DISTRIBUTION OF TRACE ELEMENTS IN OPHIOLITES FROM CAZANESHTI, METALLIFEROUS MOUNTAINS, ROMANIA

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ABSTRACT

Distribution of minor elements in ophiolites from Cazaneshti area of Metalliferous Mountains has been studied. Petrographic studies were carried out to differentiate various lithological units of the area. The analysed data was treated statistically, to find the lognormality of various populations by cumulative frequency curve method. Co, Ni and Cr appear to be formed by identical geochemical processes, whereas, V, Cu and Pb are represented by two populations. Zn is abnormally low in the rocks studied. Other important parameters like geometric deviation, coefficient of deviation and coefficient of variation, etc., have been calculated to decipher the epigenetic nature and chemical dispersion of minor elements in the rocks. A close relationship between Cu: Pb and Pb : Zn indicates that these minerals have been formed by identical geochemical process.

INTRODUCTION

Cazaneshti is a small village situated NE of Drocea Mountains, which form a part of famous Metalliferous Mountains, constituting the NW part of Romania. The village Cazaneshti can be approached from Deva, District Headquarter of the Hunedoara Province, by 43km long all weather road, through Brad, and Vata Dejos. The locality is 16km from Vata Dejos (Fig. 1).

Relief in general is mature and is characterised by medium heights which range from 400 to 720 meters. Most of the highest points are situated on the NE part of the region. The first erosional level is located at 650m and is represented by various water drainage systems. The second erosional level, which predominates the area, is below 520–560m. The rest of the heights are found below these two and gradually lower to hydrographic basins of Vata Valley and reach upto 283m, where village Cazaneshti is situated. Generally, the valleys in the area are narrow, though relatively wide at the intersection zones.



Fig. 1. Location map of Romania.

Previous Work

The region in which geochemical distribution of elements was studied has been under geological ingestigations since the 12th Century, primarily due to its gold fields. The notable contributors include Koch (1870), Petro (1885), Locazy (1885), Deolter and Papp (1902–1908) and Rozlozsnik (1905).

The above workers accumulated and elaborated the preliminary geological data about the general lithological units which constitute the Metalliferous Mountains. After World War I, the area received special attention and the geology and tectonics of the area were studied in detail with emphasis on various magmatic phases and stratigraphy. An attempt was made to establish a relationship between tectonics, magmatism and metallogenesis (cf. Atanasiu, 1936; Petrolian, 1937; Guisca and Socolescu, 1965). In 1941, Ghitulescu and Socolescu prepared the first comprehensive geological map of the area on a scale 1:75,000.

Intensive geological work on the area started after 1950 and valuable contributions on the geology of the area were made by Papiu (1952), Cioflica (1952) and others. (The old references cited above can be found in the bibliographies in these two papers).

REGIONAL GEOLOGY

The studied area lies in the southern Apuseni Mountains, which constitute the northern part of Drocea Massif that comprises of eruptives and sedimentary formations. Basic rocks were emplaced in Muresh phase as a result of initial basic magmatism of Alpine orogeny and represent oldest lithological unit exposed in the area. Initial basic magmatism in the area is represented by basalts, gabbros, microgabbros and quartz andesites. These rocks have been attributed by Guisca and Cioflica (1965) as the Jurrassic Inferior ophiolitic magmatism, whereas, andesites constitute Cretaceous Inferior magmatism. Within this basaltic complex lie several bodies of ultrabasic rocks, exhibiting stratification, depicting that these were formed by fractional differentiation of basic magmas. The initial ophiolitic magmatism covers 90% of the area under study. These rocks have been intruded by a series of subvolcanic bodies which appear to be related to subsequent Laramic magmatism represented by granodiorites, diorites, and rhyolites, collectively named as Banatites (Lupu, 1958).

On the contact of Banatites with associated rocks, contact metamorphism is well-displayed. Silicification, epidotization, and chalcopyrite mineralization has taken place on some contacts. In rare cases galena and blende are also developed. Metamorphic aureoles produced in the associated limestones constitute marbles in which lenticles of skarns and sometimes magnetite concentrations are present. Frequently, close to banatitic bodies are granitic skarns with magnetite, garnet-wollastonite and garnet pyroxenite assembleges. Besides the principal minerals in the skarns, other associated minerals include scapolite, epidote, calcite, chlorite and quartz.

Geology of the Area

The following types of rocks have been identified in the area on the basis of petrographic studies.

A. Initial Ophiolitic Rocks

This constitutes the main lithological unit of the area and forms the important geosynclinal zone of Muresh Mountains. The unit is represented by peridotites, metagabbros, gabbros, basalts, agglomeratic basalts, porphyritic basalts and andesites. The modal composition of rocks is given in Table 1.

B. Subsequent Banatitic Rocks

Banatitic magmatism in the Metalliferous Mountains extends to north in Banatitic province and forms the Banat Mountains. In the Metalliferous Mountains these rocks are found along fracture zones of Laramic age with NE-SW or E-W orientation.

Banatitic magmatism forms two important bodies in the zone and generally consists of granodiorites and porphyritic granodiorites. However, many undifferentiated magmatic bodies or veins of aplites, etc., are also encountered. The main intrusion is localised east of Magureaua Valley with EW orientation and was con-

S. No.	Rocks		Plagioclase	Augite	Diopside	Hornblende	Biotite	Olivine + Serpentine	Glass	Opaque minerals	Accessories
1.	Porphyritic Basalt		55	19	-	_	_		25	1	-
2.	Dolerite		53	28	10	7	—			3	
3.	Andesites	a)	35	15	—	5		_	45		-
		ь)	_	15		38	-		47		
4.	Peridotite				7.6	10.6	3	48.9		2.3	26.5 Act. Chl.
5.	Melagabbros		17.6-30	<u> </u>	8.1-19.8	4.5	1	36.4-55.2	-	0.6-2.7	7.7
6.	Gabbros		55,8—59	30	15.9-22.5	—	—	7.6-22.6	-	1,5-2.8	

TABLE 1. MODAL (%) COMPOSITION OF OPHIOLITES FROM CAZANESHTI

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TABLE 2. MODAL (%) COMPOSITION OF BANATITES FROM CAZANESHTI

S. No.	Rocks	Plagioclase	K. Feldspar	Quartz	Augite	Diopside	Biotite	Hornblende	Opaque Mineral	Glass
1.	Granodiorites	32	30	12	10	15	<u> </u>	<u> </u>	1	
2.	Quartz Diorites	50		17	7		10	15	-	
3.	Diorites	60	4	3	25	-	_	5	3	
4.	Aplites	30	40	17	-	_		-	3	 Melanocratio mineral 10%
5.	Rhyolites	20	_	6	-				4	70

solidated under hypothermal conditions. On the basis of petrographic studies various rocks types have been differentiated and modal composition is given in Table 2.

C. Sedimentary Rocks

The sedimentary formations of the area have been separated into Jurassic Superior and Cretaceous, and consist of recrystallized limestones and conglomerates.

Contact Metamorphic Formations

Marbles are exposed in Cerboaia and Ponor Valleys on contact with banatites. The associated rocks have been metamorphosed into skarn and limestone has been completely recyrstallized to marbles. Skarns are white coloured massive rocks. At places pyrite, chalcopyrite, galena and blende mineralization is present. Away from banatitic bodies skarns are observed with epidote and chlorite formation.

EXPERIMENTAL WORK

Geochemical study of ophiolites from Cazaneshti was done by sampling of exposed rocks in the area. Most of the samples were taken from ophiolites but banatites and metamorphic rocks were also sampled. However, trace elements behaviour was studied in ophiolites only.

Most of the samples were taken from fresh rocks, uneffected by alteration phenomena, and zones altered by hydrothermal activity were ignored. However, where unavoidable, a systematic sampling was done from fresh rocks to hydrothermally altered rocks.

A total of 212 samples were collected out of which 103 were analysed (Appendix 1). Of these, 51 samples were from ophiolites, 20 from banatites, whereas the rest were of marble, skarn and other associated rocks. The samples were analysed on spectrograph model PGS-2, in Institute of Geochemical Prospection, Bucharest, and spectrum was registered on ORWO-UVI photographic plate. The plates were studied on a densitometer and spectral line densities of the samples were compared with the prepared standards spectral lines (with a composition very similar to the rock types of the area) to determine the quantities of elements present. The results of spectral analyses are given in Appendix 1.

GEOCHEMICAL CHARACTERS OF MINOR ELEMENTS IN THE OPHIOLITES

Geochemical character of ophiolites from the Metalliferous Mountains have been studied by many workers, e.g. Savu (1962), Cioflica (1962), and Guisca and Cioflica (1965ab), and others. All the existing data in literature show that distribution of minor elements like Ni, Co, Cr, V, Ba, Sr, Cu, Pb, and Zn reflects, in general, variation of major elements due to magmatic differentiation. In this work, principal character of minor elements distribution in Cazaneshti ophiolites is presented.



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i) Cobalt

Being an element of siderophile character, it shows the tendency to preferential accumulation during early stages of differentiation, replacing Fe" in the opaque minerals, as well as within the lattices of the ferromagnesian minerals. Rankama and Shama (1970) mention that within pyroxenes (especially the orthorhombic ones) cobalt contents varies in parallel with the Mg content.

By the cumulative frequency curve (Fig. 2), it is evident that this element is longnormally distributed with a narrow range of values (3-50 ppm), which is characteristic feature of ophiolites.

ii) Nickel

The concentration of Ni in ophiolites generally decreases with the increase of silica. It is siderophile, chalcophile and even lithophile in the upper parts of lithosphere. On probability graph Ni shows a lognormal distribution but gamma concentration in the rocks analysed is higher, i.e. 10-400 ppm (Fig. 3).

iii) Chromium

Goldschmidt (1954) has shown that concentration of chromium in igneous rocks is related to the sequence of crystallization, the earlier formed rocks being rich in chromium than the later ones. The range of chromium content in the ultramafic and mafic rocks given by Goldschmidt (p. 548) is 1000–44000 and 100–4000 ppm respectively. In case of ultramafic rocks from Cazaneshti no abnormality is seen.

All the three elements, Co, Ni and Cr appear to be distributed by similar geochemical processes during the differentiation of basic magmas.

iv) Vanadium

Among all the discussed elements, V has the most interesting behaviour. Like the other trace elements associated with the ferromagnesian minerals, V separates especially in the early stages of the magmatic evolution. The ionic radius of V" is quiet similar to that of Fe" and, therefore, replaces it easily in the mineral lattice. High contents of vanadium occur within the opaque minerals (Dunacan & Taylor, 1968). On the other hand, depending on its ionic potential, V enters lattices of some ferromagnesian minerals replacing Mg and Fe" as well.

On cumulative frequency curve this element (ranging from 30 to 300 ppm) does not show lognormal distribution, but the curve shows a deflection to the left at 120 ppm (Fig. 2). This supports the existence of two populations of V in ophiolites of the area. There are two possibilities: a) Perhaps the samples taken for analysis are not homogeneous, and b) the samples analysed belong to hydro-thermally altered zones and V present in basic rocks may be concentrated in these zones.

v) Copper

Copper is a strong chalcophile element and shows a tendency of concentra-



tion in the early phases of magmatic processes. Cu" may replace Fe" and Mg in the ferromagnesian minerals (El Hinnawi, 1972). However, Wedepohl (1969) considers that the presence of disperse chalcopyrite in rocks leads to the occurrence of relatively high contents of Cu. The concentration of copper in mafic igneous rocks is several times that in felsic igneous rocks (Goldschmidt 1954, p. 178).

The cumulative frequency curve (Fig. 3) shows a deflection to the left at 250 ppm. The values of Cu in most of the analysed rocks range from 10 to 400 ppm, however, in one sample it exceeds 3000 ppm.

The relatively high concentration of Cu in samples is due to the presence of cupriferous pyrite in rocks. It was observed in the field that cupriferous pyrite occurs in two modes in the rocks of the area. In some cases it is finely disseminated in the rocks, while in other cases it occurs as fillings in the joints and fissures of the rocks. Due to this fact, two populations of copper appear on the probability graph.

By taking average concentration of Cu = 40 ppm, the values equal to or more than 200 ppm are considered as anomolous for Cu distribution in the rocks of the area.

vi) Lead

The geochemical behaviour of this element depends on the K geochemistry, due to a high similarity of their ionic radii on the one hand, and to the chalcophile character of Pb which may determine its occurrence in rocks as sulphide (Goldschmidt, 1954) on the other hand. Although it is not a characteristic element of ophiolites, nevertheless, it was studied. The concentration of Pb in the rocks analysed ranges from 3 to 150 ppm, thus indicating three populations (Fig. 3). The first population has values between 3 and 25 ppm, which is normal concentration of Pb in ophiolites. In second population the value of Pb is more than 95 ppm, indicating that samples of ophiolites have been taken from a place near the hydrothermal activity, while the third population indicates the presence of rich zone in ophiolites due to hydrothermal activity.

vii) Zinc

The geochemical behaviour of this element is intermediate between those of Cu and Pb. Its behaviour depends on the similarity of its ionic radious to that of Fe" (Goldschmidt, 1954). During the late stages of the differentiation, the chalcophile character of zinc may determine the occurrence of disseminated sphalerite in the rocks (Stiopol, 1963). The silicate rocks formed by differentiation contain Zn in the structure of magnetite and ilmenite by replacing Fe and Mg in the crystal lattice. Biotite, amphiboles and tourmaline may contain small quantities of Zn but the high concentration of Zn is usually found in minerals of late differentiates of acid magmas. The cumulative frequency curve shows relatively low values, but with lognormal distribution (Fig. 3) concentration of this element in the rocks analysed varies between 30 to 350 ppm, whereas in some cases high values are also observed.

The use of cumulative frequency curve method for interpretation of data

has enabled the author to calculate other important parameters of geochemical distribution of minor elements in the ophiolites (Table 3). The important parameters are as under:

- a. Geometric deviation (S') which is a factor obtained by dividing threshold value by background.
- b. Deviation coefficient (S) of relative deviation which is logrithm (base 10) of the geometric deviation.
- c. Coefficient of variation (S") expressed as 100s/D.

TABLE 3.	PARAMETERS	OF	GEOCHEMICAL	DISTRIBUTION	OF	MINOR	ELEMENTS
		12	IN THE OPH	IOLITES.			

El	BG (B)	B + S	G.D. (S')	D.C. (S)	R.D. (S")
Cu	40	100	1.42	0.15	0.21
РЬ	14	60	4.44	0.64	4.57
Zn	65	100	1.53	0.18	27.6
Ni	70	170	2.42	0.38	0.54
v	120	175	1.45	0.16	0.13
Cr	160	750	4.68	0.67	0.41
Co	18	45	2.50	0.39	1.16

Abbreviations: El, element; BG, Background; G.D., geometric deviation; D.C., deviation coefficient; R.D., relative deviation.

A lognormal distribution is completely determined by two parameters, the geometric mean (b) and the coefficient of deviation S' or more commonly, as a logrithmic coefficient S (Lepelter, 1969). The coefficient of variation is a dispersion index specific for the distribution of a given element in a given environment and expresses the degree of homogeneity. When rocks are considered, a similarity in the coefficient of deviation, together with similar average values, may indicate similar geochemical processes in their formation. Based on these facts, it is observed from Table 3 that for all the minor elements coefficient of deviation is low (0.15 to 0.64), thus confirming the similar geochemical processes in the distribution of the minor elements discussed above. Moreover, coefficient of deviation is related to the type of geochemical dispersion, i.e. mechanical or chemical, and consequently might give an indication about syngenetic or epigenetic conditions. It has been shown that high coefficient of deviation for the rocks under investigation is low, thus indicating that all the minerals in ophiolites are epigenetic in origin.

In case of a polymetallic mineralization, with two or more elements lognormally distributed, there is generally a positive correlation between them. Thus coefficient of correlation gives a reliable measure of their degree of dependency. The coefficient always falls between -1 and +1; if it is 0, it means a complete independence between the two elements. If the value is +1 it indicates a perfect correlation, whereas -1 indicates a perfectly invariant relation between the factors, (Siegel, 1974, p. 277). Correlation coefficient was calculated for data, for Pb : Cu and for Pb : Zn, for possible mineralized zone in ophiolites. Relative coefficient of correlation is calculated by equation :

$$\Upsilon = \frac{\Sigma X Y - \left(\frac{\Sigma X \cdot \Sigma Y}{N}\right)}{\left[\sqrt{\Sigma X^2 - \left(\frac{\Sigma X}{N}\right)^2}\right] \left[\sqrt{\Sigma Y^2 - \left(\frac{\Sigma Y}{N}\right)^2}\right]}$$

Where : γ = An estimation of correlation coefficient.

N = The number of samples of x and y.

- XY = The value of each x multiplied by the corresponding y.
- $\Sigma_{x,y}$ = The sum of all the values of x multiplied by the sum of all the values of y.

 X^2 = The square of the sum of each value of x.

 Y^2 = The square of the sum of each value of y.

For Cu and Pb the correlation coefficient calculated comes to 0.418, which indicates a direct relation between both elements. Thus it is concluded that Cu and Pb are from the same magma/mineralizing solutions. The coefficient of correlation for Pb and Zn is 0.716, indicating also a direct relationship between the two.

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S. No.	Sample	Cu	Pb	Zn	Ag	Mo	As	В	Ni	Co	Cr	v
1.	Ophiolites	40	100	130		2	70	80	110	15	70	130
2.	Limestone	15	10	30		3	100	130	30	5		50
3.	Limestone	15	3	50					. 3			Traces
4.	Dolomitic	20	70	130				100	10		10	140
5.	-do-	400	25	200		1	150		250	80	250	70
6.	Banatite	10	25			1					_	70
7.	do	15	20			1					-	60
8.	Limestone	15	15	70				300	15		20	
9.	do	25	130	130				150	30	10		
10.	Ophiolite	50	80	60		2			130	20	40	400
11.	_do-	25	30	100			70		150	30	250	150
12.	Limestone	20	10	80	0.4	1	100		20	3	11	30
13.	-do-	25	10	30	<u></u>	3			30	5	_	60
14.	Banatite	30	35	50			80		15	3	30	120
15.	Skarn	35	35	70	0.1	2	80		400	80	150	200
16.	do	10	20	60		1			80	25	200	150
17.	-do-	300	200	400		5	100		80	70	200	130
18.	Limestone	50	100	150		2	130	150	100	80	60	60
19.	Ophiolite	40	10	130		1	150	120	150	30	100	50
20.	-do-	25	20	60					60	5	70	150
21.	Banatite	15	10	80		3			35	10	35	80
22.	Limestone	20	35	3000		1		100	100	80		10

APPENDIX 1. DISTRIBUTION OF MINOR ELEMENTS (ppm) IN OPHIOLLTES BANATITES AND LIMESTONES FROM CAZANESHTI

S. No.	Sample	Cu	РЬ	Zn	Ag	Мо	As	В	Ni	Co	Cr	v
23.	Banatite	20	15	70	-				40	3	35	100
24.	Banatite	26	25	60		1			5			50
25.	Ophiolite	20	25	50			100		30	3		80
26.	do	5	10	30			•		3			70
27.	-do-	35	70	200	1.3	3	100	100	50	15		100
28.	Skarn	15	100	150			100	120	15		60	60
29.	Ophiolite	120	40	70	2.7			70	150	30	40	50
30.	Limestone	20	15	Traces		0.000			3			
31.	Ophiolite	150	40	60				80	200	25	300	400
32.	Limestone	20	3	80		1		200	150	35	-	50
33.	Banatite	5	10	Traces		•	70					30
34.	Quartzite	15	3	Traces		1	250	•	3	3		30
35.	Skarn	60	20	100	-	2	••	80	200	30	100	350
36.	do	50	10	70	—		70		50	3	100	150
37.	Ophiolite	20	20	50				15				100
38.	-do-	45	15	50			70		130	15	200	170
39.	-do-	150	30	130		20	200	150	130	60	30	70
40.	-do-	35	5	50	_			1200.0	80	5	130	150
41	do	20	15	80			70		20	3	300	200
4.2	-do-	20	10	60	_	1				-		30
43		120	15	80					100	20	250	180
44.	-do-	100	10	100					100	25	40	40
45	-do-	60	3	70	-				80	10	_	50
46	Quartzite	250	30	30	1.5	15	100	100	70	5		30
47	Ophiolite	3000	150	200	1	15			95	40		70
49	-do-	150	35	80		5		130	100	15	130	130
4.0		50	20	80	-	.,		150	70	95	35	150
50	Ophiolite	50	100	80		1		190	200	40	400	200
51	-do-	25	100			1		120	200	2012	400	200
52	-do-	15	35	60	-	.,		100	20	3	_	20
52.		20	Traces	50	0.000	0	80	100	10	50	200	900
54	-do-	20	114005	100	_			100	250	50	500	1200
55	Quartzita	110	25	70					50	20	_	100
56	-do-	3000	60	130	25		100	100	10	20		200
57	-do-	2000	10	100	4,0	8	120	100	20	50	050	30
58	do	1900	100	2000	1	1	100	140	250	50	250	200
59	do	1200	100	Traces	1	. 5	100		20	30	30	20
60	do	150	10	100	_			1 races	- 50	3	80	80
61	-do	25	50	100				80	250	20	200	08
62	-do-	45	- 50	100	-	1			15	3	86	100
63	do	90	20	100				100	150	15	770	120
64	do	25	35	100			100		200	25	350	250
65	-do	20	20	120	-		120	80	80	15	100	100
66	Ophielite	900	50	130				100	80	10	200	150
67	Banatita	200	20	130	-	1			500	20	300	100
68	Ophielite	100	10	120	-			100	50	50	43	200
00.	Opniolite	35	15	70			-	120	80	30	30	300

S. No.	Sample	Cu	Pb	Zn	Ag	Mo	As	В	Ni	Co	Cr	v
69.	Quartzite	70	15	80			_	150	70	45		100
70.	Ophiolite	70	3	70			_		300	50	25	150
71.	-do	170	200	400	0.3	2		80	150	35	500	250
72.	Banatite	20	20	60	· · · · · ·	1			30	5	60	120
73.	Ophiolite	16	15	50				100	100	25	3	200
74.	Ophiolite	40	20	70				80	150	35	80	170
75.	-do-	20	20	50	_	2	120	100	15	3		70
76.	-do-	10	20	100			100		70	10	120	150
77.	_do_	30	15	60		1	-	45	10		30	150
78.	-do-	15	80	50		3	100	100			25	100
79.	-do-	5	25	50			80		_			80
80.	do	10	20	50	-	2	130	130	5		200	60
81.	Banatite	3	10					• ••••	20		30	30
82.	Ophiolite	120	35	100	-	-	-	-	25	_	_	200
83.	Banatite	10	5	50				100	10			30
84.	Ophiolite	30	10	30		1	200	_	70	10	120	170
85.	do	70	30	130		2			70	30		80
86.	-do-	70	20	120		'			100	35	100	150
87.	-do	100	3	100			—	80	120	25	100	200
88.	-do-	15	80	60			100	120	3	Traces	100	80
89.	do	10	300	100		_		·	40	15	100	150
90.	do	20	20	60		100	÷		25	15	60	130
91.	do	110	20	120			<u></u>	120	200	25	120	130
92.	do	200	30	120				100	250	40	120	170
93.	Banatite	20	30	60			_	100	5			80
94.	Ophiolite	200	25	800		1		100	200	40	100	120
95.	Banatite	200	10	100				120	30	20		120
96.	-do-	400	5	120		2	_	100	150	100	70	150
97.	Ophiolite	15	10	100	-	Traces	_	170	20	40	40	80
98.	Banatite	35	15	100				100	80	40	40	150
99.	do	25	15	Traces					15	3	200	170
100.	do	25	10	200	_	2		120	200	70	120	120
101.	-do-	120	5	120		2		150	130	30	300	200
102.	do	5	150	50	1	2	80		5			30
103.	do	30	3	80	Traces	Traces	_		15	30	60	70

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