Ţ. S. Inst. Geol. Geofiz. vol. 72–73/1 (1985; 1986), 1987, pag. 381–397

GEOCHIMIE

TRACE ELEMENTS GEOCHEMISTRY OF THE SOUTH HARGHITA VOLCANICS (EAST CARPATHIANS): CALC-ALKALINE AND SHOSHONITIC ASSOCIATIONS [1]

BY

IOAN SEGHEDI [2], ALEXANDRU SZAKÁCS [2], CONSTANŢA UDRESCU [2], MARIA STOIAN [2], GABRIELA GRABARI [2]

Magmatic differentiation. Petrochemistry. Trace elements. Calc-alkaline associations. Shoshonitic associations. Genetic model. Rare earths. East Carpathians – Neogene-Quaternary eruptive – Harghita.

Abstract

Completions and nuances of the previously mentioned petrogenetic model (Seghedi et al., 1986) are brought on the basis of a new set of trace elements (42) and REE (14) analyses. The petrographical and petrochemical variation observed along the South Harghita Mts from N to S, from calc-alkaline to high-K calc-alkaline characters, is achieved by magma generation by more and more reduced degrees of partial melting, corresponding to ever higher depths of formation. In case of the most recent eruptive products (shoshonitic rocks) magma-mixing processes are observed between the calc-alkaline magma resulting from the lowest degree of partial melting and a new-formed, basic magma originating in the upper mantle. The differentiation processes by fractional crystallization and contamination with crustal material have not played a significant part in the magma evolution. The REE distribution points to the preponderent part of garnet and pyroxenes in their gradual fractioning as a result of partial melting. The geochemical characteristics of the calc-alkaline suites are compatible with Nicholls and Ringwood's (1973) and Ringwood's (1974) petrogenetic models.

Résumé

Géochimie des éléments mineurs des volcanites des monts Harghita de sud (Carpathes Orientales): associations calco-alcaline et shoshonitique. A base d'une nouvelle série d'analyses sur les éléments mineurs (42) et les terres rares (14) on a fait des complétions et des nuances pour

[1] Received April 19, 1986, accepted for communication and publication November 1, 1986, communicated in the meeting April 23, 1986 ("Geological Symposium" Baia Mare).

[2] Institutul de Geologie şi Geofizică. Str. Caransebeş nr. 1, R 79678 Bucureşti, 32.

le modèle pétrogénétique énoncé auparavant (Seghedi et al., 1986). La variation pétrographique et pétrochimique observée au long des monts Harghita de sud, du nord vers le sud, des caractères calco-alcalins aux caractères calco-alcalins très potassiques, est réalisée par une génération de magmas par les degrés de fusion partielle de plus en plus réduits, qui correspondent à des profondeurs de formation de plus en plus grandes. Quant aux derniers produits éruptifs (roches shoshonitiques), on a constaté l'interventions des processus de mélange entre le magma calco-alcalin, résulté à la suite de plus réduit degré de fusion partielle et le magma basique, nouvellement formé, originaire du manteau supérieur. Les processus de différenciation par cristallisation fractionnée et de contamination avec du matériel de croûte ont eu un rôle insignifiant dans l'évolution des magmas. La distribution des terres rares indique le rôle dominant du grenat et des pyroxènes dans leur fractionnement progressif observé, résulté à la suite du processus de fusion partielle. Les caractères géochimiques de la série calco-alcaline sont compatibles aux modèles pétrogénétiques de Nicholls et Ringwood (1973) et Ringwood (1974).

1. Introduction

The special attention given lately to the petrological problems o the South Harghita volcanics (Peltz et al., 1984 ; Rădulescu et al., 1984 ; Seghedi et al., 1986 ; Szakács, Seghedi, 1986 ; Peltz et al., this volume) attests their usefulness in the elucidation of the origin of the magmas generated under subduction conditions in the East Carpathians.

This paper brings completions to the existent bulk of geochemical pata by new determinations of trace elements with a view to completing and specificating the genetical model enunciated in a previous paper on the basis of the distribution of major and "incompatible" trace elements (Seghedi et al., 1986).

On the basis of the geochemical analyses carried out on rocks belonging to five volcanic structures of the South Harghita Mts several conclusions can be drawn from the above-mentioned model :

— the existence of two magma types which generated the volcanic arc, in its southern segment : (1) a calc-alkaline magma, which develops by a gradual increase of SiO_2, K_2O, Na_2O, Sr, Th, U from N to S ; (2) a shoshonitic magma, whose products show low values of SiO_2 and the highest contents of K_2O, Na_2O, Sr, Th, U, occurring in two isolated eruptive bodies, in the southernmost part of the Harghita Mts ;

— the geochemical comparison of the Harghita volcanics with geochemical features of island arcs and continental margins volcanics (regions considered different in geotectonic respect) indicates similarities with both of them. This suggests the independence of the magma generation in the Harghita Mts as against the geotectonic conditions (in this case of continental basement type) ;

— the particular geochemical features of the magmas have been interpreted as the result of the following processes : (1) partial melting (the most important), with an ever reduced degree from N to S, simultaneously with the increase of the source depth ; (2) differentiation processes (less significant), by fractional crystallization within intermediary

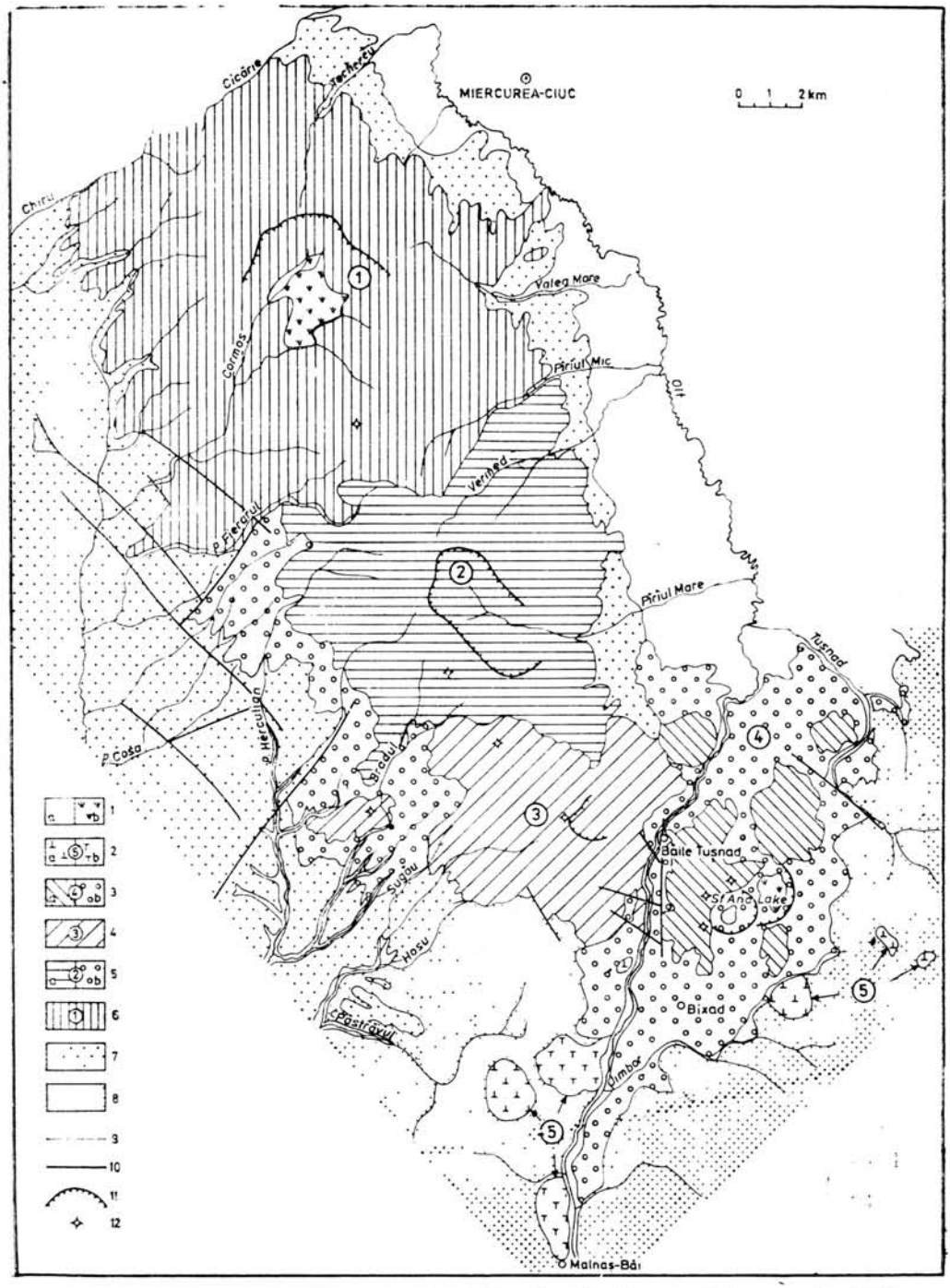

Fig. 1 — Geological sketch of the South Harghita Mts (after Rădulescu et al., 1984). 1, Quaternary deposits: a, alluvia; b, marshes; 2 a, calc-alkaline extrusive domes in the Malnaș—Bixad-Balvanyos zone (5 a); b, intrusive domes of shoshonitic rocks in the Malnaș-Bixad zone (5 b); 3, Ciomadul volcanic structure (4): a, massive volcanics; b, pyroclastics; 4, Pilișca volcanic structure (3); 5, Cucu volcanic structure (2): a, massive volcanics; b, pyroclastics; 6, Luci and Lazu volcanic structures (1); 7, lower volcanic compartment; 8, Mesozoic sedimentary deposits of the Flysch Zone; 9, geological boundary; 10, fault; 11, crater; 12, eruption centre.

TABLE 1

No.	Sample no.	SiO_2	K_2O	Sign on* diagrams	Phenocrysts **	Location
	Luci-Fagul (Lazu)					
1	T151	57.49	1.72	L_3	Pl. Opx. Cpx. Ol	Valea Mare Brook
2	H327	56.96	1.67	L_3	Pl. Opx. Cpx. Hb	Lugojul Mic Brook
3	H221	56.98	1.54	L_3	Pl. Opx. Cpx. Hb	Lugojul Mare Brook
4	H339	57.30	1.75	L_3	Pl. Opx. Hb. Cpx. Ol	Lugojul Mic Brook
5	H329	57.60	1.79	L_3	Pl. Opx. Cpx. Hb	Covacius Brook
6	H341	58.31	1.91	L_3	Pl. Opx. Cpx. Ol	Lugojul Mic Brook
7	H335	60.28	2.16	L_3	Pl. Opx. Cpx. Hb	Lugojul Mic Brook
	Cucu					
8	C3	57.41	1.61	C_3	Pl. Opx. Hb. Cpx	Aso Brook
9	H278	57.64	1.86	C_3	Pl. Hb. Opx. Cpx. Bi	Durca Brook
10	H270	58.09	1.74	C_3	Pl. Hb. Opx. Cpx	Cucu Summit
11	H281	58.25	1.84	C_3	Pl. Hb. Opx. Cpx	Durca Brook
12	C4	58.62	1.70	C_3	Pl. Hb. Opx. Cpx	Aso Brook
13	T90	58.64	1.87	C_3	Pl. Hb. Opx. Cpx	Mitaci Brook
14	C22	58.72	1.70	C_3	Pl. Hb. Opx. Cpx	Aso Brook
15	H247	59.10	2.28	C_4	Pl. Opx. Hb	Cormoş Brook
16	H276	59.76	2.16	C_4	Pl. Hb. Opx. Cpx. Bi	Durca Brook
17	H273	60.00	2.14	C_4	Pl. Hb. Opx. Cpx	Durca Brook
	Pilişca					
18	T96	54.22	1.56	P_1	Pl. Cpx. Opx. Ol	Mitaci Brook
19	T95	54.47	1.63	P_1	Pl. Cpx. Opx. Ol	Mitaci Brook
20	T77	58.95	2.02	P_3	Pl. Hb. Opx. Cpx	Olt River
21	T5A	61.04	2.36	P_4	Pl. Opx. Cpx. Hb	Hollo Brook
22	T9	61.48	2.66	P_4	Pl. Hb. Bi	Hollo Brook
23	T33	61.63	2.37	P_4	Pl. Opx. Cpx	Olt River
24	T101	61.73	2.72	P_4	Pl. Hb. Bi	Pilişca Summit
25	T16	62.28	2.57	P_4	Pl. Hb. Bi	Pilişca Summit
26	T17	64.74	3.16	P_6	Pl. Hb. Bi	Pilişca Summit
	Ciomadul					
27	T70	57.20	2.06	A_4	Pl. Hb. Cpx	Apor Summit
28	T125	59.55	2.76	A_4	Pl. Hb. Cpx, Bi	Mohoş Hill
29	T124	61.32	3.16	A_4	Pl. Hb. Bi. Cpx	Ciomadul Hill
30	T45	62.18	3.30	A_4	Pl. Hb. Bi	Bixad Brook
31	T28 B	63.43	2.98	A_6	Pl. Hb. Bi	Olt River
32	VI—2	65.07	3.14	A_6	Pl. Hb. Bi	Lake Sf. Ana
33	T36	65.42	3.16	A_6	Pl. Hb. Bi	Ciomadul Hill
34	T67	65,80	3.26	A_6	Pl. Bi. Hb	Apor Summit
35	T44	65.82	3.53	A_6	Pl. Bi. Hb	Bixad Brook
36	VI—3	66.08	4.46	A_6	Pl. Hb. Bi	Ciomadul Summit
	Bixad-Malnaş					
37	T134B	55.10	3.26	B_2	Pl. Cpx. Opx. Ol. Q. Bi. Hb	Malnaş 1 Quarry
38	T134	55.88	3.40	B_2	Pl. Cpx. Ol. Opx. Q. Bi. Hb	Malnaş 1 Quarry
39	T135	55.88	3.20	B_2	Pl. Cpx. Ol. Opx. Q. Bi. Hb	Malnaş 2 Quarry
40	T144	56.10	4.06	B_5	Pl. Cpx. Ol. Opx. Bi. Q. Hb	Bixad Quarry
41	T146	56.90	4.12	B_5	Pl. Cpx. Ol. Opx. Bi. Q. Hb	Bixad Quarry
42	T140	56.96	2.53	B_4	Pl. Bi. Hb. Cpx. Opx	Murgul Mare Hill

* Capital letters represent the affiliation to the volcanic structures: Luci-Lazu (L); Cucu (C); Pilişca (P); Ciomadul (A); Bixad-Malnaş (B); figures represent the petrographic type according to Peccerillo-Taylor chemical classification (1976): basaltic andesites (1), shoshonites (2), andesites (3), high-K andesites (4), banakites (5) and high-K dacites (6).

** Pl: plagioclase, Opx: orthopyroxene, Cpx: clinopyroxene, Ol: olivine, Hb: hornlende, Bi: biotite, Q: quartz.

TABLE 2

No.	Sample no.	Pb	Cu	Zn	Ga	Ni	Co	Cr	V	Sc	Zr	Y	Yb	La	Ba	Sr	Rb
1	151	3.5	9	60	11	3.5	10	3	85	15	130	20	2	<30	450	500	69
2	H327	10	19	70	17	6.5	12	22	105	20	120	15	1.7	30	360	260	53
3	H221	7	20	80	17	9	15	11,5	160	24	120	17	1.7	30	380	340	61
4	H339	7	15	62	16	7	11	13	95	15	125	16	1.8	<30	620	380	72
5	H329	8	11	62	15	8	11	50	115	19	115	17	1.9	30	600	400	71
6	H341	7	9.5	58	17	6	9	11	95	15	140	18	1.9	30	530	280	79
7	H335	8	12.5	55	20	6.5	10	12	80	16	185	20	1.6	32	620	310	89
8	C—3	24	34	62	18	14	14	38	140	18	120	22	1.8	40	850	530	57
9	H278	12	11	75	16	4.5	9	4.5	75	12	130	16	1.5	30	800	500	66
10	H270	12.5	18	72	15	7.5	9.5	14	75	12	110	13	1.4	30	850	600	64
11	H281	3.5	10	—	9.5	8	12	13	85	10	120	10	1.4	<30	900	670	53
12	C—4	10	40	62	17	8	10	15	100	14	95	14	1.5	<30	750	360	75
13	T90	4.5	6	44	8	5	7	5.5	54	8	80	8	1.0	<30	570	700	66
14	C22	6.5	20	65	15	11	10	38	110	16	95	18	1.5	36	530	300	76
15	H247	12.5	7.5	50	17	7.5	9.5	19	90	14	150	15.5	1.7	40	750	380	91
16	H276	12	8.5	72	17	6	8.5	7	75	10	130	15	1.6	34	700	300	80
17	H273	8.5	14	—	15	8	10	23	85	11	140	11	1.1	<30	850	370	78
18	T96	19	18	43	12	14	13	52	180	20	80	15	1.6	<30	520	1700	35
19	T95	13	24	43	10	15	12	70	130	17	75	10.5	1.5	<30	520	1500	47
20	T77	22	15	52	14	11	8	55	100	13	100	10	1.4	<30	800	1600	68
21	T5A	17	11	—	11	12	6	29	65	9	115	32	4.6	<30	1100	900	74
22	T9	20	28	85	13	6	6	5	60	7	150	9	1.0	<30	1050	720	70
23	T33	25	20	40	15	18	11	55	130	14	125	11.5	1.0	32	950	2200	57
24	T101	15	4	62	16	5	6	4.5	62	7.5	130	11	1.4	54	1700	1150	81
25	T16	12	8	48	12	3.5	3	7.5	90	8.5	120	6.5	0.8	38	1150	630	94
26	T17	24	3.5	40	13.5	3.5	3.5	5	30	3.5	130	8	1.0	32	1500	1100	112
27	T70	11	13	46	12	7	8	15	25	11	75	16	2.1	38	900	760	62
28	T125	22	8	44	11	14	6	27	28	3,5	80	6	0.6	<30	400	2000	54
29	T124	15	5	30	12	12	7	47	70	7.5	135	11	1.0	46	1300	19000	78
30	T45	21	7.5	<30	13	11	5.5	26	46	5	140	7.5	0.8	42	1800	1350	95
31	T28P	26	30	—	17	32	4	28	36	4	125	10	0.6	<30	1450	1100	76
32	VI—2	29	9	—	19.5	33	6.5	36	60	7.5	125	10	1.4	65	2300	1500	
33	T30	22	8	32	14	7	4	11	36	4.5	160	7.5	0.8	36	1500	800	100
34	T67	24	6	30	15	6	3	11	24	2	150	5.5	0.7	<30	1600	1200	101
35	T44	28	8	37	13	7.5	3	14	32	4	100	7	1.0	42	1400	2800	104
36	VI—3	32	5	—	19	13.5	13	16	36	5	140	9	1.2	65	1800	1500	

No.	Sample no.	Pb	Cu	Zn	Ga	Ni	Co	Cr	V	Sc	Zr	Y	Yb	La	Ba	Sr	Rb
37	T 134B	18	12	40	11	24	13	115	85	13	180	11	1.1	44	1600	2200	58
38	T 134	21	7.5	58	9	20	11	120	90	12	150	10	1.0	46	1400	2100	55
39	T 135	11	11	42	12	32	17	170	160	16	230	15	1.1	60	1350	2100	49
40	T 144	17	11	43	13	31	15	155	145	14	320	17	1.2	130	2800	3100	60
41	T 146	15	7	48	10	28	15	125	150	14	320	17	1.1	150	3000	3100	58
42	T 140	4.5	6.5	46	5.5	6	6	15	57	8.5	105	10	1.0	36	670	850	80

Sample location the same as in Table 1.

TABLE 3

No.	Sample * no.	Sign on diagrams	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Yb	Lu
1	H221	L_3	17	23			3.6	1.10		0.6		1.7	0.20
2	H339	L_3	16	22			3.1	1.13				1.8	0.29
3	H270	C_3	15	30			2.9	1.45		0.79		1.4	0.34
4	C—3	C_4	24	36			3.6	1.30		0.81		1.8	0.20
5	T95	P_1	17	15			3.9	1.50		0.53		1.5	0.46
6	T77	P_3	27	30			3.9	1.40				1.4	
7	T17	P_6	30	66			2.8	1.01				1.0	0.25
8	AM45	A_6	32	62			2.5	1.20		0.63		1.2	0.22
9	AM62	A_6	20	59			2.5	1.10		0.76		1.0	
10	AM34	A_6	19	56			2.1	1.12		0.61		1.1	0.25
11	T36	A_6	21	51			2.7	1.35		0.67		0.8	
12	T140	B_3	28	49			2.9	1.60				1.1	0.25
13	T135	B_2	37	52			4.9	1.50		0.56		1.1	
14	T144 **	B_5	94	200	157	99	10.7	2.90	16.7	0.82	2.2	1.1	0.16

* Sample location: AM45, AM62 — Haromul Mare Hill: AM34 — Ciomadul Mic Hill: the other samples as in Table 1.

** Analysts: M. Sălăgean: A. Pantelică (IFIN București).

magmatic chambers; (3) assimilation (less significant) during the magma cessation in intermediary magmatic chambers [3].

2. Geological Setting

The South Harghita Mts represent the southernmost part of the Călimani-Gurghiu-Harghita Neogene eruptive chain. They consist of a series of NW—SE trending volcanic structures whose products are characterized by a wide petrographic and geochemical variation. These volcanic structures cover a 40 km long area between the localities of Miercurea-Ciuc (to the north) and Malnaş (to the south). Their basement is composed of folded formations belonging to the East Carpathians Internal Units (Crystalline-Mesozoic Zone and Internal Flysch).

The magmatic activity developed within two main stages to which two structural compartments correspond (Rădulescu et al., 1964): (1) the lower volcanic compartment (volcano-sedimentary), widespread on the western border of the South Harghita Mts, where it occupies a great part of the Baraolt Basin, and less extended on the eastern border of the South Harghita Mts, up to the Mitaci Brook; (2) the upper compartment, characterized in volcanological respect by several volcanic structures with partially superposed (from N to S) products: Luci, Fagul (Lazu), Cucu, Pilişca, Ciomadul, as well as by several isolated, small volcanic apparata (Balvanyos, Puturosul, Dealul Mare, Murgul Mare) or eruptive bodies (Murgul Mic, Luget), situated in the southernmost part (Moţoi et al., 1975; Rădulescu et al., 1984) (Fig. 1).

The radiogenic age data indicate a gradual "rejuvenation" of the volcanic activity from N to S in the interval between 3.7 and 1.45 MA (Rădulescu, 1973; Peltz et al., 1985).

3. Geochemical Data

42 spectral analyses for Pb, Cu, Zn, Ga, Ni, Cr, Co, V, Sc, Zr, Y, Yb, La, Ba, Sr, Rb (Tab. 1,2) and 14 analyses for REE (Tab. 3) were effectuated.

The analysed samples, collected only from the upper compartment, were selected from a larger group of samples, being considered the most representative ones. The main criterion of selection was the chemical one correlated with the petrographic diagnosis. One could observe that among the petrotypes separated on the basis of the content of phenocrysts there is a gradual increase of the Rb, Sr, Zr, Th and U values concomitantly with the predominance of hornblende and biotite over pyroxene (Seghedi et al., 1986). Table 1 shows the change of the quantitative ratios of the main phenocrysts from pyroxene-bearing types to hornblende-bearing and biotite-bearing types. The different petrographic features of the shoshonites and banakites from Murgul Mic and Luget bodies

characterized by the presence of olivine, clino- and orthopyroxene beside magmatically corroded quartz, biotite and hornblende are pointed out. Plagioclase often shows a more basic rim (Szöke, 1963).

A mixed criterion was used for the plotting of the chemical data on diagrams taking into account, on the one hand, the appurtenance to volcanic structures and, on the other hand, the rock diagnosis according to Peccerillo, Taylor petrochemical classification (1976) (Tab. 1). In case of several analyses of the same petrographic type the average value was plotted.

Figure 2 presents Ba variation versus Rb, considered as an indicator of the degree of magmatic differentiation (Robin, 1982). It is obvious the

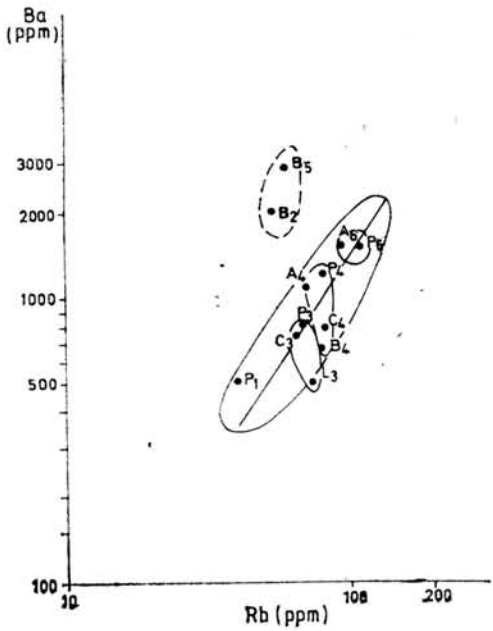

Fig. 2 — Ba(ppm) vs. Rb (ppm) diagram. Symbols as in Table 1.

tendency of a good positive correlation closely connected with separate petrochemical types. Shoshonites and banakites fall in a different area due to the relatively reduced values of Rb (50 — 60 ppm) and high values of Ba (1400 — 3000 ppm).

Sr shows a clear general tendency of increase from N to S along the volcanic chain, with maximum values for shoshonites and banakites (2100 — 3100 ppm). The Murgul Mare andesite in the Bixad-Malnaş area displays more reduced values of Sr as compared with the other andesites (Fig. 3). The sudden increase of the values from the Cucu volcanic structure (300 — 500 ppm) to the Pilişca structure (1000 — 1500 ppm) is quite obvious.

The same general tendency of increase is observed in case of Pb (Fig. 4). Shoshonites and banakites are also exceptions because of their lower values similar to those of the basaltic andesites and of the high-K

andesites from the Pilișca and Ciomadul structures. The Murgul Mare andesites occupy a special place due to their lowest values of Pb (4.5 ppm).

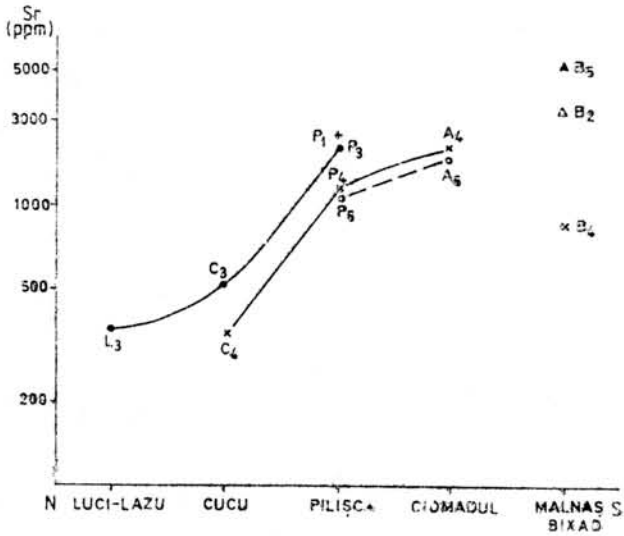

Fig. 3 — Variation of the Sr content along the volcanic structures. Symbols as in Table 1.

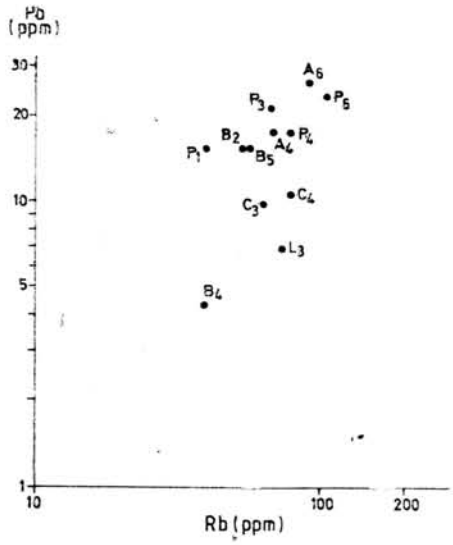

Fig. 4 — Pb (ppm) vs. Rb (ppm) diagram. Symbols as in Table 1.

The values of the transition ("compatible") trace elements Cr and Ni, versus Rb, can give information on the main processes by which the primary magmas developed (Gill, 1981 ; Robin, 1982). There is a negative correlation tendency both of Ni and of Cr versus Rb (Fig. 5). The small variation intervals of Ni (5-15 ppm) and Cr (20—30 ppm) are obviously in correlation with the petrochemical types. On both diagrams shoshonites and banakites have a special position due to the highest Ni (20—30 ppm) and Cr (120—170 ppm) values. On the other hand, Co, Sc and V

include the shoshonites and banakites into the same tendency of negative correlation versus Rb (Fig. 6).

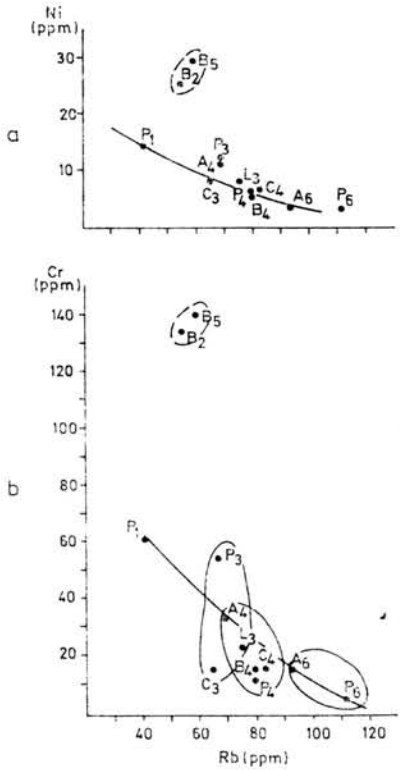

Fig. 5 (a, b) — Ni, Cr (ppm) vs. Rb (ppm) diagrams. Symbols as in Table 1.

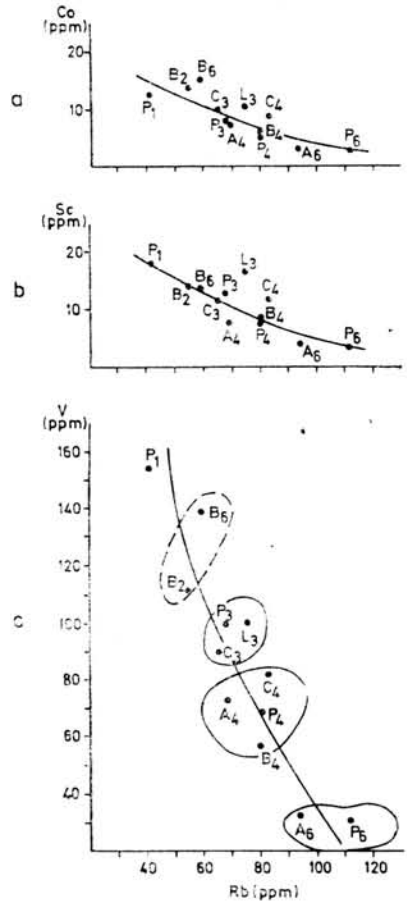

Fig. 6 — (a, b, c) — Co, Sc, V (ppm) vs. Rb (ppm) diagrams. Symbols as in Table 1.

Figure 7 shows the chondrite-normalized REE distribution in volcanics. The continuous change of the REE distribution depends both on the volcanic structure and on the petrochemical type.

The andesites belonging to Fagul and Cucu structures display a poor fractionation of both heavy and light REE. The andesites of the Cucu volcanic structure have a higher total content; one of the sample shows a slight Eu positive anomaly. The basaltic andesite and the high-K andesite and dacite of the Pilișca structure are differentiated by the different content of Ce, the higher the more acid the rocks are. The dacites of the Ciomadul structure have a similar behaviour as the Pilișca daci-

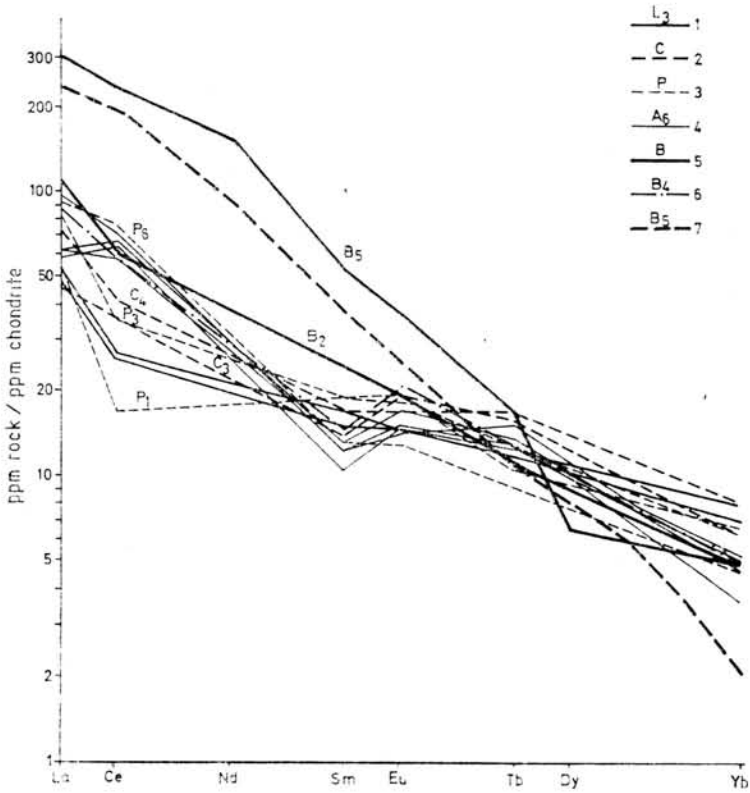

Fig. 7 — Diagram of REE distribution normalized at chondrites. For 1, 2, 3, 4, 5, 6 see Tables 3; 7, Sample R-107 (Peccerillo, Taylor, 1976 b).

tes. All the analysed samples indicate a similar distribution; unlike other rock types they show a positive Eu anomaly. The REE distribution trend in the Murgul Mare high-K andesite is similar with that of the Ciomadul high-K dacites. Shoshonites and banakites have a similar distribution, pointing to the obvious fractionation both of the light REE and heavy ones. Banakites have a higher total content in REE than shoshonites; together they differ from the other rocks by the maximum values of La, Ce and Sm.

The calc-alkaline association is characterized by the increase of the La and Ce values and the decrease of the Sm and Yb content concomitantly with the increase of the rock acidity.

At the same time we plotted the banakite sample from Murgul Mic Hill, previously analysed by Peccerillo and Taylor (1976 b). Our data are in agreement with those of Peccerillo and Taylor, confirming the accuracy of the analyses effectuated in our laboratories.

4. Discussion

Within the calc-alkaline rock associations the variation of the "compatible" trace elements versus Rb points out the relative significance of the partial melting processes and of differentiation by fractional crystallization in the outlining of the trace elements distribution in these rocks (Gill, 1981; Robin, 1982). Thus, if the processes of partial melting prevailed, the wide variation of Rb corresponds to a small variation interval of the Ni, Cr, Co, etc. values. A wide variation of Ni, Cr, Co, etc. versus a relatively constant Rb value indicates the significant part played by the fractional crystallization in the magmatic differentiation process. The Ni, Cr/Rb diagrames (Fig. 5) for the South Harghita Mts point out the partial melting as the main process responsible for the trace elements distribution in volcanics.

The REE distribution normalized at chondrites indicates that the fractional crystallization processes did not play an important part in the formation of the South Harghita volcanic suite, their geochemical characters being related to the different degree of partial melting of the primary magma source, the only process which can generate significant differences of the total REE contents (Hanson, 1980), in our case a gradual enrichment from N to S. The absence of the Eu negative anomaly or even of a slight positive Eu anomaly indicates high pressure conditions in which the partial melting and, possibly, the fractional crystallization took place.

The REE distribution in volcanics makes possible some estimations as regards the degree in which the main component minerals of the magmatic rocks are involved in the processes of partial melting or of fractional crystallization (Hanson, 1980). Thus, the increasing fractionation of the heavy and light REE along the vulcanic arc simultaneously with the mentioned petrographical and geochemical changes indicates the participation of garnet and, subordinately, of clino- and orthopyroxene and of hornblende. The significant role played by garnet in the HREE fractionation culminates in shoshonites and banakites, as previously pointed out by Peccerillo and Taylor (1976 b). The presence of garnet, as a residual phase, in the genesis of the primary magma, under conditions of a gradual decrease of the degree of partial melting, correlated with relatively low values of the $^{87}Sr/^{86}Sr$ ratio (0.7049 — 0.7062) (Peltz et al., this volume), clearly indicates — at least for the calc-alkaline association — the derivation of the magmas in the upper mantle above the subduction plane, at progressively greater depths.

The experimental petrology data concerning the genesis of the calc-alkaline magmas, in which the fusion of the upper mantle is implicated, brings evidence for the models proposed by Nicholls and Ringwood (1973) and Ringwood (1974). According to these models the suite of rocks derived from the fusion of the upper mantle has as main source the garnet-bearing lherzolites, representing its main petrologic component. According to Ringwood (1974), the dehydration of talcum, serpentine, brucite and even of micas from the composition of the subducted lithosphere took place at 100—200 km deep in the subduction zone, under

high temperature and pressure conditions. Due to the increase of the fusibility by the enrichment in volatiles there takes place the partial melting of the rocks from the suprajacent upper mantle; it generates the magmatic liquids, which leave a residual phase with garnets, pyroxenes ± amphiboles. The resulted magmas reach the surface and form calc-alkaline rock suites. This model can explain satisfactorily the genesis of the calc-alkaline rock association in the South Harghita Mts.

Due to their particular petrographic and geochemical characters the shoshonitic rocks (shoshonites and banakites) occupy a special position within the South Harghita volcanics, which suggets their different genesis.

In geochemical respect, the shoshonitic rocks display a "duplicative" character. On the one hand, the high alkalinity, the contents of Co, Sc, V, Sr, Ba, La, Ce assign them to the general geochemical trend of the calc-alkaline suite. On the other hand, they are an exception to this trend due to the decrease of acidity, and of the Rb and Pb contents and the increase of the Ni, Cr and Sm values.

From the petrographic viewpoint, the shoshonitic rocks possess particular features given by the presence of magmatically corroded quartz, biotite and hornblende (xenocrysts), beside unaffected olivine, clinopyroxene and orthopyroxene. The plagioclase phenocrysts (An_{35-45}) show more basic rims (An_{60-65}; Szőke, 1963).

Furthermore, one can also mention the petrographic and geochemical differences between the shoshonitic rocks from Murgul Mic and Luget bodies as well as the petrographic unhomogeneities within each of them.

The highest values of Sr, La, Ce and Ba indicate the presence of the partial melting process in the genesis of the shoshonitic rocks. In comparison with the calc-alkaline rocks they were formed by the lowest degree of partial melting. On the other hand, the mentioned petrographical and geochemical features do not correspond, at first sight, with their generation only by the lowest degree of partial melting of the same source as that of the calc-alkaline rocks. Therefore, the implication of another petrogenetic process must be admitted. If the chemical and isotopic data do not confirm the significant participation of the fractional crystallization and of the contamination with crustal material and taking into account the mentioned petrographical and chemical particularities, the intervention of magma-mixing processes represents the petrogenetic solution for these rocks. These data are compatible with magma-mixing petrogenetic models (Anderson, 1976; Eichelberger, 1978). Therefore, one can presume that the shoshonitic association was derived from the same source that generated the primary calc-alkaline suite, by the lowest degree of partial melting; this magma was then mixed, in different degrees for the two bodies, with a new-generated basic magma, derived from the same source (the upper mantle).

In comparison with the existent petrogenetic interpretations, according to which the South Harghita shoshonitic rocks come from a primary magma different from the calc-alkaline one (Peccerillo, Taylor, 1976 b; Peltz et al., 1984; Seghedi et al., 1986), this hypothesis achieves a better concordance between the petrographic and geochemical data.

The general petrographical and petrochemical characteristics of the South Harghita volcanic area are determined, in geotectonic respect, by its special position of "closing" and ceasing of the volcanic activity of a volcanic chain in connection with the thermic and density equilibrations between the "remains" of the subducted lithosphere and the surrounding mantle (Ringwood, 1975, in Green, 1980).

5. Conclusions

The geochemical features of the studied rocks confirm, to a large extent, the mentioned geochemical model (Seghedi et al., 1986). It is established the fact that the magma which generated the shoshonitic rocks differs from that which generated the calc-alkaline association, but not in the sense of a "primary" shoshonitic magma. They were derived from the same source which, however, underwent a much more reduced partial melting (5–10%) and was later mixed with a new-formed basic magma, originating in the upper mantle. This interpretation is based both on geochemical and petrographical data.

The succession of calc-alkaline and shoshonitic rocks, corresponding to a degree of partial melting of the source, gradually lower from N to S, proves a linear-type "migration" along the arc-trench system similar to the volcanic arcs from the Lesser Antiles, Papua and New Guinea (Arculus, Johnson, 1978).

On the basis of the REE distribution one inferred that the minerals which participated in their fractioning were : garnet, clino- and ortho-pyroxenes and, possibly, hornblende. These minerals remain in the residual phase in larger percentages corresponding to the decrease of the partial melting degree. The positive Eu anomalies point to the separation of the abore-mentioned minerals at high pressure, that is under great depth conditions of the magma generation.

In case of both associations there also results the minor implication of the differentiation by fractional crystallization processes in intermediary magmatic chambers.

The values of the $^{87}Sr/^{85}Sr$ ratio (0.7049–0.7062 ; Peltz et al., this volume) indicate the upper mantle as source of the primary magmas and confirm the unsignificant implication of the assimilation processes.

Considering the significant participation of the partial melting process and the unsignificant one of the fractional crystallization and assimilation in establishing the geochemical features of the volcanics, there results that the magma did not remain a long time in intermediary magmatic chambers and it did not undergo significant chemical changes during its rising through the continental lithosphere (30–35 km).

---

[3] Recently $^{87}Sr/^{86}Sr$ data confirm the insignificant participation of the assimilation processes in the configuration of the magma composition (Peltz et al., this volume).

REFERENCES

Anderson A. T. (1976) Magma mixing : petrological process and volcanological tool. *Journ. of Volc. and Geoth. Res.*, 1,p. 3—33, Amsterdam.

Arculus R. J., Johnson R. W. (1978) Criticism of generalized models for the magmatic evolution of arc-trench system. *Earth Planet. Sci. Lett.*, 39, p. 118—128, Amsterdam.

Dupuy C., Dostal J., Verniéres J. (1977) Genesis of volcanic rocks related to subduction zones ; geochemical point of view. *Bull. Soc. géol. France* (7), XIX, 6, p. 1233—1243, Paris.

Eichelberger J. C. (1978) Andesitic volcanism and crustal evolution. *Nature*. 275/7, p. 21—27.

Gill J. B. (1981) Orogenic andesites and plate tectonics. 398 p., Springer Verlag, Berlin-Heidelberg-New York.

Green T. H. (1980) Island arc and continent building magmatism — a review of petrogenic models based on experimental petrology and geochemistry. *Tectonophysics*, 63, p. 367—385, Amsterdam.

Hanson G. N. (1980) Rare earth elements in petrogenetic studies of igneous sistem. *Ann. Rew. of Earth and Planet. Sci.*, 8, p. 371—407, Palo Alto.

Moţoi G., Szakács Al., Setel A., Vrăşmaş N., Setel M. (1976) Report, the archives of I.P.G.G. Bucharest.

Nicholls I. A., Ringwood A. E. (1973) Effect of water on olivine stability in tholeiites and the production of silica saturated magmas in the island arc environment. *J. Geol.*, 81, p. 285—300.

Peccerillo A., Taylor S. R. (1976 a) Geochemistry of Eocene calc-alkaline volcanic rocks from Kastamonu area, northern Turkey. *Contr. Mineral. Petrol.*, 58, p. 63—83, Heidelberg.

— Taylor S. R. (1976 b) Rare earth elements in East Carpathians volcanic rocks. *Earth Planet. Sci. Lett.*, 32, p. 121—126, Amsterdam.

Peltz S., Grabari G., Stoian M., Tănăsescu A. (1984) REE, Rb, Sr and K distribution in volcanic rocks from the East Carpathians (Călimani—Harghita and Perşani Mts.). Petrogenetic significance. Magmatism of the molasse-forming epoch and its relation to endogenous mineralization. *Geol. Ustav Dionysa Stura*, p. 47—58, Bratislava.

— Vâjdea E., Balogh K., Pécskay Z. (1985) Contributions to the chronological study of the Neogene volcanic processes in the Călimani and Harghita Mountains. In *Abstracts of VIII-th RCMNS Congress*, Budapest.

— Seghedi I., Grabari G., Popescu G. (1987) Strontium isotope composition in volcanic rocks from Călimani, Harghita and Perşani Mts. *D. S. Inst. Geol. Geofiz.*, 72—73/1, Bucureşti.

Rădulescu D., Vasilescu A., Peltz S., Peltz M. (1964) Contribuţii la cunoaşterea structurii geologice a munţilor Gurghiu. *An. Com. Stat Geol.*, 33, Bucureşti.

— (1973) Contribuţii asupra cronologiei proceselor vulcanice neogene din munţii Călimani, Gurghiu şi Harghita. *D. S. Inst. Geol.*, LIX/4, Bucureşti.

— Peltz S., Stanciu C., Seghedi I., Szakács Al., Ionescu F. (1984) Report, the archives of the I.G.G. Bucharest.

Ringwood A. E. (1974) Petrological evolution of island arc system. *J. Geol. Soc. London*, 130, p. 183—204.

Robin C. (1982) Relation volcanologie-magmatologie-géodinamique : aplication au passage entre volcanismes alcalin et andesitique dans le sud Méxicain. *An. Sci. de L'Univ. de Clermont Ferrand*, 70, 31, 503 p.

Seghedi I., Grabari G., Ianc R., Tănăsescu A., Vâjdea E. (1986) Rb, Sr, Zr, Th, U, K in the Neogene volcanics from the South Harghita Mountains. *D. S. Inst. Geol. Geofiz.*, 70—71/1 (1983—1984), p. 453—473, Bucureşti.

Szakács Al., Seghedi I. (1986) Chemical diagnosis nature of the volcanics in the southeasternmost part of the Harghita Mountains — Proposal for a new nomenclature. *Rev. Roum. Géol. Géophys. Géogr., sér. Géol.*, 30, p. 41—48, București.

Szöke A. (1963) Studiul petrografic asupra rocilor andezitice din Valea Oltului între Tușnad și Malnaș. *Acad. RPR, Stud. cerc. geol.*, VIII/2, București.

GEOCHIMIA ELEMENTELOR MINORE ÎN VULCANITELE MUNȚILOR HARGHITA DE SUD (CARPAȚII ORIENTALI): ASOCIAȚIILE CALCOALCALINĂ ȘI SHOSHONITICĂ

(Rezumat)

1. *Introducere*

Lucrarea de față aduce completări fondului de date geochimice existent, cu noi determinări de elemente minore efectuate pe 42 probe, și de pămînturi rare, pe 14 probe, în intenția de a completa și de a nuanța modelul petrogenetic enunțat într-o lucrare anterioară (Seghedi et al., 1986).

2. *Cadrul geologic*

Activitatea magmatică a avut loc în cadrul a două etape principale, cărora le corespund două compartimente structurale (Rădulescu et al., 1964): (1) compartimentul inferior (vulcano-sedimentar), larg extins în Harghita de Sud pe rama vestică și mai puțin pe cea estică, și (2) compartimentul vulcanic superior, caracterizat prin prezența unor structuri vulcanice aliniate pe direcția NE—SV, cu produse parțial suprapuse, de la nord la sud: Luci, Fagul (Lazu), Cucu, Pilișca, Ciomadul, precum și o serie de corpuri eruptive mici, izolate, situate în extremitatea sudică, în zona Bixad-Malnaș (Moțoi et al., 1975; Rădulescu et al., 1984).

3. *Date geochimice*

Au fost executate un număr de 42 analize spectrale pentru Pb, Cu, Zn, Ga, Ni, Cr, Co, V, Sc, Zr, Y, Yb, La, Ba, Sr, Rb, și 14 analize de pămînturi rare (tab. 1, 2, 3).

Elementele minore cele mai reprezentative pentru interpretări petrogenetice au fost proiectate într-o serie de diagrame, în raport cu Rb, considerat ca bun indicator al gradului de diferențiere magmatică.

Ba prezintă o tendință de corelare pozitivă în cadrul rocilor calcoalcaline, față de care rocile shoshonitice contrastează prin conținuturi mult ridicate de Ba la valori reduse ale Rb (fig. 2).

Sr prezintă o clară tendință de creștere de-a lungul Harghitei de Sud, cu valori maxime pentru rocile shoshonitice (fig. 3). Aceeași tendință generală de creștere o prezintă și Pb, cu excepția rocilor shoshonitice, cu valori mai scăzute (fig. 4).

Ni și Cr au tendință de corelare negativă cu Rb, variind în cadrul unor intervale reduse, iar rocile shoshonitice distingîndu-se prin valorile cele mai ridicate de Ni (fig. 5). În privința conținutului în Co, Sc și V, rocile shoshonitice se conformează tendinței generale de corelație negativă față de Rb (fig. 6).

Distribuția pămînturilor rare, normalizate la chondrite, (fig. 7) indică variații în funcție de apartenența la structurile vulcanice și în funcție de tipurile petrografice ale rocilor analizate. Conținutul total în pămînturi rare crește de la nord la sud. Rocile shoshonitice se deosebesc de asociația de roci calcoalcaline prin valorile cele mai ridicate în La și Sm.

4. *Discuția și interpretarea datelor*

Conform modului de variație a elementelor minore „compatibile", față de Rb, care indică importanța relativă a proceselor de topire parțială și cristalizare fracționată în diferențierea magmatică a rocilor calcoalcaline (Gill, 1981; Robin, 1982), se constată faptul că procesele de topire parțială au jucat rolul preponderent în imprimarea caracterelor geochimice observate ale vulcanitelor din munții Harghita de Sud (fig. 5, 6).

Distribuția pămînturilor rare indică rolul preponderent al granatului și al piroxenilor (Hanson, 1980) în fracționarea progresivă observată a pămînturilor rare, rezultate în urma procesului de topire parțială, cu grad tot mai redus de la nord la sud.

Trăsăturile geochimice ale suitei calcoalcaline sînt compatibile cu modelul petrogenetic al lui Nicholls și Ringwood (1973) și Ringwood (1974), conform căruia aceasta se formează prin topirea parțială a unor porțiuni din mantaua superioară de deasupra planului de subducție, îmbogățite în volatile în urma deshidratării rocilor din componența litosferei subduse.

Pentru explicarea caracterelor geochimice diferite ale rocilor shoshonitice (fig. 2, 5, 7) este nevoie să se apeleze la ipoteza unei geneze diferite a acestora. Caracterul „duplicitar" al comportamentului geochimic al rocilor shoshonitice (pe de o parte tendința lor de a se încadra în trendul geochimic al suitei calcoalcaline — Co, Sc, V, Sr — iar pe de alta, tendința de a se deosebi de acesta — Ni, Cr, Rb, Pb) și unele particularități mineralogice (prezența cuarțului, biotitului și hornblendei corodate magmatic — xenocristale — alături de olivina, clino- și ortopiroxenul neafectate, ca și prezența unor coroane de supracreștere mai bazice — An_{60-65} pe cristalele de plagioclaz — An_{35-40}) sugerează intervenția procesului de amestec de magme (Anderson, 1976; Eichelberger, 1978). Diferențele geochimice observate între cele două corpuri de roci shoshonitice (Sr, Ba, Zr, pămînturi rare), ca și neomogenitățile petrografice din interiorul acestora, întăresc această interpretare. Amestecul de magme s-a produs între magma calcoalcalină cu cel mai scăzut grad de topire parțială și o magmă bazică nou formată, provenită probabil din aceeași sursă (mantaua superioară).