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CAMPTONITES FROM THE DITRĂU ALKALINE MASSIF, ROMANIA: GEOCHEMISTRY AND PETROGENESIS

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Abstract: 20 cm to 2 m wide camptonite dykes occur at the northern part of the Ditrău Alkaline Massif [DAM] (Eastern Carpathians, Romania) intersecting granitoids, syenitoids and hornblendites. Based on their low SiO_2 and high alkali, TiO_2, LILE and LREE content, high Yb/Nb, Ti/V, $(La/Yb)_N$ ratios, Zr/TiO_2 *vs.* Nb/Y distribution, nepheline and olivine normative composition they are silica- and alumina-undersaturated, alkaline basic rocks and basanitic in composition. The Mg#, Cr, Ni, Co and Sc concentration, and low S.I. and high D.I. values of the DAM camptonites indicate that they could be fractionates of primary melts. Based on strongly incompatible trace element composition the DAM camptonites derive from an OIB mantle source containing HIMU and EM I mantle components. The high LREE and low HREE content of the DAM camptonites (La/Yb=15-24) can indicate both a metasomatised mantle source for the magma generation and a garnet lherzolite source by very low degrees (~1-2 %) of partial melting. The latter mean that the camptonite magma must have originated at a great depth, around 60-80 km.

Keywords: Camptonite, Geochemistry, Petrogenesis, Ditrău Alkaline Massif, Eastern Carpathians

1. Introduction

Camptonites are alkaline lamprophyres with more plagioclase than alkali feldspar, can include Na-foids and containing essential amphibole which dominates over biotite (Rock, 1991). They are a group of alkali-rich igneous rocks and form sub-volcanic dykes, sills, plugs, stocks, vents or margins to larger intrusions. They have ‘basanitic to nephelinitic’ compositions, low-Si (41–43 % SiO_2), high-Na (3–4 % Na_2O) content, usually Na » K, and are rich in Sr, Rb, Ba, Th, Zr, LREE and volatiles (Rock, 1991).

While several scientific studies concerning the mineralogy, petrology, structure, formation and time of origin of the DAM, as well as the economic potential of its rock and ores have been made, the camptonites intersecting different rock types of the Massif, have slightly been discussed (Mauritz, 1912; Mauritz et al., 1925; Streckeisen, 1954; Anastasiu and Contantinescu, 1982). So far, only petrographical and a few chemical analyses were made on camptonite bodies, hence, the petrological and tectonical interpretation of these rocks would greatly contribute to understand the genetics of DAM.

This paper presents whole rock major, trace and rare-earth element data of camptonites occurring at the northern part of the DAM, and discusses variation in their chemical composition and their petrogenesis.

2. Geological setting

The DAM is a Mesozoic alkaline igneous complex and situated in the S-SW part of the Giurgeu Alps belonging to the Eastern Carpathians (Romania) (Fig. 1). The diameter of its surface mass in a NW-SE and NE-SW direction is 19 and 14 km, respectively. Including the border zones its total extension is approximately 225 km^2. According to our present knowledge, the DAM is an intrusive rock body (Fig. 2) with an eastern, north eastern tilt, built up by several tectonic blocks providing the massif a complex form. Magnetotelluric and telluric gravimetry along a Paşcani – Tg.-Neamț – Ditrău – Reghin geotraverse (Visarion, 1987) displayed an allochthon body till a depth of 2–2.5 km, which belongs to the Bukovina Nappe.

The DAM outcrops right east of the Neogene-Quaternary Călimani-Gurghiu-Harghita calc-alkali volcanic belt by breaking through the pre-Alpine metamorphic rocks of the Bukovina Nappe. The massif is partly covered by the andesitic pyroclastic rocks and lava flows of the volcanic arc and the Pliocene-Pleistocene sedimentary rocks of the Gheorgeni and Jolotca Basins. The DAM intruded the central crystalline rock mass of the Eastern Carpathians, and it participated later in the Alpine tectonic events along with metamorphic rocks (Pál-Molnár, 2000).

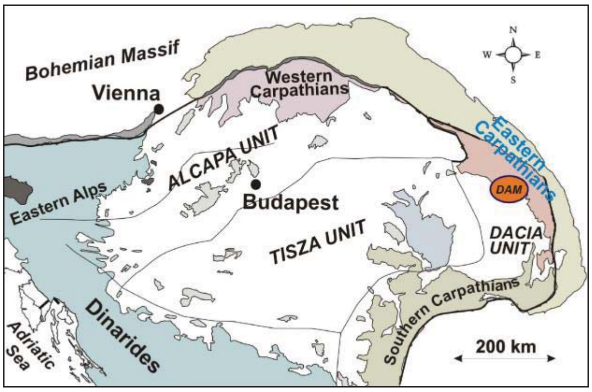

Fig. 1. Schematic map of the Carpathian-Pannonian region after Săndulescu et al. (1981).

From a petrographic point of view the DAM is exceptionally diverse. Great number of different rock types appears on the surface (ultrabasites, gabbros, diorites, monzonites, syenites, nepheline syenites, granites, lamprophyres). Based on 30 K/Ar data originating from various mineral fractions of different rock types Pál-Molnár and Árva-Sós (1995) and Pál-Molnár (2000) has shown that the massif is the result of a long lasting (Middle Triassic – Lower Cretaceous) two phase (Middle Triassic – Upper Triassic and Lower Cretaceous) magmatic process. With additional Ar/Ar age data Dallmeyer et al. (1997) reinforced the Middle Triassic origin of ultrabasic rocks, while Kräutner and Bindea (1998) stressed again the long and multi-phase magmatic activity of the DAM, which started during the Triassic by the opening up of the Tethys and the detachment of the Getida-Bukovina Microplate from the Eurasian Plate.

3. Petrography

Since the occurrence of camptonites can be studied better at the northern part of the DAM, and the contacts of camptonites with the most

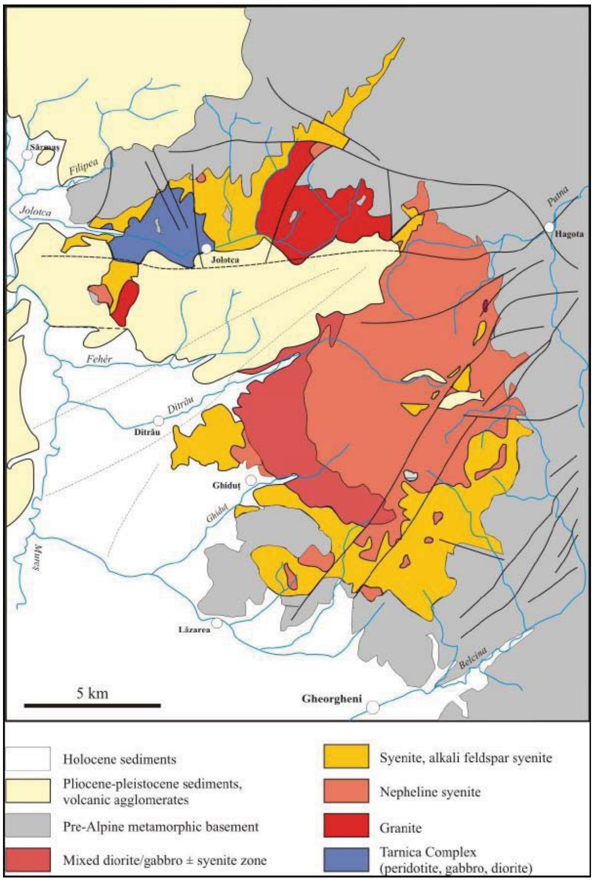

Fig. 2. Geological map of the Ditrău Alkaline Massif (Pál-Molnár, 2008; modified after Kräutner and Bindea, 1998).

rock type in natural outcrops can be found at this part as well, the Jolotca Creek and its northern affluents have been chosen as the studied area.

The 20 cm to 2 m wide camptonite dykes and dyke swarms intersect granitoids, syenitoids and hornblendites. Contacts of camptonite dykes with the wall rocks are sharp. Both camptonites and the country rocks are less or largely altered. There are numerous faults on the territory, from which several cut the camptonite dykes, too. The studied rocks (35 samples) were collected from nine natural outcrops of seven creeks. Field relations suggest late stage emplacement of camptonite in the DAM's magmatic evolution (Batki et al., 2004).

The studied camptonites are dark-grey, greenish-grey. Their texture is mostly panidiomorphic, porphyritic and at some places vitrous in contact zones. They do not contain any kind of xenoliths. Based on petrographic investigations two types of camptonites occur in the studied area. The first type of camptonites (Type I.) consists of subsilicic aluminian ferroan diopside phenocryst, groundmass kaersutite and Mg-biotite, interstitial albite-oligoclase and ocelli filled with euhedral calcite in the core and anhedral plagioclase at the rim. The dominant component of the second type of camptonites (Type II.) is hastingsite – magnesiohastingsite in the groundmass. The other main rock-forming mineral is Fe-Mg-biotite. The interstitial plagioclase is albite-andesine. This type is pyroxene free and has silica-rich felsic globular structures filled with the same mineral assemblages as in the groundmass. Accessories are apatite, titanite, magnetite and zircon (Batki & Pál-Molnár, 2006).

4. Analytical methods

Whole-rock major oxide compositions for 26 selected samples were analysed on a Finnigan MAT Element spectrometer by HR-ICP-MS, trace and rare-earth elements were determined by ICP-AES using a Varian Vista AX spectrometer at the Department of Geology and Geochemistry, University of Stockholm.

5. Geochemistry

Major, trace and rare-earth element analyses are given in table 1 and table 2. The DAM camptonites are characterized by low SiO_2 contents (in the range of 43-51 wt.%) (Fig. 3, 4) and variable Mg values (0.5-0.7). MgO, Cr and Ni contents range from 4.9-10.0 wt.%, 42-277 ppm and 40-214 ppm, respectively. They have low S.I. and high D.I. values (Table 1). The DAM camptonites are typically alkaline as shown by high concentrations of TiO_2 (Fig. 3), alkalies (Fig. 4) and incompatible trace elements such as LREE, Zr, Nb, Y, Ba, Sr and by high Ti/V, $(La/Yb)_N$ and low Y/Nb ratios (Table 2). They are silica-undersaturated (ne = 5.6-13.8), alkaline basic to ultrabasic rocks (Fig. 4) and basanitic (ol = 7.6-17.6) (Fig. 5) in composition. Their alumina-undersaturated or metaluminious character (Fig. 6) and their primitive mantle-normalized trace element patterns (Fig. 7) agree well with average alkaline lamprophyres (Rock, 1987; 1991). The camptonite dykes show strong enrichments in LILE relative to the primitive mantle and negative anomalies for Cr and Ni (Fig. 7). The primitive mantle-normalized (Sun and McDonough, 1989) REE patterns of camptonites show a decrease from La to Yb (Fig. 8), and do not have Eu anomaly (Eu/Eu^*=0.54-0.68). While the camptonites have just 5- to 9-fold higher HREE content, they have 50- to 100-fold higher LREE content than the primitive mantle. Such fractionation of the LREE and HREE (La/Yb=15-24) show that during partial melting the lamprophyric magma was enriched in LREE much more than in HREE. The high LREE content of the camptonites must be related to their extremely high volatile content (Szabó et al. 1993). Experimental data of Wendlandt and Harrison (1979) suggest that most LREE become soluble under mantle pressure when an H_2O-rich fluid coexists with partial melt. Green (1979) detected Ti, Rb, Sr, Ba, Ce and Pb in CO_2 inclusions in upper mantle rocks and suggested

Table 1. Representative major element composition (wt%) of camptonites from the northern part of the Ditrău Alkaline Massif.

Rock	Camptonite Type I.						Camptonite Type II.				AL average
Sample	ÁGK-6715	ÁGK-7292	ÁGK-7296	ÁGK-7297	ÁGK-7301	ÁGK-7302	ÁGK-7287	ÁGK-7289	ÁGK-7290	ÁGK-7351	Rock,1991
SiO_2	45.29	45.22	46.26	48.61	43.27	46.54	50.80	44.35	43.32	44.79	42.5
Al_2O_3	14.7	12.52	15.68	15.16	14.47	16.07	16.67	15.42	14.82	15.64	13.7
TiO_2	3.59	2.07	2.16	2.12	3.42	2.93	2.85	3.42	3.45	3.77	2.9
Fe_2O_3	2.49	1.88	1.80	1.81	2.45	2.03	1.78	2.61	2.57	2.49	12.0
FeO	9.46	7.73	7.21	7.33	9.42	7.71	6.52	10.24	9.98	9.28	
MgO	7.05	10.01	6.52	7.14	6.60	4.87	5.37	5.91	6.01	6.41	7.1
MnO	0.16	0.16	0.17	0.15	0.20	0.18	0.18	0.26	0.25	0.19	0.2
CaO	8.88	8.85	8.28	7.30	8.83	8.79	6.83	7.68	9.49	9.56	10.3
Na_2O	3.99	3.01	4.56	4.49	3.02	4.08	5.35	2.92	3.45	3.24	3.0
K_2O	1.96	2.36	2.36	2.25	3.57	2.43	1.63	3.29	1.89	2.59	2.0
Total	98.64	94.67	95.81	97.18	96.3	96.49	98.71	97.25	96.35	99.01	93.7
$Al_2O_3/(Na_2O+K_2O)$	2.47	2.33	2.27	2.25	2.20	2.47	2.39	2.48	2.78	2.68	2.74
Mg#	0.57	0.70	0.61	0.63	0.55	0.53	0.60	0.51	0.52	0.55	0.67
D.I.	37.3	34.9	43.7	46.2	37.4	42.7	51.3	39.0	33.7	35.1	
S.I.	27.1	38.8	28.0	30.0	25.3	22.1	25.2	22.6	24.0	25.6	
CIPW norms											
or	11.88	14.82	14.69	13.81	22.11	15.03	9.85	20.25	11.74	15.7	
ab	14.65	11.74	15.21	24.19	1.66	17.73	35.81	10.56	11.64	9.22	
an	16.78	14.63	16.12	15.13	16.14	19.15	16.78	19.98	20.25	20.73	
ne	10.8	8.29	13.75	8.19	13.62	9.93	5.62	8.2	10.29	10.16	
cpx	23.0	25.9	22.0	18.2	24.3	21.6	14.3	16.1	23.9	22.5	
ol	12.2	17.6	11.2	13.6	11.6	7.6	9.5	14.2	11.4	10.7	
mt	3.7	2.91	2.74	2.73	3.73	3.08	2.64	3.94	3.91	3.68	
il	7.0	4.2	4.32	4.17	6.83	5.83	5.53	6.76	6.88	7.33	

Table 2. Representative trace and rare-earth element composition (ppm) of camptonites from the northern part of the Ditrău Alkaline Massif.

Rock			Camptonite Type I.					Camptonite Type II.			AL average
Sample	ÁGK-6715	ÁGK-7292	ÁGK-7296	ÁGK-7297	ÁGK-7301	ÁGK-7302	ÁGK-7287	ÁGK-7289	ÁGK-7290	ÁGK-7351	Rock,1991
Be	1.2	1.2	1.6	1.4	1.1	2.1	5.2	3.3	2.2	1.6	1.0
Sc	15.4	17.1	12.6	13.3	17.2	13.3	9.0	12.3	13.4	16.3	21.0
V	233	150	164	142	224	192	155	214	208	249	285
Cr	100	277	208	201	138	69	58	51	53	42	97
Co	38	45	28	36	40	30	28	32	32	37	38
Ni	72	214	101	134	74	41	40	43	50	52	65
Cu	32	49	31	51	32	32	22	17	25	35	50
Zn	146	104	105	104	146	111	145	137	124	126	98
Sr	903	695	1142	826	1049	837	1047	725	875	873	990
Ba	442	597	1816	781	620	597	377	816	680	851	930
Rb	147	184	172	174	215	186	279	437	186	173	50
Zr	264	168	230	358	179	338	357	306	277	302	313
Nb	93	53	94	68	69	105	125	108	106	112	101
Y	26.2	14.7	16.9	16.8	20.2	21.9	27.0	27.3	27.0	26.4	31.0
Hf	12.1	8.0	5.2	9.0	7.9	10.5	10.0	10.7	9.2	10.3	6.9
Mo	4.5	7.8	1.9	5.9	3.2	7.0	11.0	2.8	3.4	2.7	8.5
S	541	595	393	288	703	566	86	87	164	254	—
La	58	32	56	38	40	59	69	74	72	63	66
Ce	118	55	107	78	80	110	127	134	130	123	125
Nd	53	22	38	24	40	34	48	56	54	50	54
Sm	11.0	4.8	7.0	5.8	8.8	8.5	9.7	12.0	11.0	11.0	10.8
Eu	3.3	1.5	2.1	1.8	2.7	2.4	2.6	3.3	3.3	3.0	3.1
Dy	5.9	4.0	3.6	3.6	5.1	5.0	5.4	6.7	6.5	6.1	5.4
Yb	3.2	2.2	2.5	2.4	2.6	2.8	2.9	3.1	3.2	3.3	1.8
ΣREE	252	122	216	154	179	222	265	289	280	259	266
$(La/Yb)_N$	13.1	10.6	16.1	11.5	11.1	14.9	17.47	17.06	16.02	13.7	
La/Yb	18.1	14.5	22.4	15.8	15.4	21.1	23.8	23.9	22.5	19.1	36.6
(Eu/Eu*)	0.68	0.54	0.65	0.62	0.65	0.63	0.66	0.63	0.67	0.62	
Y/Nb	0.28	0.28	0.18	0.25	0.29	0.21	0.22	0.25	0.25	0.24	0.31
K/Nb	175	370	208	275	429	192	108	253	148	192	
Ti/V	92	83	79	90	92	92	110	96	99	91	

that these elements were previously dissolved in the CO_2. Roedder (1972) and Stosch (1982) also found evidence for the transport of REE by dense CO_2. The REE's migrate from fluid into the silicate melt under subsequent lower pressures (Fesq et al. 1974). In contrast, H_2O is better understood as a solvent, compared to CO_2, especially, in fluid mobile LIL element transfer under upper mantle conditions (Williams et al., 1995; Prouteau et al., 2001).

6. Petrogenesis

The studied camptonites lack mantle xenoliths, do not have modal olivine, and most of them show whole-rock Mg# 0.5-0.7 supposing that they could be fractionates of primary melts. Their differentiated nature is confirmed by their low S.I. and high D.I. values.

The OIB-normalized REE patterns (Fig. 9), and the Ti/100 *vs.* Zr *vs.* Y*3 distribution of the camptonites show (Fig. 10), that they are related to an intraplate magmatic activity. The La/Nb, Zr/Nb, Ba/Nb, Ba/La, Rb/Nb and K/Nb ratios of the camptonites (Table 3; Weaver 1991; Sun and McDonough 1989; Ngounouno et al. 2006; Perini et al., 2004) indicate the presence of HIMU and EM I mantle components in the source region of the DAM camptonites. Both of the camptonites (Type I. and Type II.) have the same primitive mantle- and OIB-normalized REE patterns which mean that they are co-magmatic.

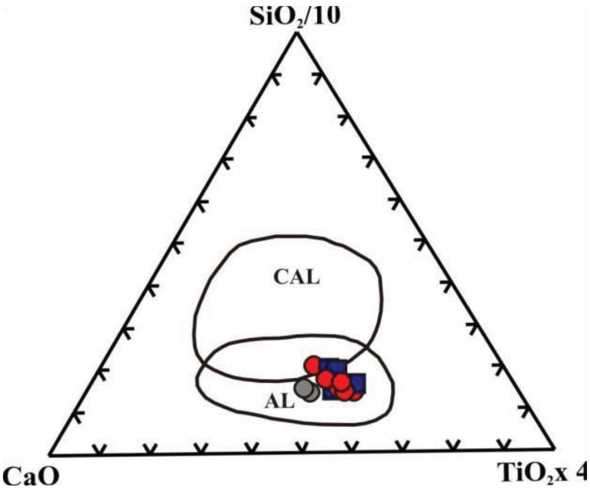

Fig. 3. Discrimination diagrams of camptonites from the Ditrău Alkaline Massif based on Rock (1987) ● Camptonite Type I. ■ Camptonite Type II. ● average alkaline lamprophyres [AL], CAL – calc alkaline lamprophyre (Rock, 1991)

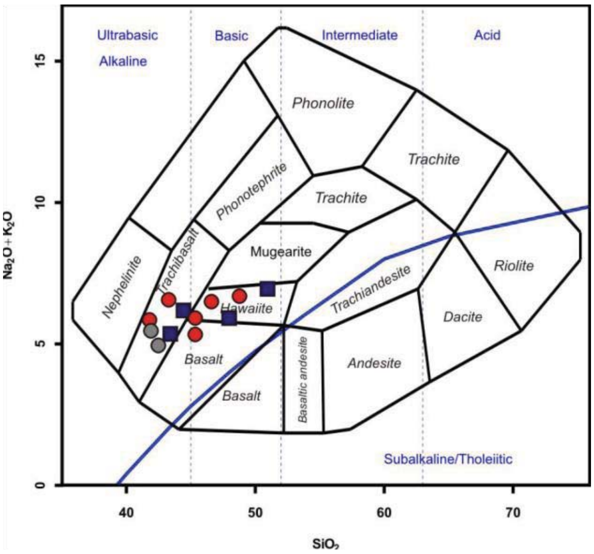

Fig. 4. Lithological classification of camptonites from the Ditrău Alkaline Massif (Cox et al., 1979). ● Camptonite Type I. ■ Camptonite Type II. ● average AL (Rock, 1991).

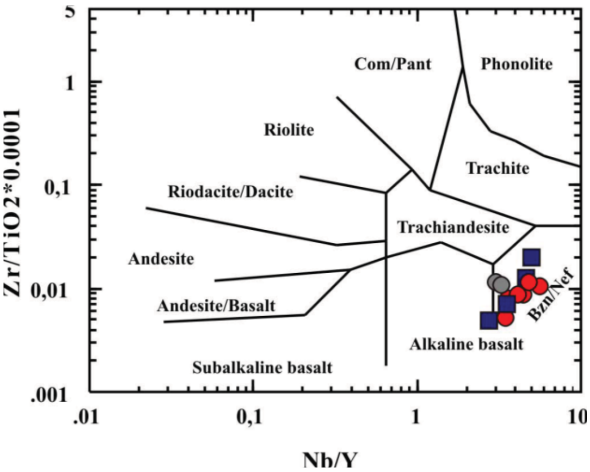

Fig. 5. Nb/Y *vs.* Zr/TiO2*0.0001 discrimination diagram of camptonites from the Ditrău Alkaline Massif based on Winchester and Floyd (1977) ● Camptonite Type I. ■ Camptonite Type II. ● average AL (Rock, 1991).

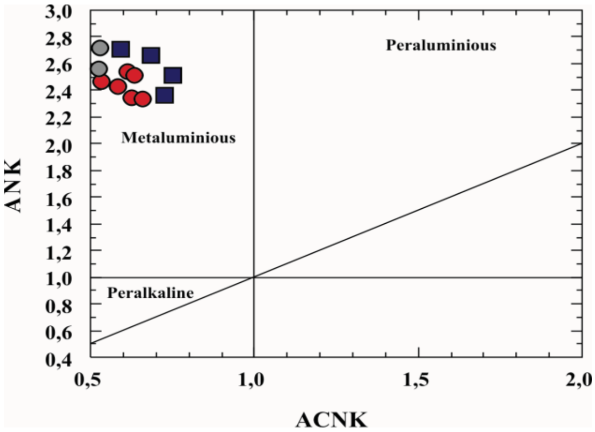

Fig. 6. $Al_2O_3/(Na_2O+K_2O)$ *vs.* $Al_2O_3/(CaO+Na_2O+K_2O)$ distribution of camptonites from the Ditrău Alkaline Massif based on Shand (1943) and Maniar and Piccoli (1989). ● Camptonite Type I. ■ Camptonite Type II. ● average AL (Rock, 1991).

The low HREE content of the camptonites indicates the presence of residual garnet in the source region. The enrichment in LREE suggests very low degrees (~1-2 %) of partial melting (Kay and Gast, 1978). Therefore the camptonite magma should derive from garnet lherzolite mantle source by very low degrees of partial melting. In this case the camptonite magma must have originated at a great depth (60-80 km) (Watson and McKenzie, 1991). The enrichment in LREE and LILE can indicate a metasomatised mantle source of the camptonites as well (Wendlandt and Harrison, 1979).

7. Conclusion

Whole-rock major oxide compositions, trace and rare-earth element concentrations were determined on camptonite dykes intersecting granitoids, syenitoids and hornblendites at the northern part of the DAM, Eastern Carpathians (Romania). Based on their chemical composition they are silica- and

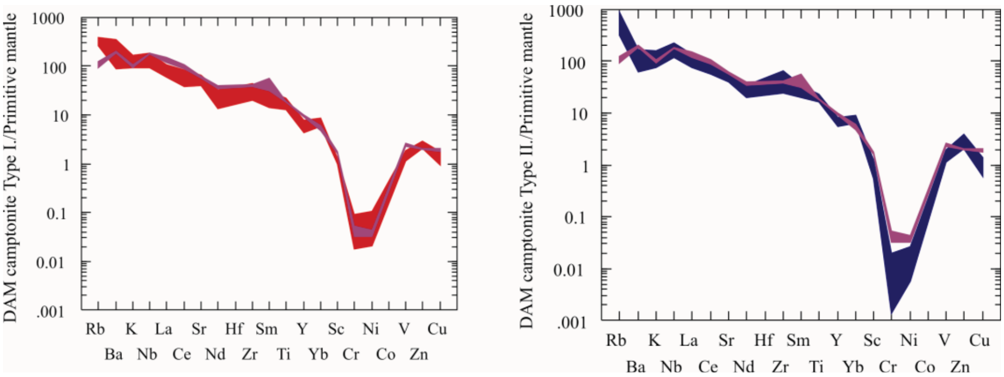

Fig. 7. Primitive mantle-normalized (Sun and McDonough, 1989) trace element patterns of camptonites from the Ditrău Alkaline Massif, ■ Camptonite Type I. ■ Camptonite Type II. ■ average AL (Rock, 1991).

Table 3. La/Nb, Zr/Nb, Ba/Nb, Ba/La and Rb/Nb ratios of camptonite Type I. and Type II. of the Ditrău Alkaline Massif, and some of the mantle reservoirs after Weaver (1991). K/Nb ratios after Sun and McDonough (1989).

	Camptonite Type I.	Camptonite Type II.	OIB	HIMU	EM I	EM II
La/Nb	0.56-0.66	0.55-0.69	0.77	0.66-0.77	0.64-1.19	0.89-1.09
Zr/Nb	2.45-5.26	2.61-2.86		2.6-5.0	3.8-8.2	3.9-7.9
Ba/Nb	4.8-19-3	2.7-7.6	9.46	5.4-6.5	5.6-17.7	7.3-10.9
Ba/La	7.6-32.4	4.3-13.5	9.46	6.8-8.7	8.8-16.9	8.3-11.3
Rb/Nb	1.58-3.47	1.54-4.16	0.65	0.35-0.38	0.88-1.17	0.59-0.85
K/Nb	175-429	108-253		< 200		> 200

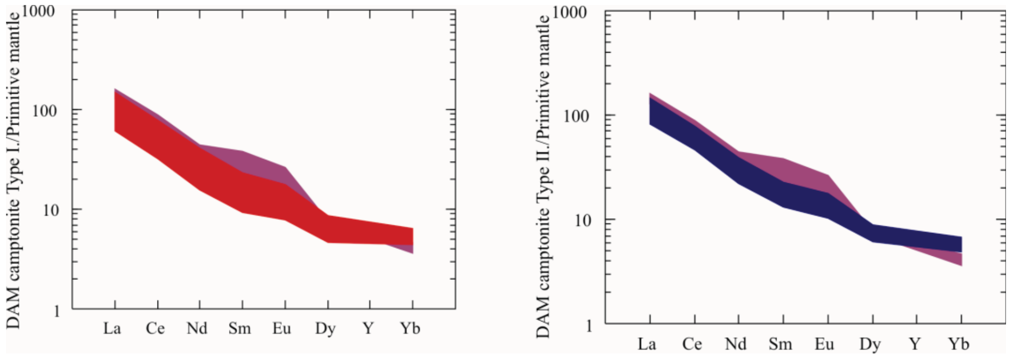

Fig. 8. Primitive mantle-normalized (Sun and McDonough 1989) REE patterns of camptonites from the Ditrău Alkaline Massif, ■ Camptonite Type I. ■ Camptonite Type II. ■ average AL (Rock, 1991).

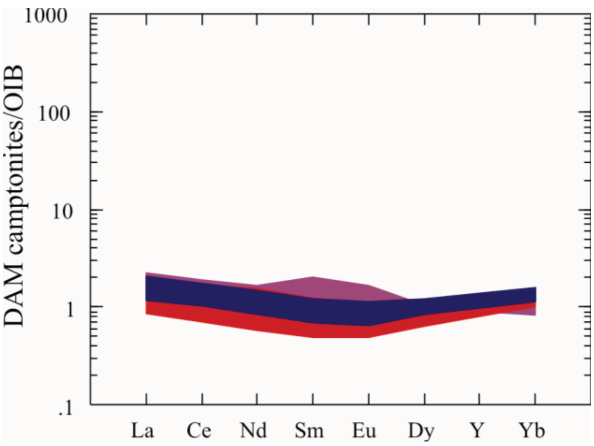

Fig. 9. OIB-normalized (Sun and McDonough 1989) REE patterns of camptonites from the Ditrău Alkaline Massif, ■ Camptonite Type I. ■ Camptonite Type II. ■ average AL (Rock, 1991)

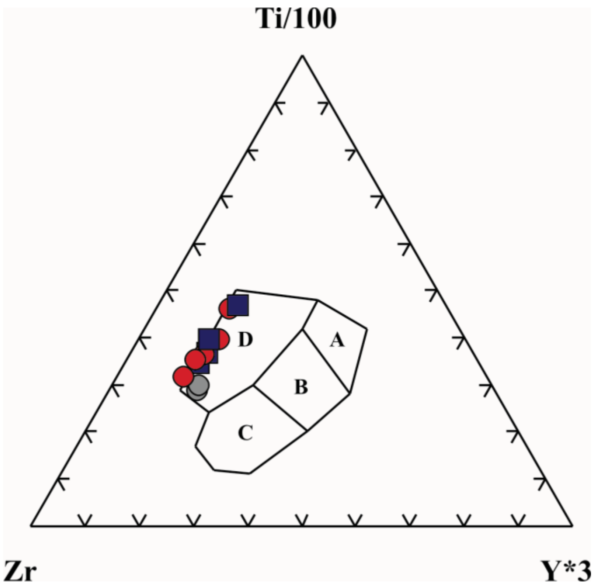

Fig. 10. Ti/100-Zr-Y*3 distribution (Pearce and Cann 1973) of camptonites from the Ditrău Alkaline Massif, ● Camptonite Type I. ■ Camptonite Type II. ● average AL (Rock, 1991). A-B low K-tholeiites, B – ocean floor basalts, B-C calc-alkaline basalts, D – within plate basalts.

alumina-undersaturated, alkaline, basanitic rocks. They derive from a differentiated melt, and could be fractionates of primary melts. They originate from an OIB mantle source containing HIMU and EM I mantle components. The camptonite magma derived from a garnet lherzolite mantle source by very low degrees (~1-2 %) of partial melting which means that it must have originated at a great depth, around 60-80 km.

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