/La	2.69	1.75	1.95	-	2.12
Σ _L /Σ _H	157	104	38	-	38

1. Homogenous allanite (Mórág, megacryst cont. gr. on Fig. 3A., No. 1.); 2. Inhomogenous allanite (Mórág, megacryst cont. gr. on Fig. 3B., No. 4.); 3. Rim of the zoned allanite (Erdősmecke, megacryst cont. gr.); 4. Epidote, outermost rim of zoned allanite (Erdősmecke), 5. Zoned allanite (innerpart, Erdősmecke, restite); n.d. = not determined

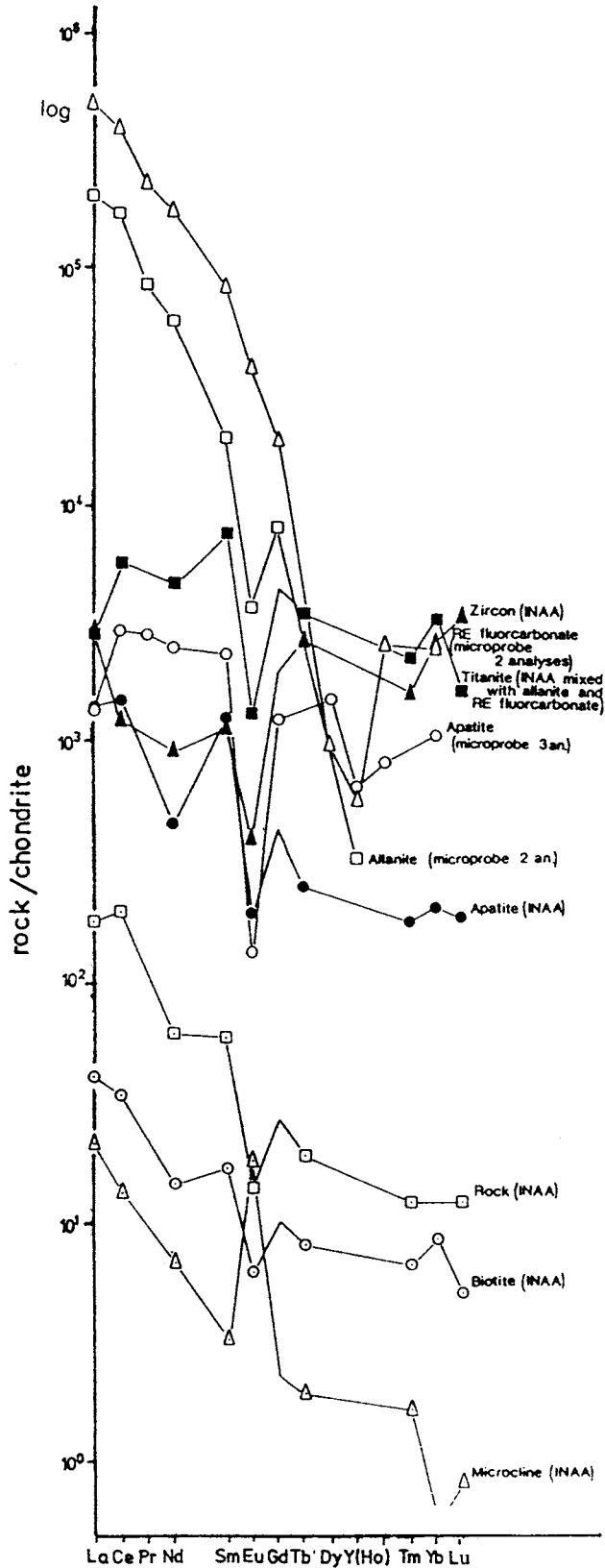


Fig. 2. Chondrite-normalized REE(+Y) patterns of rock, rock-forming minerals and accessories (Mecsek Mts.: Mórág; INAA = Instrumental Neutron Activation Analyses).

Table 3: Microprobe analyses of RE-fluorcarbonate minerals (Mecsek Mts., Mórág).

	1.	2.
Y ₂ O ₃	0.08	0.22
La ₂ O ₃	15.87	14.31
Ce ₂ O ₃	29.69	34.20
Pr ₂ O ₃	2.89	2.08
Nd ₂ O ₃	9.91	7.84
Sm ₂ O ₃	1.54	1.49
Eu ₂ O ₃	0.26	0.19
Gd ₂ O ₃	0.51	0.43
Dy ₂ O ₃	0.00	0.00
Er ₂ O ₃	0.00	0.00
Yb ₂ O ₃	0.04	0.02
CaO	5.19	5.45
ThO ₂	5.14	2.24
F	8.26	8.68
Σ	79.38	77.15
Numbers of ions on the basis of 12 oxygens		
Y	0.012	0.035
La	1.707	1.577
Ce	3.171	3.742
Pr	0.307	0.226
Nd	1.033	1.837
Sm	0.155	0.153
Eu	0.026	0.019
Gd	0.050	0.043
Dy	0.000	0.000
Er	0.000	0.000
Yb	0.003	0.002
Ca	1.621	1.744
Th	0.341	0.153
F	7.623	8.204

1. Röntgenite-(Ce)? in K-silicate (on Fig. 4A., No. 3);

2. Parisite-(Ce)? in calcite (on Fig. 4B., No. 4)

at the Hungarian Academy of Sciences. For REE analyses, the L_{α} lines were measured but in the case of Pr and Tm their L_{β} lines were used on the LiF crystal. The artificial glass standards of Drake & Weill (1972) were used for comparison.

In order to determine the "rough" concentrations a program was written in JASCAL the special language of JEOL, JCA-733 probe. The main steps are (Nagy 1993): 1. determination of overlap; 2. standardization; 3. correction of spectrometer shifts determining the nominal vs. true peak positions; 4. measurement of unknown specimen; a. scanning the spectrometer to peak or background position; b. calculation of backgrounds at analytical peaks; c. overlap correction; d. calculation of first approximations followed by ZAF correction using off-line program.

Instrumental neutron activation analyses were carried out on separated minerals of titanite, apatite, zircon, biotite and feldspar at the Training Reactor of the Technical University, Budapest. The REE data have been normalised using the chondritic



Fig. 3A. Back-scattered electron images (BEI) of homogeneous allanite with thorite grains (white spots) from porphyroblastic granitoid (see Tab. 2, No. 1 analysis, Mecsek Mts.: Mórágý).

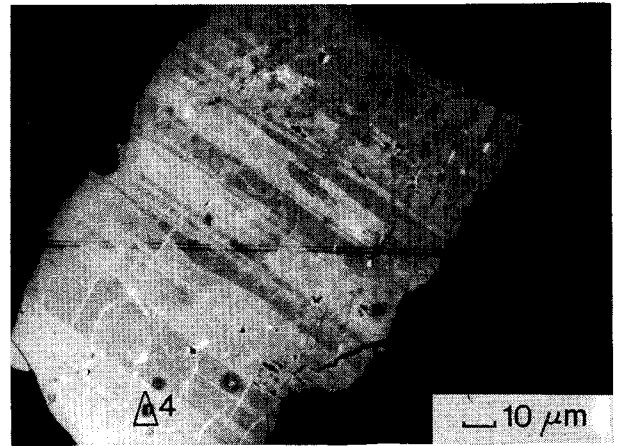


Fig. 3B. BEI of inhomogeneous REE-bearing allanite (see Tab. 2, No. 4 analysis, Mecsek Mts.: Mórágý).



Fig. 4A. BEI of RE-fluorcarbonate [röntgenite-(Ce)?] in K-silicate (see Tab. 3, No. 3 analysis, Mecsek Mts.: Mórágý).

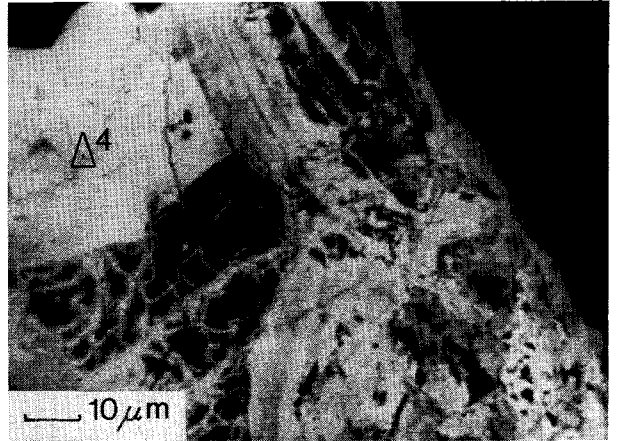


Fig. 4B. BEI of RE-fluorcarbonate [parisite-(Ce)?] in calcite (see Tab. 3, analysis of No. 4, Mecsek Mts.: Mórágý).

values of Sun & McDonough (CI chondrite, 1989). Yttrium has been plotted at the Holmium position on ionic radius criteria.

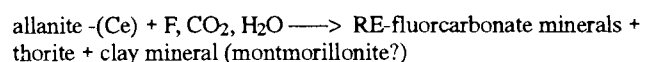
REE-rich accessory minerals in syncollision granitoids (Mecsek Mts.)

The megacryst microcline-bearing granitoids are very rich in accessory minerals: allanite-(Ce), unknown REE silicate (britholite?), apatite, zircon, titanite, thorite, monazite, uraninite, rutile and secondary rare earth fluorcarbonate group minerals such as röntgenite-(Ce) or parisite-(Ce) (determined by only microprobe analyses). The REE enrichment (average of rock: 241 g/t; Tab. 1) is due to these accessories, the most abundant being allanite, because the rock-forming minerals are actually low in REE (e.g. REE in biotite = 57 g/t, in microcline = 26 g/t; Tab. 1, Fig. 2). The bulk REE content of accessory minerals separated by heavy liquid was measured by INAA. According to these measurements the titanite rich fraction has the highest REE content (8400 g/t). Zircon (2800 g/t) and apatite (1700 g/t) have considerably lower REE (Tab. 1).

The titanite-rich heavy liquid fraction was examined by microprobe. According to these investigations this fraction contains about 10 wt. % of allanite-(Ce) (confirmed by X-ray powder diffraction),

unknown REE silicate (britholite?), thorite and secondary RE-fluorcarbonate minerals. These minerals are responsible for the REE enrichments since titanite contains small amount of REE ($\text{La}_2\text{O}_3 = 0.11$, $\text{Ce}_2\text{O}_3 = 0.20$, $\text{Nd}_2\text{O}_3 = 0.04$ wt. %).

Allanite-(Ce) is rather common in the microcline-bearing granitoids but it can be found in the amphibole rich restite as well. It is euhedral or subhedral, zoned with inhomogeneous or sometimes homogeneous (Fig. 3A, 3B) composition. The cores of the zoned crystals are often metamict. Sometimes the outermost rim is entirely depleted in REE, and an epidote overgrowth (Tab. 2) is present which was also observed by Pantó (1975). The allanite commonly contains RE-fluorcarbonate minerals and thorite as alteration products due to later processes. Crystals with homogeneous cores contain high Ce ($\text{Ce}/\text{La} = 2.7$), whilst the rims ($\text{Ce}/\text{La} = 2.0$) and inhomogeneous allanites ($\text{Ce}/\text{La} = 1.8$) are enriched in La and HREE. This is due to leaching by acidic fluorine and carbonate-bearing solution formed either at the later stage of crystallization or originated hydrothermally after crystallization. These processes resulted in RE-fluorcarbonate minerals (Tab. 3, Fig. 4A, 4B), thorite and clay mineral formation from allanite, according to the following reaction:



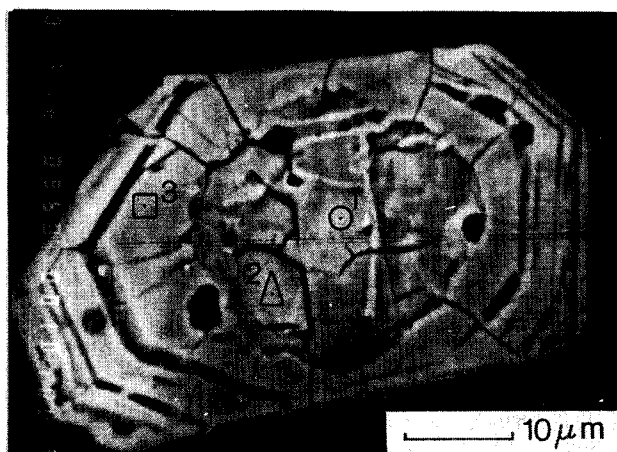


Fig. 5A. BEI of zoned zircon with relatively U, Th, REE-rich cores (see Tab. 4, analyses of No. 1, No. 2) and depleted outer zone (No. 3, Mecsek Mts.: Mórágý).

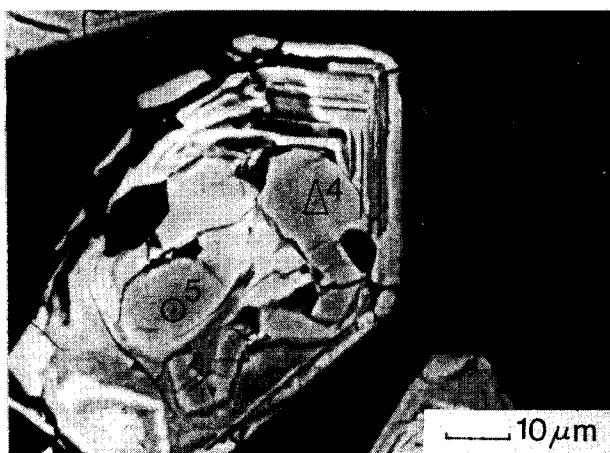


Fig. 5B. BEI of zoned zircon with rather high Hf-bearing cores (see Tab. 4, analyses of No. 4 and No. 5, Mecsek Mts.: Mórágý).

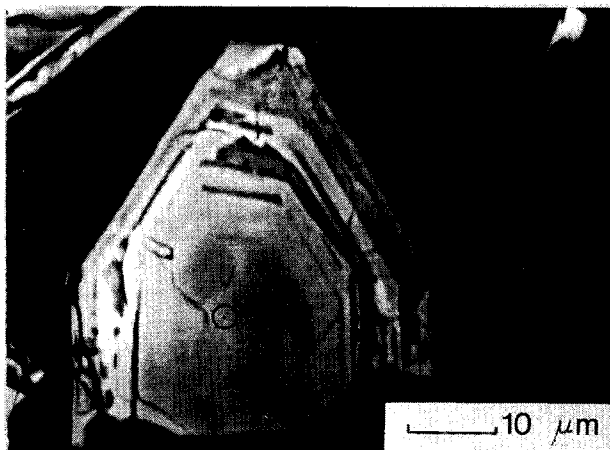


Fig. 5C. BEI of zoned zircon with REE depleted core (see Tab. 4, and analysis of No. 7, Mecsek Mts.: Mórágý).

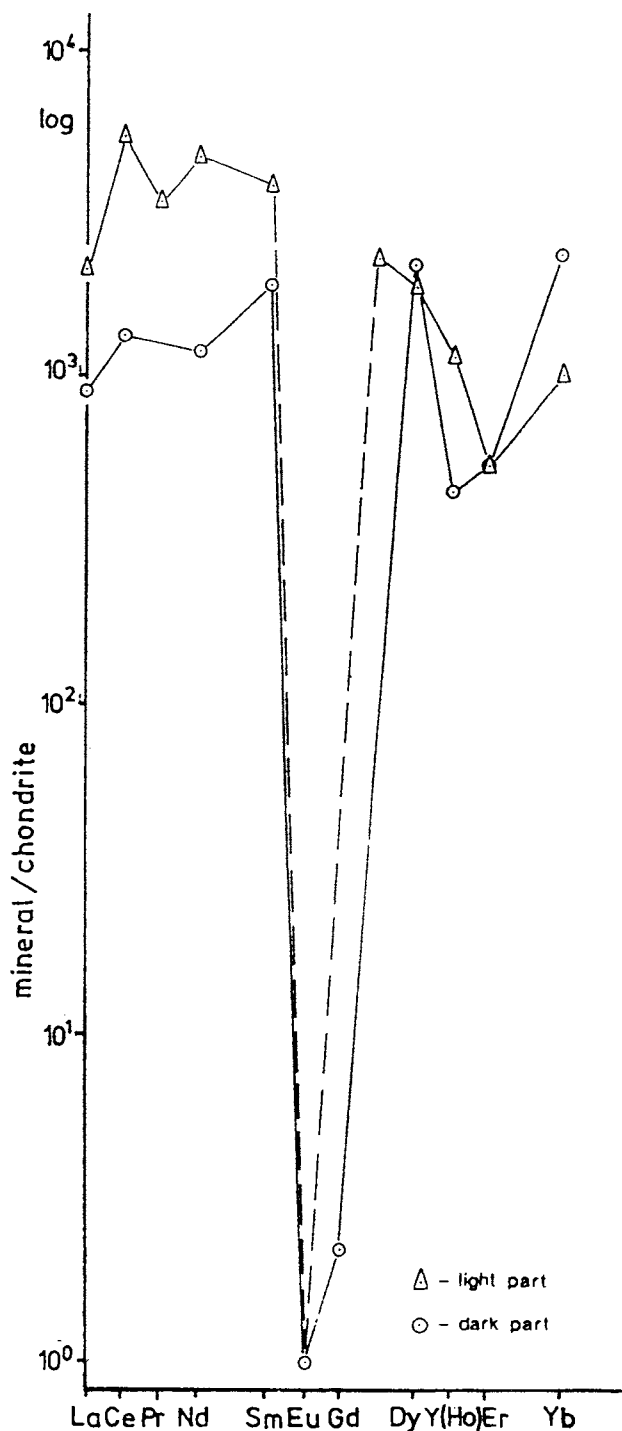


Fig. 6. Chondrite-normalized REE(+Y) patterns of dark and light part of apatite on BEI (Mecsek Mts.: Mórágý).

($Y/Hf < 1.90$, $Y/Hf = 0.004$) corresponding to heterogeneous origins. Most of the cores are enriched in REE (Tab. 4) with a relatively HREE enrichment ($\Sigma REE_L / \Sigma REE_H = 3.2$) compared with allanite (84). On the basis of their varying Ca content, two populations were also detected by Pantó (1975).

Fluor-apatite: is always zoned, with the cores and the rims sometimes enriched in REE, (Fig. 6, 6A, 6B). REE enrichment in the core is more common. The light parts on the BEI image are enriched in REE, whereas in the dark parts ΣREE are lower and

Zircon: is very often zoned with one or more cores (Fig. 5A, 5B, 5C). Most of the cores are hydrozircon enriched in U, Hf. According to Y/Hf ratios two populations can be distinguished

Table 4: Microprobe analyses of zircons (Mecsek Mts., Mórág).

	1.	2.	3.	4.	5.	6.
ZrO ₂	54.02	49.01	66.71	65.75	65.70	65.13
SiO ₂	30.89	29.43	32.02	32.52	32.00	31.83
HfO ₂	1.45	1.62	1.84	2.18	1.82	1.61
FeO	0.93	1.94	0.10	0.04	0.04	0.03
CaO	1.58	1.44	0.03	0.01	0.01	0.02
ThO ₂	1.52	1.56	0.12	0.02	0.02	0.00
UO ₂	1.16	1.11	0.16	0.18	0.12	0.11
Al ₂ O ₃	1.27	1.64	0.05	0.00	0.00	0.00
Y ₂ O ₃	1.70	1.96	0.00	0.00	0.02	0.00
Ce ₂ O ₃	0.51	1.84	0.00	0.00	0.10	0.00
Pr ₂ O ₃	0.12	0.28	0.00	0.00	0.01	0.00
Nd ₂ O ₃	0.64	1.91	0.00	0.00	0.00	0.00
Sm ₂ O ₃	0.25	0.67	0.00	0.00	0.00	0.00
Gd ₂ O ₃	0.23	0.55	0.00	0.00	0.00	0.00
Dy ₂ O ₃	0.24	0.29	0.00	0.00	0.05	0.00
Er ₂ O ₃	0.13	0.18	0.00	0.00	0.08	0.00
Yb ₂ O ₃	0.23	0.21	0.00	0.00	0.03	0.00
Σ	96.87	95.64	101.03	100.70	100.00	98.73
Numbers of ions on the basis of 16 oxygens						
Si	3.989	3.934	3.921	3.980	3.953	3.968
Al	0.193	0.259	0.008	0.000	0.000	0.000
Y	0.116	0.140	-	-	0.001	-
Zr	3.401	3.195	3.983	3.923	3.957	3.959
Hf	0.062	0.072	0.075	0.089	0.075	0.067
Fe	0.101	0.217	0.010	0.004	0.004	0.003
Th	0.045	0.047	0.003	0.000	0.000	0.000
U	0.033	0.033	0.004	0.005	0.003	0.003
Ce	0.024	0.090	-	-	0.004	-
Pr	0.006	0.014	-	-	0.000	-
Nd	0.030	0.091	-	-	0.000	-
Sm	0.011	0.031	-	-	0.000	-
Gd	0.010	0.024	-	-	0.000	-
Dy	0.010	0.013	-	-	0.002	-
Er	0.005	0.008	-	-	0.003	-
Yb	0.009	0.008	-	-	0.001	-
Ca	0.219	0.206	0.004	0.001	0.002	0.003
ΣREE+Y	0.221	0.419	-	-	0.11	-
Σ _L /Σ _H	2.1	4.3	-	-	0.7	-
Th/U	1.3	1.4	0.75	0.11	0.17	0.0

1. Inner part of the crystal (hydrozircon on Fig. 5A., No. 1); 2. Inner part of the same crystal (hydrozircon on Fig. 5A., No. 2); 3. Outer part of the same crystal (on Fig. 5A., No. 3); 4. Core of the crystal (on Fig. 5B., No. 4); 5. Other core of the same crystal (on Fig. 5B., No. 5); 6. Core of the crystal (on Fig. 5C., No. 7).

LREE content is decreased (Tab. 5). Both show negative Eu anomalies and are relatively enriched in HREE ($\Sigma_L/\Sigma_H = 2.7$). The REE distribution of apatite implies a metamorphic origin (Cruft 1966). A negative Ce anomaly was not observed (Puchelt & Emmermann 1976). Consequently the negative Eu anomaly in apatite and biotite as well as the low oxidation ratio in biotite

(Buda 1990) can be explained by a low oxygen fugacity during crystallization.

The other identified accessory minerals are pyrite, monazite, uraninite, (galena, molybdenite, rutile) etc., but they are mostly small grains and their occurrences are not as widespread as the described ones.

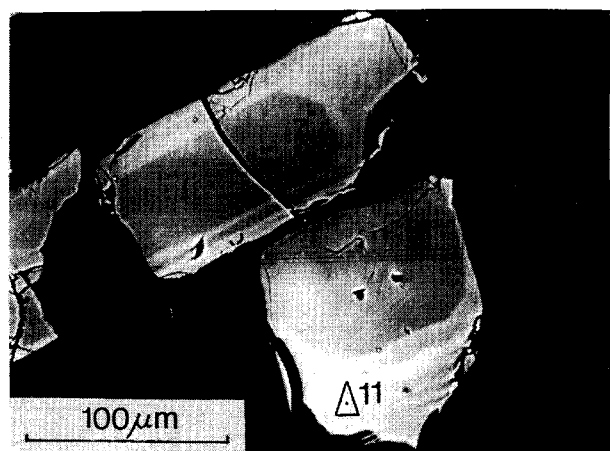


Fig. 6A. BEI of zoned apatite with REE poor core (dark part, see Tab. 5, analysis of No. 7) and REE rich rim (white part, see Tab. 5, analysis of No. 11, Mecsek Mts.: Mórágý).

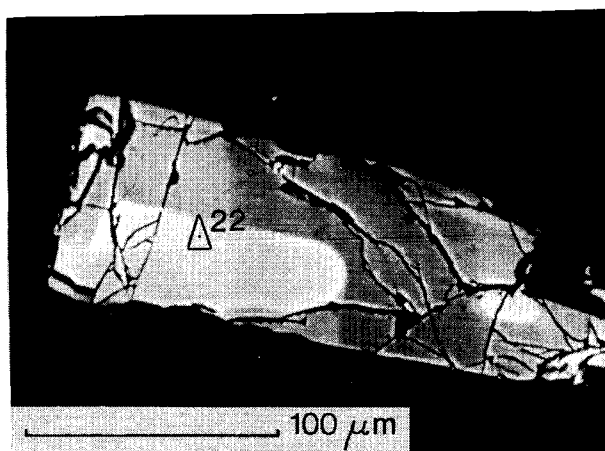


Fig. 6B. BEI of zoned apatite with REE rich core (white part, see Tab. 5, No. 22 analysis).

Table 5: Representative microprobe analyses of apatites (Mecsek Mts., Mórágý).

	1.	2.	3.	4.
CaO	55.35	55.20	54.76	54.60
P ₂ O ₅	42.63	42.72	41.68	41.35
F	2.49	2.64	2.74	2.68
Y ₂ O ₃	0.12	0.06	0.15	0.30
La ₂ O ₃	0.00	0.05	0.00	0.12
Ce ₂ O ₃	0.05	0.14	0.24	0.56
Pr ₂ O ₃	0.00	0.00	0.03	0.05
Nd ₂ O ₃	0.04	0.09	0.20	0.33
Sm ₂ O ₃	0.04	0.03	0.06	0.08
Eu ₂ O ₃	0.00	0.00	0.00	0.00
Gd ₂ O ₃	0.02	0.00	0.05	0.06
Dy ₂ O ₃	0.12	0.01	0.06	0.05
Er ₂ O ₃	0.08	0.00	0.02	0.00
Yb ₂ O ₃	0.07	0.02	0.04	0.00
O=F	-1.05	1.11	1.15	1.13
Σ	99.96	99.85	98.88	99.05
ΣREE+Y ₂ O	0.54	0.40	0.85	1.55
Σ _L /Σ _H	0.32	3.4	4.66	2.6
Numbers of ions on the basis 26 (O + F)				
Ca	10.037	9.992	10.077	10.112
P	6.119	6.121	6.072	6.062
F	1.332	1.410	1.488	1.465

1. Dark apatite on BEI, (on Fig. 6A., No. 7); 2. Dark apatite on BEI (an. No. 24); 3. Light apatite on BEI, (on Fig. 6A., No. 11); 4. Light apatite on BEI (on Fig. 6B., No. 22)

REE-bearing minerals in postcollision granitoids (Velence-Balaton tectonic line)

Two granitoid occurrences were investigated along the Velence-Balaton tectonic line: *a*. Granodiorite from Buzsák (core sample); *b*. Monzogranite from Sukoró (Rigó Hill, Velence Mts., surface samples; Fig. 1).

Table 6: Trace element content of granitoids and biotite measured by INAA (Balaton-Velence tectonic line).

	1.	2.	3.
La	12.00	41.60	17.9
Ce	34.20	77.00	42.3
Nd	11.10	27.60	15.6
Sm	5.10	8.90	9.5
Eu	0.67	0.51	0.77
Tb	0.90	1.00	1.30
Tm	0.40	0.50	0.60
Yb	2.10	2.60	9.50
Lu	0.49	0.44	1.28
ΣREE _M	66.96	160.15	98.75
ΣREE _C	84.84	185.49	-
Σ _L REE	66.04	162.25	-
Σ _H REE	18.80	23.24	-
Σ _L /Σ _H	3.51	6.98	-
Eu/Eu*	0.41	0.19	-
Sc	7.8	4.4	74.7
Cr	10.3	81.3	57.0
Co	5.7	3.0	28.8
Rb	181.0	215.0	390.0
Cs	6.6	4.5	32.8
Hf	3.6	3.7	2.3
Ta	1.3	1.4	15.6
Th	11.1	24.2	5.9
U	4.2	5.3	9.3

1. Granodiorite (Buzsák 1200–1206 m); 2. Monzogranite, (Velence Mts., Sukoró, Rigó Hill); 3. Biotite from monzogranite (Sukoró, Rigó Hill)

a - Granodiorite (Buzsák): The REE content of this rock is rather low (ΣREE 67 g/t determined by INAA; Tab. 6) and the ΣREE_L/ΣREE_H ratio is also low (3.5) which means relative enrichment of HREE (Fig. 7). The main REE-bearing mineral is allanite which forms euhedral, zoned greenish crystals with apatite and zircon inclusions. The inner part of the crystal is

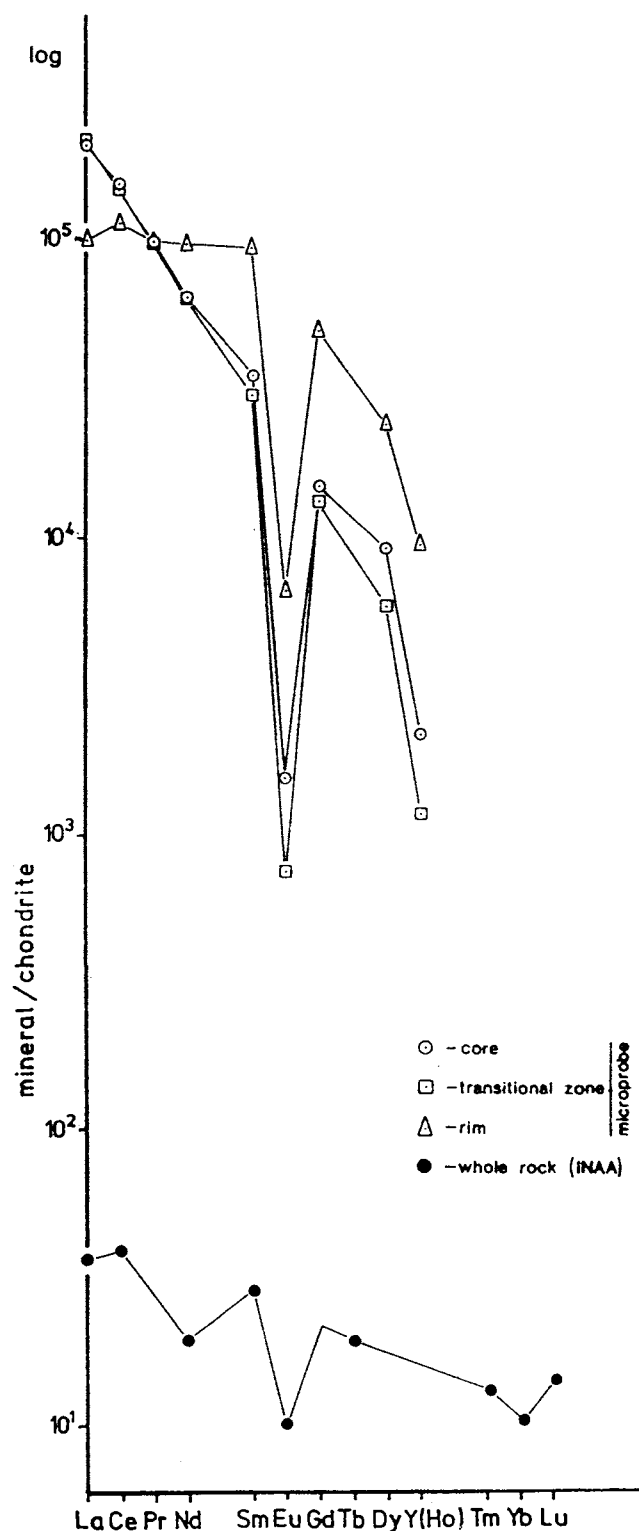


Fig. 7. Chondrite-normalized REE(+Y) patterns of granodiorite and allanite (Balaton-Velence tectonic line: Buzsák).

slightly inhomogenous, and near to the rim a metamict zone occurs with small thorite grains (Fig. 7A). Fourteen spot microprobe analyses have been carried out on one grain: of these, six gave acceptable total oxides of more than 97 wt.%. Total oxides in the metamict zone are considerable lower (95–81 wt.%) but thorium (2.78 wt.%), fluorine (0.61 wt.%) and chlorine (0.25 wt.%) en-

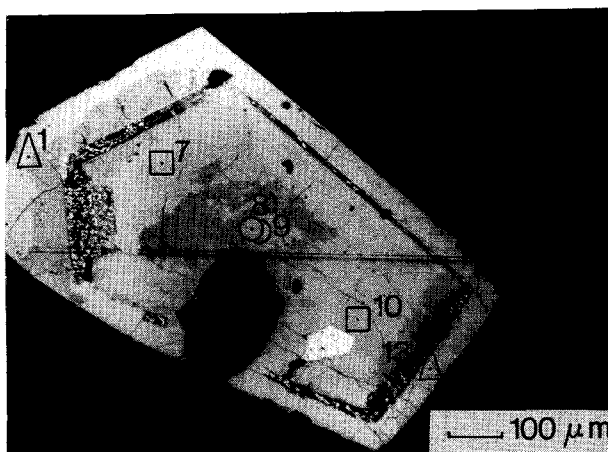


Fig. 7A. BEI of euhedral allanite with metamict (dark) and thorite (white spots in dark zone) content zone (granodiorite occurring in Buzsák, numbers are analysed points, see Tab. 7).

richments were detected and OH content may also be higher. In the rim Fe, Mn, Nd, Sm, Eu and HREE(Y) are enriched and strong La, Ce, Al and Ti depletion can be recognised (Tab. 7).

b - Monzogranite (Velence Mts.: Sukoró, Rigó Hill); The Σ REE content of this granite is considerable higher than that of the granodiorite (Σ REE = 160 g/t). LREE and HREE enrichments and Eu depletion can be observed (Tab. 6, Fig. 8), and these REE patterns correspond well with the latter stage of crystal differentiation of monzogranite compared with granodiorite.

The granite is not as rich in accessory minerals as the South-Hungarian granitoids. The most common accessory minerals are allanite, zircon, apatite, RE-fluorcarbonate minerals. Monazite, xenotime, ilmenite, rutile etc. were identified only in pelitic xenoliths (Buda 1993) occurring in the upper part of a monzogranite intrusion, near the thermal contact zone.

Allanite-(Ce): is euhedral, partly metamict in different zones of the crystal, and brown in colour (Fig. 8A). Six analyses have been carried out on one grain but three had total oxides around 98 wt.% (Tab. 8). The total oxides of others were between 86 and 95 wt.%, which is most probably due to H_2O enrichment as a consequence of metamictization. Thorium is presumably responsible for metamictization because Th enrichment ($ThO_2 = 3.0$ wt.%) can be measured in metamict zone. The total REE distribution does not change significantly from the core towards the rim (Fig. 8), with mostly oscillatory zoning observed. A slight enrichment of Fe, Ce, Pr, Eu and Si depletion can be observed from core to rim.

Summary and conclusions

The REE distribution of granitoids is controlled by the accessory minerals (allanite, zircon, apatite, titanite, monazite, xenotime, etc.). The total REE content of whole-rock will be high, if the granitoids are enriched in accessories and the rocks are depleted in REE, if they are poor in accessories, because the rock-forming minerals contain very low REE (e.g. biotite, microcline, etc.). Only Eu is enriched in feldspars (Fig. 2).

The South-Hungarian syncollisional migmatitic granitoids are rich in accessories, consequently the whole-rock has a high content of Σ REE. One of the most REE-rich minerals is allanite, which has a widespread occurrence in the granitoids and con-

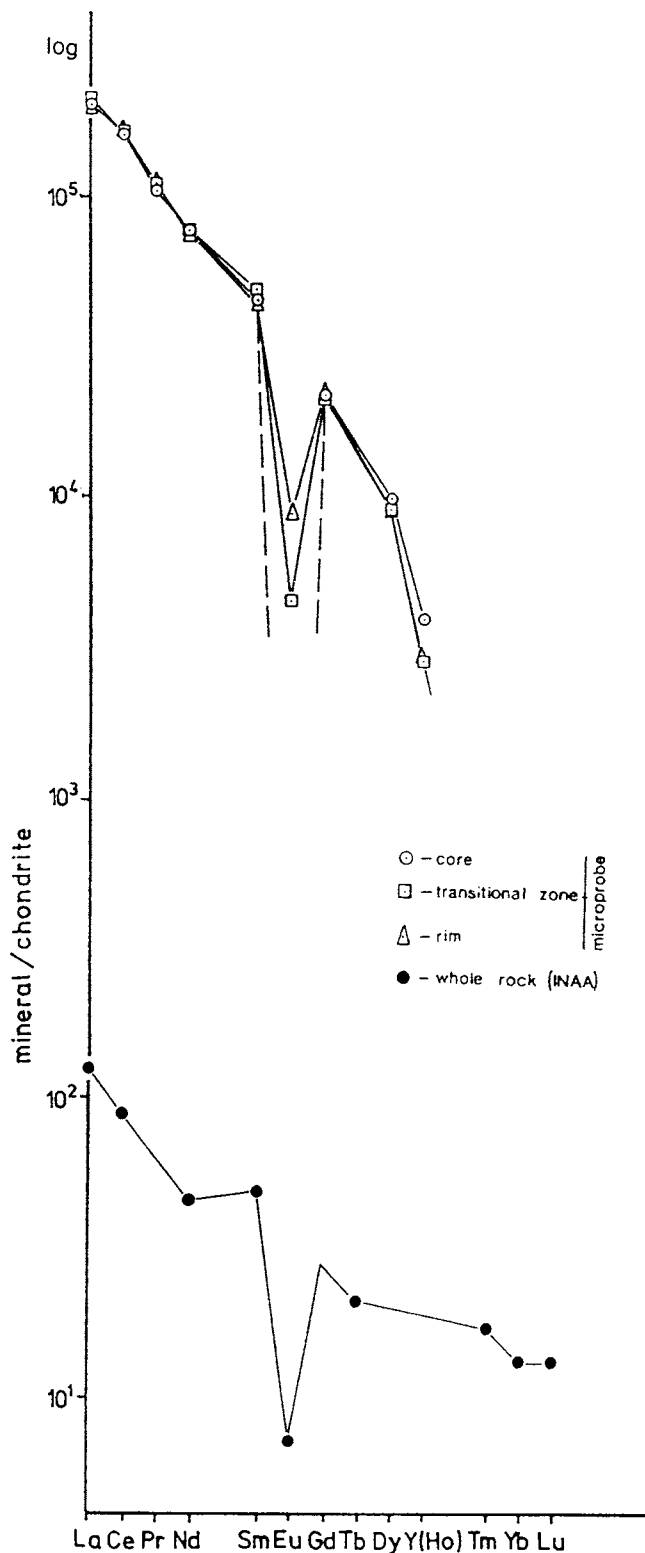


Fig. 8. Chondrite-normalized REE(+Y) pattern of monzogranite and allanite (Velece Mts.: Sukoró, Rigó Hill).

controls whole-rock REE patterns. Allanite of granitoids in the Mecsek Mts. (syncollisional-type) is LREE enriched ($\Sigma_L/\Sigma_H = 100$), as is the whole-rock ($\Sigma_L/\Sigma_H = 11$).

In the postcollisional granodiorite of Buzsák, LREE decreases in both allanite ($\Sigma_L/\Sigma_H = 39$) and in the whole-rock (3.5). The allanite of the monzogranite of the Velece Mts. (postcollisional-



Fig. 8A. BEI of allanite with metamict patches (Velece Mts.: Sukoró, Rigó Hill, numbers are analysed points, see Tab. 8).

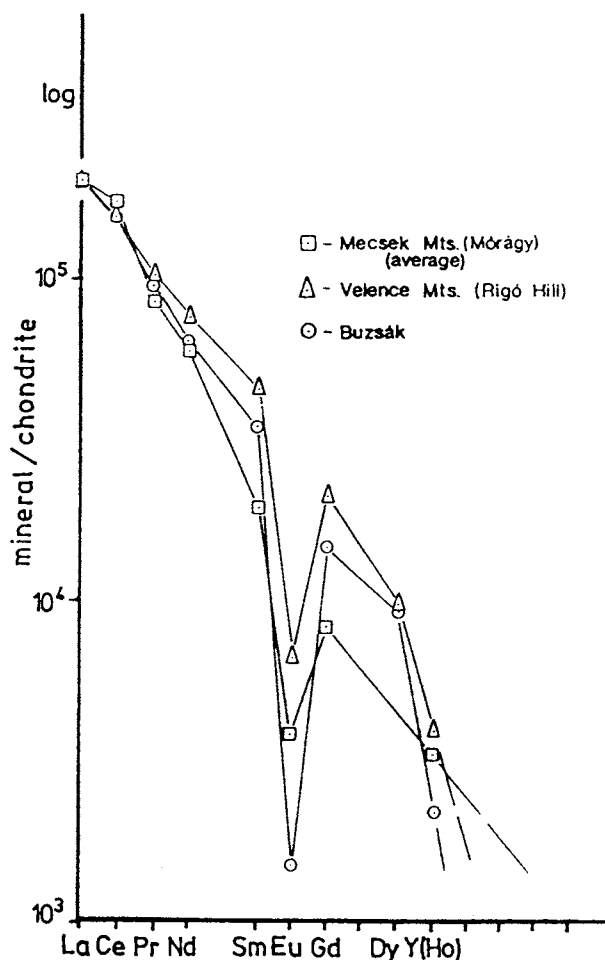


Fig. 9. Chondrite-normalized REE(+Y) patterns of allanite cores in some Hungarian granitoids.

type) is enriched in HREE and Y ($\Sigma_L/\Sigma_H = 32$). Only the cores of allanite have been compared because the outer parts of the crystals were affected by later processes which could have changed the compositions (Fig. 9).

The other accessories contain insufficient REE to have influenced whole rock REE distribution patterns; the REE-bearing

Table 7: Microprobe analyses of allanites (Buzsák).

	1.	2.	3.
SiO ₂	32.15	30.63	31.28
Al ₂ O ₃	17.18	17.13	16.58
FeO	11.11	12.50	12.99
MgO	0.65	0.80	0.64
CaO	10.79	10.79	10.17
MnO	0.39	0.38	0.72
TiO ₂	0.80	0.70	0.47
Y ₂ O ₃	0.43	0.23	1.93
La ₂ O ₃	5.70	5.86	2.76
Ce ₂ O ₃	10.78	10.66	8.16
Pr ₂ O ₃	1.05	1.04	1.11
Nd ₂ O ₃	3.41	3.40	5.24
Sm ₂ O ₃	0.60	0.52	1.66
Eu ₂ O ₃	0.01	0.01	0.05
Gd ₂ O ₃	0.35	0.31	1.14
Dy ₂ O ₃	0.26	0.17	0.70
ThO ₂	1.73	1.95	1.53
UO ₂	0.10	0.10	0.10
Cl	0.03	0.07	0.11
F	0.35	0.52	0.45
Σ	97.87	97.77	97.79
Numbers of ions on the basis of 12.5 oxygens			
Si	3.062	2.964	3.023
Al	-	0.036	-
Al	1.929	1.918	1.889
Fe ²⁺	0.885	1.012	1.051
Mg	0.092	0.115	0.092
Ca	1.101	1.119	1.054
Mn	0.031	0.031	0.059
Ti	0.058	0.051	0.034
Y	0.022	0.012	0.099
La	0.201	0.209	0.098
Ce	0.376	0.378	0.288
Pr	0.037	0.037	0.039
Nd	0.116	0.118	0.181
Sm	0.020	0.018	0.056
Eu	0.0003	0.0003	0.0002
Gd	0.011	0.010	0.037
Dy	0.008	0.005	0.022
Th	0.037	0.043	0.034
ΣREE+Y	0.83	0.79	0.82
Sm/Nd	0.172	0.152	0.309
Ce/La	1.87	1.81	2.94
Σ _I /Σ _H	39	59	11

1. Core (average of analyses on Fig. 7A., Nos. 8, 9); 2. Intermediate part (average of analyses on Fig. 7A., Nos. 7, 10); 3. Rim (average of analyses on Fig. 7A., Nos. 1, 13)

Table 8: Microprobe analyses of allanites (Velence Mts., Sukoró, Rigó Hill).

	1.	2.	3.
SiO ₂	30.72	30.24	30.06
Al ₂ O ₃	14.36	14.49	14.37
FeO	14.97	14.95	15.18
MgO	0.75	0.74	0.71
CaO	9.36	9.26	9.24
MnO	0.36	0.33	0.36
TiO ₂	1.11	1.11	1.29
Y ₂ O ₃	0.73	0.54	0.57
La ₂ O ₃	5.60	5.88	5.57
Ce ₂ O ₃	11.16	11.35	11.64
Pr ₂ O ₃	1.13	1.20	1.23
Nd ₂ O ₃	4.13	4.13	4.06
Sm ₂ O ₃	0.80	0.86	0.78
Eu ₂ O ₃	0.00	0.03	0.06
Gd ₂ O ₃	0.51	0.50	0.54
Dy ₂ O ₃	0.28	0.26	0.26
ThO ₂	1.74	1.97	1.82
UO ₂	0.10	0.05	0.10
Cl	0.00	0.00	0.00
F	0.40	0.40	0.50
Σ	98.21	98.29	98.34
Numbers of ions on the basis of 12.5 oxygens			
Si	3.031	2.999	2.986
Al	-	0.001	0.014
Al	1.671	1.693	1.669
Fe ²⁺	1.236	1.240	1.261
Mg	0.110	0.109	0.105
Ca	0.990	0.984	0.984
Mn	0.030	0.028	0.030
Ti	0.080	0.083	0.096
Y	0.039	0.029	0.031
La	0.204	0.215	0.204
Ce	0.403	0.412	0.424
Pr	0.041	0.043	0.045
Nd	0.146	0.146	0.144
Sm	0.027	0.030	0.027
Eu	0.000	0.001	0.002
Gd	0.017	0.017	0.018
Dy	0.009	0.008	0.008
Th	0.039	0.045	0.041
ΣREE+Y	0.89	0.88	0.90
Sm/Nd	0.185	0.205	0.188
Ce/La	1.98	1.92	2.08
Σ _I /Σ _H	32	34	33

1. Core (on Fig. 8A., No. 4.); 2. Intermediate part (on Fig. 8A., No. 3.); 3. Rim (on Fig. 8A., No. 2)

zircon ($\Sigma_L/\Sigma_H = 3.2$) and apatite ($\Sigma_L/\Sigma_H = 2$) are enriched in HREE in the Mecsek Mts., but this enrichment cannot be detected in whole-rock $L_{\text{REE}}/H_{\text{REE}}$ ratios. The REE contents of the cores of zircons are variable ($\Sigma\text{REE} + \text{Y} = 0.42\text{--}0.00$ wt. %). Those cores which have higher REE content usually contain higher Th, U ($\Sigma\text{REE} = 0.32/16_{\text{oxy}}$, Th = $0.046/16_{\text{oxy}}$, U = $0.033/16_{\text{oxy}}$) while the low REE content cores are depleted in Th, U with slight Hf enrichment. The different composition of zircon cores suggests a different source compatible with a migmatitic origin. Two different ΣREE contents of apatite cores ($\Sigma\text{REE} = 0.47$ wt. %, $\Sigma\text{REE} = 1.2$ wt. %) also support the idea of different sources of parental rocks.

The zoning of allanite has not influenced the whole-rock REE patterns significantly, but can give information on the REE geochemistry of the later stage of crystallization and hydrothermal alteration. In the migmatitic granitoids of the Mecsek Mts., the later stage of crystallization of the melt was entirely depleted in REE and epidote crystallized instead of allanite. The late hydrothermal solutions (CO_3^{2-} , F^- , H_2O) affected the LREE rich allanite, and altered them into RE-fluorcarbonate minerals, thorite and clay minerals. The transportation distances of these REE-rich solutions were not significant, because usually these secondary minerals occur together with allanite. It is suggested that K-metasomatism was older and the hydrothermal alteration was a younger process.

In the postcollisional granitoids, allanites display zoning with well developed metamict zones (enriched in Th). In the case of granodiorite (Buzsák) depletion of Ce, La and enrichment of Nd, Sm, Eu, HREE (Y) occur in the rim, which corresponds to Exley's (1980) observations that the fluids became more HREE-rich during the later stage of evolution of fluid phases. Allanites in Velence monzogranite show oscillatory zoning, with a slight depletion of silica, and enrichment of Fe, Ce, Pr, Eu in the rim.

The ΣREE content of allanites increases with the SiO_2 content of granitoids excepting cerium. The cerium content is considerably enriched in the allanite of the migmatitic-anatectic granitoids in Mecsek Mts.; this is the reason why secondary Ce-rich fluorcarbonate minerals are more common in these rocks than in the other granitoids. HREE are considerably enriched in allanites of the well differentiated granitoids occurring along the Velence-Balaton tectonic line. This is due to HREE acidic fluorine and carbonate-bearing solutions becoming enriched at the later stage of crystal differentiation (Fig. 9).

According to Bea (1994) metaluminous granitoids are enriched in allanite, titanite and occasionally RE-carbonates. Strongly peraluminous granitoids contain monazite and, xenotime while peralkaline granites are very rich in bastnäsite, allanite, monazite, xenotime and niobates all over the world. Due to their mixed meta-, and peraluminous character, the granitoids occurring in Mecsek contain both allanite and monazite, whereas the slightly peraluminous granitoids of Velence have allanite and RE-carbonates. We found monazite and xenotime only in the partly digested pelitic enclaves, but Pantó (1977) described these minerals from the granite too. Enrichment of allanite in more basic, least differentiated granitoids were also observed by Broska & Uher (1991) which is probably due to the higher Ca content of these rocks. The more common occurrences of primary monazite, xenotime in the highly differentiated granitoids were not proved by our observations. The presence of these minerals can

presumably be explained by the partly or entirely melted monazite, xenotime rich pelitic xenoliths in the peraluminous granitoids of Velence Mts.

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