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SULFUR ISOTOPES AND TRACE ELEMENTS IN COPPER ORES AND PYRITIC SCHISTS FROM BĂLAN (EAST CARPATHIANS)

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Key words: Ore deposits. Sulphides. S-Isotopes. Minor elements. Metamorphism. Lithostratigraphic control. Model. East Carpathians - crystalline zone - Hăghimaș Mountains.

Abstract: *Sulfur Isotopes and Trace Elements in Copper Ores and Pyritic Schists from Bălan (East Carpathians).* At Bălan metamorphosed pyrite-chalcopryrite ores and pyritic schists occur at different lithostratigraphic levels. The distribution of sulphur isotopes and trace elements in pyrite of ores and pyritic schists show lithostratigraphic control, no regional metamorphic homogenization is recognisable. There is no isotopic equilibrium between pyrite-chalcopryrite pairs of the ore, due probably, at least partly, to metamorphic isotopic fractionation, especially in the chalcopryrite phase. In a vertical profile through the ore lenses a continuous variation of $\delta^{34}\text{S}$ values and trace elements in pyrite was recognised. A genetic model is proposed based on refluxing convective circulation of hydrotherms charged by reduced sea water sulphur and metals leached from volcanic or nonvolcanic rock assemblages in the source area.

General Remarks

The ore deposits at Bălan are represented mainly by disseminated pyrite and chalcopryrite ores concordantly interlayered with low grade metamorphites of the Tulgheș Group, Cambrian in age (Fig. 1). Massive sulfide ores occur only subordinately in discontinuous thin pyrite-chalcopryrite bands and locally in small Cu-Zn-Pb ore lenses (Bălan, Medias). The ore deposits are considered of hydrothermal-sedimentary (or volcano-sedimentary) origin, metamorphosed in the greenschist facies during an early Caledonian event (Sardic phase). Together with other similar copper and base metal ore deposits of the East Carpathians (Leșul Ursului, Fundul Moldovei, Baia Borșa) the ore deposits from Bălan have been assigned to an ore (metallo-genetic) province associated with a Cambrian rhyolitic volcanism, mainly of submarine character. Therefore the ore deposits were assumed to be of Kuroko type, in spite of the fact that some of them present peculiarities linked especially to their depositional type (Kräutner, 1984, 1989).

In the Slovakian Carpathians (Spiš-Gemer Mts) similar ore deposits are mined from the Gelnica Group at Smolník and Mníšek. Their resemblance with the ores from Bălan was recognized some time ago (Földvari, Panto, 1950). Due to equivalence in age and geological setting they were assigned to the same Cambrian ore province (Kräutner, 1984).

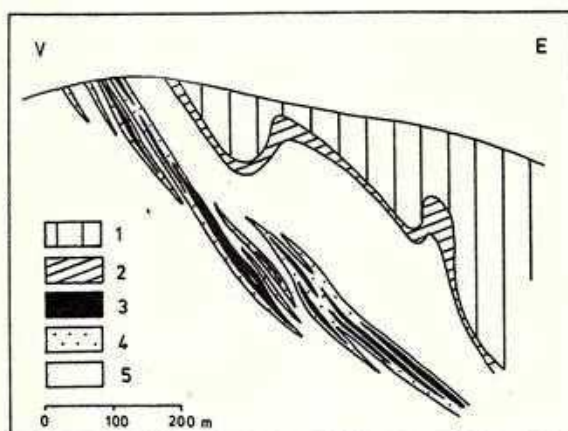


Fig. 1 - Geological cross section through the upper part of the Bălan ore deposit (acc. to Kräutner, Popa, 1972). 1, Valea Băii Member, sericite-chlorite schists; 2, Bălan metarhyolites; 3-5, Bălan ore member; 3, disseminated copper ore; 4, chlorite quartzites and chlorite schists $\pm$ pyrite, locally with magnetite and/or iron carbonates; 5, sericite-chlorite phyllites with local intercalations of graphite phyllites.

According to the proposed depositional model (Kräutner, 1989) the Bălan ores were formed at the water-sediment interface from outflowing hydrotherms in marine environment. An intensive dispersion, of the

sulfides concomitant with/or subsequent to their deposition (intraformational resedimentation), is suggested by: 1) lenticular shape of the ore deposits; 2) predominance of disseminated ore and scarce, incomplete development of massive ore; 3) change in the lithologic support of the disseminated ore; 4) relict sedimentary structures as banding, breccia-like mixing of different types of massive ore; 5) locally interlayered iron carbonate or magnetite-bearing schists, indicating unstable Eh and pH conditions; 6) lithostratigraphic control at the rank of a member in a volcano-sedimentary formation. Thus the whole ore member from Bălan has been considered a "hydrothermal-sedimentary sulfide ore sequence" (Kräutner 1989).

Disseminated ores (Fig. 2) are the most frequent type. Usually they consist only of sulfide + chlorite + quartz. The sulfides, represented mainly by pyrite and chalcopyrite, are disseminated in chlorite schists or chlorite quartzites. Pyrite appears usually blastic in idiomorphic crystals, unevenly distributed, or concentrated parallel to the primary banding. Chalcopyrite is xenomorphic, it migrated on the metamorphic schistosity or was mobilized in metamorphic quartz and carbonate veinlets, or lenses, disposed both concordantly and discordantly to the schistosity, suggesting successive stages of metamorphic mobilisation. Sphalerite and galenite do appear only subordinately. Bournonite, tetrahedrite, mispickel, galenobismuthite, jamesonite, teallite and cubanite, as well as native bismuth, gold and silver have been mentioned (Petruian et al., 1971, Kräutner, Popa, 1972, unpubl. report) as sporadic components.

the metamorphic sequence (Fig. 3). They are represented by chlorite-sericite schists, sericite-chlorite-quartz schists, white sericite-quartz-feldspar schists (epiclastic volcanic material) and graphite sericite phyllites. Pyrite usually forms idiomorphic blasts, but sometimes large porphyroblasts have been noticed.

Isolated idiomorphic pyrite crystals were found locally in graphite quartzites (metalydites), blastodetriral quartz-feldspar schists and greenschists (basic metavulcanics).

Magnetite or iron carbonates (siderite, ankerite) appear locally in the chlorite-quartz rocks instead of pyrite, suggesting temporal changes of the Eh and pH conditions during the ore deposition.

Data on the isotopic sulfur composition of Bălan ores have been available only since 1981 (Borcoş, Gaftoi, 1981; Popa, Şerbănescu, 1984, unpubl. report). Considering these first data the mentioned authors remarked a relatively wide spreading of δ values and suggested either different genetic processes or late modifications of the isotopic ratio (Borcoş, Gaftoi, 1981, unpubl. report), as well as bacterian activity in sedimentary deposits (Popa, Şerbănescu, 1984, unpubl. report).

The new analytical data are presented in tables 1, 2, 3, 4, 5, as well as some of the older isotopic data (Borcoş, Gaftoi, 1981, unpubl. report; Popa, Şerbănescu, 1984, unpubl. report) that could be attributed to the collectivites used for the present purpose. All data refer to a quantity of about 0.2 g of sulfide crystals, or crystal fragments, selected carefully under the stereoscope from a rock volumes of about 100 cm³. Therefore the values of tables 1-5 represent average values for the respective sulfides and thus refer to the global geochemical character of each sulfide phase from hand specimen volumes. No information is available on the degree of geochemical homogeneity at both intra- and intergranular levels.

The samples were collected systematically from profiles through selected ore bodies as well as informatively from different lithostratigraphic levels: Bălan member, Valea Băii member, Arama Oltului member and the graphite phyllite member below the Pingărat blastodetriral schists. The latter belongs to the top sequence of the Tulgheş Group (upper part of Tg₄ formation in the Sindomic Sequence) and is in tectonic contact with the other sulfide-bearing levels assigned to the Tg₃ formation of the Bălan Sequence (Bălan nappe). The tectonic and lithostratigraphic setting of the analysed samples is shown in Fig. 3.

A general look on the trace element distribution and the ratios of sulfur isotopes in pyrite and chalcopyrite (Tabs. 1-6, Fig. 3) shows a rather unhomogeneous picture with a $\delta^{34}\text{S}_{\text{py}}$ spread of 56.47 ‰, from -18.27 ‰ to +38.20 ‰. From Figures 3 and 4 it is obvious

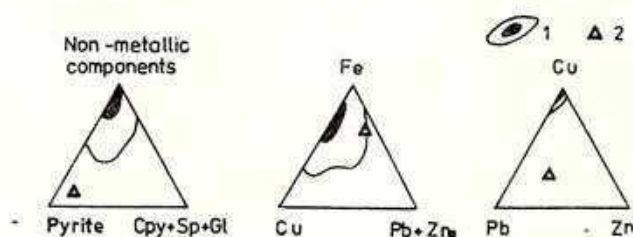


Fig. 2 - Main components of the Bălan ores.

1, disseminated copper ores (statistic distribution); 2, massive polymetallic ore (average).

Massive ores (Fig. 2) occur only locally in centimetric and decimetric concordant bands or small lenses. The amount of sulfides may exceed 80 %. Pyrite-chalcopyrite, sphalerite-galenite and polymetallic (Cu, Pb, Zn, Fe) varieties are known. Relict sedimentary structures may be reorganized in these ores, for example banding, breccias a.o.

Schists with disseminated pyrite ± chalcopyrite (pyritic schists) occur associated with the ore deposits, but also at different lithostratigraphic levels of

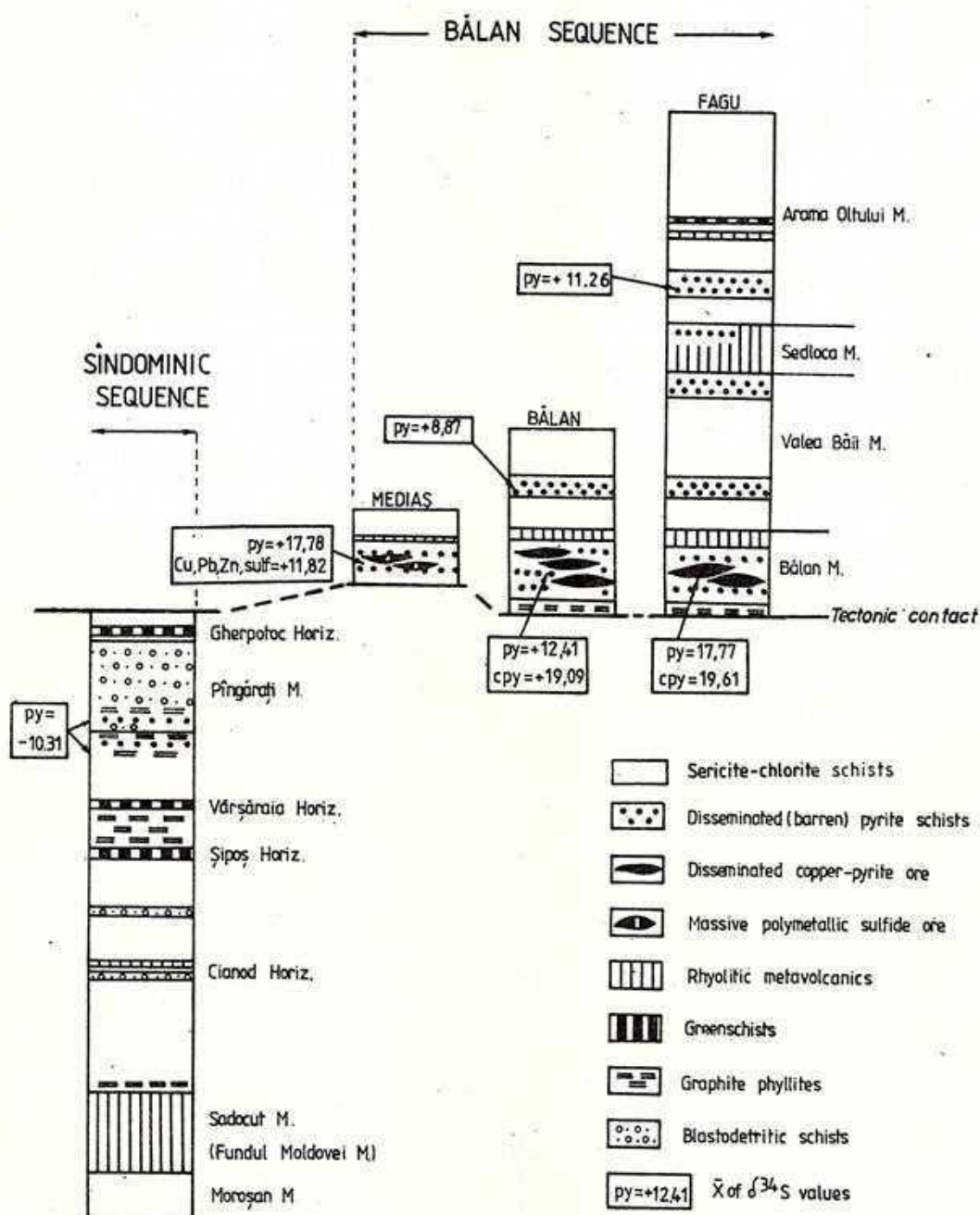


Fig.3 - Lithostratigraphic position of ores and pyritic schists at Bălan.

that there are some correlations between the lithostratigraphic position and the $\delta^{34}\text{S}$ distribution. Similar correlation results also from the trace element picture (Tab. 6, Figs. 8, 9, 10, 11). Therefore it seems evident that the recrystallizations due to the early Caledonian regional metamorphism and the subsequent Variscan overprint did not produce a homogenization of sulfur isotopes and trace elements in the sulfide phase of the metamorphic pile. Oppositely,

the mentioned unhomogeneities can never be explained only by metamorphic differentiation. Thus, one may admit that the actual picture reflects the main geochemical characters of the primary (premetamorphic) stage and requires interpretation on these terms. As a matter of fact, it is widely accepted that the greenschist grade metamorphism was not of sufficient intensity to alter significantly the $\delta^{34}\text{S}$ values and that the degree of lack of equilibrium noticed in low meta-

Table 1
 $\delta^{34}\text{S}$ values for pyrite and chalcopyrite samples from ores and pyritic schists of the Blan area

No Sample	Rock	Provenance	Sample	$\delta^{34}\text{S}_{\text{I/CDT}} \text{‰}$
BALAN ORE MEMBER				
Disseminated ore				
375	Py+cpy in chlorite quartz schist	Fagu; level+440S; br.15	Pyrite	+10.67
375	" "	Lense 26 m.234.0	Chalcopyrite	+23.68
377	" "	" m. 233.6	Pyrite	+16.56
377	" "	" m. 233.6	Chalcopyrite	+29.29
378	" "	" m. 233.1	Pyrite	+16.58
380	" "	" m. 231.5	Chalcopyrite	+7.56
381	" "	" m. 231.0	Chalcopyrite	+29.35
383	Cpy in ankerite lense	" m. 229.5	Chalcopyrite	+15.73
384	Py+cpy in chlorite quartz schist	" m. 229.5	Pyrite	+20.05
385	" "	" m. 227.5	Pyrite	+22.68
385	" "	" m. 227.5	Chalcopyrite	+25.17
386	" "	" m. 225.5	Pyrite	+22.44
387	" "	" m. 222.5	Pyrite	+16.29
388	" "	" m. 218.0	Pyrite	+16.75
389	" "	" m. 216.5	Pyrite	+10.63
390	Py+cpy in chlorite quartz schist	Idem, lense 25 m. 195.0	Pyrite	+21.77
391	" "	" m. 188.5	Pyrite	+16.97
392	" "	" m. 185.0	Pyrite	+16.11
393	" "	" m. 178.0	Pyrite	+16.48
393	" "	" m. 178.0	Chalcopyrite	+10.52
394	" "	" m. 177.8	Pyrite	+24.26
297/3(P)	Py+cpy in chlorite quartz schist	Fagu; drillhole 297	Chalcopyrite	+18.31
297/5(P)	" "	" "	Chalcopyrite	+18.36
297/7(P)	" "	" "	Chalcopyrite	+18.64
A	Py in chlorite quartz schist	Fagu; level+590N	Pyrite	+19.39
B	" "	" "	Pyrite	+22.06
5(B)	Py+cpy in chlorite quartz schist	Bălan (Central)	Pyrite	+12.41
5(B)	" "	" "	Chalcopyrite	+19.09
512/2(P)	Py in chlorite quartz schist	Medias; drillhole 512	Pyrite	+18.64
512/3(P)	" "	" "	Pyrite	+17.08
512/8(P)	" "	" "	Pyrite	+17.52
512/9(P)	" "	" "	Pyrite	+18.95
510/3(P)	" "	Medias; drillhole 510	Pyrite	+16.89
Massive ore				
3(B)	Polymetallic ore	Medias, Gal. 35; lense 1	Chalcopyrite	+11.76
3(B)	" "	" "	Galena ore	+12.39
-(P)	" "	" lense 2	Galena ore	+11.60
VALEA BĂII MEMBER (pyritic schists)				
B-156	Py sericite chlorite schist	Bălan; nivel -435; tr.0 m.129	Pyrite	+3.42
B-156A	" (py porphyroblasts)	" " "	Pyrite	+32.52
B-158	Py sericite chlorite schist	" " m. 150	Pyrite	+14.33
B-158B	" (py porphyroblasts)	" " "	Pyrite	+32.65
B-158A	2 cm band massive py.	" " "	Pyrite	+7.54

Table 1 (continued)

No Sample	Rock	Provenance	Sample	$\delta^{34}\text{S}_{\text{I/CDT}} \text{‰}$
ARAMA OLTULUI MEMBER (pyritic schists)				
604	Py sericite chlorite quartz schist	South Olt; gal.18 Sabo	Pyrite	+6.99
		Dir. 2S; Br. m. 78		
605	" "	" " m.76	Pyrite	+5.72
606	" "	" " m.75	Pyrite	+9.27
608	" "	" " m.37	Pyrite	+16.61
609	" "	" " m.36	Pyrite	+14.50
607	" "	" " m.21	Pyrite	+9.70
610	" "	Dir. 2S; Br. 4V; m. 9	Pyrite	+10.13
611	" "	" " m.12	Pyrite	+14.52
612	" "	" " m.41	Pyrite	+16.94
613	" "	" " m.44	Pyrite	+7.23
408	Py sericite chlorite quartz schist	South Olt; drill. 335; m. 106	Pyrite	+35.77
349	White py sericite quartz schiste	" " drill. 337; m. 710	Pyrite	+38.20
SÎNDOMIC SEQUENCE (Pyritic schists)				
509/13(P)	Py sericite graphite schist	Medias; drill. 509	Pyrite	-7.58
514/29(P)	" "	" drill. 514	Pyrite	-3.18
523/ 5(P)	" "	" drill. 523	Pyrite	-9.51
523/ 5(P)	" "	" " "	Pyrite	-8.30
523/6A(P)	" "	" " "	Pyrite	-7.14
523/ 7(P)	" "	" " "	Pyrite	-7.90
406/ 6(P)	" "	" drill. 406	Pyrite	-8.64
409/25(P)	Py±cpy sericite graphite schist	" drill. 409; m.870	Pyrite	-15.93
409/20(P)	" "	" " "	Pyrite	-14.40
1(B)	Py sericite graphite schist	" drill. 205; m.875	Pyrite	-18.27
2(B)	" "	" drill. 16	pyrite	-12.54

Abreviation: (B) = Data from Borcoş, Gaftoi (1981); (P) = Data from Păpa, Şerbănescu (1984);

Py = pyrite; cpy = chalcopyrite.

morphic ores is mainly due to the original conditions of deposition (e.g. Gregory, Robinson, 1984; Gehrisch et al., 1975). This means that during the low grade metamorphism the system was closed for sulfur on regional scale, but it could be open on local scale, due to recrystallization and metamorphic mobilisations by siliceous and carbonatic fluids.

Bearing in mind the mentioned facts it seems appropriate to discuss the $\delta^{34}\text{S}$ values and trace element distribution according to the lithostratigraphic assignment of the samples. This means that each sample collectivity represents synchronous ores and/or pyritic schists, whereas sulfides from different collectivities did originally deposit during different time periods; but all collectivities were submitted to the same metamorphic events.

DISSEMINATED AND MASSIVE SULFIDE ORES OF THE BĂLAN ORE MEMBER (BĂLAN, FAGU AND MEDIAŞ ORE DEPOSITS)

Spread of $\delta^{34}\text{S}$ values

$\delta^{34}\text{S}$ values for pyrite range from +10.63 ‰ to +24.26 ‰, and for chalcopyrite from +7.56 ‰ to

+29.35 ‰. Pyrite has a δ spread of 13.63 ‰ around an average value of $\bar{x} = +17.77$ ‰, while the chalcopyrite spread is of 21.79 ‰ around an average of $\bar{x} = 19.61$ ‰ (Tab. 6). This is the δ range within which many of the stratabound sulfide ores are placed as well as the modern hydrotherms (Nielsen, 1979)(Fig. 4).

Average differences from the Cambrian sea water ($\delta^{34}\text{S}=+30$ ‰), as can be inferred from Cambrian sulfate deposits (Nielsen, 1979), are of ($\Delta = \delta^{34}\text{S}(\text{SO}_4^{2-} - \text{S}^{2-}) = 12.23$ ‰ for the Bălan pyrite and of $\Delta = 16.73$ ‰ for the pyrite of Smolnik (Kantor, Rybar, 1970). Thus the Bălan ore deposits and the equivalent Smolnik ores in Slovakia are not exceptions from the fact mentioned by Sangster (1968) that in most cases the $\delta^{34}\text{S}$ average in sulphide ore deposits is about 15 ‰ lower than in the sea water sulfate of the same age. Sangster (1976) suggests that the differences between $\delta^{34}\text{S}$ values recorded in different (volcanic or sediment hosted) hydrothermal sedimentary sulfide ore deposits are controlled by the global change of $\delta^{34}\text{S}$ in sea water sulfate, and that there is in fact no real statistic difference between the sulfur populations of the mentioned ore deposits, if these are related to the synchronous sea

Table 2

Trace elements in pyrite samples from ores and pyritic schists of the Bălan copper ore deposit

Sample	Cu	Pb	Zn	Ni	Co	Ag	Sn	Bi	As	Ti	Mn
FAGUL CETĂȚII SOUTH (disseminated ore)											
8	12500	550	300	40	300	3.0	115	65	700	110	170
8A	300	320	260	3	170	4.0	10	30	900	1300	30
10	30000	1200	1000	65	340	5.5	150	70	500	170	550
204	1000	21000	6000	38	370	24.0	17	75	1100	105	83
205	4400	6200	260	40	320	26.0	22	130	600	105	115
203	2700	1900	1000	48	380	12.0	17	48	500	130	26
84	430	25	100	180	350	1.0	10	10	900	370	45
85	6500	60	150	55	500	2.0	16	40	600	140	225
A	1300	650	160	100	560	6.0	10	72	500	700	120
B	2600	5600	3400	42	260	13.0	16	10	2600	4200	50
375	11000	19000	6500	24	650	24.0	38	90	1100	1200	120
370	30000	22000	24000	24	420	120.0	150	500	2600	110	320
378	30000	30000	2600	26	850	135.0	170	400	2300	970	150
379	7700	4300	3800	40	380	14.0	30	60	2400	4000	95
381	14000	950	800	105	260	7.5	85	70	500	700	72
384	1700	600	220	30	190	2.5	18	28	500	400	18
385	15000	850	260	58	800	22.0	50	62	850	670	65
386	28000	600	560	70	870	15.0	360	63	850	280	670
387	24000	320	220	52	850	23.0	180	115	1000	100	80
388	30000	2500	1500	58	320	70.0	260	46	500	140	520
389	30000	600	650	65	670	92.0	750	46	650	125	550
390	15000	11000	4400	55	620	44.0	35	250	1100	500	42
391	30000	1500	460	90	650	34.0	380	60	500	270	280
392	2400	1700	130	155	430	10.0	18	70	700	1200	230
393	30000	2000	1400	100	370	40.0	500	110	550	135	420
394	30000	8000	4400	38	520	70.0	120	180	500	190	55
B-72	1000	1200	110	95	600	8.0	10	44	1500	530	70
438	4000	2000	1600	26	210	24.0	10	75	1300	140	30
B-73	1400	170	340	100	520	5.0	70	32	1050	200	55
B-73A	11000	170	280	80	480	4.0	105	26	1200	150	80
B-74	5300	270	100	16	360	3.6	570	29	500	30	16
B-75	13000	1400	110	20	160	19.0	280	50	1000	320	47
B-76	340	34	100	650	350	1.0	10	10	500	2600	10
B-77	2200	3000	4000	90	105	5.5	10	13	500	370	32
B-78	50	100	100	170	160	1.3	10	10	14000	185	11
BĂLAN CENTRAL (disseminated ore)											
B-107	13000	100	10	58	620	70.0	24	35	2800	125	48
B-108	4200	1700	110	280	700	4.0	10	17	900	280	23
B-109	1600	85	100	65	1400	5.5	28	42	2600	150	40
B-110	1900	180	100	65	650	2.2	100	50	2000	200	52
B-120	4200	900	100	70	1600	6.0	10	36	500	290	14
6(B)				220	110	3.0		10	3000		10
42(B)		2500		46	135	54.0	1000	100	500		63
69(B)		1000		42	260	15.0	150	120	500		1030
16(B)		1300		33	770	18.0	120	240	3000		125
17(B)		2300		42	450	33.0	70	240	3000		165
23(B)		3000		40	540	50.0	180	100	3000		210
31(B)		210		160	230	23.0	80	90	3000		220
16(P)	5000	380	600	42	255	6.5	130	200	2200	230	90
18(P)	30000	7000	4100	10	100	26.0	62	120	300	680	55

Table 2 (continued)

Sample	Cu	Pb	Zn	Ni	Co	Ag	Sn	Bi	As	Ti	Mn
PYRITE DISSEMINATED IN DIFFERENT ROCK TYPES OF THE ORE SEQUENCE											
In limestones											
B-79	1600	1800	11000	34	270	8.5	190	14	1250	52	55
In white quartz-sericite schists											
B-82	420	190	100	44	40	1.0	10	10	550	210	330
502	50	2400	360	17	38	6.0	10	20	1100	46	21
In grey ($\pm$ grafitic) sericite schists											
503	140	900	170	280	125	2.0	10	10	1300	600	12
Big crystals in chlorite schists											
439	100	40	90	200	135	10.0	10	10	1400	1100	48
Big crystals in carbonate ore											
206	120	70	400	380	130	1.0	10	10	500	120	95
In pyritic schists below the ore:											
Graphite chlorite phyllite											
482A	300	1200	1100	44	230	2.0	10	15	500	900	38
483	1100	4500	260	650	380	4.5	10	15	2000	360	32
4	105	500	160	160	380	1.0	10	10	750	500	55
Quartz chlorite schists											
437	400	470	100	110	140	1.5	10	10	500	280	460
MEDIAS (massive ore)											
20(P)	22000	20000	5750	18	140	15.0	65	48	300	565	290
12(P)	1500	900	2350	18	175	2.0	10	32	300	1750	1100

Provenance: 375 - 389 = level +440 S, breşa 15, lense 26

390 - 394 = level +440 S, breşa 15, lense 25

B-72 - B-78 = level +440 S, transv. puţ. 5

B-107 - B-120 = below level Ferdinand

(B) = levels Wetter; +50; -50; -85

(P) = levels Ruţoc 0; Ruţoc +50

water sulfate. Therefore accepting sea water sulfur as a source for both volcanic and sediment hosted stratabound sulfide ore deposits, a similar evolution of sulphur fractionation may be supposed for all these deposits.

Figure 5 shows the $\delta^{34}\text{S}$ of pyrite from Bălan ore comparatively to pyrite of representative volcanic hosted (Kuroko) and sediment hosted (Rammelsberg) stratabound sulfide deposits. By shifting the $\delta^{34}\text{S}$ values of the mentioned deposit for equilibration with the Precambrian sea water value, a good concordance may be obtained for the pyrites from Bălan and from the two "classic" sulfide deposits (Fig. 5, dashed lines). The same conclusion is drawn on a larger scale by comparing Sangster's (1976) $\delta^{34}\text{S}$ average distribution pattern for 110 stratabound "volcanic" and "sedimentary" sulfide ore deposits, equilibrated in Fig. 5 with the Bălan ores by Cambrian sea water equivalence.

From Figure 5 results a narrower $\delta^{34}\text{S}$ spread in volcanic hosted sulfide ore deposits comparatively to the larger scattering in sediment hosted ores. This may indicate for the latter a supplementary sulfur fractionation due to the local sedimentation environment and bacterial activity. Comparatively to the mentioned

data the $\delta^{34}\text{S}$ distribution in the Bălan pyrites (Fig. 5) shows an intermediate picture, suggesting volcanic hosted distribution extended to a low populated larger spread as noticed in sediment hosted deposits. This conclusion fits well the mentioned deposition model (Kräutner, 1989) which presumes for the Bălan ores dispersion and resedimentation of sulfides due to an active hydroenergetic environment.

According to the genetic model (Kräutner, 1966, 1984, 1989) the Bălan ores were deposited from out-flowing hydrotherms. The $\delta^{34}\text{S}$ spread indicates that these fluids do not bear mantle sulfur nor "volcanic" sulfur. It is mostly assumed that the metal-bearing thermal fluids belong to convective systems of ocean water which gather their sulfur and metal charge by leaching deeply seated rock formations. In such geological environments the mentioned related acid volcanism may act as heat engine promoting the convective circulation and metal extraction. Thus, even for volcanic hosted deposits, for example the Kuroko type, models have been imagined in which the ascending hydrotherms are charged by sulfur of sea water origin (Ohmoto, Kajiward, fide Sasaki, 1974). The $\delta^{34}\text{S}$ patterns of these ore deposits may be explained by kinetic

Table 3
Trace elements in pyrite samples from the pyritic schists of the Arama Oltului and
Valea Băii member

Sample	Cu	Pb	Zn	Ni	Co	Ag	Sn	Bi	As	Ti	Mn
ARAMA OLTULUI MEMBER (pyrite in sericite-chlorite schists)											
604	160	1800	6500	230	320	4.0	10	52	1000	720	46
602	260	1250	5500	420	650	4.0	10	65	1100	650	65
606	480	1000	9000	230	380	2.5	10	105	1000	800	35
607	360	420	250	200	120	2.0	10	68	1000	850	12
608	90	2200	4200	220	180	3.5	10	32	3600	650	32
609	280	2400	11000	170	220	3.5	10	30	3700	630	25
610	190	1100	600	180	175	5.5	10	75	1000	1400	15
611	150	1350	11000	300	270	2.0	10	19	3200	750	48
612	150	1150	2800	280	210	2.0	10	16	1000	1300	50
613	150	1600	4800	260	240	5.5	10	13	1000	1450	13
614	145	650	185	260	220	5.0	10	10	2500	1000	10
22	650	19000	22000	320	260	12	10	24	1900	950	50
23	95	2400	1600	210	340	1.5	10	10	1200	620	10
57	900	750	500	160	660	3.0	10	180	500	480	40
58	1600	620	14000	250	620	3.5	10	130	850	800	95
59	1100	200	180	165	150	2.5	10	39	500	460	10
B-226	1800	2500	210	110	280	17	10	220	750	700	32
408	270	1800	2600	240	140	10	10	10	1100	1000	22
410	750	11000	12000	300	440	7.5	10	10	1050	700	68
463	720	140	85	160	180	1.0	10	10	500	950	42
B-141	1900	340	135	370	440	3.0	10	100	670	650	18
B-142	1000	320	100	380	350	1.5	3	70	500	750	10
pyrite in white sericite schists)											
349	550	440	3000	110	480	5.0	10	10	500	150	46
VALEA BĂII MEMBER (pyrite in sericite-chlorite schists)											
479	230	650	100	220	180	1.0	10	10	1250	700	10
480	220	570	130	340	210	1.5	10	10	1000	1500	13
481	30	280	100	150	54	1.0	10	10	500	1500	10
505	320	600	150	200	275	1.5	10	10	1000	900	16
477	320	250	100	210	340	1.5	10	10	550	750	12
lower level (pyrite in sericite-chlorite schists)											
504	30	400	100	65	135	1.0	10	10	500	950	10
B-154	220	700	120	320	260	2.0	10	10	1500	720	60
B-156	190	400	125	300	250	2.5	10	10	1200	1750	11
B-157	460	310	110	190	150	1.5	10	10	1300	500	36
B-158	37	210	100	120	60	1.0	10	10	800	1350	10
(pyrite porphyroblasts)											
B-154A	100	350	110	120	210	3.0	10	18	630	2300	60
B-156A	20	260	100	100	85	4.0	10	10	520	900	60
B-158B	550	370	260	180	90	1.0	10	10	1450	1500	12
(pyrite band)											
B-158A	45	250	110	95	90	7.0	10	10	1450	2000	10

Table 4

Trace elements in pyrite samples from graphite phyllites, graphite quartzites and blastodetrital rocks of the Sindomic sequence (Tg₄ formation of the Tulgheș Group) in the Bălan area

Sample	Cu	Pb	Zn	Ni	Co	Ag	Sn	Bi	As	Ti	Mn
GRAPHITE PHYLLITES											
500	220	460	250	17	170	5	<10	<10	<500	1100	27
32(P)	75	115	100	190	340	<1	<10	<10	600	300	70
28(P)	50	75	100	285	110	<1	<10	<10	<500	2000	100
8(P)	360	5000	6200	57	150	2	<10	<10	<500	1000	20
15(P)	110	270	100	270	245	<1	<10	<10	600	1500	19
17(P)	75	270	100	15	75	<1	<10	<10	900	150	13
GRAPHITE QUARTZITES											
136	2200	150	200	450	240	3	<10	<10	<500	1300	750
29(P)	3000	160	100	550	550	<1	<10	<10	<500	200	325
30(P)	30	55	100	80	100	<1	<10	<10	600	2250	65
BLASTODETRITAL ROCKS											
26(P)	14000	7800	8000	46	75	21	210	110	<500	600	530
25(P)	4000	6000	11500	35	130	20	36	190	<500	550	2000

8(P) - 32(P): Data from Popa, Șerbănescu (1984)

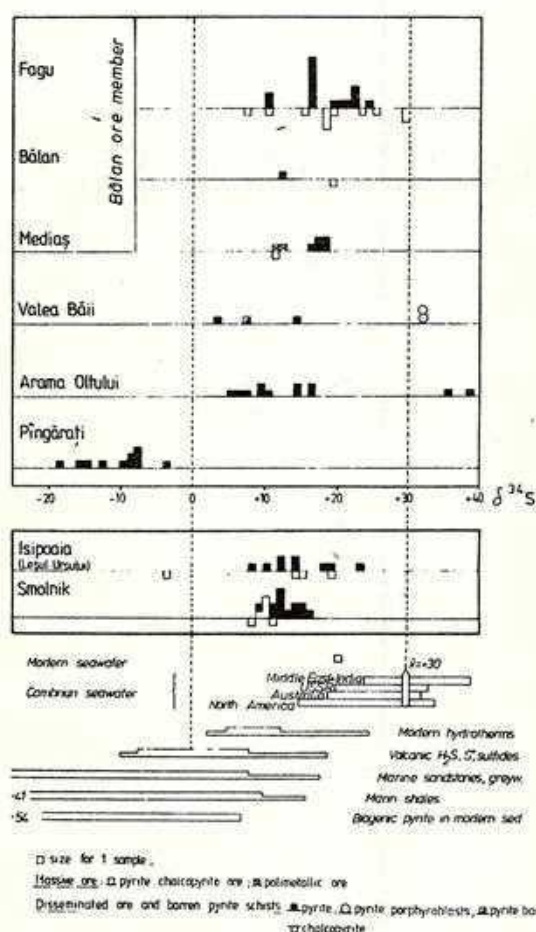


Fig. 4 $\delta^{34}\text{S}$ distribution in ores and pyritic schists at Bălan (Synopsis patterns of natural geochemical systems after Nielsen, 1979; Smolnik after Kantor, Rybar, 1970; Isipoaia-Leșul Ursului after Kräutner, Gaftoi, unpubl. data).

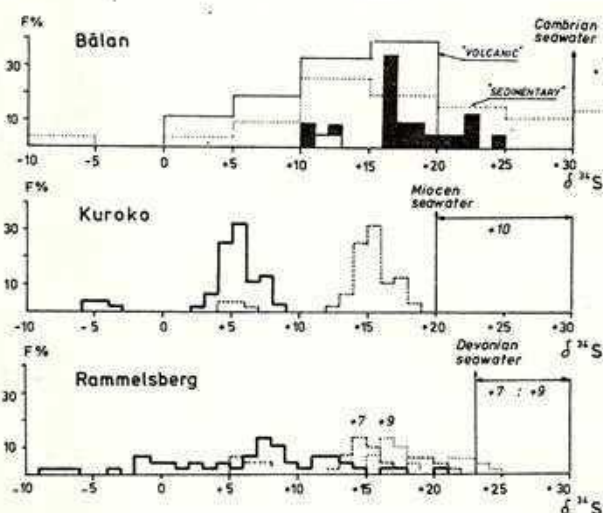


Fig. 5 Comparative histograms for $\delta^{34}\text{S}$ frequency in pyrite from ores at Bălan, Kuroko province and Rammelsberg. Broken lines indicate the $\delta^{34}\text{S}$ values for the Miocene Kuroko deposits and the Devonian Rammelsberg deposit shifted for Precambrian sea water by adding $\Delta = \delta^{34}\text{S}(\text{Cambrian sea water}) - \delta^{34}\text{S}(\text{x sea water})$. Average values used: Δ Miocene sea water = +10‰; Δ Devonian sea water = +7‰ for central Europe and +9‰ on global scale (Kuroko data Sasaki, 1974; Rammelsberg from Anger et al., 1966; sea water from Nielsen, 1979). The "sedimentary" and "volcanic" lines represent the distribution of average $\delta^{34}\text{S}$ values from 110 Phanerozoic volcanic hosted and sediment hosted deposits, equated for Precambrian sea water (data from Sangster, 1976).

fractionation due to inorganic reduction of sulfate at depth (Nielsen, 1979). According to the experimental data of Ohmoto (1976) temperatures of 300-500°C may promote such reactions.

Table 5
Trace elements in chalcopyrite samples from ores of the Bălan deposits

Sample	Ore type	Zn	Pb	Ni	Co	Ag	Sn	Bi	As	In	Ti	Mn
FAFUL CETATII (Sect. south, +440, br.15, lenses 25,26)												
357	A	16000	29000	<10	75	74	380	130	<500	4.5	110	200
381	A	3000	550	<10	<10	31	420	16	<500	3.0	30	86
385	A	3600	155	<10	70	28	185	14	<500	6.0	150	150
393	A	2700	1150	<10	56	80	1200	78	<500	28.0	40	500
380	A	29000	30000	<10	12	95	800	90	<500	7.5	42	125
383	D	1700	60	<10	<10	19	820	<10	<500	34.0	65	60
60(B)	-			22	30	280	190	<10	<300			32
BĂLAN CENTRAL (sect. Ferdinand)												
B-116	B	320	2400	<10	31	75	650	190	<500	57.0	760	23
B-122	B	<100	900	<10	<10	43	520	240	<300	27.0	96	<10
B-123	B	<100	170	<10	<10	48	310	240	<300	19.0	105	12
B-126	B	180	500	<10	12	63	750	900	<500	36.0	110	20
B-113	C	550	220	<10	34	62	750	180	<500	55.0	30	42
B-115	C	730	140	<10	17	53	800	60	<500	46.0	30	60
B-121	E	160	90	<10	28	72	135	130	<500	19.0	58	<10
103(B)				<10		44	1100	10	<300			50
1(B)			3000	<10	120	120	1050	130	<300			175
15(B)			2300	<10	<10	65	360	10	<300			50
47(B)				<10		36	1300	10	<300			300
57(B)			3000	<10	60	160	120	290	<300			28
61(B)				66	400	35	70	350	2000			56
64(B)			360	<10	30	74	100	10	<300			250
66(B)			2500	15	185	115	370	1600	850			1100
19(B)				<10	<10	19	350	10	<300			30
22(B)			280	175	175	85	130	140	600			90
77(B)				200	600	45	30	20	1700			35

Cd <30; Ga <3; Tl <10; Ge <; Mo <10; V <10; Cr <30; Sb <100

Ore types: A Disseminated chalcopyrite in quartz-chlorite schists

B Disseminated chalcopyrite in chlorite schists (partly mobilized)

C Chalcopyrite in veins and lenses of mobilized quartz

D chalcopyrite in veins and lenses of mobilized carbonates

E Massive chalcopyrite mobilized in chlorite schists

77(B) - 1(B) Data according to Botez *et al.* (1971)

As it is shown in figure 5, for the Bălan ores the $\delta^{34}\text{S}$ spread and the average difference with respect to the isotopic ratio of sulfur from Cambrian sea water fit well this sea water convective system model. As it was mentioned the large scattering of $\delta^{34}\text{S}$ in the disseminated ores may reflect local deposition conditions. This could explain also the tendency of values to form more than one statistic collectivity, suggesting a polygenetic evolution of the pyrite sulfur isotopes.

The narrower δ spread in massive ore at lower $\delta^{34}\text{S}$ values as in disseminated ores (Figs. 4, 5, Tabs. 6, 7) seems to be a common features for both Bălan and Smolnik ore deposits, as well as for other stratiform sulfide ore deposits (e.g. Sulitjelma; Tab. 7). Massive ores are probably closer in their isotopic ratio to the primary ore fluids, due to the fact that fast and abundant precipitation of nearly the whole sulfide content of the solution may reduce to a minimum the isotopic

fractionation under the influence of the sedimentation environment. If this holds true, a range of $\delta^{34}\text{S}$ from about +9 ‰ to +13 ‰ can be supposed for the isotopic ratio in the metal and sulfur carrying ore fluids from Bălan and Smolnik.

The enrichment of heavy sulfur in pyrites of disseminated ores (Tab. 7) can be explained neither by closed system deposition conditions (Sangster, 1976) nor by temperature fall and fO_2 increase due to the outflow in the marine environment. In opposition with the first presumption is the geological evolution requiring an open, ventured depositional system for the Bălan ores. The second model would contrarily produce an enrichment of lighter sulfur (Kajiwara, *vide* Sasaki, 1974) in the disseminated ore. A possible explanation may be suggested by Sakai's statement (Sakai, 1968, *vide* Gehrisch *et al.*, 1975) that Fe_2S_3 in isotopic equilibrium with an ore solution will be enriched in $\delta^{34}\text{S}$ with

Table 6
Average values for $\delta^{34}\text{S}$ and trace elements from pyrite and chalcopyrite samples of the ores
and pyritic schists of the Bălan area.

LITHOSTRATIGRAPHIC POSITION ROCK TYPE	SAMPLE	n	$\bar{x} \delta^{34}\text{S} \%$ COT ($\delta^{34}\text{S} \%$ Spread)	n	$\bar{x} \text{Cu}$ ($\delta n-1$)	$\bar{x} \text{Pb}$ ($\delta n-1$)	$\bar{x} \text{Zn}$ ($\delta n-1$)	$\bar{x} \text{Ni}$ ($\delta n-1$)	$\bar{x} \text{Co}$ ($\delta n-1$)	$\bar{x} \text{Ag}$ ($\delta n-1$)	$\bar{x} \text{Sn}$ ($\delta n-1$)	$\bar{x} \text{Bi}$ ($\delta n-1$)	$\bar{x} \text{As}$ ($\delta n-1$)	$\bar{x} \text{Ti}$ ($\delta n-1$)	$\bar{x} \text{Mn}$ ($\delta n-1$)
Bălan M. Disseminated copper ore in chlorite schists: Bălan and Fagu	PYRITE	17	+17.77 (+10.63 +24.3)	42	13 318 (11784)	4152 (6832)	2833 (5836)	71 (56)	429 (222)	26.3 (31)	135 (204)	99 (101)	988 (648)	605 (936)	175 (213)
	CHALCOPYRITE	11	+19.61 (+7.56 +29.95)	25	—	4041 (9074)	4472 (8515)	13 (12)	63 (91)	72.8 (54)	516 (382)	195 (348)	546 (417)	123 (194)	140 (230)
Disseminated ore in chlorite schists: Medias	PYRITE	5 ^x	+17.78 (+16.89 +18.95)	2	11 750 (14495)	10450 (19505)	4050 (2406)	18 (0)	157 (25)	8.5 (9.2)	375 (39)	40 (11)	300 (0)	1157 (837)	695 (572)
	CHALCOPYRITE	1 ^x	+11.76												
Massive polymetallic ore: Medias	ORE	2 ^x	+11.99 (+11.60 +12.39)	1 ^x	22000	20000	5750	18	140	15	65	48	300	565	290
Pyritic ser.-chl. schist Fagu	PYRITE			4	487 (421)	1667 (1918)	405 (468)	241 (276)	282 (118)	2.2 (1.5)	<10	12.5 (2.9)	937 (718)	510 (275)	146 (209)
Valea Băii M. Lower pyritic ser.-chl. schist Bălan	PYRITE	2	+ 887 (+342 +1439)	5	187 (175)	404 (183)	111 (11)	199 (110)	171 (84)	1.6 (0.6)	<10	<10	1060 (403)	1054 (500)	25 (22)
Idem: massive pyrite band	PYRITE	1	+ 754	1	45	250	110	95	90	7	<10	<10	1450	2000	<10
Idem: pyrite porphyroblasts	PYRITE	2	+3257 (+3252 +3263)	3	223 (285)	326 (58)	156 (89)	133 (41)	128 (70)	26 (15)	<10	≈12	866 (508)	1566 (702)	44 (27)
Upper pyritic ser.-chl. schist	PYRITE			5	224 (118)	470 (89)	116 (23)	224 (70)	212 (107)	13 (0.3)	<10	<10	860 (323)	1070 (999)	12 (25)
Arama Oltului M. Pyritic ser.-chl. schist	PYRITE	10	+11.26 (+5.72 +11.69) (+35.77)	22	600 (567)	2454 (4308)	4956 (5919)	246 (79)	311 (162)	4.6 (4)	<10	58 (58)	1346 (989)	830 (269)	34 (23)
Pyritic white sericite schist	PYRITE	1	+3820	1	550	440	3000	110	480	5	<10	<10	<500	150	46
Sîndaminic sequence Pyritic graphite phyllite	PYRITE	11 ^x	-10.31 (-3.18 -18.27)	6 ^x	148 (120)	1031 (1949)	1141 (2479)	139 (125)	181 (96)	1.9 (1.8)	<10	<10	600 (155)	1018 (691)	41 (35)
Pyritic graphite quartzite	PYRITE			3 ^x	1743 (1536)	122 (58)	150 (71)	360 (247)	269 (230)	1.6 (1.3)	<10	<10	533 (58)	1250 (1026)	380 (346)
Pyritic blastodetrital schist	PYRITE			5 ^x	3780 (5938)	2840 (3761)	3960 (5421)	76 (58)	133 (76)	92 (10.3)	55 (87)	66 (82)	560 (134)	580 (385)	607 (805)

^x Data according to: Popa, Șerbănescu (1984), Borcos, Gaffel (1981)

respect to the dissolved species. This fractionation is higher by increasing pH and decreasing temperature (e.g. 2‰–7‰ $\delta^{34}\text{S}$ in neutral and alkaline conditions at 250°C) and fits the order of values from Table 7. Therefore the enrichment of $\delta^{34}\text{S}$ in the disseminated ores from Bălan ($\bar{x}\delta^{34}\text{S}_{\text{py}}=17.77$) could be explained by a preferentially $\delta^{34}\text{S}$ bound in lately and/or slowly precipitating Fe_2S (isotopic fractionation by precipitation). Surely addition of heavy sulfur from sea water or coincidence with δ variation in ore solutions cannot be excluded as alternative or supplementary explanation.

The problem of isotopic equilibrium

Between the two main sulfide phases of the ores from Bălan (pyrite and chalcopyrite) there is no isotopic equilibrium (Fig. 6). Both pyrite and chalcopyrite show a large $\delta^{34}\text{S}$ spread (Fig. 4) which could be partly inherited from the premetamorphic sulfide deposit. The $\delta^{34}\text{S}$ scattering in pyrite results mainly from trends of $\delta^{34}\text{S}$ increase and decrease during the

deposition of the ore bodies (Pl. 1). On the contrary $\delta^{34}\text{S}$ of chalcopyrite shows no such regular trends and spread in domains of both higher and lower δ values as pyrite. This peculiar character of S isotope ratios in chalcopyrite is shown in Figure 6 by the plotting of the pyrite-chalcopyrite pairs on either side, externally to the equilibrium domain in hydrothermal systems in the range of 100–450°C. This suggests two types of chalcopyrite in the ore, both lacking in isotopic equilibrium with the ore pyrite. Due to the fact that during metamorphism chalcopyrite is more mobile than pyrite, the mentioned lack of isotopic equilibrium might be explained, at least partly by metamorphic isotopic fractionation.

Metamorphic isotopic fractionation

Metamorphic isotopic fractionation may be recognized in chalcopyrite and pyrite phases due to both metamorphic mobilization and local (in situ) growth. As reactions go faster with the lighter S isotope (^{32}S) it

Table 7
 $\delta^{34}\text{S}$ average for pyrite from massive ore and disseminated ore

	$\delta^{34}\text{S}$ (pyrite) ‰ massive ore	$\delta^{34}\text{S}$ (pyrite) ‰ disseminated ore	$\Delta\delta$
Bălan	+11.99 (n=2)	+17.77 (n=17)	5.78
Smolnik (Kantor, Rybar, 1970)	+10.1 (n=4)	+10.10 (n=4)	3.20
Sulitjelma (Gerisch <i>et al.</i> , 1975)	+3.2	+7.14	3.94

$$\Delta\delta = \delta^{34}\text{S} (\text{disseminated ore pyrite}) - \delta^{34}\text{S} (\text{massive ore pyrite})$$

Table 8
 Comparative average values for $\delta^{34}\text{S}$ and trace elements in common sulphides and in sulphides migrated (mobilised) during the regional metamorphism of the Bălan areas.

	$\delta^{34}\text{S}$ ‰	Ni	Co	Ag	Sn	Bi	As	In	Ti	Mn
CHALCOPYRITE (Bălan)										
Mobilized:										
In quartz veins or lenses (B-113; B-115)		<10	25	57	775	120	<500	50	30	51
In ankerite veins or lenses	+15.73	<10	10	19	820	<10	<500	34	65	60
Common ore:										
Migrated on schistosity in chlorite schists (380; 393)	+9.04	<10	34	87.5	1000	84	<500	17.5	41	312
Recrystallized in chlorite schists (357; 377; 381; 385)	+9.04 (+22.7*)	<10	52	43	328	53	<500	4.5	97	145
PYRITE (Valea Băii Member)										
Large porphyroblasts (B-154A; B-156A; B-158B)	+32.5	133	128	3.5	<10	13	867		1567	44
Common pyrite in the same samples (B-154; B-156; B-157; B-158; B-158A)	+8.4	205	162	2.8	<10	<10	1250		1264	25

* Including data of Popa, Șerbănescu (1984) and Borcoș, Gaftoi (1981).

All values are in ppm.

may be theoretically presumed that the sulfides formed from sulfur migrated in fluids during metamorphism are enriched in ^{32}S and consequently ^{34}S increases relatively in "remanent" sulfides.

Chalcopyrite. The mentioned statement holds true for the mobilised chalcopyrite sample (380) from the Fagu ore ($\delta^{34}\text{S}=+7.56$ ‰). Therefore it may be suggested that the group of low $\delta^{34}\text{S}$ chalcopyrite ($\delta^{34}\text{S}=+7.56$ ‰ to $+15.75$ ‰) represent metamorphic mobilisates, while the high $\delta^{34}\text{S}$ chalcopyrites ($\delta^{34}\text{S}=+18.31$ ‰ to $+29.35$ ‰) are recrystallized remanent sulfide phases (only "mechanically" migrated on schistosity planes). The trace element content in chalcopyrite only poorly suggests some geochemical differentiation by such metamorphic mobilisations. The most evident correlation with the mentioned sulfur isotope fractionation is shown by a Sn increase in low $\delta^{34}\text{S}$ chalcopyrite (Fig. 7). The Sn content in

these "mobilised" chalcopyrite exceeds by more than 10 times the possible amount of isomorphic substitution (Tabs. 8, 9). It seems therefore that Sn migrates together with Cu in metamorphic fluids and form Sn mineral inclusions in the mobilised chalcopyrite. A similar trend is suggested for In, not related to concomitant Zn increase. On the contrary, the Co, Mn, Ti contents decrease in this mobilised chalcopyrite, due to the depletion of some mineral inclusions (e.g. the Co content reaches values below the limit of isomorphic substitution).

Pyrite. In the Valea Băii Member a remarkable $\delta^{34}\text{S}$ difference of about 24 ‰ appears between disseminated pyrite ($\phi = 0.3-1.0$ mm) and large pyrite crystals ($\phi = 5-15$ mm) formed by blastic growth in the same rock volume of about 0.5 m^3 (Tabs. 6, 8). It is assumed that the mentioned large crystals consumed remanent sulfur of small rock volume, depleted of the

more mobile ^{32}S by the generation of metamorphic fluid phases migrated towards sulfur deficient parts. The $\delta^{34}\text{S}$ spread between these "remanent" porphyroblastic pyrites and the "remanent" chalcopyrite of the Bălan ore is narrow ($\delta^{34}\text{S}_{\text{py}} - \delta^{34}\text{S}_{\text{cpy}} = +3.2$ to $+7.3$) but it does not plot in the domain of isotopic equilibria (Fig. 6). This implies again isotopic fractionation due to the kinetic reactions by which sulfur is included in metamorphic fluids. Trace element differentiation between the mentioned pyrite types is not obvious (Tab. 8).

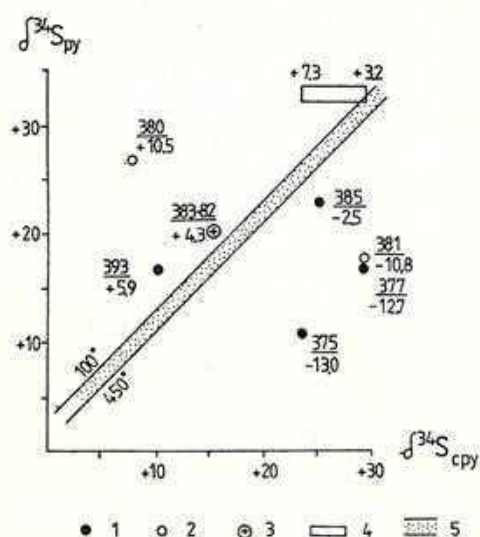


Fig. 6 - $\delta^{34}\text{S}$ ratio in pyrite + chalcopyrite pairs from the Bălan ores.

1, pyrite + chalcopyrite pairs; 2, interpolated pairs; 3, interpolated mobilised (vein) chalcopyrite-rock pyrite; 4, interpolated "remanent" chalcopyrite and "remanent" pyrite; 5, domain of isotopic equilibrium in the temperature range 100° – 450° C (acc. to data from Nielsen, 1979); values are sample numbers and differences between $\delta^{34}\text{S}$ values of pyrite-chalcopyrite pairs ($\Delta^{34}\text{S}_{\text{py}} - \delta^{34}\text{S}_{\text{cpy}}$).

Trace element content

The trace element content in the disseminated ore (whole rock), as well as in pyrite, chalcopyrite, magnetite and chlorite (monomineral samples) from the same ores are shown in Table 9. There is a clear tendency of selective concentration (marked in Table 9) for Ni, Co, As in pyrite, for Ag, Sn in chalcopyrite, for Cr, Ga in chlorite, for V in magnetite and for Bi, Mo, Ti, Mn in independent minerals (native bismuth, molybdenite, rutile, carbonate). Generally, it is worth noting the relatively constant Ni:Co ratio between 0.1 – 0.4 for all the main mineralogical constituents of the copper ores (pyrite, chalcopyrite, chlorite, magnetite) as well as for the respective whole ores (Tab. 10).

This reflects a strong and persistent Co predominance in the Bălan ore member, contrasting to the tendency of higher Ni content in the pyrite of pyritic schists from other lithostratigraphic levels.

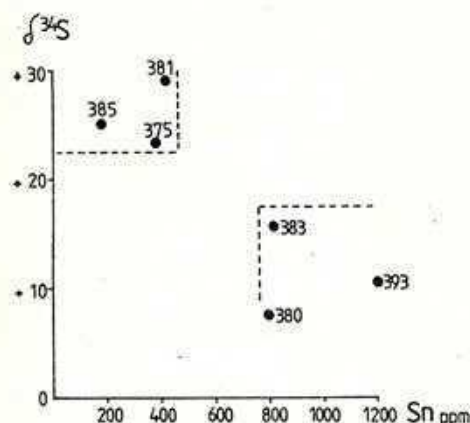


Fig. 7 - $\delta^{34}\text{S}$:Sn correlation in chalcopyrite (values are sample number)

The ore pyrite

The distribution of the main trace elements is represented by histograms in Figures 8, 9, 10, 11.

Ni and Co show an obvious concordance with the general distribution pattern in syngenetic (stratiform) sulfide ores according to Cambel, Jarkovsky (1967) (Fig. 8). The Ni and Co contents probably do not exceed the limit of isomorphic substitution. It is worth noting that pyrites with low Co content (<100 ppm) are lacking. This reflects the relatively high Co content all over the ore province; Co:Ni ratios > 1 have been mentioned also for the other main ore deposits of the province, both in pyrite and whole ores (Fundul Moldovei, Kräutner et al., 1973; 1974, unpubl. report; Leșul Ursului, Kräutner et al., 1976, 1978, unpubl. report; Baia Borșa, Zincenco et al., 1973; Smolnik, Cambel, Jarkovsky, 1967). This regional geochemical peculiarity may be due to the primary character of the source.

The Ni:Co ratios in pyrite from ores and different pyritic schists are represented in Figure 12. The ore pyrites scatter around the Ni:Co = 0.1 line while those from pyritic schists plot near the Ni:Co = 1 ratio. The pyrite from disseminated ores spreads near the Ni:Co clark intervals for pyrites from stratiform and hydrothermal sulfide ores, with some tendencies towards higher Co and Ni contents. Thus the ore pyrite from Bălan resembles with respect to Ni:Co contents the Co-rich pyrites from Rio Tinto (10:480), Zlaté Hory (76:458) in Czechoslovakia, some Scandinavian ores as Oblarn (29:410), Rörös (12:600) or Falun (20:600) or

Table 9
Average of trace elements in disseminated ores and pyrite, chalcopryrite, magnetite
chlorite samples from the Bălan ore deposit

	Disseminated ore (n=98)	Pyrite (n=42)	Chalcopryrite (n=22)	Magnetite (n=5)	Chlorite (n=6)
Ni	26,8 (10-70)	<u>71</u> (10-50) (<3-280)	13 (<10-200)	16,2 (13-20)	17 (16-22)
Co	113 (8-1300)	<u>429</u> (10-500) (100-1600)	97 (<10-400)	37 (27-56)	108 (55-170)
Ag	4,9 (<1-14)	26,3 (0-10) (<1-135)	65,9 (19-160)	—	—
Sn	36 (<10-140)	135 (<10-750)	539 (30-1300)	12 (10-22)	101 (22-300)
Bi	<u>210</u> (<10->1000)	99 (<10-500)	199 (<10-1600)	—	17,3 (10-48)
As	—	<u>988</u> (<500-2600)	536 (<300-3000)	—	—
Sb	—	<10	<10	—	—
Ti	<u>2409</u> (600->10000)	605 (10-50) (100-4200)	129 (13) (?)	464 (290-620)	—
Mn	<u>865</u> (30-2700)	175 (0,10-50) (14-670)	156 (<10-1100)	102 (52-200)	—
Mo	2,5 (2-3)	<10 (0,10-50)	<10	—	—
V	47 (<30-100)	<10 (0,10-50)	<10	131 (100-180)	42 (25-50)
Cr	26 (5-46)	<30	<30	45 (30-80)	75 (46-90)
Ga	155 (5-27)	<3	<3	3,6 (3-6)	<u>30,3</u> (16-46)
In	—	<10	<10	—	—
Ge	—	<10	<10	—	—
Tl	—	<10	<10	—	—
Cd	—	<10	<30	—	—

Expl.:

 — 65,9 — 55 — clark
 (19-160) 30 — supposed limit for isomorph substitution
 spread

Canadian ores as for example Noranda (93:600) (data according to Cambel, Jarkovsky, 1967; Mercer, 1976). Pyrite from pyritic schists shows Ni values above the mentioned clark domain and lower Co content, excepting the Arama Oltului pyrites placed around the Co clark interval. Pyrite from schists not related to the sulfide bearing horizons scatters in a relatively large

area around Ni:Co=1 and differs from the ore pyrites especially by the low Co content.

In massive ores most of the pyrites plot at lower Ni content compared to pyrites from disseminated ores (Fig. 12). The statistics distribution of the Ni:Co ratio in pyrites of these two ore types is shown in Figure 13. Thus a tendency of preferential Co concentrations in

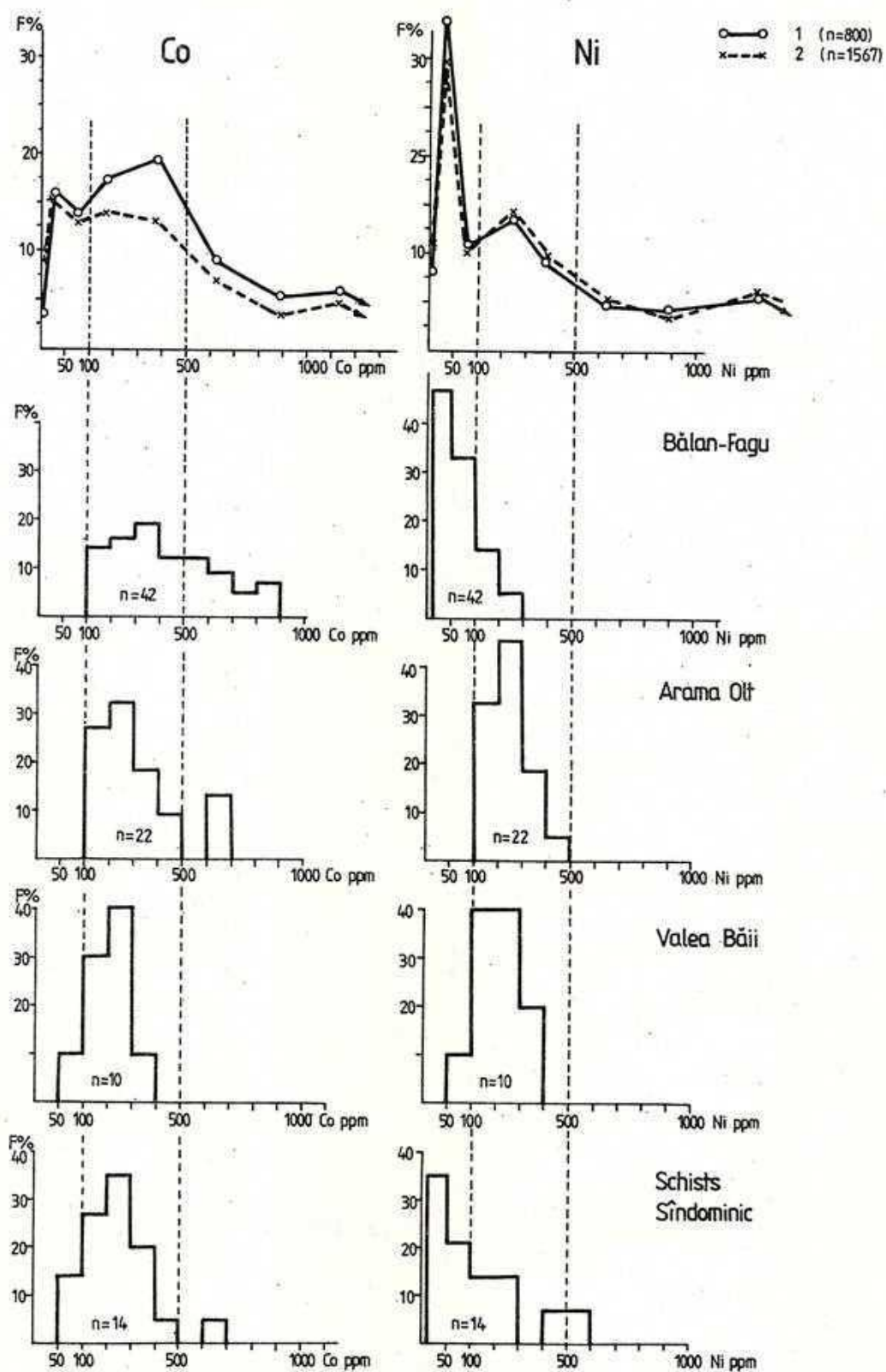


Fig. 8 - Ni and Co in pyrite: histograms for ores and pyritic schists from Bălan and comparative frequency curves according to Cambel, Jarkovsky (1967).
1, "syngenetic" pyrites; 2, "syngenetic" + hydrothermal pyrites.

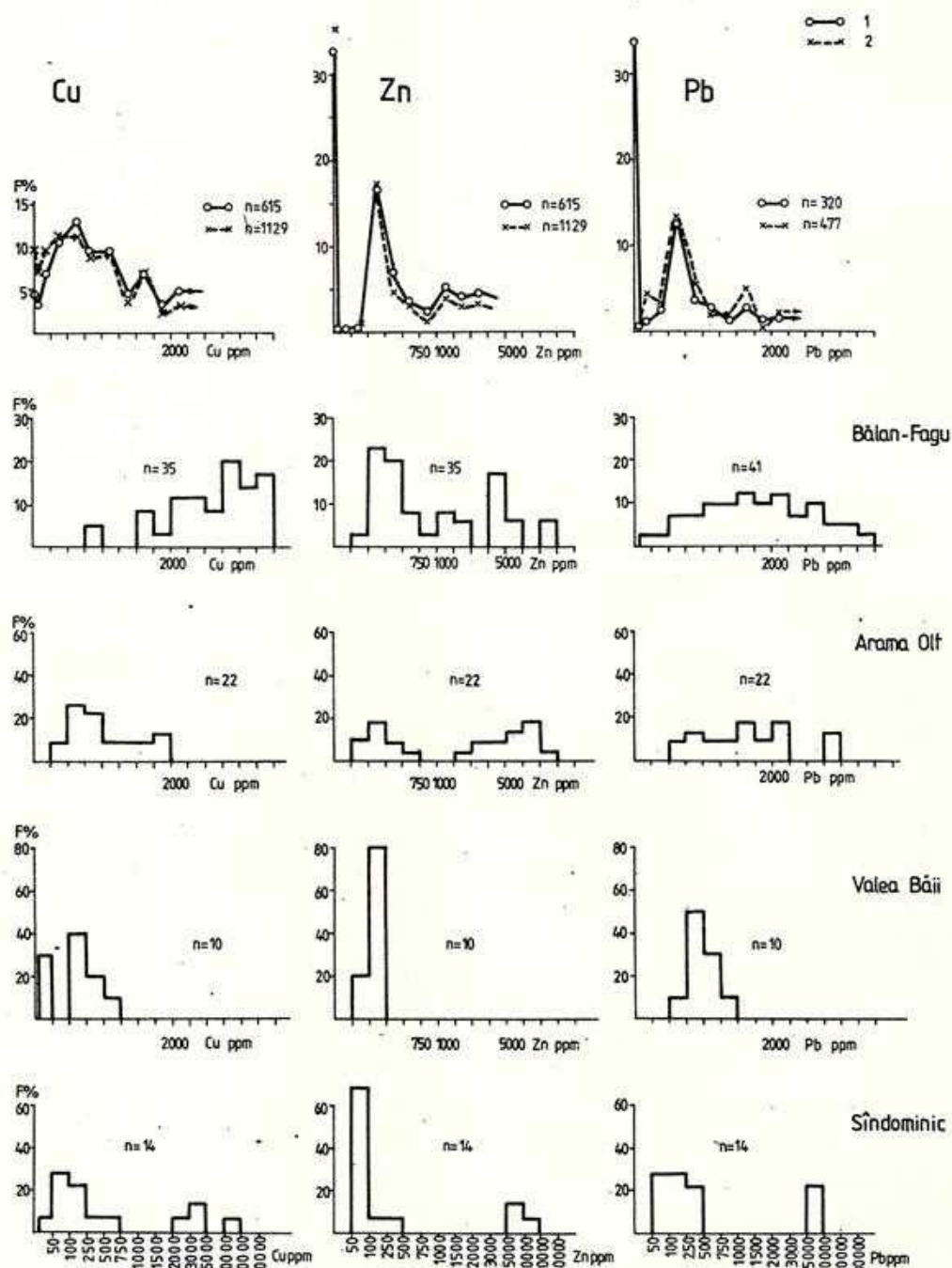


Fig. 9 - Cu, Zn and Pb in pyrite: histograms for ores and pyritic schists from Bălan and comparative frequency curves according to Cambel, Jarkovsky (1967).
1, "syngenetic" pyrites; 2, "syngenetic" + hydrothermal pyrites.

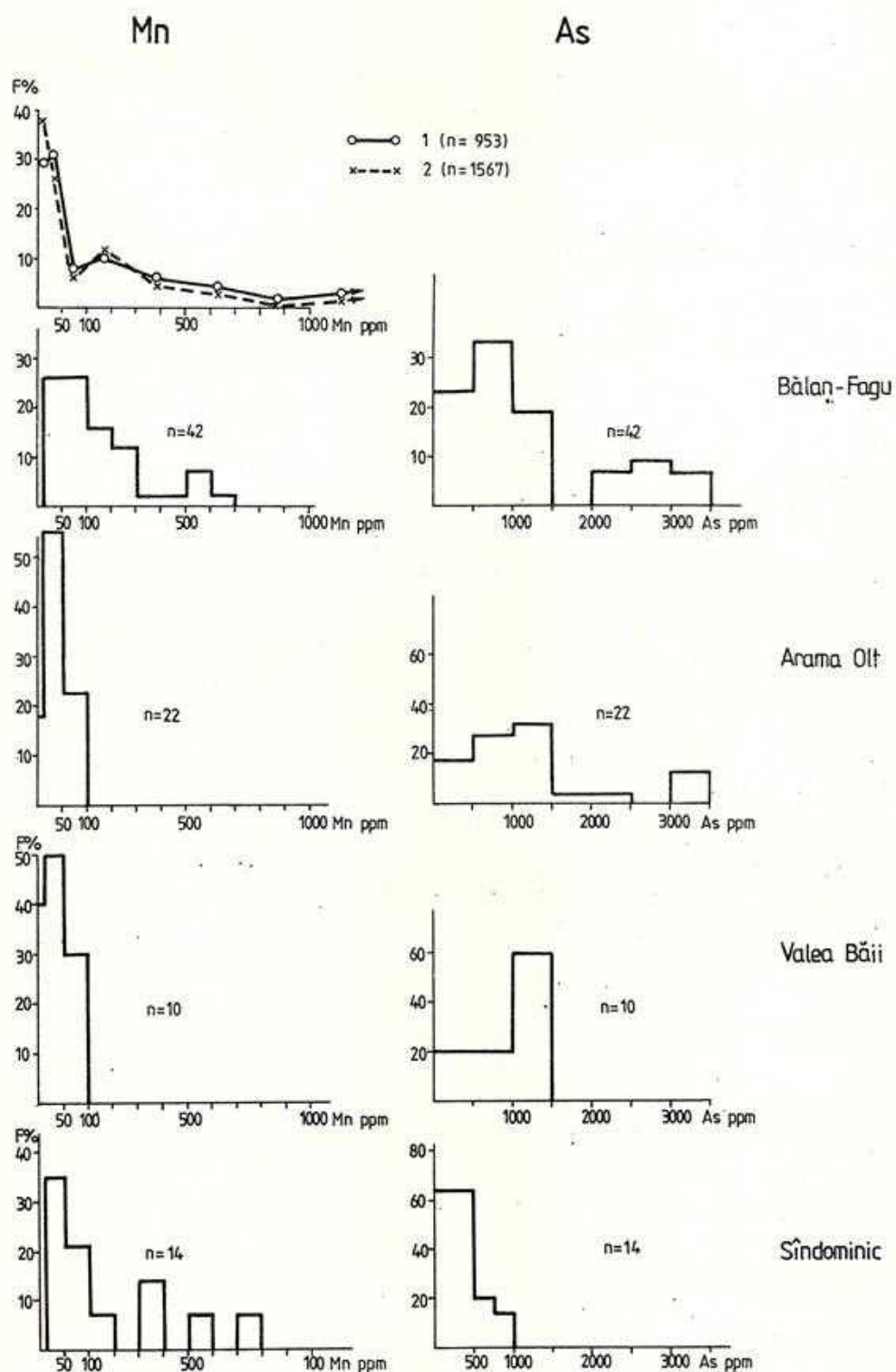


Fig. 10 - Mn and As in pyrite: histograms for ores and pyritic schists from Bălan and comparative frequency curves according to Cambel, Jarkovsky (1967).
1, "syngenetic" pyrites; 2, "syngenetic" + hydrothermal pyrites.

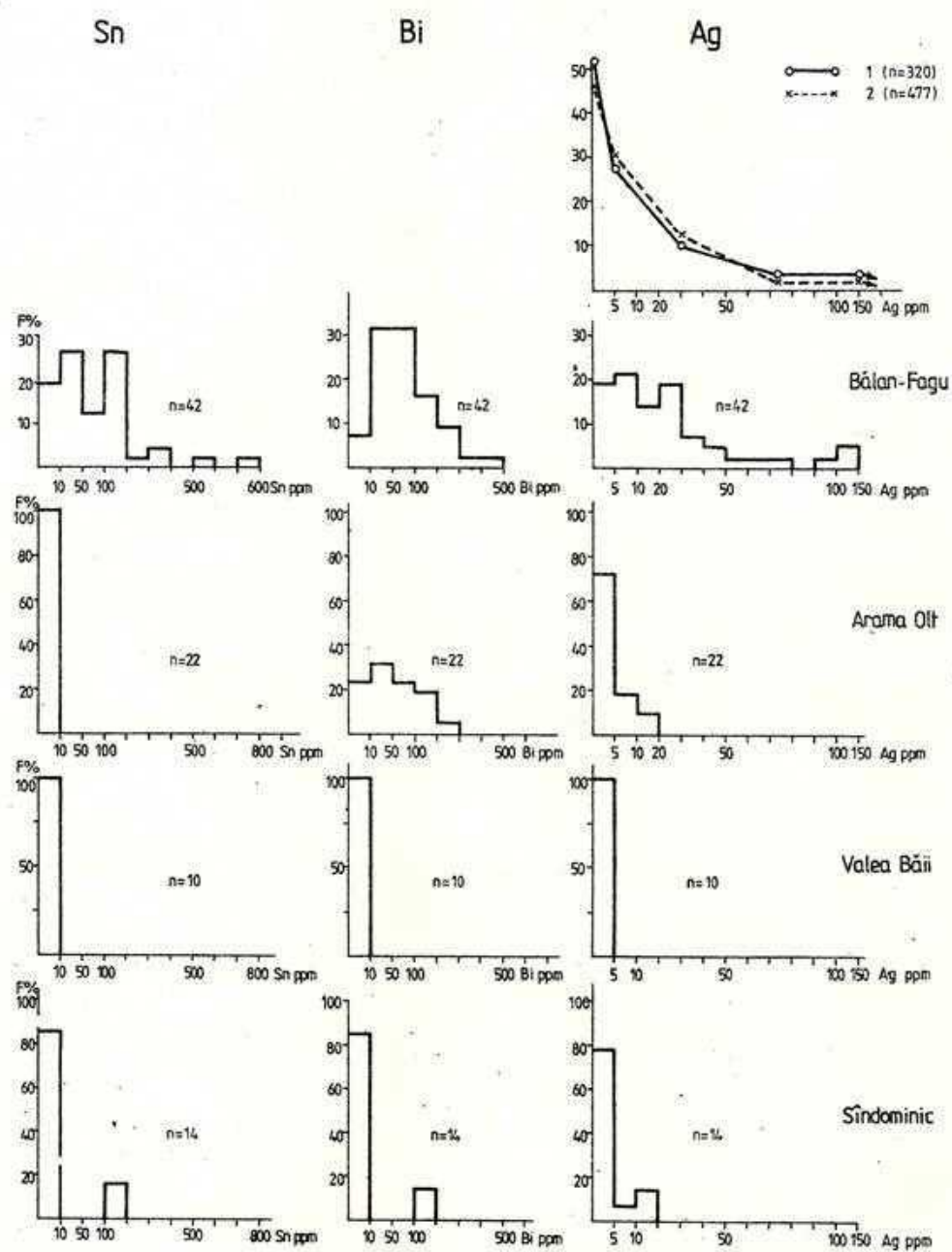


Fig. 11 - Sn, Bi and Ag in pyrites: histograms for ores and pyritic schists from Bălan and comparative frequency curves according to Cambel, Jarkovsky (1967).

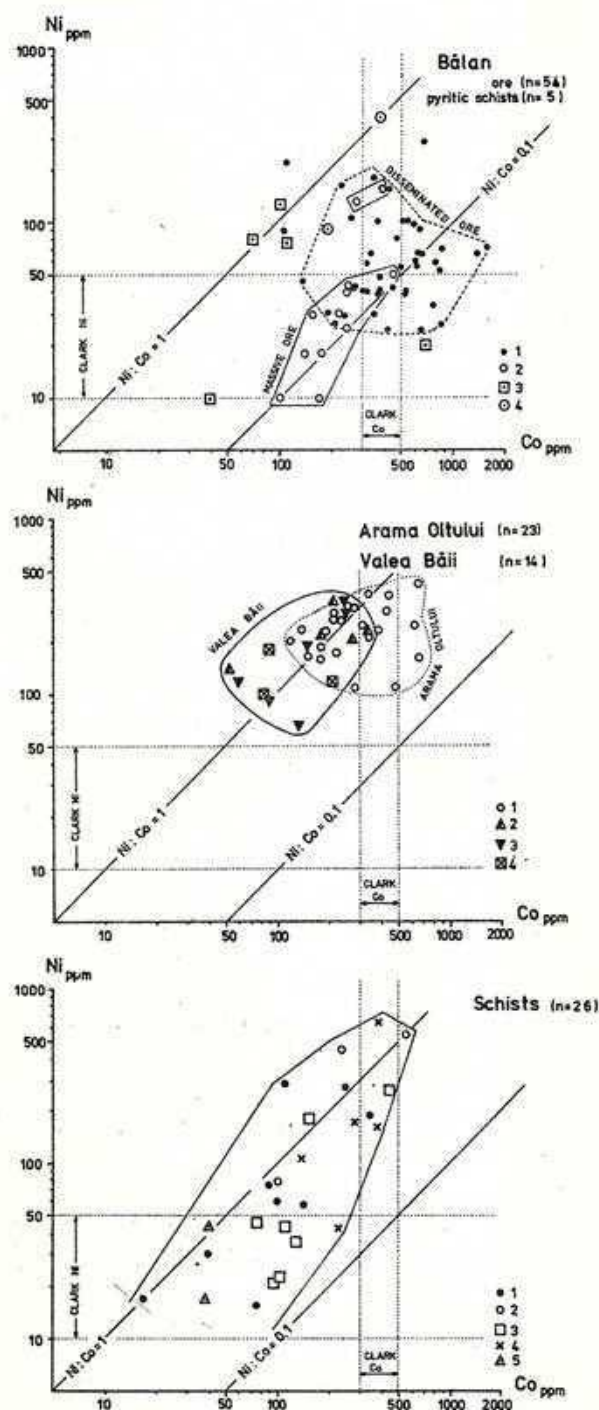


Fig. 12 - Ni : Co ratio in pyrite of ores and pyritic schists from Bălan (Clark values according to Cambel, Jarkovsky, 1967). Bălan: 1, disseminated ore; 2, massive ore; 3, pyritic sericite-chlorite schists near the ore; 4, large pyrite porphyroblasts in pyritic ore; Arama Oltului and Valea Băii: 1, Arama Oltului pyritic sericite-chlorite schists; 2, upper (Salamas) and 3, lower pyritic sericite-chlorite schists of the Valea Băii Member; 4, large pyrite porphyroblasts in the lower Valea Băii pyritic schists; Schists with pyrite crystals (outside the sulfide bearing horizons): 1, sericite-graphite schists and phyllites; 2, graphite quartzites (metalyditic rocks); 3, blastodetrital rocks; 4, sericite-chlorite schists; 5, white sericite-quartz±feldspar schists (metaepiclastic rocks).

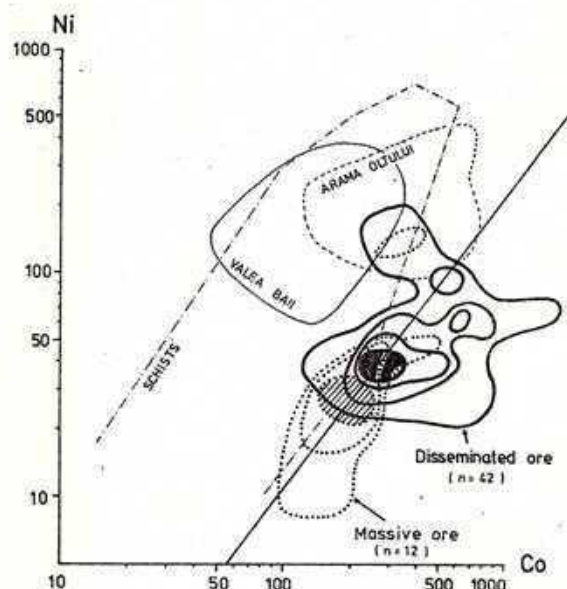


Fig. 13 - Ni : Co ratio of pyrite from disseminated and massive Bălan ores comparatively to pyrite from the Arama Oltului and Valea Băii pyritic schists. (Isolines: disseminated ore: 15 %; 7 %; 5 %; 2 %; massive ore = 33 %; 15 %; 8 %).

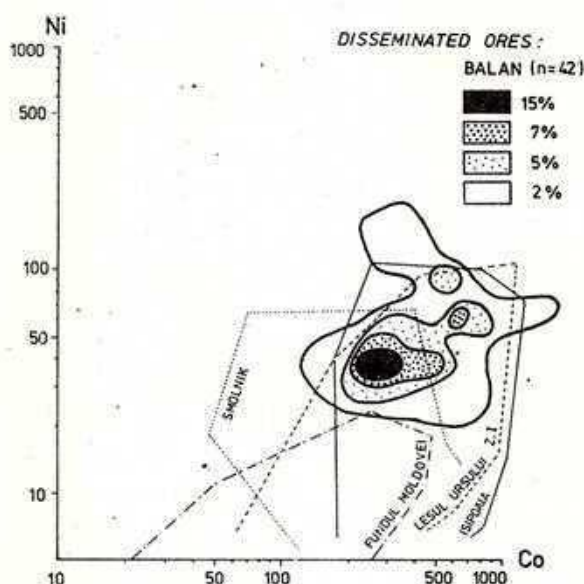


Fig. 14 - Ni : Co ratio of pyrite from disseminated ores from Bălan and similar ores from other main deposits of the same metallogenic province (data used: Fundul Moldovei, Kräutner et al., 1973, 1974; Leșul Ursului, Kräutner et al., 1976, 1978; Smolnik, Cambel, Jarkovsky, 1967).

chlorite rich ores is suggested. A similar trend was mentioned by Zencenco et al. (1973) for the chlorite

copper ores from Baia Borşa. This conclusion may be supported also by the relatively high Co content in the chlorite of the Bălan ore (Tab. 9).

Figure 14 shows the statistic distribution of the Ni:Co ratio in pyrite of disseminated copper ores from Bălan compared with other similar ores of the same metallogenetic province. The low Ni content in pyrites from the Fundul Moldovei sulfide horizon may be related to its higher lithostratigraphic position (Kräutner, 1984). Thus a change in time of the Ni:Co ratio in the source may be suspected. At Bălan a lithostratigraphic control of the Ni:Co ratio in different sulfide bearing horizons is evident (Fig. 13). A similar conclusion resulted also from the isotopic composition of the pyrite sulfur (Fig. 3). At present there is no proof of these facts being really due only to the mentioned lithostratigraphic control or whether they point in fact to differences between ore deposits and barren pyritic schists. In favour of the last hypothesis is a general trend of concomitant Co and Cu increase including pyrites from Valea Băii and Arama Oltului pyritic schists as well as from Bălan ores (Fig. 15). This suggests a Co-Cu correlation irrespective of the lithostratigraphic position. Therefore it seems that the mentioned lithostratigraphic control delimits sulfide horizons with different Cu concentration and only the latter controls Co distribution, both below and over the clark values (Fig. 15). It is worth noting that pyrite crystals from different schists external to the mentioned sulfide levels, as graphite phyllites, graphite quartzites, quartz sericite-chlorite schists (excepting the two blastodetrital schists, Table 4) plot along the same trend (Fig. 15).

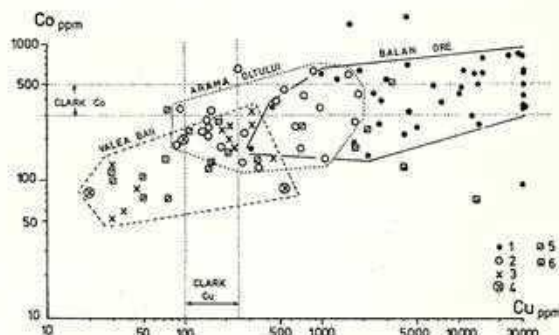


Fig. 15 Co-Cu correlation in pyrite from ores and schists. 1, Bălan ore; 2, Arama Oltului pyritic schists; 3, Valea Băii pyritic schists; 4, the same, large pyrite porphyroblasts; 5, sericite graphite phyllites, graphite quartzites, quartz sericite-chlorite schists; 6, blastodetrital schists.

Comparatively to Ni:Co ratios in pyrite from sulfide ore deposits of different genetic types and geological environments (Bajwah et al., 1987) the pyrite from

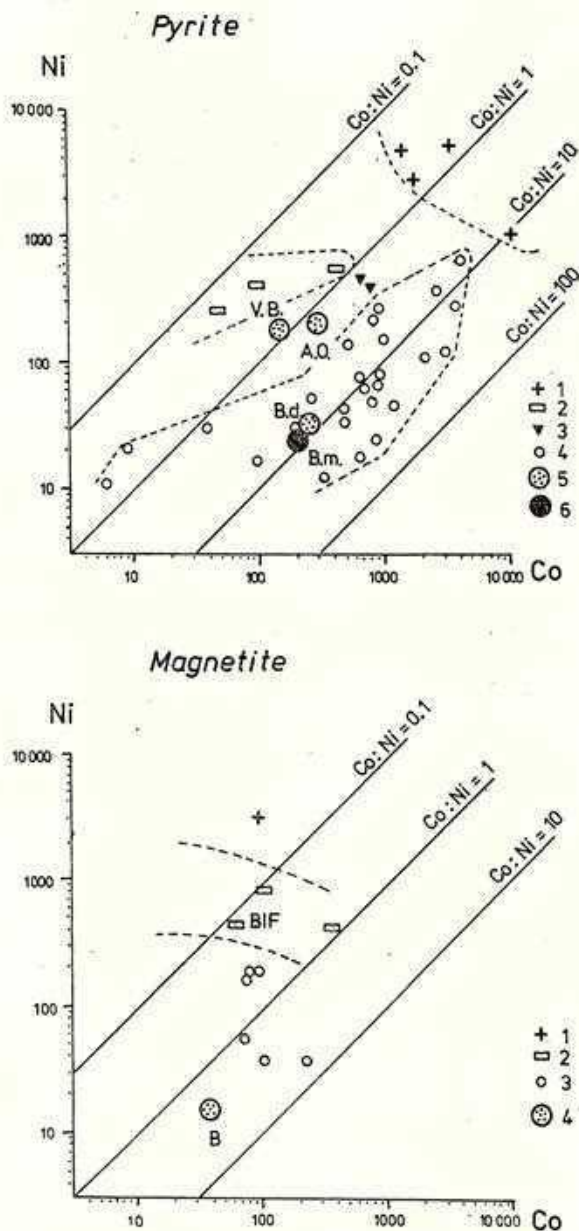


Fig. 16 - Ni : Co distribution in pyrite and magnetite from Bălan comparatively to ore deposits of different genetic type and geological environments. Average values. (redrawn from Bajwah et al., 1987).

Pyrite: 1, magmatic deposits; 2, sedimentary deposits; 3, skarn deposits; 4, submarine hydrothermal-sedimentary deposits; 5, disseminated ores and pyritic schists (Bălan); 6, massive ore (Bălan); V. B., Valea Băii; A. O., Arama Oltului; B. d., Bălan disseminated ore; B. m., Bălan massive ore. *Magnetite*: 1, magmatic deposits; 2, sedimentary deposits; 3, submarine hydrothermal-sedimentary deposits; 4, disseminated magnetite; B, Bălan; BIF, Banded Iron Formation.

Bălan ores is placed between the submarine (exhalative) hydrothermal-sedimentary deposits (Fig. 16), in concordance with the accepted genetic model (Kräutner, 1966, 1984, 1988). The pyrite of the Arama Oltului and Valea Băii pyritic schists plots between the sedimentary and hydrothermal-sedimentary ores (Fig. 16). This fits well with their geological environment from which a metal charge dispersed by submarine transport or intraformational resedimentation may be supposed. The Ni:Co ratio in magnetite from the ore chlorite schists plots again near the submarine (exhalative) hydrothermal-sedimentary deposits selected by Bajwah et al. (1987) (Fig. 16).

Cu, Zn, Pb are systematically highly concentrated in ore pyrites, exceeding isomorphic substitution and clark values. The nonconcordance with Cambel and Jarkovsky's (1967) frequency curves (Fig. 9) is due to chalcopryite, sphalerite and galena inclusions sometimes seen under the microscope. These mineral inclusions are not separable by current technics. They either have been included by the blastic growths of the pyrite crystals or were infiltrated through fissures by metamorphic mobilisation. Pyrite from schists not related to ores, as for example from the Valea Băii member or from the Sindomic sequence (Fig. 9) systematically has lower Cu, Pb, Zn content (in approximate clark values) than the ore pyrites.

Mn shows a distribution similarly to the general pattern for "syngenetic" ore pyrites according to Cambel, Jarkovsky (1967) (Fig. 10). It does not exceed the isomorphic substitution in pyrite.

As has a tendency to bimodal distribution, suggesting two pyrite types in the ores (Fig. 10). Pyrites rich in As occur either locally or systematically in ores enriched in Pb and Zn, as for example in the upper part of lens 26 (Pl. I).

Sn, Bi, Ag (Fig. 11). As no isomorphic substitution in the pyrite lattice is possible, these elements are due to microscopic and submicroscopic inclusion of other mineral phases. This is proved for Ag by its positive correlation with the Pb content (Fig. 17) suggesting a Pb sulfide as mineral support. The general behaviour corresponds to Cambel's (1967) frequency curve for ore pyrites (Fig. 11). Sn increases with Cu (Fig. 18) and is probably related to chalcopryite inclusions. Its concentration in ore pyrites is definitely higher than in pyritic schists (Fig. 11). Bi shows no evident correlation with other trace elements, it forms independent mineral inclusions, as for example native Bi, noticeable at microscopic scale.

Chalcopryite

Excepting the low Ni content, the main trace elements are above the clark values and the limit of isomorphic substitution suggested by Cambel et al. (1977) (Tab. 9). Thus in the analysed samples most

of the trace elements are due to heterogeneous mineral inclusions. Such inclusions are partly visible under the microscope (e.g. native Bi, sphalerite, etc.), but they lie below separation technics. The mentioned mineral inclusions resulted from metamorphic growth, recrystallisation or mobilisation and are not products of immiscibility segregation.

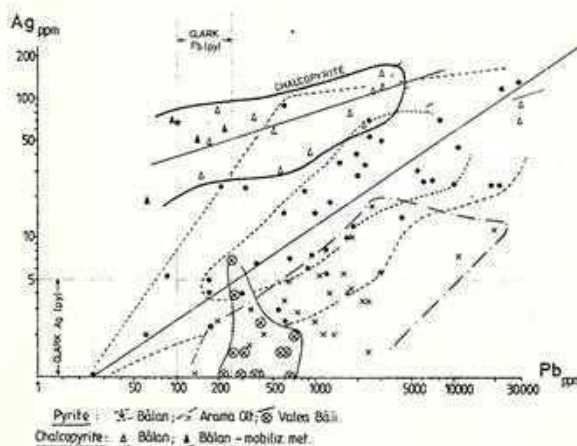


Fig. 17 Ag-Pb correlation in pyrite and chalcopryite.

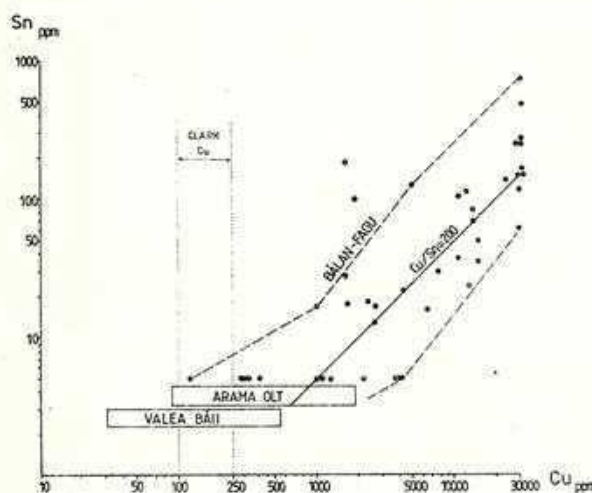


Fig. 18 - Sn-Cu correlation in pyrite.

Co and Ni follow the general distribution pattern in chalcopryite as it is inferred from data collected by Cambel et al. (1977) (Fig. 19).

Bi displays a bimodal distribution in concordance with the two frequency peaks marked on the general curve in Figure 19. This means that in the analysed samples there is a population with Bi-bearing inclusions and another population lacking in such inclusions. The relatively high frequency of chalcopryite

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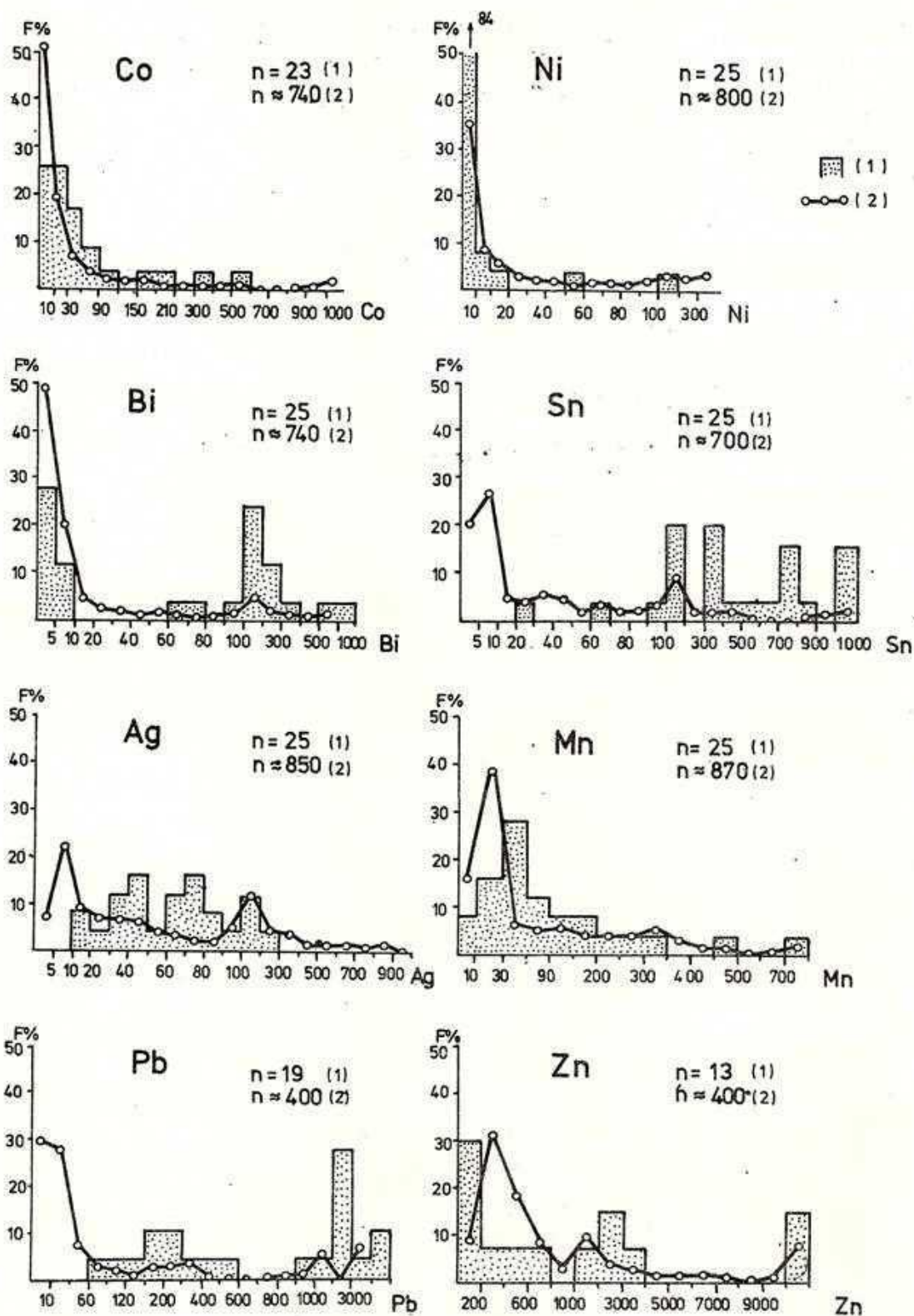


Fig. 19 - Co, Ni, Bi, Sn, Ag, Mn, Pb, Zn in chalcopyrite: histograms and comparative frequency curves according to Cambel et al. (1977).
1, chalcopyrite from Bălan; 2, chalcopyrite from different deposits according to Cambel, Rose, Bunham et al. (vide Cambel et al., 1977).

with Bi inclusion (Fig. 19) is a peculiarity of the Bălan ores. Bi in chalcopyrite shows no correlation with the Pb content (Fig. 20). This pattern is in concordance with microscopic data indicating native-Bi, contrary to other deposits of the same province in which galenobismuthite is mentioned.

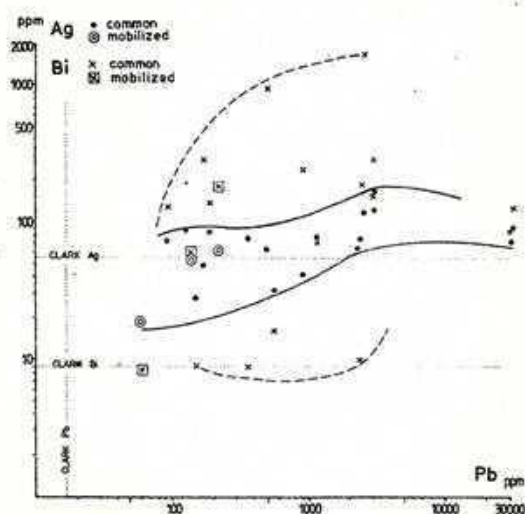


Fig. 20 - Ag : Pb and Bi : Pb correlation in chalcopyrite.

Sn displays a different distribution with respect to the general frequency curve for chalcopyrite (Fig. 19). The most frequent low Sn chalcopyrites are lacking at Bălan. Relatively high Sn content in chalcopyrites seems to be another geochemical peculiarity of the Bălan ores. There is a tendency of bimodal distribution in the ranges of 100–400 ppm and 700–1000 ppm which is also marked by the sulfur isotopes (Fig. 7). The two mentioned populations are suspected to represent mobilized and "remanent" chalcopyrites.

Ag shows also a different distribution compared to the general frequency curve for chalcopyrite (Fig. 19). This is probably due to galena inclusions in the analysed samples as it is suggested by the Ag-Pb correlation represented in Fig. 20.

Mn trend to a normal distribution pattern in chalcopyrite (Fig. 19). The position of the maximal frequency at Bălan in a neighbouring class may be due to the relatively low number of data for statistic aims.

Pb is systematically above the clark content in chalcopyrite (Fig. 19). This is due to the mentioned galena inclusions. Chalcopyrite mobilized in quartz and carbonate veins has relatively low Pb content being the most depleted in mineral inclusions. This might be a means to explain, at least partly, the tendency of bimodal distribution shown in Figure 19.

Zn has also a tendency to bimodal distribution; "normal" low contents contrast with high Zn content

due to sphalerite inclusion (Fig. 19).

Magnetite

In the ore deposits from Bălan magnetite occurs mostly as idiomorphic crystals disseminated in the same quartz-chlorite schists as the ores, but only on local levels depleted of sulfides. It is presumed that these levels correspond to periods of temporary Eh (fO_2) increase during the ore deposition due to ventured oxygenated ocean water. The trace element content of these magnetite crystals is indicated in Tables 11 and 12 by comparison with the average values for magnetite from other schists of the Tulgheș Group as meta-jaspilites, sericite-chlorite schists and greenschists (basic metavolcanics).

Compared to magnetite from the other mentioned environments, the ore magnetite from Bălan has systematically higher Cu, Sn, Mg and Al contents. This proves both the affiliation to the copper ore sequence and to the peculiar chlorite-quartz rock assemblage of this sequence, rich in Mg and Al. Noteworthy is also the Ni:Co ratio specifically lower than 1 in all ore components (Tab. 10), contrary to the Ni prevalence in magnetite from all the other mentioned environments (Tab. 11). On the Ni:Co diagram of Bajwah et al. (1987) the magnetite from Bălan plots between ("exhalative") hydrothermal sedimentary deposits (Fig. 16).

Table 10

Co: Ni ratio in the whole rock and in the main mineralogical components of the disseminated pyritic copper ore from Bălan

	Co: Ni	Ni: Co
Whole ore (n=98)	113:26.8=4.2	0.24
Chalcopyrite (n=25)	63:13=4.8	0.21
Pyrite (n=42)	429:71=6.0	0.17
Chlorite (n=6)	108:17=6.3	0.16
Magnetite (n=5)	37:16.2=2.3	0.44

The ore magnetite from Bălan differs from the magnetite of basic metavolcanics by its lower content in all siderophile elements: Ni, Co, Cr, V, Ti. Compared with the iron metajaspilites the ore magnetite from Bălan has higher average trace element content, excepting Mn, Ni and V.

Chlorite

Chlorite is besides quartz the main non-metallic component of the ore (Fig. 2). It is presumed that chlorite crystallized from the primary "ore mud" deposited on the sea floor by hydrothermal ore fluids. The trace element content and the average values are indicated in Tables 9 and 13. Specifically high Cu and Sn contents stress out the appurtenance to the ore.

Table 11
Average values for trace elements in magnetite samples from the Bălan ore and other Paleozoic schists

	Cu	Pb	Zn	Ni	Co	Cr	V	Ti	Mg	Mn	Al	Sn	Ga	Zr
Dissem. ore ¹ (Bălan-Ferd. lev.)	219	3	308	16	37	45	131	464	1224	102	3939	12	3.6	86
Schists ² (Bălan)	8	<3	315	13	<10	92	130	955	520	290	1300	<10	<3	92
Metajaspilite ³ (Sindominic)	19	<10	<100	22	<10	<30	150	<30	850	150	2500	<10	<3	<10
Greenschists ⁴ (Sindominic)	34	<10	150	235	85	150	110	2700	400	290	1950	<10	<3	52
Greenschists ⁵ (Poiana Ruscă)	5	<3	300	90	70	130	620	4800	635	52	2550	<10	8.3	180

1, n=5; 2, n=2; 3, n=1; 4, n=29; 5, n=2

All values are in ppm

Table 12
Trace elements in magnetite from the quartz-chlorite schists of the top sequence from the disseminated ore of the Central Bălan ore deposit (Ferdinand level)

	Cu	Pb	Zn	Ni	Co	Cr	V	Ti	Mg	Mn	Al	Sn	Ga	Zr
B-124	58	4	300	14	32	46	140	290	700	57	1750	22	3	56
B-125	51	5	340	13	37	80	180	450	950	52	4200	<10	6	60
B-128	135	<3	<300	16	27	<30	105	420	920	82	2400	<10	<3	115
B-129	460	<3	<300	18	34	<30	130	540	1450	120	4800	<10	<3	86
B-130	390	<3	<300	20	56	38	100	620	2100	200	6500	<10	73	115

All values are in ppm

Table 13
Trace elements in chlorite samples from disseminated pyrite-copper ores in quartz-chlorite schists (Bălan and Leșu Ursului ore deposits)

	Cu	Zn	Pb	Bi	Sn	Ti	Mn	Ni	Co	Cr	V	Ga	Sc	Zr	Y	La	Ba	Sr
B-111	180	110	2	<10	22	3400	1500	16	60	82	38	16	7	380	21	44	<10	<10
B-112	550	240	2	<10	62	2300	460	16	55	72	43	20	5	115	19	32	<10	25
B-120	500	165	20	<10	55	4200	950	14	110	70	48	22	10	240	15	38	145	<10
B-122	1000	260	18	16	135	2000	1100	22	170	90	50	46	5	190	12	37	55	<10
B-123	750	260	2	<10	300	2100	850	18	150	90	50	38	5	160	18	33	135	14
B-125	200	380	24	48	34	1850	950	17	105	46	25	40	6	150	17	34	10	10
$\bar{x}$ B (n=6)	530	236	11	17	101	2641	968	17	108	75	42	30	6	206	17	36	61	13
(Gn-1)	317	92	10	15	105	944	338	3	46	16	10	12	2	95	3	4	63	6
$\bar{x}$ LU (n=5)	522	1158	56	10	30	1190	3520	<2	16	4	4	36	4	166	31	51	90	<10
(Gn-1)	473	1087	71	1	10	65	988		12	2	2	4	1	15	6	23	91	

B - Bălan; $\bar{x}$ B average for Bălan, $\bar{x}$ LU average for Isipoaia (Leșu Ursului)

All values are in ppm

Noteworthy is also the Ni:Co ratio (0.16) as mentioned similar with the same ratio in the ore pyrite (Tab. 10). Variable and relative high amounts of Cu, Zn, Sn and Zr result from mineral inclusions. Peculiar are the systematically high Sn, Ni, Co, Cr and V contents, compared with chlorites of the other similar disseminated copper ores of the same province, as for example from the Isipoaia horizon at Leșu Ursului (Tab. 13).

Trends in the vertical change of $\delta^{34}\text{S}$ and in the chemical constitution of the ores

Variations of $\delta^{34}\text{S}$ from bottom to the top are evident in the ore bodies from Bălan and have already been described from other stratiform ore deposits (e.g. Rammelsberg, Anger et al., 1966; Shakanai - Kuroko type, Sasaki, 1974; Sulitjelma - Scandinavian type, Gehrisch et al., 1975). Such changes in time of $\delta^{34}\text{S}$ during the deposition of ore have been referred either to the source or to the depositional conditions.

a) $\delta^{34}\text{S}$ variations in the source were differently explained. Supporters of the magmatic origin suggest sulfur isotopic fractionation favouring the light isotope to be accumulated in the early differentiates and precipitates (Anger et al., 1966). Adepts of refluxing cells suppose: 1) distillation in closed systems according to the Rayleigh equation (Gehrisch et al., 1975); 2) change of position and depth of the convective cells; 3) change of temperature, pH, $f\text{O}_2$ and admixture of sea water (Kajivara, 1971; Sato, 1973; Coomer, Robinson, 1976); 4) mixing of different convecting cells (Secombe et al., 1985) or of volcanic sulfur with sea water sulfur (Lusk, 1972).

b) $\delta^{34}\text{S}$ variations due to depositional effects may involve: 1) physico-chemical changes in the sedimentation area; 2) variable amounts of the supply; 3) bacterian activity.

No systematic or general sense of vertical $\delta^{34}\text{S}$ variations may be recognized from literature data, but in many cases a trend to light sulfur enrichment towards the top of the deposits is mentioned (e.g. Shakanai, Sasaki, 1974; Sulitjelma, Gehrisch et al., 1975; Rammelsberg, Anger et al., 1966).

For testing the stratigraphic (vertical) $\delta^{34}\text{S}$ variations in the Bălan ores a geochemical profile through the Bălan deposit of the Fagu mine was sampled (two superposed ore lenses). Plate I shows the $\delta^{34}\text{S}$ variation and the concomitant changes of trace elements content in pyrite and chalcopryrite, as well as of the bulk mineralogical composition of the sulfide phases, deduced from chemical analyses. A prevailing trend to ^{34}S enrichment may be recognized in both lenses (L.25 and L.26, Pl. I) and a strong ^{32}S increase on the top of lense 26, therefore at the end of ore deposition. For pyrite this trend covers a $\delta^{34}\text{S}$ spread of about 12‰.

Concomitantly with the mentioned ^{32}S increase on the top of the ore sequence an increase of Pb and Zn appears both in the sulfide phase of the whole ore and in pyrite (Pl. I).

Trace elements in pyrite show some systematic trends following roughly the increasing Cu, Pb, Zn supply (Cu, Pb, Zn content in ore). Co and Sn follow the Cu trend, while Bi, Ag and As follow the Pb-Zn trend. Ni is constant and shows no correlations with other elements. Thus most of the mentioned trends of

trace elements reflect the amount of mineral inclusions in pyrite.

Models for the source and the vertical geochemical trend

As it was mentioned, for the Bălan ores a sedimentary deposition fed by a continuous supply from hydrotherms in an open basinal system is accepted. Therefore it seems suitable to suppose the mentioned $\delta^{34}\text{S}$ variation mainly from the source and only subsidiarily from depositional conditions (e.g. local deviations from the general trend). This is strongly supported by the concomitant change of the ore fluid chemistry, indicated by variations of the metal and trace element content in pyrite, chalcopryrite and in the bulk composition of the sulfide phases (Pl. I). If we accept as source of the sulfide-sulfur anorganic kinetic reduction of previous sea water sulfate, as it was suggested by Nielsen (1979), then the time-bound isotopic fractionation may be explained by the faster reacting light sulfur. Thus the refluxing cells carry firstly preferentially light sulfur and later enrich in ^{34}S . This implies sulfur extraction from a closed system. Resetting of $\delta^{34}\text{S}$ values in different ore lenses (L 25, L 26) as well as different senses of $\delta^{34}\text{S}$ trends could suggest change of the sources area (mobile source). Therefore we can suppose either (Fig. 21) 1) changes in time of the "source position", as for example the depth and/or the place of sulfur and metal extraction, or 2) changes of the physical conditions in the same source area (e.g. increasing T and pH will enlarge the sulfur and metal extraction), as well as 3) mixing of ore fluids from two different sources.

1) According to the first model the $\delta^{34}\text{S}$ variation recorded from Bălan could be explained as follows: at the beginning lens 25 was fed by a deep seated preferential extraction of anorganically reduced light sulfur, followed by a persistent depletion of the remanent ^{34}S enriched sulfur from the same rock volume (extraction from a closed system). As no geochemical and space-time continuity exists between lenses 25 and 26, the cell of lens 25 died out and lens 26 was fed later by a new convective circulation. In the lower part of lens 26 the $\delta^{34}\text{S}$ trend resembles that one of lens 25. Therefore in the new source the history of the previous source (of lens 25) was roughly repeated. But to the end of the ore deposition a gradual change of the source position is suggested by the increasing supply of Pb, Zn and As, Bi, Sn, Ag, Co, concomitantly with a strong increase of light sulfur (Pl. I).

2) According to the second model a continuous increase of temperature and pH during the life of the convective cell of lens 26 favoured a more and more intensive metal and sulfur extraction in the same source

area, or a continuous growth of the source region. Consequently the ionic charge of fluids increases and sulfur becomes lighter due to preferentially ^{32}S depletion in the growing source area. An alternative explanation for the trend of increasing light sulfur may be the increase of $f\text{O}_2$ and/or pH of the ore solutions in the source, or during their ascension to the surface. Such a model was proposed by Kajiwa (1971) for the Shakanai deposit of Kuroko type (at a temperature of 250°C an isotopic fractionation of about 8 ‰ may be performed by a pH variation from 5 to 6 or by a log $f\text{O}_2$ increase from -35.5 to -33).

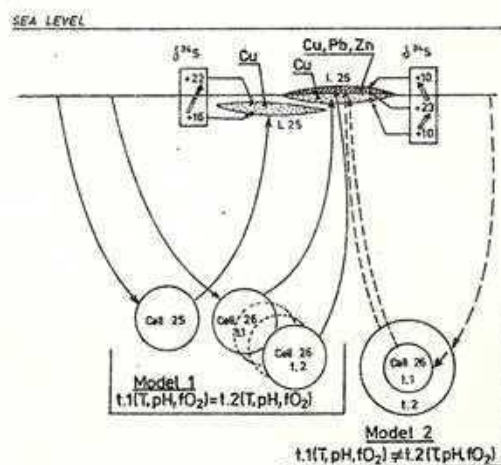


Fig. 21 – Models for sulfur and metal extraction by convective cells that may explain the vertical geochemical trends in the ore deposits from Bălan (explanation in the text).

3) The third model assumes in the last stage of ore deposition (lens 26) a mixing with fluids of another convective cell, rich in Pb, Zn and in the other mentioned trace elements.

The mentioned trends are recorded only for pyrite sulfur. The chalcopyrite sulfur shows an irregular scattering, probably due to the suspected metamorphic fractionation. Only the ^{32}S increase in the uppermost part of the ore sequence may be recognized concomitantly in both pyrite and chalcopyrite sulfur (Pl. I). A supplementary organic fractionation cannot be excluded for the top of the ore deposit.

Pyrite-copper deposition, followed by Pb and Zn supply towards the final deposition stages have been described from some prominent ore deposits (e.g. Rammelsberg, Kuroko type ores). In most cases the Pb, Zn supply develops concomitantly with a systematic increase of light sulfur. If such trends really are a common feature of some types of stratiform sulfide ore deposits, a similar change of the source position (according to model 1) in all cases is less probable. Therefore the second model that explains the mentioned geo-

chemical evolution of the ore fluids by changes of physical factors (T , pH , $f\text{O}_2$) in the same source area seems to be more suitable. Thus modification of the geothermal gradient might be one of the main promoters of the mentioned geochemical trend during the ore deposition.

Similar geochemical constitution of volcanic hosted (Kuroko type) and sediment hosted (Rammelsberg type) sulfide ore deposits as well as similar trends in the vertical zoning of such ore bodies, suggest that the source of metals is not strictly related to volcanic environments.

PYRITIC SERICITE-CHLORITE SCHISTS OF THE VALEA BĂII AND ARAMA OLTULUI MEMBERS

Isotopic data are scarce, therefore only informative and not conclusive (Tabs. 1, 6; Fig. 3). Differences with respect to the disseminated ores of the Bălan member are evident for $\delta^{34}\text{S}$, Ni, Co, Sn, Bi, Ag (Tab. 6, Figs. 8, 9, 10, 11).

For the *Arama Oltului* pyrites the higher amounts of Cu, Zn, Pb, Co and Bi suggest deposition from metal carrying hydrotherms, as it is proved by some small and local copper ore accumulations south of the Fagu Mine (Bore holes 337, 317). The $\delta^{34}\text{S}_{\text{py}}$ average is similar to that of the Mediaș massive ore from the Bălan Member, but the spread is definitely larger and includes lower values (Tab. 6), semblable with those of the Valea Băii pyrite. An informative geochemical profile (Gal. 18, Sabo) of 10 samples show no systematic vertical variation of $\delta^{34}\text{S}$ values as in the ore lenses of the Bălan Member. Therefore in the Arama Oltului horizon more constant source and/or depositional conditions may be presumed. Difficult to explain are the two isolated high $\delta^{34}\text{S}$ values (+35.77 and +38.20 ‰) which would suggest Cambrian sea water sulfur ($\delta^{34}\text{S} = +30$ ‰), locally shifted to the sulfide stability field due to increasing temperature and $f\text{O}_2$ (Nielsen, 1979).

For the *Valea Băii* pyrites the $\delta^{34}\text{S}$ average is slightly below that one of the ore pyrites. A similar sea water sulfur source could be presumed, but not associated with metal carrying hydrotherms as the ore fluids had been in earlier connective cells (Fig. 3). For this counts also the low trace element content of those pyrites.

For both Arama Oltului and Valea Băii pyrites the trace element distribution is in good concordance with the general data of Cambel, Jarkosky (1967): Cu, Zn, Pb show maximal frequency around clark values, with some tendencies to higher values in the Arama Oltului pyrites (Fig. 9). The same clark distribution may be noticed for Ag and Mn (Figs. 10, 11). Both Arama Oltului and Valea Băii pyrites fit for Co and Ni the second (high value) maximum of Cambel's frequency

curves (Fig. 8). For Ni this is an obvious difference comparatively to the Bălan-Fagu and Sindominic pyrites (Fig. 8).

SERICITE-GRAPHITE SCHISTS WITH DISSEMINATED PYRITE IN THE SINDOMINIC SEQUENCE

Generally pyrite does not exceed a 10–15 volume percentage of the rock. Only locally scarce chalcopyrite dissemination may occur (Popa, Serbănescu, 1984, unpubl. report), sometimes associated with chlorite schists. Pyrite $\delta^{34}\text{S}$ values range from about -18‰ to -3‰ (Tab. 1) ($\bar{x}\delta^{34}\text{S} = -10.31\text{‰}$). Popa (1975) suggested that these pyritic schists represent the northern extension of the Bălan ore member, assuming that the Pingărați blastodetrital schists could be an equivalent of the Bălan acid metavolcanics. Such a correlation has no real lithostratigraphic, lithologic and geochemical support (Fig. 3).

For the pyrite sulfur of the Sindominic schists a biogenic reduction of sea water sulfate, supposed by Popa (1981, unpubl. report; 1982), is suggested by the scarce pyrite dissemination in graphitic phyllites, as well as by the higher amount of ^{32}S than in pyrites from sulfide disseminations of the ore-bearing levels. The average $\bar{x}\delta^{34}\text{S}_{\text{py}}$ differences to the mentioned pyritic schists are of 28.08‰ (Bălan), 19.18‰ (Valea Băii) and 21.57‰ (Arama Oltului).

Comparatively with the $\delta^{34}\text{S} = +30\text{‰}$ of Cambrian sea water, as it can be inferred from Cambrian sulfate deposits (Nielsen, 1979), an isotopic fractionation of $\delta^{34}\text{S}$ $33\text{--}48\text{‰}$ ($\bar{x}=40.31\text{‰}$) does result. This value exceeds the experimental and theoretical data for dissimilatory ("respiratory") bacterial sulfate reduction (-25‰) but fits the order of the studied natural systems (-40 to -65‰) in which a more advanced fractionation develops due to the slow rate of the process and possible steady state replenishment of sulfate nutrient (Nielsen, 1979; Schwarcz, Burnie, 1973).

By comparison to the theoretical $\delta^{34}\text{S}$ distribution in open and closed natural systems with bacterial reduction proposed by Schwarcz, Burnie (1973) the histogram of pyrite sulfur from the Sindominic graphitic schists fits an open system distribution with a narrow $\delta^{34}\text{S}$ range around $\Delta\bar{x} = 40\text{‰}$ (Fig. 22). Such open systems may be either sedimentation in anoxic sea water or permeable wet sediments in which sulfate can diffuse from overlying oxygenated sea water as fast as it had been consumed by reduction or precipitation. In such conditions the spread of $\delta^{34}\text{S}$ values can be enlarged (skewed to higher Δ) by reduction of sea water sulfate trapped in the sediment below the depth of diffusion of fresh sulfate. This could account for the tendency of bimodal distribution in the mentioned histogram (Fig. 22). But the low number of analytic

data and the metamorphic overprint render such conclusions only speculative.

Generally $\Delta(\delta^{34}\text{S}_{\text{sw sulfate}} - \delta^{34}\text{S}_{\text{biog. sulfide}})$ varies as a function of the specific acting bacteria. According to Schwarcz, Burnie (1973) Δ appears to be larger in quiet, undisturbed marine environments than in more agitated, higher energy systems. In this model the relatively low ($\bar{x}=40.31\text{‰}$) and narrow $\delta^{34}\text{S}$ range of the pyrite below the Pingărați Member fit well the sedimentologic environment in the Sindominic sequence, where the pyritic graphite phyllites have local intercalations of blastodetrital schists, showing temporary high energy disturbances.

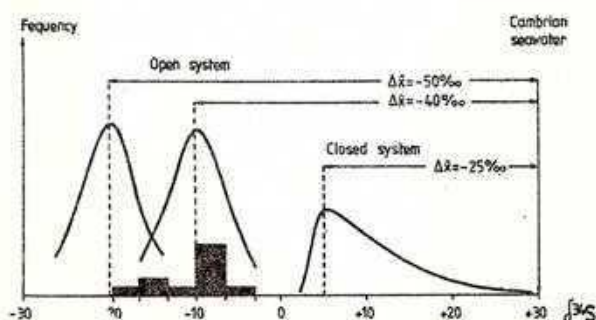


Fig. 22 — $\delta^{34}\text{S}$ histogram for pyrite from Sindominic sericite-graphite schists (black) compared to the theoretical $\delta^{34}\text{S}$ distribution in open and closed natural systems with bacterial reduction according to Schwarcz, Burnie (1973).

The mentioned data suggest strongly the provenance of pyrite sulfur in the graphite phyllites north of Bălan by biogenic reduction of sea water sulfate in spite of the fact that a broad and nonsystematic $\delta^{34}\text{S}$ spreading required according to Nielsen (1979) as test for bacterial activity is lacking. This could be explained by both the "open" character of the system requiring a narrower $\delta^{34}\text{S}$ spread and by a tendency of local isotopic homogenisation by metamorphic crystallisation (blastesis). A relict tendency to nonsystematic spreading in locally distributed "closed cells" could be speculatively supposed in the bimodal distribution of $\delta^{34}\text{S}$ (Fig. 22).

As a supplementary explanation it may be supposed that concomitantly, but only locally, the system was fed by convective cells of hydrotherms, carrying from depth dissolved biogenic sulfur and copper. This may account for local occurrences on the same lithostratigraphic level of small lenses of chlorite schists with scarce pyrite and chalcopyrite disseminations (e.g. Bore hole 205, Belcina).

The trace element distribution in pyrite is shown in Figs. 8, 9, 10, 11. For all the elements relatively low contents are prevailing, close to Cambel's (1967)

distribution patterns. This is the main geochemical difference from the ore pyrite with higher amounts of trace elements (Fig. 23). Ni is an exception with its similar distribution, but the Co:Ni ratio is below 1, due to the low Co content. Among different types of pyritic schists the blastodetrital rocks show the lowest Co content.

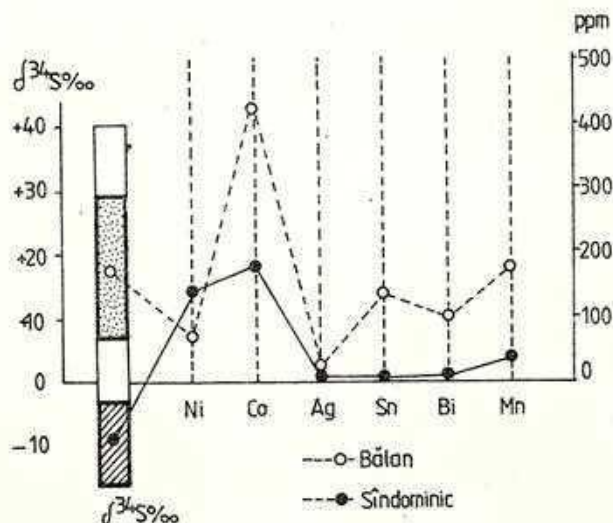


Fig. 23 - Differences in $\delta^{34}\text{S}$ and trace elements average values between the Bălan ore pyrite and pyrite from the Sîndominic graphite-sericite schists.

Conclusive remarks

Sulfur isotopes and trace elements in pyrite of ore and pyritic schists show lithostratigraphic control. No metamorphic (greenschist facies) homogenisation is recognisable on regional scale.

A concordance in the $\delta^{34}\text{S}$ values of the Bălan ores and of other syngenetic sulfide ore deposits may be obtained by equilibration of the recorded ore $\delta^{34}\text{S}$ values for the sea water $\delta^{34}\text{S}$ values during the respective ore deposition.

There is no isotopic equilibrium between sulfur of pyrite-chalcopyrite pairs in the ore. This may be explained either by an initial disequilibrium in the premetamorphic ore, or by metamorphic isotopic fractionation (mainly in the chalcopyrite phase).

Local metamorphic isotopic fractionation of sulfur and trace element differentiation is suggested for mobilised chalcopyrite and for large porphyroblasts of pyrite.

A continuous change of $\delta^{34}\text{S}$ and trace element content occurs in a transversal section through the ore lenses. This may be explained by variable leaching (extraction) conditions in a growing source area from

which a convective circulation of hydrotherms was charged by sulfur and metals. The sulfide sulfur of the ore is presumed to originate in sea water sulfate by kinetic isotopic fractionation at depth. Metals could be extracted from both, volcanic or nonvolcanic rock associations.

Organic reduction of sea water sulfate is suggested for the pyrite sulfur of the Sîndominic sericite-graphite schists.

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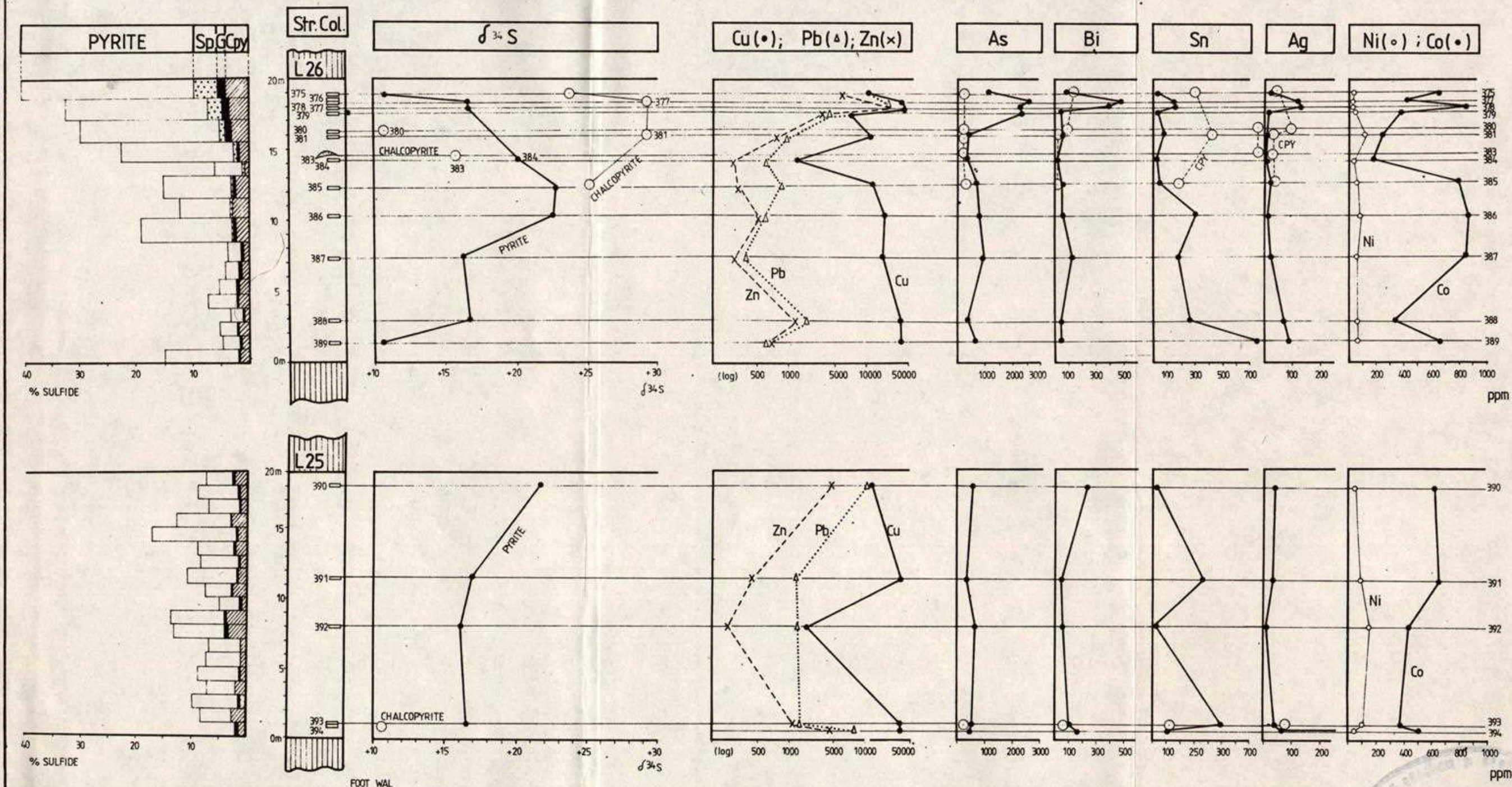
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GEOCHEMICAL PROFILE THROUGH TWO SUPERPOSED ORE LENSES OF THE FAGU ORE DEPOSIT



METALLOGENY OF THE CENTRAL SOUTH CARPATHIANS AND SOME REMARKS ON THE SOURCE OF GOLD IN METAMORPHITES

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Key words: Metallogeny. Metamorphic rocks. Gold sources and bearers. Au. Neutron activation analysis. South Carpathians – Getic and Supragetic realms – Lotru and Căpăţina Mts, Cibin Mts, Sebeş Mts.

Abstract: *Metallogeny of the Central South Carpathians and Some Remarks on the Source of Gold in Metamorphites.* Four major types of mineral deposits have been recognized in the Upper Proterozoic metamorphics of the South Carpathians, i. e. (1) regionally metamorphosed sedimentary and magmatic deposits (true protoliths), (2) metamorphic deposits, (3) shear-zone related ore occurrences, (4) sulfide disseminations in ultramafics tectonically pierced into supracrustal rocks. As concerns the gold sources (mainly for alluvial concentrations) the following hierarchy has been established: I, the shear-zone related ores; II, titanian hematite inclusions in kyanite and nests within quartz lenses in micaschists accompanying the manganiferous belt; III, accessory magnetite in schists and chromian spinel in ultramafics. Additional gold bearers in the mature alluvial deposits are the greigite (microconcretions up to 300 μm in size) and the framboidal pyrite.

The Precambrian metamorphites occurring in the central South Carpathians (the Getic Crystalline area) are usually poor in relevant mineral accumulations, the only exception to the rule being the pegmatites. However, there are several occurrence types, of different structure and genesis, assigned to several metamorphic sequences. They are of different importance, if one considers that the deposition of mineral resources took place during several stages, by extremely varied geological processes. According to the prevailing character of the metallogenetic process, the mineral occurrences are grouped as follows (Udubaşa, 1987; Udubaşa, in Balintoni et al., 1989).

1. Regionally metamorphosed sedimentary or igneous occurrences

1.1 Manganese-bearing rocks (Sebeş-Lotru Series, Sebeş-Cibin-Lotru Mts)

1.2 Pb-Zn ores (Suru Formation, Făgăraş Mts)

1.3 Ni-Cu-Co ores (Mioarele Formation, Făgăraş Mts)

2. Metamorphic occurrences

2.1 Pegmatites (Sebeş-Lotru Series, Sebeş-Cibin-Lotru Mts)

2.2 Kyanite (the same)

2.3 Iron ores in retromorphic metamorphites (Sibişel Series, Lotru and Sebeş-Cibin Mts)

3. Ore occurrences related to shear zones

3.1 Au-Cu ores (Căpăţina Mts)

3.2 Iron sulphide ores (Căpăţina Mts)

4. Ni-Fe-Cu sulphides in exotic ultrabasite bodies (Sebeş-Cibin-Lotru Mts)

Although almost all these types of mineral deposits played a more or less important part in the accumulation and redistribution of gold, it is difficult to present them thoroughly. Therefore, special attention will be paid to those of particular metallogenetic significance to the gold.

Manganese-bearing rocks. The axial area of the Central South Carpathians (CSC) contains a manganese belt generally trending E-W which delimits two independent realms of the Sebeş-Lotru Series: (1) one lying south of the manganese belt, consisting mainly of metapelites which abound in pegmatite bodies, kyanite and exotic ultrabasite bodies, quartz-feldspar gneisses and eclogitic rocks and (2) another one in the north of this belt, consisting mainly of partly migmatized paragneisses (Pl. I). It has not been proved yet that the manganese-bearing rocks yield relevant gold contents (a sample of nearly monomineral spessartinite from the Cugir Valley shows only 0.0025 ppm Au), but it is interesting to note the local occurrence of titanian hematite near the manganese ores; this mineral is one of the important gold bearers in the CSC meta-

morphites (Tab. 1).

Table 1
Gold content in minerals and rocks (RNAA method)

A. Minerals		
Minerals	Sample No.	Au (ppm)
Titanian hematite (hem _{ss})	S-87	0.0541
(ditto)	S-4	0.0326
Kyanite	S-10	0.0326
Muscovite (pegm.)	1058	0.0293
Garnet	1033	0.0195
Spessartine	1059	0.0025
Microcline (pegm.)	1063	0.0010
Biotite	1067	0.0007
B. Rocks		
Rock type	Locality	Au (ppm)
Amphibolite (retrogressed)	Pianu Valley	0.1300
Garnet amphibolite	Valea lui Stan	0.0446
Amphibolite (retrogressed)	Vasilatu Valley	0.0305
Ultrabasite	Canciu	0.0086
Biotite gneiss	Valea lui Stan	0.0075
Micaschist	Valea lui Stan	0.0037
Red gneisses	Valea lui Stan	0.0025
Ultrabasite	Valea lui Stan	0.0022
Ultrabasite	Căldarea brook (trib. Sebeș Valley)	0.0011

Kyanite deposits. There are kyanite micaschists in which the kyanite amount ranges from 2 to 20 % and constitutes in places megablasts of 10 cm; according to Hărtopan (1982) the kyanite-bearing rocks occurring in the CSC show a marked preference for the Upper metapelitic unit of the Sebeș-Lotru Series forming here a tabular, nearly horizontal primary structure. Hărtopan (1978) gives a detailed description of the relationships between kyanite and staurolite, as well as of massive disthenites, apparently with no foliation. It is important to note that kyanite exhibits systematically titanian hematite inclusions, which point to coexistence PT domains and also account for some relatively high gold contents of kyanite (Tab. 1).

Iron ores in retromorphic metamorphites. According to Hann and Balintoni (1988) the Sibîșel Series in the Lotru Mts is equivalent to the Căpâlna-Cărpiniș one (Chivu, 1964), these authors also proving the retromorphic character of metamorphites and suggesting their Precambrian age. In this view, the Sibîșel Series is an independent metamorphic sequence, characterized by iron (magnetite) ores, considered by Minecan et al. (1979) and Chivu (1980) to represent regionally metamorphosed syngenetic ores, but proved to be formed as a result of intense retromorphism (Hann, Szasz, 1984). The latter opinion is confirmed

by the relationships between ilmenite and magnetite (Fig. 1); the magnetite porphyroblasts have resulted from the deferrization of ferromagnesian silicates, synchronous with ilmenite destabilization within a complex metamorphic process of prevailing static and essentially retrograde nature.

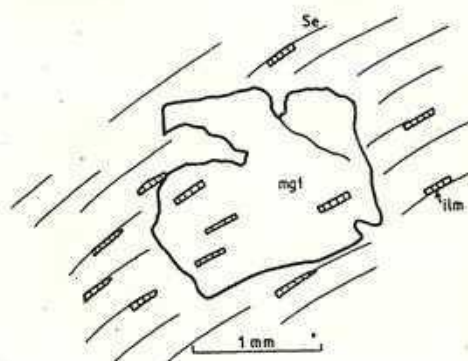


Fig. 1 - Magnetite (mgt) porphyroblast exhibiting elongated ilmenite (ilm) inclusions partly altered to rutile+titanite aggregates (similar alteration both inside the porphyroblasts, where ilmenite parallels S_{e1} , and outside them). Retrogressed amphibolites of the Sibîșel formation, Cărpiniș, Cîbin Mts.

The Sibîșel Series on the whole is viewed as a Precambrian green schists belt which acted as gold-bearing protore in the CSC (Udubașa, 1987), generating the "tectogenetic" Au-Cu ores from Valea lui Stan in the Căpâlna Mts by means of processes related to alpine (probably pre-alpine, too) shearing zones (Udubașa, Hann, 1988).

Au-Cu ores and Au ores. So far, primary gold deposits are known at Valea lui Stan (Udubașa, Hann, 1988) and in the Costești Valley in the Căpâlna Mts (Apostoloiu et al., 1987; unpublished data); they are related to intense shearing zones of different ages which affected the above mentioned green schists belt (Valea lui Stan) or a similar sequence of the Sebeș-Lotru Series (Costești Valley). In the last case, the blastomylonitic protore was later reactivated and affected by intense metamorphic differentiation processes resulting in gold-bearing quartz bodies.

Important alluvial concentrations are reported from the north of the Sebeș Mts (Valea Pianului) and from the Lotru and Olt Valleys; the source of alluvial gold will be treated further on.

Iron sulfide ores. In the Căpâlna Mts iron sulfide ores have been identified by Trifulescu et al. (1962, unpublished data); according to Hann et al. (1988) they are associated with the mylonites occurring in the contact area between Ursu and Vaideeni forma-

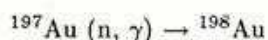
tions. The main component is pyrrhotite, partly altered to pyrite, marcasite (via Zwischenprodukt), to which different amounts of chalcopyrite, graphite, ilmenite, picroilmenite, rutile, titanite, sphalerite, tosilite (?) are added; magnetite occurs only as inclusions in the pyrite formed at the expense of pyrrhotite (Udubaşa et al., 1988, unpublished data). Within the shear zone there are decimetric lenses of fine carbonate rocks exhibiting numerous graphite inclusions, as well as nonmetamorphosed dolerite bodies. Pyrrhotite-dominated ores occur also in the Cerna Valley (Danubian realm). Unlike the above mentioned occurrences, the pyrrhotite ores in the Cerna Valley contain also graphite, pyrite and chalcopyrite but show a strong transformation of pyrite into pyrrhotite as a result of thermal effect produced by Late Precambrian granitoids. A massive pyrrhotite sample from Cerna ores has yielded 0.0276 ppm Au.

Ni-Fe-Cu sulfides in ultrabasites. The Getic Crystalline in the CSC contains numerous partly serpentinized ultrabasic bodies of varying size, which together with the eclogites and the granulitic rocks represent deep-seated bodies tectonically included in the supracrustal metamorphic rocks of the Sebeş-Lotru Series (Iancu et al., 1987). The metallic components of these rocks are represented by chrome spinels, pyrrhotite, pentlandite, chalcopyrite, magnetite (subordinate, as coronas round the chromite grains or filamentous, arranged in serpentinic cells or veinlets substituting olivine); millerite occurs in places. Some ultrabasic samples have been analysed for gold and the contents yielded are generally low (Tab. 1). It is, however, to note the presence of gold inclusions in the chromite of some alluvial concentrates, keeping the ultrabasites among potential gold bearers as the ultimate source of this metal in the mantle.

Analytical Method

The gold contents of the rocks, minerals and alluvial concentrates have been determined by radiochemical neutron activation analysis (RNAA). This method is particularly sensitive to all concentration levels; for the lower limit of 0.1 ppb (10^{10} or 0.1 mg/t) the accuracy of measuring is of 7-8 %.

The gold ratio is inferred from the nuclear reaction:



by means of which ^{198}Au is obtained, subsequently to the sample irradiation inside the reactor; $T_{1/2}=65$ hours, $E=0.412$ MeV. A NaI crystal detector coupled with an 800 channel analyser have been used. The spectra have been calculated by using the photopeak area method. The standard used was pure spectral gold (produced by Johnson and Matthey Chem. Ltd.)

dissolved in aqua regia. The samples weighing 100-200 g have been finely ground and homogenized to be simultaneously used for determining both the gold content by RNAA and the trace elements (titanium included) by emission spectroscopy. The sample amount undergoing neutron activation was of 0.2 g after 24 hours drying at 105°C .

Gold Distribution in Metamorphites

While the source of alluvial gold in the Lotru and Olt Valleys is relatively easily detected (mainly the Valea lui Stan ore occurrence), in the other areas the alluvial gold is of still unknown origin. In order to elucidate this problem and to make progress in the geochemical study of gold in metamorphites, a systematic investigation of the alluvial deposits has been carried out. For obtaining significant geochemical results second and third order tributaries have been chosen. Thus, the sampling included both areas with known alluvial concentrations and the adjoining zones. Informative sampling of different rocks and minerals was also added. The analyses of gold by neutron activation have been associated with quantitative spectrographic analyses, partial chemical analyses and minute microscopic studies, especially of polished sections obtained by resin inclusion of concentrates. The analytical flow generally included magnetic separation (for certain samples at several intensities of the magnetic field) and the simultaneous analyses of both the magnetic fractions and the bulk samples or the non-magnetic remnants.

The analytical data are presented here either as synthetic markers noted on the map (Pl. 1) or as maximum and minimum values (Tab. 2). These synthetic markers on the map point formerly to the presence of the free gold (bulk samples or non-magnetic fraction with high gold content) or gold inclusions in different minerals (higher gold content of the magnetic fraction). The latter is most frequent, the immature alluvia containing gold inclusions mainly in other minerals.

It is to mention that the gold was observed under the microscope in relatively few samples; the main cause is its aleatory distribution and sometimes its being very fine-grained; for the latter, the name of "analytical gold" is more appropriate, at least till its investigation by the electronic microscope or by microprobe analysis which represent the second stage of the geochemical study of the CSC gold occurrences.

By using the RNAA and the microscopic investigation the main bearers of "included gold" in metamorphites have been identified. According to frequency, the main gold bearers are: magnetite, titanite, hematite, chromite, goethite and framboidal pyrite (the last two minerals from mature alluvia or/and

formed at the expense of sedimentary rocks). The "optical" proof of the occurrence of gold in these minerals will be given in a separate paper.

Table 2
Some data concerning the gold geochemistry
of the stream sediments

I. Highest(H) and lowest(L) values				
	Whole samples (A)	Magnetic concentrates(B)		
H	0.1294	0.3248		
L	0.0007	0.0005		
II. Enrichment factors				
Sample No.	A:B	Sample No	A:B	
S-75	1:319	S-110	35:1	
S-105	1:39	S-96	13:1	
S-28	1:31	S-77	10:1	
S-102	1:21	C-140	6:1	
C-126	1:1	L-127	3:1	
III. Variation of gold content versus magnetic intensity*				
	M ₁ (0.1 A)	M ₂ (**)	M ₃ (7.5-8A)	N (***)
1.	0.2655	0.0178	0.0645	0.0085
2.	0.0190	1.3279	0.0177	0.0123

* In an electromagnetic separator M₁, M₂, M₃, N - from the same sample).

** The remaining portion from M₂.

*** Non-magnetic fraction.

As regards the "analytical gold" certain relationships between the gold contents and other elements have been sought; the successive testing has shown positive correlations between gold and titanium and between gold and some other elements. The diagram of Figure 2 illustrates the positive Au/Ti correlation and implicitly the preference of gold for titanian hematite. It is interesting to note also the positive correlation between the gold content and the sum of the following elements Cu, Pb, Zn, Sn, Mo, Cr, Ni, Co (Fig. 3), its significance - statistically determined - being not wholly elucidated yet.

The gold protore nature of the Precambrian green schists belt represented by the Sibişel Series is statistically confirmed. Several alluvial concentrate samples from the developing areas of these metamorphites yield higher contents as compared to the Sebeş-Lotru Series. The gold contents exhibit in both cases great variations. It is presumed that the Sibişel Series was primarily inhomogeneous as regards the gold content; it forms an elongated belt several tens of km long (see Fig. 4). For the Sebeş-Lotru Series gradual gold concentration on restricted areas (blastomylonite belts, locally developed quartz lenses with titanian hematite

nest) must be taken into account.

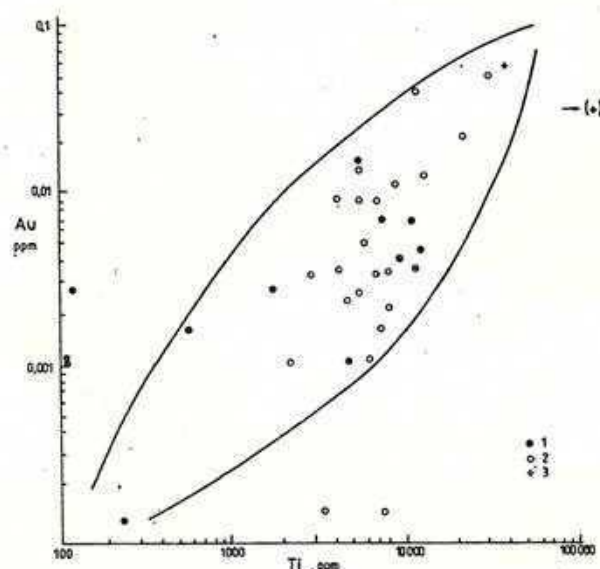


Fig. 2 - Au/Ti correlation diagram.
1, rock samples; 2, alluvial concentrates (magnetic fractions); 3, minerals (particularly titanian hematite). Positive correlation disturbed mainly with respect to the very reduced gold contents (next to the Clarke).

Discussions

Starting from the very non-uniform distribution of gold in rocks, it has been considered that the study of alluvial concentrates from small hydrographic basins can inform, to a greater extent, on the primary sources of gold in metamorphites. This premise has been confirmed. The systematic investigations led to the conclusion that metamorphites should contain preferential gold bearers, i.e. minerals including elements with geochemical affinities for this metal or rocks exhibiting wide geochemical spectra which also include gold. Some types of amphibolite rocks and certain rock sequences also containing amphibolite rocks (eg. Sibişel Series) play this role in the CSC. As regards the minerals, the available data show that, at present, magnetite, titanian hematite and chrome spinel frequently associate with gold.

It is more difficult to discuss the nature of the protoliths yielding the metamorphic rocks or rock sequences which exhibit at present anomalous gold contents. If according to Petrovskaja (1973) the geochemical spectrum of alluvial gold as a mineral reflects the geochemical features of the primary ore, the same is true for our samples of alluvial concentrates; the samples yielding relevant gold contents usually contain

such elements as Cu, Pb, Zn, Sn, Mo, Cr, Co, Ni, the correlation being positive in case their sum total is considered. Thus the source rocks or formations are supposed to contain all these elements. There are several samples yielding anomalous contents of one or two of these elements and lacking in significant gold amounts, thus accounting for the fact that the primary sources contain a well defined association of elements. The common factor is $Ti(\pm Fe)$ for which the positive correlation with gold is preserved independently of the fraction type (global, magnetic) pointing to the importance of these elements to the primary fixation of gold in sediments.

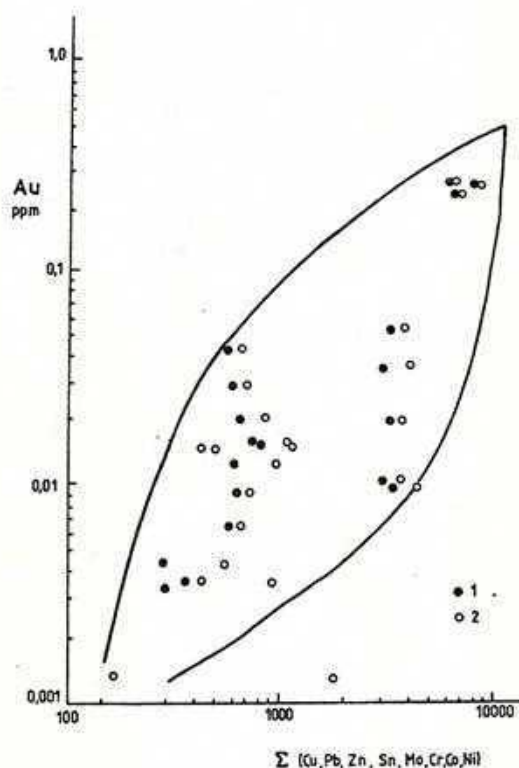


Fig. 3 - Au/sum total of Cu, Pb, Zn, Sn, Mo, Cr, Co and Ni correlation diagram.

1, variant without Co and Ni (better positive correlation); 2, variant including Co and Ni (poor positive correlation especially with respect to the reduced gold contents). For details, see the text.

Iablokova (1972) emphasizes the role of colloidal iron hydrate and of organic carbon to the migration and deposition of gold in sediments, as well as the active role of ferruginous microconcretions to the "coprecipitation" of gold. Therefore, it is easily understood how the gold-iron association is preserved during the metamorphism, finally resulting in gold inclusions in magnetite. A similar association can be supposed between colloidal gold and the cryptocrystalline titanium hydrated oxide of the α -titanium acid (present in nature,

acc. to Marcu, 1979, as $TiO_2 \cdot H_2O$). This may account for the gold-titanium-hematite association in kyanite-bearing rocks. Saager et al. (1982) calculated an average value of 0.0130 ppm Au for the ferruginous rocks of the greenstone belt in Southern Africa (ranging from 0.00005 to 0.667 ppm) and of 0.0011 ppm (0.00001–0.0372 ppm) for the associated basic volcanics.

Accepting the hypothesis that the ultimate source of gold is the mantle and, by direct observation, the rocks originating in the mantle (Anhaeusser et al., 1969), the CSC ultrabasites considered of deep, infracrustal nature (Iancu et al., 1987) can be viewed as potential source of gold. However, as the analyses of ultrabasic samples have not pointed to significant gold contents (Tab. 1) and as far as the alluvial concentrates contain gold inclusions in chromite, it is supposed that the role of ultrabasites in generating or increasing the gold content of metamorphites is mediated by their degree of "processing" in areas with blastomylonites or mylonites.

There are numerous data which account for the preferential concentration of gold in melanocratic minerals and particularly in magnetite; the magnetite of some granitoids may yield as much as 0.8 ppm Au (Scerbakov, 1974), by contrast to quartz (0.0018 ppm at the most), feldspars (0.0020), biotite (0.0207), chlorite (0.0412) etc. Saager et al. (1982) suppose that in the Archean basic volcanics from South Africa sulfides are the main gold bearers, although the analyses were performed on rock samples; no gold inclusions have been observed in the rocks analysed nor in the sulfides encountered so such a conclusion seems to be purely speculative. It is however true that the metamorphosed Ni-Cu-Co ore occurrences in the Vilsan Valley (Udubaşa et al., 1988) have shown gold inclusions in sulfides, while the alluvial concentrate samples from the area adjoining to the ore deposit yield gold contents higher than those in the adjacent areas.

The primary gold sources can be thus numerous, the available data on the CSC metamorphites suggesting that the main gold bearers are: metamorphic sequences of green schists type (Sibişel Series) rich in magnetite; titanian hematite associated with quartz lenses resulting from metamorphic differentiation within the kyanite-bearing micaschists; the chromite of ultrabasites occurring in blastomylonite areas; blastomylonites themselves containing slight gold concentrations of shear-zone type.

Considering these possible sources and the shear zone related gold concentrations such as in Valea lui Stan and Costeşti Valley (Căpăţina Mts), the distribution of alluvial gold in the CSC is easily understood (Fig. 4). Moreover, "anomalous areas" can be delimited within the metamorphites of the Getic realm (exhibiting free gold or gold inclusions in other miner-

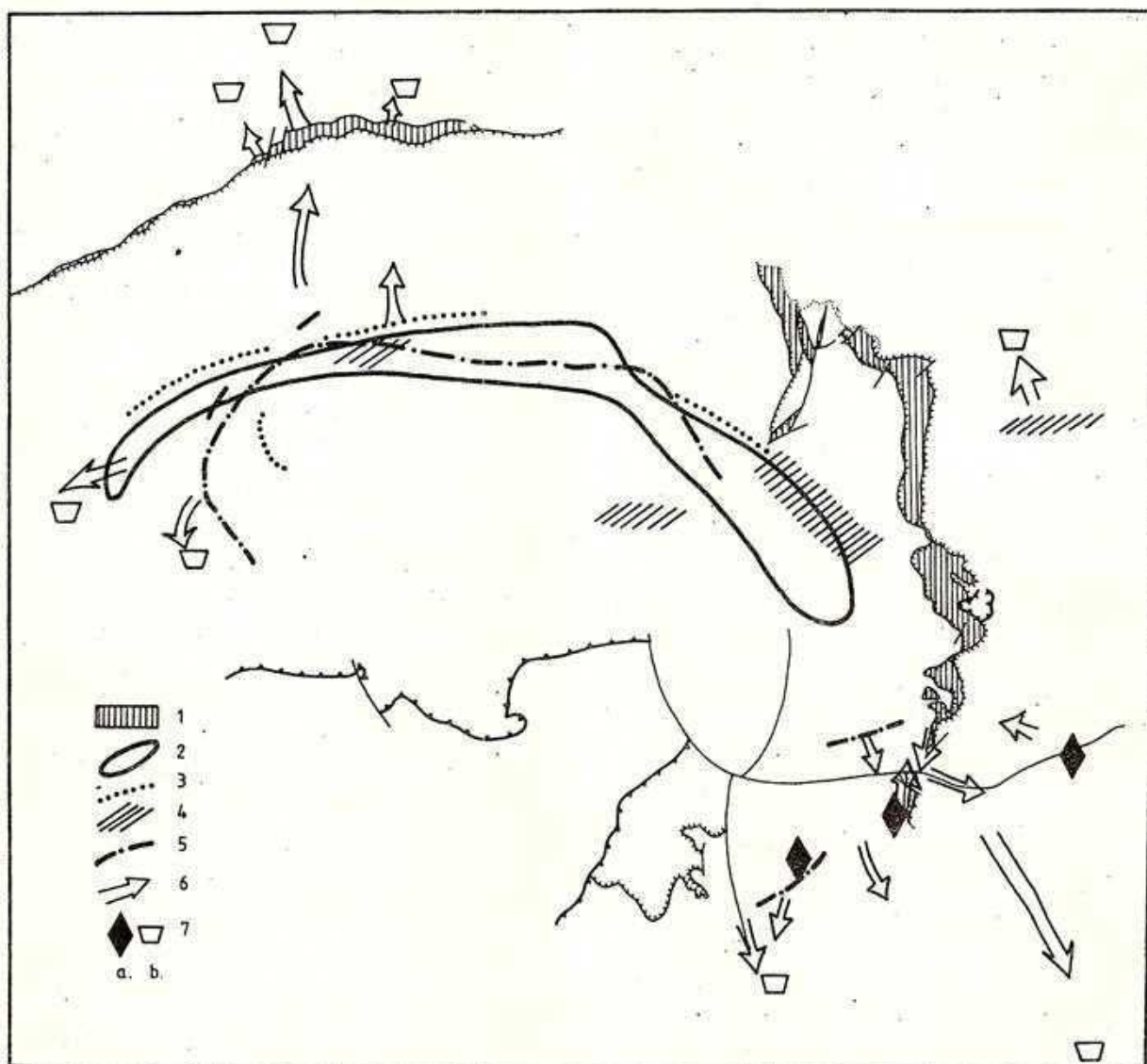


Fig. 4 - Sketch of the Central South Carpathians showing the main gold protores and the gold migration within stream sediments.

1, Sibîşel Series; 2, manganiferous belt; 3, titanite hematite nests in quartz lenses; 4, kyanite-rich rocks; 5, blastomylonite belts; 6, gold migration from protores; 7, gold concentrations: a, primary (mainly shear-zone related); b, secondary (alluvial).

als) which include formations similar to those mentioned above as well as probable paleoplacers (?). Taking into account the constant association of gold with other elements, in these "anomalous areas" one can discover possible primary metal-bearing concentrations of complex composition.

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STRUCTURAL MAP OF CENTRAL SOUTH CARPATHIANS

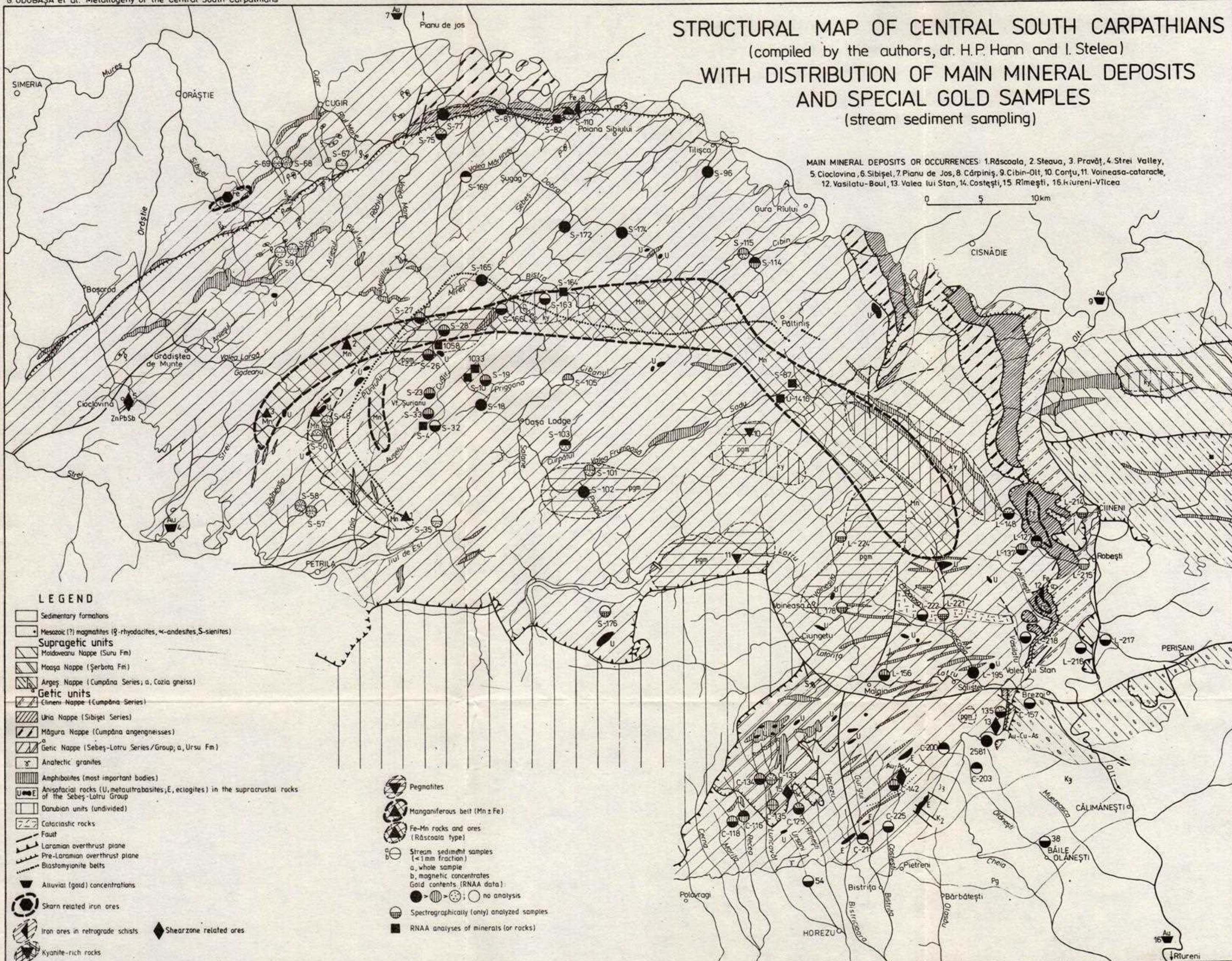
(compiled by the authors, dr. H.P. Hann and I. Stelea)

WITH DISTRIBUTION OF MAIN MINERAL DEPOSITS AND SPECIAL GOLD SAMPLES

(stream sediment sampling)

MAIN MINERAL DEPOSITS OR OCCURRENCES: 1. Râscaala, 2. Steaua, 3. Pravăț, 4. Strei Valley, 5. Cioclovina, 6. Sibișel, 7. Pianu de Jos, 8. Cărpiniș, 9. Cămin-Olt, 10. Conțu, 11. Voineasa-cataracte, 12. Vasilatu-Boul, 13. Valea lui Stan, 14. Costești, 15. Rimești, 16. Rureni-Vilcea

0 5 10 km



ISOTOPIC COMPOSITION OF OXYGEN, CARBON AND SULPHUR IN SIDERITE ORE DEPOSITS ASSOCIATED TO NEOGENE VOLCANISM IN THE EAST CARPATHIANS - PRELIMINARY DATA.

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Key words: Mineral deposits. Siderite. Volcanic rocks. Neogene. Stable isotopes. ^{18}O . ^{13}C . ^{34}S . East Carpathians - Neogene-Quaternary eruptive - Călimani, Harghita Mts.

Abstract: *Isotopic Composition of Oxygen, Carbon and Sulphur in Siderite Ore Deposits associated to Neogene Volcanism in the East Carpathians - Preliminary Data.* The isotopic composition of oxygen and carbon in siderites and of sulphur in associated marcasites, from siderite ore deposits related to the Neogene volcanics in the East Carpathians, has been measured. The obtained $\delta^{18}\text{O}$ values (-7.56 – 9.16 ‰PDB) are consistent with the meteoric origin of water in the carbonate forming hydrotherms. Siderite formation temperatures (ca. 60°C), obtained using Epstein's isotopic thermometer, are in agreement with both mineralogical features of siderites and geothermal data concerning their occurrence areas. The ^{13}C values in the samples from the Harghita Mts can be explained - as in the case of free CO_2 from the actual thermomineral systems in the same area - by thermal decomposition of marine carbonates. The isotopic composition of sulphur from marcasites is consistent with their magmatic origin but also other hypotheses (filtration of hydrotherms through sulphate-bearing formations for instance) may be taken into account.

1. Introduction

By the courtesy of Dr. Wang Zhonggang and Dr. Yu Xueyuan preliminary ^{18}O and ^{13}C data have been obtained in the Institute of Geochemistry - Academia Sinica - from Guiyang (People's Republic of China) on siderite samples collected in the Harghita and Călimani Mts., Romania. Simultaneously Sulphur isotopic composition of marcasite associated to siderite in the Harghita Mts. has been determined in the Institute of Geology and Geophysics, Bucharest.

Informations concerning isotopic composition of Oxygen, Hydrogen and Carbon have recently been obtained for hydrogeological systems in the area of the Neogene Volcanic chain (Crăciun et al., 1989).

2. Geological and metallogenetical framework

Two major siderite occurrences forming accumulations of economic interest at Lueta-Vlăhița and Mădăraș, and a large number of minor occurrences scattered along the western and eastern sides of the volcanic range are known in the Harghita Mts. Small-scale siderite outcrops have also been found within a

limited area in the southern part of the Călimani Mts (near Toplița).

The siderite deposits occur either at the contact zone between Neogene andesitic volcanic rocks and their pre-volcanic basement or within the Volcaniclastic formation produced during the first phase of volcanic evolution. They have been denominated as the "Lueta type" and "Vlăhița type" respectively (Peltz et al., 1982).

The deposits essentially consists of sideritized rocks of various original composition: Precambrian metamorphics (at Mădăraș), Neogene sedimentary rocks (at Lueta-Vlăhița and Mădăraș) and Neogene volcanics (in all occurrence areas). The mineral paragenesis includes, besides host-rock mineral assemblage, siderite $\pm$ opal $\pm$ marcasite, as neoformation, the monomineral siderite deposits being however the most frequent ones.

Siderite genesis has largely been debated, the opinions differing from one author to another or even at the same author from one ore type to another. Thus, for instance, Tănăsescu (1967) stressed the hydrothermal origin for the Mădăraș siderites. Peltz et al. (1983) stated different genesis for various ore

types: volcano-sedimentary (Lueta type), volcano-sedimentary + hydrothermal-metasomatic (Vlăhița type) and hydrothermal-metasomatic (Chirui type siliceous siderite deposit). Szakács (1988, unpubl. report) assumed a hydrothermal genesis for all types of siderite deposits in the Harghita and South Călimani Mts.

3. Sampling localities

Three siderite samples have been analysed for their stable isotope composition: sample V-1 Vlăhița-type sideritized clay, Tîrbuc brook, Băile Homorod (Harghita Mts); sample L-2 Lueta-type sideritized clay, Lueta mine (Harghita Mts); sample Ro-37 Vlăhița-type sideritized clay "soft pebble" from volcanoclastic deposit, Piriul Popii brook, Toplița (Călimani Mts). The marcasite samples are localised as follows: sample Fe-29 Vlăhița-type ore, borehole 733 Selters m. 232-235, Vlăhița; sample Fe-39, Lueta-type ore, Lueta mine; sample Fe-47, Lueta-type ore, borehole 25133 m. 522-524, Mădăraș.¹

4. Analytical method

Isotopic composition of Oxygen and Carbon has been analysed at the Departament of Isotopic Geochemistry of the Institute of Geochemistry - Academia Sinica - from Guiyang, People's Republic of China by the analysts Qiu Xiuhua and Liu Deping. After testing their mineralogical composition by X-ray diffractometry the samples have been chemically disaggregated by etching with H_3PO_4 100 % at 75° C for five hours. ^{18}O and ^{13}C have been measured using a MAT 230-C type mass-spectrometer yielding an instrumental error of 0.04 %. The obtained results are rendered as $\delta^{18}O$ (‰) and $\delta^{13}C$ (‰) values² according to the PDB International Standard. $\delta^{18}O$ is given according to the SMOW Standard as well.³

Sample processing and analytical method for Sulphur isotope analysis used at the Institute of Geology and Geophysics, Bucharest have already been published (Udubaș, Gaftoi, 1985). The analytical results are given as $\delta^{34}S$ (‰) according to the CDT International Standard.

¹The sample has been taken off from borehole core kept in the Lithoteque of the Institute of Geology and Geophysics with the contribution of dr. Mușat Gheorghian to whom we are grateful.

²The isotopic composition of an element X is rendered as δ_x representing the relative difference between isotopic ratios of the sample and that of the Standard, according to the formula:

$$\delta_x = \frac{R_{Sample} - R_{Standard}}{R_{Standard}} \times 10^3 \text{ (‰)},$$

where R is the isotopic ratio for sample and standard respectively.

³The transformation is made using the formula:

$$\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$$

5. Analytical results and discussion

5.1. Oxygen isotopes

A narrow range of ^{18}O in CO_2 of the three analysed siderite samples ($\delta^{18}O = -7.56$ to -9.16 ‰PDB) can be observed. This becomes obvious as compared with the wide variation field in different types of carbonatic rocks (+0.6 to +34 ‰, Degens, 1967) suggesting the formation of the discussed siderites under similar conditions of isotopic equilibrium, in similar thermodynamic conditions respectively.

In most natural media the isotopic equilibrium between aqueous solutions and minerals precipitating from them is reached for Oxygen and Hydrogen due to the high rates of their isotopic exchange reactions. Thus minerals usually preserve isotopic composition of the fluid at precipitation temperature (Ohmoto, 1986). For this reason Oxygen and Hydrogen isotopic composition is frequently used for water origin determination in mineralizing solutions. Since the great deal of hydrothermal solutions have been proved to be formed of meteoric water (Sheppard, 1986) and since Crăciun et al. (1989) reached the same conclusion for hydrogeothermal systems associated to the Neogene volcanic areas in Romania, the exogene origin of water in hydrothermal solutions from which the study siderites have been generated, can also be presumed. A simple calculation based upon experimental data concerning ^{18}O fractionation in the calcite-water system (O'Neil et al., 1969) points to the fact that our siderites could be in isotopic equilibrium with a water having $\delta^{18}O = +0.93$ ‰ at a temperature of 60° C. This value is consistent with the hypothesis of meteoric origin of water in the ore generating hydrotherms.

The higher $\delta^{18}O$ in geothermal systems as compared with unheated local meteoric waters - the so called "oxygen-shift" - is largely explained by heavy isotope enrichment as a result of reactions between geothermal waters and percolated crustal rocks. The higher ^{18}O content of our analysed siderites and their generating hydrotherms respectively - assuming isotopic equilibrium between them - with respect to that of waters from the actual geothermal systems of the areas (Crăciun et al., 1989) could be explained by the same mechanism.

The isotopic composition of Oxygen from siderites in base-metal hydrothermal veins at Rudnany (Slovakia) (-11.7‰ PDB) has been interpreted by Cambel et al. (1984) as indicating the magmatic origin of water in the generating hydrotherms.

The Oxygen isotopic geothermometer has been stated by Epstein et al. (1953, fide Sheppard, 1984) and it is widely used especially in sedimentary petrology. It has also been used in the study of thermal conditions of hydrothermal carbonate mineral genesis

(e. g. Cornides et al., 1966). Taking into account that Epstein's geothermometer has been calibrated for the calcite-water system, its use in our case would not be justified. There are, however, several favourable circumstances for such an attempt even only to test the consistency of the obtained thermic parameter, as order of magnitude, with that suggested by the paragenetic and mineralogical features of the siderite ore. The structural identity of siderite and calcite makes possible the use of the isotopic reaction constants of the latter as already has been done by other authors (Cambel et al., 1984, for instance). Furthermore, the high probability that an isotopic equilibrium state has been reached as suggested by chemical equilibrium inferred from mineralogical studies (Szakács, 1988, 1989, unpubl. reports), the mineralogical and chemical simplicity of the system and the recent age of the ore forming process (Szakács, 1988, unpubl. report) making improbable isotopic exchange reactions subsequent to ore deposition, are all in favour of the use of the isotopic thermometer.

Table 1 presents isotopic temperatures obtained for each sample using Epstein's equation:

$$T(^{\circ}\text{C}) = 16.5 - 4.3(\delta\text{c} - \delta\text{w}) + 0.14(\delta\text{c} - \delta\text{w})^2 \quad (1)$$

where $\delta\text{w} \sim 0$. The obtained values of about 60°C (61.24°C in average) are in agreement with both the thermal domain suggested by the mineral paragenesis (siderite + marcasite + opal) and the mineralogical features of siderite (Szakács, 1988, unpubl. report). They are also consistent with regional thermal features in the occurrence areas, as reflected in heat-flow anomalies (Veliciu, 1988).

abundance of ^{13}C in the mantle (ca. -5‰ in average) (Ohmoto, 1986) points to a high participation of the heavy Carbon isotope in the Vlăhița siderites exceeding the common values of carbonate rocks.

Carbon, unlike Hydrogen and Oxygen but like Sulphur, tends to preserve its initial isotopic composition during precipitation process of minerals from solutions because the low rate of the isotopic exchange reactions at low temperatures that usually makes impossible isotopic equilibrium to be reached (Ohmoto, 1986). Thus, $\delta^{13}\text{C}$ data are interpreted rather in terms of Carbon (CO_2) source than in terms of thermodynamic and chemical conditions of precipitation. Consequently, a possible explanation for high ^{13}C content of Harghita siderites has to be looked for in connection with CO_2 source.

Using published data, Degens (1967, Fig. 2) presented a sketch showing ^{13}C fractionation in carbonatic systems from different natural media. In order to explain ^{13}C enrichment in travertines the origin of CO_2 by thermal decomposition of marine limestones has been admitted. The increase of ^{13}C content takes place during CO_2 dissolution in thermal water, the precipitated carbonate from these solutions having $\delta^{13}\text{C}$ of ca. $+7 - +8\text{‰}$. Such a hypothesis is worth considering for the CO_2 origin in the Harghita siderites as well.

Considering $\delta^{13}\text{C}$ data Crăciun et al. (1989) presumed Carbon origin in thermal waters of the Pannonian Plain in carbonate deposits. They also assign the isotopic values obtained for free CO_2 on the Tușnad and Poiana Coșnei mineral waters ($\delta^{13}\text{C} = -2.9 - -5.2$

Table 1
Isotopic composition of oxygen and carbon from siderites

No	Sample	Siderite %	$\delta^{18}\text{O} \text{ ‰ PDB}$	$\delta^{18}\text{S} \text{ ‰ SMOW}$	$\delta^{13}\text{C} \text{ ‰ PDB}$	$t(^{\circ}\text{C})$
1	RO-37	95	-9.16 ± 0.2	21.42	-0.18 ± 0.2	67.63
2	L-2	90	-7.88 ± 0.2	22.74	$+4.27 \pm 0.2$	59.07
3	V-1	90	-7.56 ± 0.2	23.07	$+6.81 \pm 0.2$	57.01
	Average		-8.20	22.41		61.24

5. 2. Carbon isotopes

The two samples from the Harghita Mts. present close positive $\delta^{13}\text{C}$ values whereas that from Toplița shows a low negative value with respect the PDB Standard (Tab. 1). The comparison of these results with the isotopic composition of Carbon in various natural media (ca. -7‰ for atmospheric CO_2 , -2 to 4‰ for marine limestones, -22‰ in average for organic Carbon in marine environment and -26‰ for organic Carbon in terrestrial environment) or with the inferred

‰) either to the "probably thermal transformation" of certain carbonatic formations or to mixing processes between CO_2 originating in carbonatic rocks with juvenile CO_2 in proportion of 3/1 (p. 35).

The isotopic composition of Carbon in siderites of hydrothermal veins at Rudnany (Slovakia) with an average $\delta^{13}\text{C} = -4.2 \text{‰}$ is interpreted by Cambel et al. (1984) as indicating the mixing of 2/3 deep-seated Carbon (with $\delta^{13}\text{C} = -6.5 \text{‰}$) and 1/3 sedimentary carbon (with $\delta^{13}\text{C} = 0 \div +1 \text{‰}$).

The value of $\delta^{13}\text{C} = -0.18 \text{‰}$ obtained for the Toplița siderite sample is clearly influenced by the organic Car-

⁴ δc and δw represent the isotopic composition of Oxygen from carbonate and water respectively.

bon pointed out in the composition of the initial sideritized clay (Szakács, 1988, unpubl. report).

5. 3. Sulphur isotopes

Two of the analysed marcasite samples present positive $\delta^{34}\text{S}$ values (+2.32‰ and 1.54‰) close to the CDT Standard. The third sample shows a higher positive value (+10.76‰) (Tab. 2).

Table 2

Isotopic composition of sulfur from marcasite samples

No	Sample no.	$\delta^{34}\text{S}$ ‰ CDT	$^{32}\text{S}/^{34}\text{S}$
1	Fe-29	+1.54	22.186
2	Fe-30	+2.32	22.169
3	Fe-47	+10.67	21.983

A value of $\delta^{34}\text{S} = -3.60$ ‰ has been measured earlier for a marcasite sample occurring within a siderite occurrence hosted in a fault clay localised in metamorphic formations near Frumoasa (Ciuc Mts) (Runceanu, Voicu, 1988). This outcrop is considered to be genetically linked with the nearby Harghita Neogene volcanism (Runceanu, Voicu, 1988).

Udubaşa and Gaftoi (1985) presented Sulphur isotopic data for numerous hypogene Neogene ore sulphide deposits from Metaliferi Mts. According to these data $\delta^{34}\text{S}$ varies from +1.46 to +3.60‰ in pyrites, +0.25 to +4.43‰ in sphalerites and -1.52 to +2.32‰ in galenas. The $\delta^{34}\text{S}$ values for the Lueta-Vlăhiţa marcasites are placed in the variation domain of pyrites from the Neogene hydrothermal ores in the Metaliferi Mts. The marcasite from Mădăraş displays higher ^{34}S content.

Genetical interpretation possibilities of our analytical results are strongly limited by the lack of information concerning ^{34}S distribution in several associated sulphidic and/or sulphatic phases. The low $\delta^{34}\text{S}$ values close to the Standard are usually considered to be consistent with the magmatic origin of Sulphur. Although our Sulphur isotope analyses on marcasite samples from the Harghita Mts are not contrary to a deep-seated (magmatic) origin, other interpretations can also be taken into account, especially if we consider the probable non-magmatic origin of Carbon in siderites as suggested by Carbon isotopic data. Cambel et al. (1984) for instance explained the $\delta^{34}\text{S}$ range (-2.0 - +2.5‰) measured in pyrites in siderite gangue of the hydrothermal ores at Rudnany (Slovakia) by the deep-seated origin of Sulphur; the high values (+4.5 to +12‰) obtained for pyrites in the main ore body are assigned to a possible filtration process of the hydrothermal solutions through sulphate bearing Paleozoic rocks. The influence of a sulphate phase during the generation and movement of ferriferous hy-

drotherms is not out of question in the Harghita Mts, at Mădăraş especially.

Further detailed isotopic investigations involving larger number of samples, both carbonates and sulphides, would provide more accuracy in genetic studies of siderite deposits associated to the Neogene volcanism in the East Carpathians.

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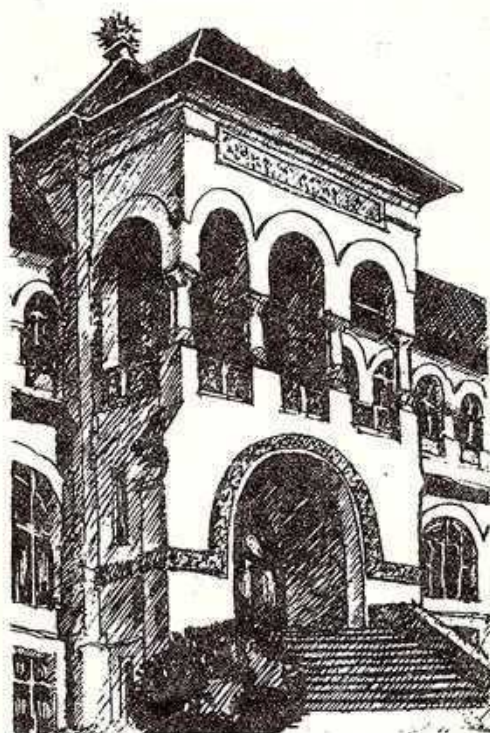
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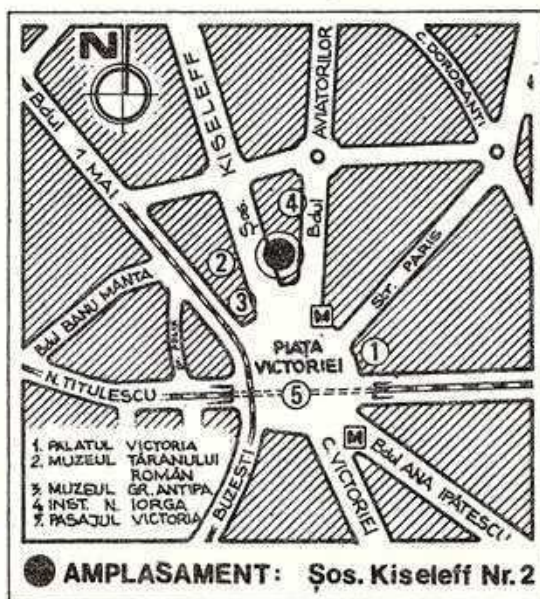
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METASOMATITE OCCURRENCES IN THE UPPER BASIN OF THE MRACONIA VALLEY (ALMĂJ MTS.) AND THE SUPERPOSED MINERALIZATION

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Key words: Mineralization. Skarn. Metasomatism. Optical mineralogy. Infrared spectra. X-Ray data. Lithologic control. Structural control. South Carpathians - Almăj Mts.

Abstract: *Metasomatite occurrences in the upper basin of the Mraconia Valley (Almăj Mts.) and the superposed mineralisation.* The mineral parageneses identified in the calcic metasomatites from the upper basin of the Mraconia Valley account for a pyrometamorphic evolution followed by a hydrometamorphic one; thus the rocks were defined as pseudoskarns. A mineralization of hypo-mesothermal temperature, genetically related to granodioritic intrusions, which generated the mentioned thermal and metasomatic contact phenomena is spatially superposed. A tectonic control of the ore mineral location as well as some recurrence and rejuvenation phenomena have been pointed out. The P-T conditions estimated for the Mraconia pseudoskarns are compatible with a "classical" evolutionary model hinting at decrease of temperature under a varying pressure of the fluid phase.

1. Introduction

In the upper basin of the Mraconia Valley, north of its confluence with the Neamțului Valley, metasomatite occurrences of limited areal extent have been identified (Vlad et al., 1984) and investigated by mining works, in the contact area between some granite-granodiorite dykes of uncertain age (Gunnesh, Gunnesh, 1977, Vlad et al., 1984) and crystalline limestones and calcschists of the Corbu Series (Codarcea, 1940).

The Mraconia metasomatites are represented by pseudoskarns as defined by Korzhinskii (1965), with hydrothermal reaction minerals superposed on the primary skarn paragenesis. Their presence both in the thermal contact aureole of igneous bodies and in areas with no obvious contact between granitoids and crystalline limestones, suggests a tectonic controlled afflux of pneumatolytic and hydrothermal fluids.

Therefore the practically monomineral character of the paleosome (92-96 % carbonates containing 4-8 % quartz, muscovite, chlorite and opaque minerals as isolated crystalloblasts) account for the relatively poor mineral parageneses of the primary Mraconia metasomatites. Calcite is the only carbonate phase in the mentioned limestones, as it was pointed out by differential thermal analysis. The calcic character of the Mraconia metasomatites was obviously determined by the mentioned facts.

2. Pseudoskarn Mineralogy

Garnet occurs as a relict mineral of the initial pneumatolytic stage. It is frequently substituted by late pyrometamorphic minerals (i.e. vesuvianite) or by hydrothermal minerals such as pistacite, clinozoisite, calcite, quartz, albite. The microscopic study points out the following characteristic features:

a) Garnet are commonly "cataclased";
b) Two fissure systems may be recognized: a "primary" system affecting garnet crystals with rhomboidal dodecahedron (110) and cubic trapezohedron (211) faces, usually filled by calcite and epidote; and a "secondary" system extended in the whole groundmass of the metasomatites. Calcite, quartz with typical "en flammes" extinction, pennine and hematite are frequently disposed on this system.

c) Optical anomalous garnets are scarce. They show sectorial ("sector twinning"), concentric-lamellar ("polysynthetic lamellae") or mixed anomalies but most of the Mraconia grandites are isotropic. Sectorial anomalous garnet exhibiting isotropic nucleus and extremely anisotropic sectors ("garnet type V" sensu Zimmernink, 1985) occurs locally. Their distribution seems to be controlled by some paleofractures or areas of pressure discharge which favoured the development of a late grandite generation. In garnets showing concentric - lamellar anomalies (Pl. I, Fig. 1) an

evolution of the crystal habit from rhombic dodecahedron – the typical high temperature form (Kalinin, 1966 fide Vlad, 1974) – to cubic trapezohedron – the stable form at low temperatures is obvious. The optical anomalous garnet may be assigned to a late, low temperature generation as it is suggested by heating experiments showing that birefringent crystals invert at about 800–860°C to strictly isotropic ones (Kozu et al., 1940; Zimmernink, 1985).

characterizes andraditic terms. Pyralspitic moles are in reduced amounts, below the limit of the grandites–pyralspites miscibility gap on Boeck's (1914) diagram (Fig. 1). Occurrences of andraditic garnet have been previously mentioned in Mraconia metasomatites (Vlad et al., 1984). The relatively high TiO_2 content of some samples, but with lower values than in melanitic and schorlomic varieties (Moore, White, 1971) accounts for their specific optical behaviour: dark brown

Table 1
Wet-chemical Analyses of Grandites (in wt %)

Sample no.	3(1)	25(b)(2)	30(3)	832(4)	846(5)
SiO_2	33.75	35.84	36.01	37.67	42.89
TiO_2	0.17		0.86	0.18	0.84
Al_2O_3	1.89	4.00	2.89	1.35	2.00
Fe_2O_3	23.58	22.74	26.71	28.92	24.82
FeO	0.65	1.98	0.49	0.24	0.91
MnO	2.00	0.17	0.65	0.55	0.61
MgO	0.07	1.40	0.27	0.07	0.07
CaO	32.30	29.61	31.68	30.46	28.32
K_2O		2.30	0.23	0.02	0.04
Na_2O	0.14	1.14	0.12	0.03	0.05
P_2O_5^*	0.03				0.01
CO_2^*	5.58				
H_2O^+	0.37		0.03	0.02	0.06
Total		99.18	99.94	99.51	100.12
Cation Based on 24 Oxygens					
Si^{4+}	6.3142	6.0319	5.9917	6.2716	6.8564
$\text{Al}^{3+(IV)}$			0.0083		
$\text{Al}^{3+(VI)}$	0.4167	0.7934	0.5584	0.2649	0.3768
Ti^{4+}	0.0239		0.1076	0.0225	0.1010
Fe^{3+}	3.3197	2.8799	3.3443	3.6231	2.9857
Fe^{2+}	0.1017	0.2787	0.0682	0.0334	0.0548
Mn^{2+}	0.3169	0.0242	0.0916	0.0776	0.0826
Mg^{2+}	0.0195	0.3512	0.0670	0.0174	0.0167
Ca^{2+}	5.0255	5.3393	5.6477	5.4334	4.8438
K^+		0.4938	0.0488	0.0042	0.0082
Na^+	0.0508	0.3720	0.0387	0.0097	0.0155
O^{2-}	23.5398	24.0000	23.9667	23.9778	23.9365
$(\text{OH})^-$	0.4602		0.0333	0.0222	0.0635
grossularite	3.06	10.69	10.06	4.47	7.80
andradite	88.92	78.40	86.08	93.23	89.12
pyrope	0.36	5.86	1.14	0.31	0.33
almandine	1.86	4.65	1.16	0.60	1.10
spessartite	5.80	0.40	1.56	1.39	1.65

* P_2O_5 was eliminated as hydroxyl – apatite with stoichiometric formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ and CO_2 as CaCO_3 .

d) Some anisotropic lamellae in concentric-lamellar anomalies are substituted by calcite and quartz arranged according to (211) or (110) planes. Lamellar pseudomorph zones resulted, alternating with isotropic garnet lamellae (Pl. I, Fig. 2).

Wet-chemical analyses of four Mraconia garnets (Tab. 1) reveal an end-members participation which

megascopic colour and brown-yellowish hue in thin section.

Cell parameter refinements, based on X-ray powder data (Tab. 2) show lower values than those reported by Huckenholz and Yoder (1971) for the andraditic end-member ($a=12.056\pm0.003$ Å). This may be explained by the pyralspite content, which determine obvious de-

crease of the cell parameter in granditic solid solution (Constantinescu, 1980).

1971; Vlad, 1974) and a ferrogrossularite spectrum (Dimanche, 1969), due to isomorphic substitutions in

Table 2
Powder Diffraction Data for some Mraconia Grandites*

Nr. crt.	25b		233		30		832		846		25a		(hkl)
	d/n (Å)	I/I ₀	d/n (Å)	I/I ₀	d/n (Å)	I/I ₀	d/n (Å)	I/I ₀	d/n (Å)	I/I ₀	d/n (Å)	I/I ₀	
1	4.255	8	4.25	11	4.255	18	4.234	20	4.24	25	4.253	14	(220)
2	3.01	35	3.015	50	3.005	70	3.00	70	3.013	95	3.00	60	(400)
3	2.69	100	2.695	100	2.687	100	2.68	100	2.686	100	2.682	100	(420)
4	2.569	7	2.568	10	2.563	11	2.56	10	2.561	10	2.560	8	(332)
5	2.455	45	2.456	50	2.453	60	2.451	50	2.451	65	2.442	45	(422)
6	2.359	16	2.36	14	2.357	18	2.352	18	2.35	17	2.344	12	(431)
7	2.196	12	2.198	13	2.196	16	2.193	14	2.19	14	2.187	12	(521)
8	1.953	18	1.951	25	1.950	20	1.948	20	1.948	25	1.941	17	(611)
9	1.906	10	1.906	10	1.901	15	1.900	10	1.902	20	1.898	8	(620)
10	1.738	7	1.738	10	1.735	7	1.734	8	1.733	10	1.732	7	(444)
11	1.672	14	1.670	20	1.667	16	1.667	20	1.667	25	1.661	15	(640)
12	1.609	35	1.607	50	1.607	50	1.605	80	1.605	65	1.601	30	(642)
13	1.507	10	1.505	9	1.503	7	1.502	13	1.501	13	1.503	7	(800)
14	1.346	10	1.346	15	1.343	10	1.342	12	1.342	15	1.334	7	(840)
15	1.314	12	1.314	12	1.312	12	1.311	10	1.310	11	1.304	6	(842)
16	1.283	9	1.283	6	1.281	7	1.280	8	1.280	7	1.277	8	(664)
a ₀ (Å)	12.0406 Å		12.0411 Å		12.0213 Å		12.0058 Å		12.0097 Å		11.9839 Å		

* CuK α , $\lambda = 1.5418$ Å, analyst C. Cristea, IGG

Samples location: 25b, m 9, 14/9 Tr.; 233, m 45, 1/12 Tr.; 30, m 23, 30/7 Tr.; 832 and 836, Mraconia waste.

Samples 25b, 233, 30, 832, 846: andradites; sample 25a: hydrogarnet (?)

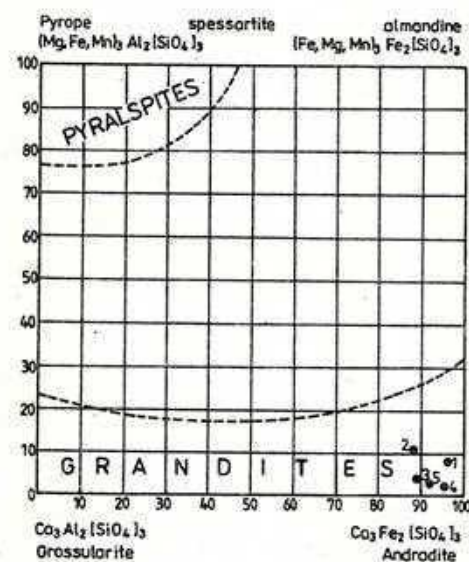


Fig. 1 - Plot of the Mraconia grandites in the Boeck diagram.
(percentage values of end-members moles %):
2-5, personal analyses; 1, acc. to Vlad et al. (1984).

IR absorption spectra recorded for three Mraconia andradites in the frequency range between 400-1300 cm^{-1} show some peculiarities by comparison to others andradites spectra (Moore et al. 1971; Moore, White,

sixfold coordinated cations position (Fig. 2, Tab. 3).

The occurrence of *hydrogarnet* in the Mraconia metasomatites was supposed due to an obvious "doubling" of the characteristic andradite peaks in X-ray powder patterns. For sample no. 25 refined cell-parameters correspond to an andraditic member with $a=12.0406$ Å and to an another garnet with $a=11.9839$ Å, which may represent a hydrogarnet (Ito and Arem, 1970 described synthetic hydrogrossularite with $a=11.92$ Å) (Tab. 2). The infrared absorption study of this sample, within the frequency range of 3000-4000 cm^{-1} , pointed to a single absorption band, around the 3420 cm^{-1} value (Fig. 3). This band is due to stretching vibrations of a virtually free hydroxyl group, showing a different character by comparison to the bands obtained for a Bushveld hydrogarnet (Dimanche, 1969). The just mentioned things make us feel unconfident on the hydrogarnet occurrence at Mraconia.

Vesuvianite occurs as a late hypothermal product in the Mraconia metasomatites. Crystalloblasts with anhedral, amoeba-like contours, of low but not anomalous birefringence, penetrate as inlets into the garnet groundmass. These morphologic features suggest the formation of vesuvianite at the expense of hydrogarnet. The garnet-vesuvianite boundary is marked by a reaction zone where the vesuvianite birefringence considerably increase. This fact is probably due to a Fe-enrichment of vesuvianite, as supposed by Constantinescu (1980).

Table 3
Position of Absorption Bands for Grandite Samples within the 400–1000 cm^{-1} Frequency Range

No.	Location	Mineral (variety)	Position of bands (cm^{-1})										
1 ¹	Dognecea	Andradite (90.3%)	433		476	507	587			810	830	886	925
2 ²	Ginevro (Elba)	Ferrogrossularite (77.8% Gr; 15.6% Al)		455	475	545	619			850	863	918	925
3 ³		Andradite (An 93)	438		438	510	589			811	831	888	929
4 ³		Titaniferous andradite	435		477	513	589	670	734	810	826	866	924
5 ⁴	Mraconia V.	Andradite*	430	450	470	520	600			800		915	
6 ⁵	Mraconia V.	Andradite**	430	460	480	530	605	605			830	910	
7 ⁶	Mraconia V.	Andradite**	435		482	516	595				825	900	930

1, Vlad (1974); 2, Dimanche (1969); 3, Moore et al. (1971); 4, Sample 25; 5, Sample 233; 6, Sample 30

* analyst C. Crăciun; ** analyst T. Drăghiciu.

Vesuvianite idiomorphs of short prismatic habit (Pl. I, Fig. 3) or sheaf-like vesuvianite aggregates have been observed locally. In both cases a sporadically recognised relict cleavage along the vesuvianite prism face suggests vesuvianite pseudomorphs after wollastonite.

Minerals of the *epidote group* occur in important amounts in the Mraconia pseudoskarns. They either substitute garnet in microcrystalline aggregates of "manteau d'arlecquin" type, in association with chlorite, calcite, quartz and hematite, or develop independently, in proper epidotites. Varieties of pistacite (yellow-greenish to yellow pleochroism, extinction angle $\alpha : n_g = 25-27^\circ$, optically positive) and clinozoisite (colourless to light yellow pleochroism, extinction angle $\alpha : n_g = 14-21^\circ$, optically negative) locally coexist in aggregates where clinozoisite relicts are surrounded by a pistacite groundmass.

Apatite is constantly present in the Mraconia metasomatites. Occurrences in metasomatic contact areas have also been reported (e.g. in the Moldova Nouă skarns; Gheorghiu, 1975). Its crystal morphology is characterized by anhedral, "corroded" amoeba-like contours, which suggests a hydrothermal transport, a process similar to the one described by Williams and Cesbron (1977).

Actinolite typically occurs as pseudomorphs after calcic pyroxene. It is represented by a member of the tremolite-ferroactinolite group with extinction angle $\alpha : n_g = 13-15^\circ$, very slightly pleochroic in yellow green shades after Ng-light yellow after Np. Long prismatic amphibole crystals develop as pseudomorph aggregates after calcic pyroxene, somewhere being accompanied by quartz (which it corrodes in places), calcite, minerals of the epidote group and chlorite. In some cases this mineral assemblage surround *diopside* relicts (with extinction angle $\alpha : n_g = 41-43^\circ$ and $(+)2V =$

$58-60^\circ$).

Chlorite occurs either as an alteration product of the garnet and diopside (in complex pseudomorph zones) or as precipitate from late hydrothermal solutions. Pennine with lamellar habit, sometimes forming radial aggregates, was observed in both cases. It is optically negative, with a small $2V$ angle, exhibits anomalous birefringence with brown and indigo interference colours as well as a strong pleochroism in blue green (after Ng) – light green (after Np) shades.

Wollastonite was only locally observed in the Mraconia metasomatites, as small relicts in a groundmass of quartz + calcite that presumably represent a product of its supergene alteration. But wollastonite has been probably more abundant as it is suggested by "wollastonite shadows", consisting in optically continuous quartz with linalite included calcite, crystallographically oriented along the (100) planes of the host wollastonite.

A "clear" *orthose* (with extinction angle $Np : (001) = 6^\circ$) scarcely occurs in the Mraconia metasomatites within a mineral assemblage which characterise an apogranitic periskarn: garnet + sericitized alkali feldspar. This occurrence suggests the superposition on the periskarn zone of some minerals assumables to a granitoid alteration halo, which can be related to the "potassic facies" model of Lowell, Guilbert (1970) or to the "phyllitic facies, biotitic type" of Burnham (1962) model.

3. Mineralization

Disseminated (impregnation) ores hosted by the Mraconia metasomatites are related to some pseudoveins resulting in a "fossil" fracture system. The mineral assemblage in the mineralized zones consist

of scheelite, magnetite, hematite, pyrite, pyrrhotite, chalcopyrite, galena, sphalerite, molybdenite and tetraedrite.

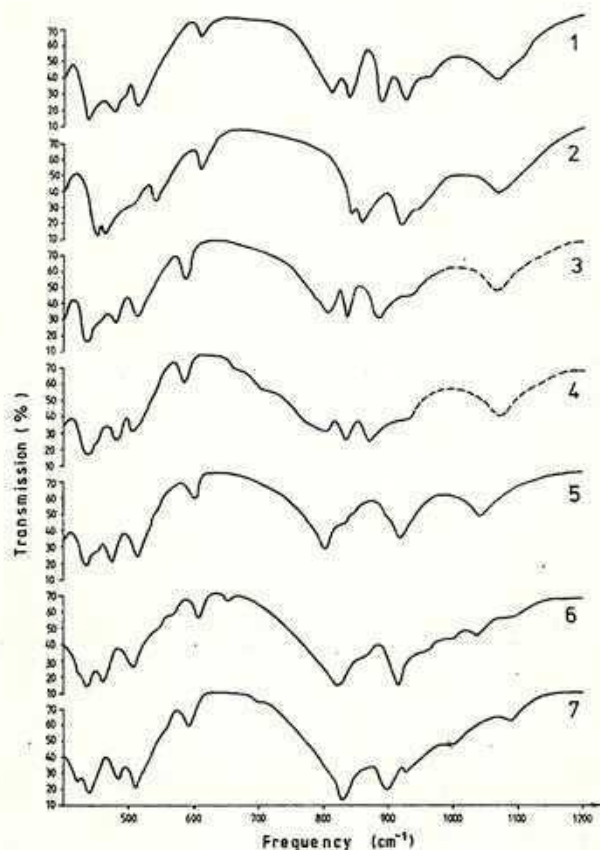


Fig. 2 - Infrared absorption spectra of some garnets, recorded within the 400-1300 cm^{-1} frequency range: 1, andradite (Vlad, 1974); 2, ferrogrossularite (Dimanche, 1969); 3, andradite (Moore, White, 1971); 4, titaniferous andradite (Moore, White, 1971); 5, Mraconia andradite (Sample 25); 6, Mraconia andradite (sample 233); 7, Mraconia andradite (sample 30).

Scheelite occurs frequently as submillimetric crystals of short prismatic habit and idiomorphic contours. Investigations with ultraviolet rays ($\lambda = 254$ nm wavelength) points out the presence of two scheelite generations:

- an early generation, showing yellow luminiscence, which points to molybdoscheelite (Vlad et al., 1984) is exclusively associated with andradite. Crystals of this generation occurs sometimes in partial pseudomorphs after garnet (Pl. I, Fig. 4).
- a late generation, with blue-violeous luminiscence occurs in a quartz-sulphides-carbonates association (Pl. I, Fig. 5).

Hematite shows morphological features which indicate two different geneses:

- oligiste with tabular habit, associated with magnetite and andradite, frequently occurs as inclusions

in the pyrite or chalcopyrite groundmass. Its muskovitisation has a typical character, due to magnetite advancing along lamellar twin planes (0112). Complete magnetite pseudomorphs after oligiste have been frequently observed (Pl. II, Fig. 1).

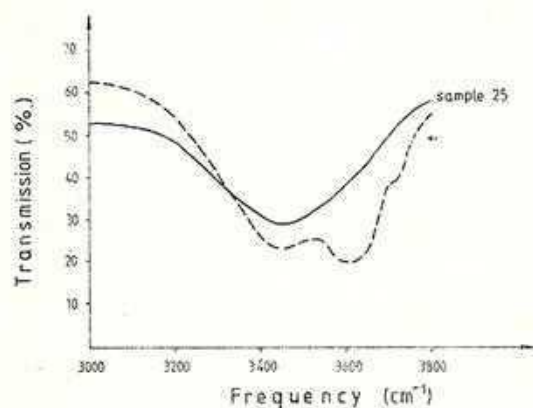


Fig. 3 - Infrared absorption bands of a Bushveld hydrogarnet - OH stretching vibrations - (Dimanche, 1969) compared to a Mraconia garnet (sample 30).

- specularite occurs in secondary mineral associations. Sometimes rosette-like specularite aggregates (Pl. II, Fig. 2) are superposed on hydrothermal alteration areas (with quartz, calcite, pennine). Commonly fine hematite plates are disposed on "secondary" fissures in andradite.

Magnetite frequently forms complete pseudomorphs after oligiste as it was mentioned. Excepting pyrite II, magnetite shows the strongest idiomorphism tendency, octahedral crystals being frequently observed. Besides the magnetite + oligiste assemblage, magnetite + pyrite I and magnetite + chalcopyrite assemblages are developed. Some times the magnetite crystals show an allotriomorphic contour due to corrosion by the mentioned sulphides (Pl. II, Fig. 1).

Pyrite is the most widespread mineral in metallic mineral associations. It shows morphologic features which suggest at least two generations:

- pyrite I is characterized by allotriomorphic or hypidiomorphic contours. It is frequently engulfed by chalcopyrite, quartz, carbonates, galena, tetraedrite or sphalerite, which commonly border it. All these minerals penetrate along the fissures which affect the pyrite I groundmass (Pl. II, Fig. 4). Pyrite I seems to be disposed along a fossil fracture system on which mineralised veins were formed in the skarn areas.

- pyrite II is characterized by idiomorphic, only seldom hypidiomorphic contours. Mostly cubic crystals have been identified. It occurs as disseminations in the

granitoid, metasomatites or in crystalline limestones, being probably the result of a late pyritisation process.

Pyrrhotite occurs in minor amounts in the mineralised zones. Extremely small pyrrhotite inclusions have been observed in magnetite, as well as in pyrite I.

Molybdenite occurs in a typical "quartz and molybdenum" association, developed in anastomosed and highly fasciculated quartz veinlets, mostly disposed nearby the contact between granitoids and the Corbu crystalline. Molybdenite impregnations in granitoids and metasomatites, commonly associated with quartz and "clear" K-feldspar (Gunnesch, Gunnesch, 1977), occur only scarcely. In both mentioned situations lamellar molybdenite crystals usually form sheaves-like, rosette-like or scaly aggregates (Pl. II, Fig. 5) in which the mineral is mechanically translated (slightly bended). Molybdenite aggregates moulding pyrite crystals suggests a molybdenite-pyrite I crystallisation sequence. Due to the absence of direct relationships with the other sulphides it is not possible to recognise the exact position of molybdenite in the general deposition sequence of minerals. The relatively high rhenium contents in molybdenite (50-75 ppm, determined by high-resolution gamma spectrometry; I. Tiepac, personal communication) indicate however a high crystallisation temperature.

Chalcopyrite morphology also suggest two possible generations of different genesis:

- chalcopyrite I (a high temperature generation ?) occurs as finely exolved tear-like inclusions on (111) twin planes of sphalerite. According to Betehtin (1953) such exsolution process need temperatures of 350-400°C.

- chalcopyrite II occurs as disseminations in metasomatites or granitoids, where it is always associated with ilmenite. Massive aggregates of chalcopyrite II enclose pyrite I, oligiste, magnetite, sphalerite and penetrate along fissures in the pyrite I groundmass. It exhibits allotriomorphic contours and is locally bordered by calcosine. Generally the aspects of chalcopyrite II point to a late remobilisation of chalcopyrite I.

Sphalerite usually occurs in association with galena, (centripetally engulfed, by advancing along (111) twin planes) or with chalcopyrite and pyrite I. Polysynthetic twin planes (easily pointed out by chemical attack) are frequently delimited by linear chalcopyrite I exolutions. Morphological features show that the chalcopyrite II inclusions in sphalerite are not oriented intergrowths within the high temperature range as defined by Ramdohr, 1969, but they are of exsolution origin (Pl. II, Fig. 6).

Galena seems to be a late product in the crystallisation sequence of sulphides. It frequently enclose chal-

copyrite II, sphalerite with chalcopyrite I exolutions, pyrite I (Pl. II, Fig. 3) tetrahedrite and even carbonate metacrystals with rhombohedral habit. The characteristic "dull" lustre of the Mraconia galena is correlatable with its relatively high Ag (240-900 ppm), Bi (6-90 ppm) and Sb (270-1000 ppm) contents.¹

Tetrahedrite. Relation with galena suggest a synchronous crystallisation. Both minerals engulfed magnetite, sphalerite, chalcopyrite II and pyrite I. A striking feature of the tetrahedrite are olive hues superposed on his characteristic grey microscopic colour, indicating a stibian member of the tetrahedrite-tennantite series.

Remarks on Thermo-baric Evolution and of the Geochemical Environment of the Mraconia Pyrrhotite-metasomatites and Hydrometasomatites

It is difficult to specify the thermodynamics of pyro- and hydrometamorphic evolution of the Mraconia pseudoskarns due to the fact that the depth at which the igneous bodies were intruded and implicitly the thermobaric environment of the initial thermal metamorphism and metasomatism can not be accurately determined. The mineral parageneses correlated with some experimental topologies lead to an evolutionary model comparable to the classical one proposed by Korzhinskii (1965). The presence in endocontact assemblages (endoskarns and apogranitoid periskarns) of some minerals which characterize the hydrothermal alteration halo of granitoids, might be due to a spatial superposition caused by telescoping phenomena. Mutual relationships between minerals of such alteration halos and the minerals of the hydrometamorphic stage in pseudoskarns allowed a comparison between intra- and extramagmatic retrograde evolution.

There are several successive stages in the evolution of metasomatites in respect with the continuous temperature decrease subsequently to the emplacement of the magmatites.

A. Pneumatolytic Stage

The maximum temperature admitted for the reactions in this stage is of ca. 750°C (the granodioritic magma temperature at P=1 kb, according to Turner, Verhoogen, 1963). The temperature was however lower than that delimited by the tremolite out-enstatite in curve (Schreyer, 1976) (Fig. 4). Based on mutual relationships between minerals, it may be accepted that the evolution during the pneumatolytic stage took place in the P-T conditions within the wollastonite + grossularite in - vesuvianite out (Ito, Arem, 1970) and the calcite + quartz out - wollastonite in (Schreyer,

¹Analyst Ana Șerbănescu, IGG. The contents was determined by emission spectrometry.

1976) curves (Fig. 4). These P-T conditions generally correspond to those of the pyroxene hornfels facies (Winkler, 1967). Any reaction which take place at temperatures and pressures between these curves and which state the stability of a metasomatic phase is possible. These reactions are influenced by the pressure of volatile phases, the presence and mobility of cation supply, the mole fractions of CO_2 , H_2O and other volatile phases etc. This multiple interdependence imposes a thermal model to be adopted, which follows a temperature decrease under varying pressure conditions.

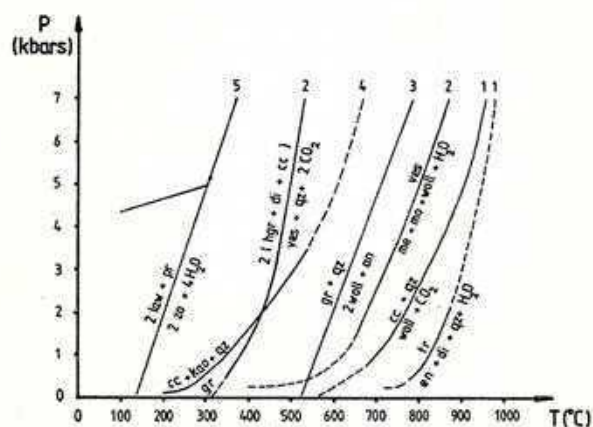


Fig. 4 - P-T stability field of the main minerals involved in metasomatic processes (according to experimental data).

1, acc. to Schreyer (1976); 2, acc. to Ito, Arem (1970); 3, acc. to Miyashiro (1975); 4, acc. to Burnham (1962); 5, acc. to Strens (1965). law=lawsonite; pr=prehnite; zo=zoisite; cc=calcite; kao=kaolinite; qz=quartz; gr=grossularite; hgr=hydrogarnet; di=diopside; ves=vesuvianite; woll=wollastonite; an=anorthite; me=melilite; mo=monticellite; tr=tremolite; en=enstatite.

The prograde crystallisation sequence of the pneumatolytic stage minerals is calcic pyroxene-grandite I (isotropic)-wollastonite, identical with that one described by Seki, 1961, fide Miyashiro, 1975 in calcic hornfels.

The high Fe^{+3} content in andradites, ($\text{Fe}_2\text{O}_3/\text{FeO}$ ratio between 11.46 and 120.50) accounts for an alkaline sindepositional pH and for a positive Eh (Zharikov, 1966), which characterize the "early alkaline stage" as defined by Korzhinskii (1965).

B. Hypothermal stage

The P-T limits which define this stage in the evolution of the Mraconia metasomatites can be approximate by the curves hydrogarnet out-vesuvianite in and vesuvianite out-wollastonite in (Ito, Arem, 1970) in Fig. 4. The temperature in this range generally

correspond to the amphibole hornfels facies (Winkler, 1967). The characteristic paragenesis for this stage includes vesuvianite + grandite II (anisotropic) + diopside. Like in calcic hornfels (Seki, 1961 fide Miyashiro, 1975) the occurrence of wollastonite seems to be conditioned by the local decrease of carbon dioxide pressure. The crystallisation of the clinozoisite + pistacite assemblage, stable at temperatures lower than 550°C (Strens, 1965) (Fig. 5), also may be assumed to this stage. It points to an increase of the $\text{Fe}^{+3}/\text{Al}^{+3}$ ratio, prior to hematite crystallisation. The assignment to this stage of the end of apatite migration, based on its relations with the epidote group minerals, agrees with the assumptions of Williams and Cesbron (1977) that the mineral migration is early started in the hydrothermal system.

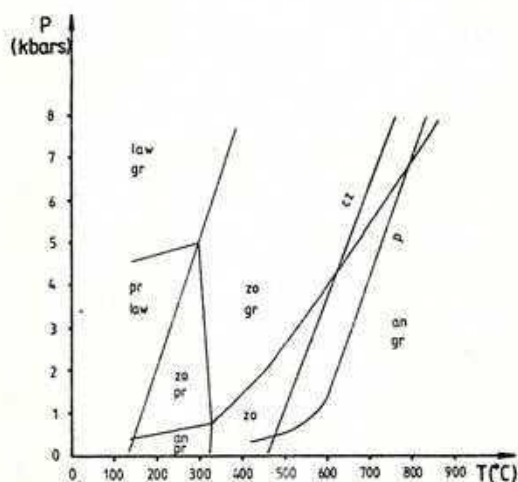


Fig. 5 - P-T stability field of the main epidote group minerals (acc. to Strens, 1965) an=anorthite, gr=grossularite; zo=zoisite; cz=clinozoisite; p=pistacite; law=lawsonite, pr=prehnite.

A W and Mo supply in high oxygen fugacity conditions allows the crystallisation of scheelite I (molybdenoscheelite). Its presence, as well as the abundant occurrence of hematite and vesuvianite (vesuvianite crystallisation being compatible with low alkaline solutions; Kosals, 1968 fide Vlad, 1974) point to an oxidizing (Eh) and alkaline (pH) environment. The initial oxidizing character is obviously reduced by reactions between fluids and the Corbu limestones, leading to musketovitization of hematite.

C. Mesothermal stage ("subsequent stage" Korzhinskii, 1965).

To this stage corresponds a P-T interval between the curves lawsonite + prehnite out-zoisite in Strens, 1965) and hydrogarnet out-vesuvianite in (Ito, Arem,

1970) (Fig. 4). The mentioned thermal range generally corresponds to the conditions of the epidote hornfels facies (Winkler, 1967). During this stage in the evolution of the metasomatic system mineral assemblages of the pseudoskarns were formed. The characteristic paragenese includes hydrogarnet (?) actinolite, pistacite, pennine. The replacement of hydrogarnet by vesuvianite can be normally regarded as a prograde transformation, but it is also compatible with a pressure decrease under isothermal conditions. Thus a retrograde hydrogarnet-vesuvianite sequence in the Mraconia metasomatites may be satisfactorily explained by a relevant decrease in fluid pressure (mainly in CO₂ pressure), do to a possible activation of some fractures.

To this stage may be assigned also some transformations in granitoids, where minerals of the hydrothermal alteration halo, assignable to the biotitic type of the phyllic facies ("clear" orthose + quartz I) and to the propylitic and sericitic types of argillic facies (epidote + chlorite + calcite + quartz II + albite + actinolite and sericite + quartz III) (Burnham, 1962), crystallized. These parageneses integrally or partly occur in hydrometasomatites, pointing out the synchronous evolution of the subsequent intra- and extramagmatic transformations.

The previously mentioned mineral assemblages suggest a continuous pH decrease in low positive Eh conditions. Initially the Eh was higher, as proved by the crystallisation of pistacite, actinolite and hematite II (specularite). It is presumable that hematite II is formed at temperatures of ca. 470° C nearby the lower limit experimentally determined for its crystallisation, at important aqueous vapor pressures (Martin, Piwinski, 1969). The decrease of oxygen fugacity simultaneous with a substantial sulphur fugacity increase, favour the stability of the scheelite II + molybdenite assemblage. The base metal sulphides developed later, initially the pyrite I + chalcocopyrite I + molybdenite assemblage being stable. A gradual increase of sulphur fugacity determines the successive initiation of pyrrhotite, sphalerite, chalcocopyrite II, pyrite II, galena and tetrahedrite crystallisation.

D. Epithermal stage

The pressure-temperature conditions which control the evolution of metasomatites during this stage are theoretically superposed on a P-T field situated at the left side of the zoizite out-lawsonite + prehnite in curve (Strens, 1965, Figs. 4, 5). In fact lower pressures determine a reaction of zoizite out-zeolite in type and the adequate P-T curve. Due to a slightly decrease of temperature, hydrothermal residual solutions of colloidal character formed during this stage. They produced in the skarns wollastonite replacement by carbonate and quartz. Deposition of quartz + carbonate on "second generation" fissures (Pl. I, Fig. 6) can also be assumed

to this stage. The negative Eh and the low pH values correspond to the "late alkaline stage" (Korzhinskii, 1965) and are compatible with chalcocine crystallisation.

5. Conclusions

The presented mineralogical data, correlated with the general geologic setting, point out the following conclusions:

- The ore mineral deposition was controlled by local, ruptural tectonic factors, as proved by the spatial relation between the "quartz and molybdenum" association and some fractures near the contact between granitoids and crystalline rocks or between the other mineralised zones and some paleofractures (fossil fracture system). Both fractural systems (oriented N-S or NE-SW) seem to be parts of a fractural network conjugated to a regional ruptural dislocation, the Dubova fault (Cristescu et al., 1975 fide Gunnesch, Gunnesch 1977).

- The ore mineral deposition was also controlled by petrographical factors, as proved by the molybdenite affinity for the silicatic host-rock or by the scheelite, sphalerite and galena affinity for the carbonatic rocks.

- The Mraconia skarn system is spatially associated with a near vertical swarm of granodiorite porphyry dykes, trending N-S. These are intensively hydrothermally altered and the Mraconia mineralisations are genetically related to them. A late generation of lamprophyre dykes (kersantites, spessartites) is considered to be intruded after the mentioned mineralisation, because it is not significantly hydrothermally altered.

- Some inversions in the normally deposition order of ore minerals are due to a recurrence phenomenon. The occurrence of two chalcocopyrite, hematite and pyrite "generations" suggests rejuvenation phenomena which are obviously due to a polyascendent mineralising process.

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Planșa I



Fig. 1 - Concentric-lamellar optical anomaly of garnet II. N +, x 10.

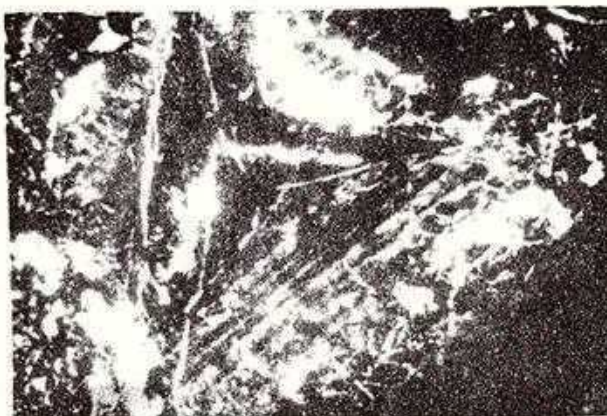


Fig. 2 - Quartz + calcite pseudomorphs on birefringent garnet II lamellae. N +, x 10.

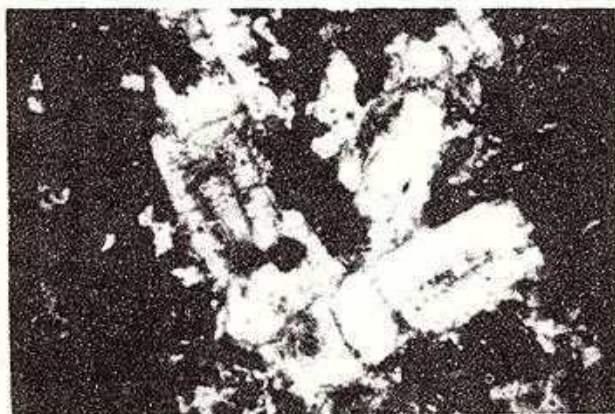


Fig. 3 - Vesuvianite pseudomorph after wollastonite. N +, x 10.



Fig. 4 - Scheelite I pseudomorph after garnet. N +, x 10.

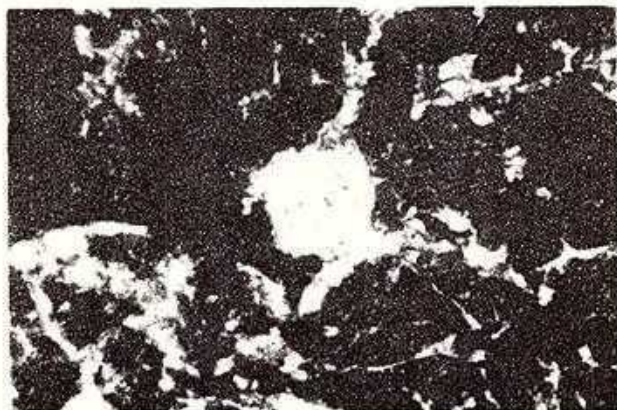


Fig. 5 - Scheelite crystal in a sulphide (black) groundmass. N +, x 20.



Fig. 6 - Calcite and quartz showing "en flammées" extinction, on second generation fissures. N +, x 20.

Planșa II



Fig. 1 – Musketovite and chalcopyrite (cp). Magnetite penetrate along oligiste twin planes. N II, x 10.



Fig. 2 – Specularite. N II, x 10.



Fig. 3 – Galena (ga) in association with pyrite I (py). N II, x 20.



Fig. 4 – Pyrite I with chalcopyrite deposition on fissures. N II, x 10.



Fig. 5 – Scaly crystalline molybdenite aggregate. N II, x 20.



Fig. 6 – Sphalerite (sph) with partly remobilized chalcopyrite I, exolutions in association with chalcopyrite II (cp). N II, x 20.

GEOCHEMISTRY AND MINERALOGY OF ALTERED ROCKS AND PYRITES ASSOCIATED WITH THE PORPHYRY COPPER-GOLD MINERALIZATION OF THE TERTIARY SUBVOLCANIC BODY FROM TĂLAGIU, ZARAND MOUNTAINS

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Key words: Porphyry copper. Andesites. Calderas. Hydrothermal alteration. Zoning. Major elements. Minor elements. Apuseni Mts - Neogene Volcanism - Vața-Sebiș area.

Abstract: *Geochemistry and Mineralogy of Altered Rocks and Pyrites Associated with the Porphyry-Gold Mineralization of the Tertiary Subvolcanic Body from Tălagiu, Zarand Mountains.* Intensive hydrothermal alteration of rocks accompanied by significant migration of elements in the Tertiary subvolcanic andesite-microdiorite body with porphyry copper mineralization remove strongly Na, Ca and Mg while Al and Si were released only slowly. The altered rocks were enriched in K_2O , H_2O and S. A significant horizontal and vertical zonality of the hydrothermal alteration and mineralization has been remarked. Horizontally it ranges from propylitic to advanced argillic stages and from a py-Au (Ti, Co) zone to a Pb-Zn-Cu-Au-Ag(Ti, Co) zone. Towards the depth it covers the advanced and intermediate argillic stage (with py-Au) through the propylitic to the phyllic-feldspathic (potassium) alteration as well as a transition from the Pb-Zn-Cu-Au-Ag(Ti, Co) veins and stockwork zone to the Cu-Au(Co) porphyry type zone.

Geological Setting

At Tălagiu, in the eastern part of the Zarand Mts an important caldera is probably present (Savu, Neacșu, 1962; Berbeleac et al., 1979, unpubl. report, 1981). This caldera is built up, by the following rock types: 1. hornblende and hypersthene±augite andesites (Upper Badenian ?), 2. pyroxene andesites with augite±hypersthene or with hypersthene±augite±hornblende (Upper Badenian-Sarmatian ?) and 3. hornblende and hypersthene andesites and microdiorites (Sarmatian-Pannonian ?). These rocks appear in lava pyroclastics and intrusions. The basement is formed especially by Tertiary and Cretaceous sedimentary deposits.

The Tălagiu caldera (9/4 km) comprises an inner collapsed part, characterized by an important andesite-microdiorite subvolcanic body, and some pre- and post-collapse volcanoes, and an outer part with post-collapse volcanic centers and minor microdiorite bodies (Fig. 1a). The subvolcanic body, as well as other small intrusions of andesite-dioritic composition show a polyphase evolution. They intruded later than

the andesitic rocks from the volcanic centers and are surrounded on large areas by thermal metamorphism (hornfels) and hydrothermal alteration. Some faults are present in the caldera (Fig. 1). The caldera has been recently investigated by boreholes. Thus a large extend, and a wide range of alterations have been identified, as well as their connection with a postmagmatic activity, closely associated with a subvolcanic andesite-dioritic body.

Mineralogical Data

Mineralogical and geochemical studies enabled us to identify a horizontal and a vertical zonality of the hydrothermal alteration: 1. As regards the horizontal zonality from the outer to the inner part of the caldera and of the subvolcanic body, the following products of hydrothermal alteration have been recognised: propylitic rocks - intermediate argillitic rocks - advanced argillitic rocks; 2. As regards the vertical zonality, in the central part of the caldera and in the subvolcanic body five types of alteration have been remarked (from

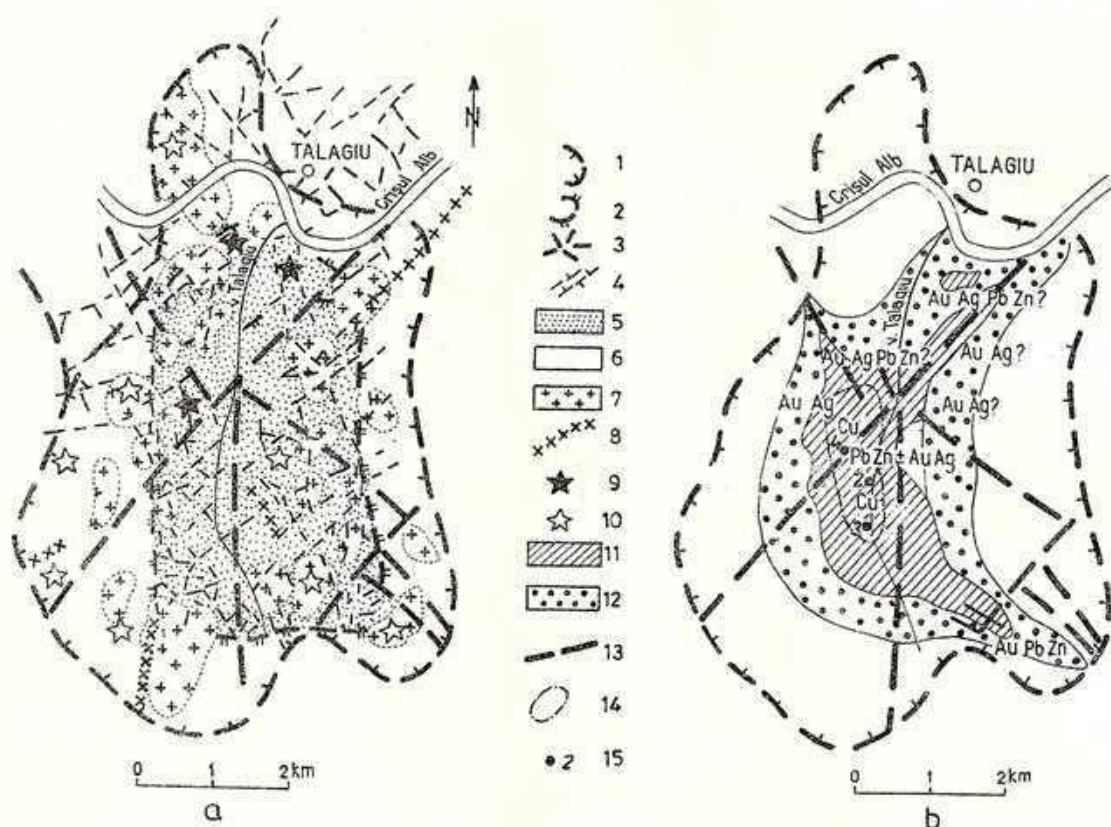


Fig. 1 - Geological (a) and metallogenetical (b) sketch of the Tălagiu area.

1, possible caldera border; 2, possible border of collapsed inner part of the caldera; 3, major fracture; 4, minor fracture; 5, possible collapsed inner part of the caldera; 6, possible border part of the caldera; 7, intrusion; 8, small dyke; 9, possible precollapse volcanic centre; 10, possible post-collapse volcanic centre; 11, advanced argillic alteration; 12, intermediate argillic alteration; 13, important faults; 14, horizontal projection of the porphyry copper-gold body; 15, location of sample.

surface to depth): advanced argillic - intermediate argillic - propylitic - phyllic - feldspathic (Fig. 3). Between the mentioned alteration types transition zones (Fig. 2, IIa, IIIa, IVa) with mixed mineral assemblages occur. The position of a quartz-alunitic alteration in the scheme presented above remains uncertain.

The rocks are affected by different intensity, from partial to total alteration. The following main mineral assemblages have been recognised: 1. chlorite+albite+carbonates±opaque minerals (pyrite, chalcopyrite, magnetite) and chlorite+albite+epidote+quartz+anhydrite±opaque minerals±adular, biotite, sericite, argillic minerals in the propylitic altered rocks (Fig. 3, II); 2. quartz+sericite+chlorite, biotite+argillic minerals+anhydrite+opaque minerals and quartz+sericite+albite+adular+argillic minerals+anhydrite(gypsum)+opaque minerals(pyrite+other sulphides+magnetite) in the phyllic and feldspathic altered rocks (Fig. 3, III); 3. quartz+argillic

minerals+anhydrite(gypsum)+opaque minerals (sulphides) and quartz + argillic minerals+anhydrite+sulphides±adular+albite±sericite+alunite in the intermediate (Fig. 3, IIIa) and intense argillic altered rocks (Fig. 3, IV), and 4. quartz + argillic minerals±alunite+pyrite in alunitic rocks (Fig. 3, V).

In the propylitic alteration plagioclase, was partially replaced by albite, adular, epidote, carbonates, anhydrite±argillic minerals, sericite, while hornblende, augite, hypersthene were sometimes wholly altered and pseudomorphosed by fine flake of chlorite to small aggregates of carbonates and quartz, pyrite and magnetite±chalcopyrite. It is supposed that the chloritisation and pyritisation proceeded simultaneously. In some parts of the andesite-dioritic body, epidote and actinolite develop as aggregates or fill small cracks. The groundmass of the rock is highly altered, but there are some parts with preserved primary minerals and original structure. Quartz aggregates resulted both

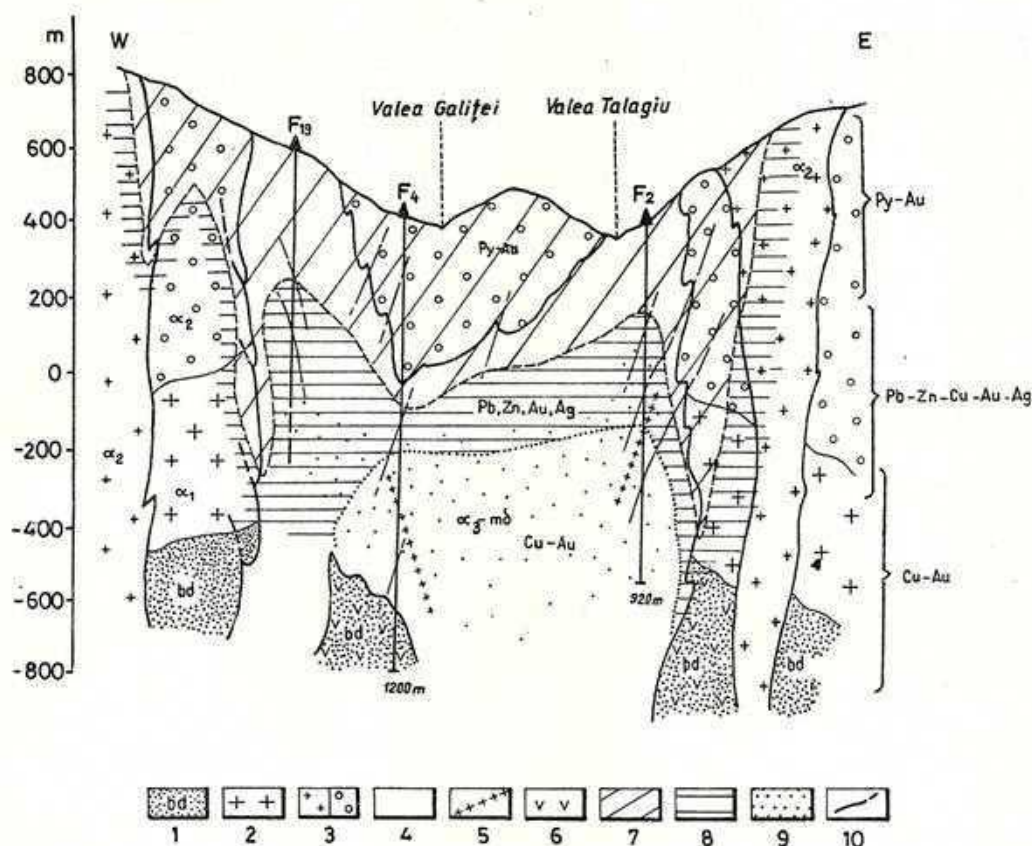


Fig. 2 - Geological cross-section in the Tălagiu area.

1, Badenian; 2, hornblende-pyroxene andesite (pyroclastics and lava- α_1); 3, pyroxene andesite (a, intrusion; b, pyroclastics and lava- α_2); 4, andesite-microdioritic subvolcanic body (α_3 -m δ); 5, late andesite dyke; 6, hornfels; 7, intermediate and advanced argillic zone; 8, propylitic; 9, phyllic-feldspathic zone; 10, veins and fractures; F2 - borehole.

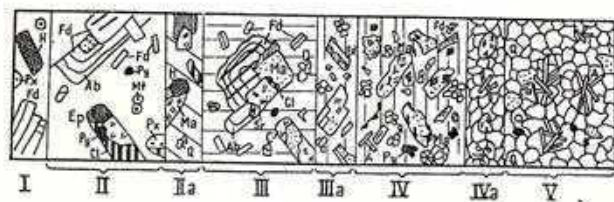


Fig. 3 Mineralogical details of alteration zones.

I, fresh rocks; II-V, hydrothermal alterations: II, propylitic; IIa, propylitic-phyllic; III, phyllic-feldspathic (potassic); IIIa, phyllic-feldspathic-intermediate argillic; IV, advanced argillic; IVa, argillic-quartz-alunitic; V, quartz-alunitic; H, hornblende; Px, pyroxene; Fd, feldspar; Ab, albite; Ep, epidote; Py, pyrite; Mt, magnetite; Sr, sericite; Cl, chlorite; Ma, argillic minerals; Q, quartz; A, alunitic.

from the alteration of primary minerals and of the groundmass.

From propylitic to argillic and alunitic alteration the substitution of primary minerals and groundmass increase in intensity. Thus, in the phyllic and feldspathic alteration plagioclases are preserved only in small amounts and dark minerals are substituted completely by sericite, chlorite, argillic minerals etc. In zones of intensive alteration chlorite was leached and decomposed into light-coloured fine flaked aggregates exhibiting multicoloured interference. Also a decrease of carbonate content may be noticed in zones of intensive alteration.

The potassic alteration, developed in the depth (400-900 m) inside the porphyry copper deposit. The primary minerals are rarely preserved, the biotite and adular form small aggregates within the substituted phenocrysts and groundmass; sometimes quartz fills the cracks.

More intensive argillic and alunitic alterations are

Table
Statistical parameters of major chemical components in fresh

Type of rock	α px I; n=23				α hpx I; n=10				α hpx II; n=10			
	A	$\bar{x}$	s		A	$\bar{x}$	s		A	$\bar{x}$	s	
SiO ₂	54.71-59.01	57.36	1.21		59.03-60.37	59.53	0.39		53.23-60.54	57.52	4.46	
TiO ₂	0.68-0.97	0.78	0.08		0.60-0.80	0.62	0.09		0.48-0.84	0.57	0.15	
Al ₂ O ₃	17.28-19.07	17.85	0.39		10.87-18.10	17.58	0.33		11.86-17.75	15.84	5.88	
Fe ₂ O ₃	2.69-5.77	4.04	0.75		3.37-6.39	4.05	0.88		0.94-4.55	2.33	1.45	
FeO	1.49-4.24	3.23	0.73		0.74-3.19	2.45	0.73		0.88-4.55	2.69	1.47	
MnO	0.11-0.17	0.14	0.02		0.11-0.17	0.13	0.02		0.01-0.31	0.08	0.09	
MgO	2.08-4.16	3.47	0.51		2.25-3.46	2.81	0.43		1.14-2.98	2.23	0.73	
CaO	7.01-8.78	7.67	0.43		6.35-7.29	6.89	0.34		1.03-6.70	4.61	1.68	
K ₂ O	0.82-1.36	1.09	0.17		0.49-1.48	1.09	0.27		1.10-4.57	2.35	0.94	
Na ₂ O	2.81-3.42	3.09	0.16		2.82-3.39	3.02	0.19		0.84-2.97	2.84	1.15	
P ₂ O ₅	0.16-0.32	0.21	0.04		0.16-0.25	0.20	0.04		0.14-0.25	0.15	0.05	
H ₂ O	0.19-1.25	0.65	0.34		0.72-1.65	1.17	0.36		1.31-4.85	2.61	1.12	
CO ₂	u-1.16	0.25	0.28		0.10-1.26	0.26	0.34					
S	0.03-0.23	0.09	0.06		0.03-0.18	0.07	0.04		0.77-7.59	2.49	2.85	
Fe(S)	u-0.19	0.06	0.05		u-0.15	0.06	0.03		0.67-6.61	2.18	2.48	
SO ₃									0.14-4.36	1.36	1.53	

Symbols: α px I, pyroxene andesites; α hpx, hornblende-pyroxene andesites; Altered rocks: II, propylitic; III, phyllic-feldspathic; IIIa, intermediate argillic; IV, advanced argillic;

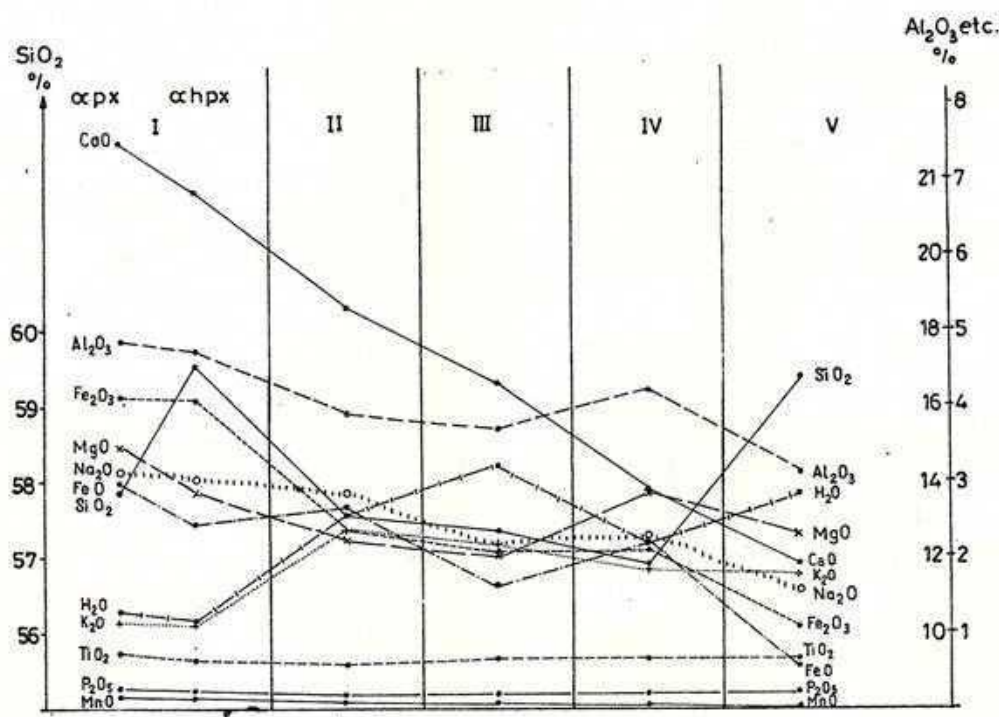


Fig. 4 - Variation of oxides in fresh and altered rocks.
I, fresh rocks; α py, pyroxene andesite; α hpy, hornblende-pyroxene andesite; Altered rocks: II, propylitic; III, phyllic-feldspathic (potassic); IV, intermediate argillic; V, advanced argillic.

1

and altered andesites from Tălagiu

α hpx III; n=8			α hpx IIIa; n=6			α hpx IV; n=5		
A	$\bar{x}$	s	A	$\bar{x}$	s	A	$\bar{x}$	s
51.74-70.70	57.39	6.93	52.98-62.15	56.88	3.33	48.05-63.44	59.38	3.68
0.44-0.82	0.62	0.09	0.50-0.66	0.62	0.08	0.34-0.80	0.64	0.19
11.69-16.91	15.48	1.59	15.36-17.80	16.58	0.19	5.64-18.00	14.23	4.90
0.29-5.30	2.07	1.44	0.81-3.30	2.09	1.15	0.50-1.45	1.02	0.54
0.24-5.53	1.69	1.45	1.69-3.68	2.23	0.77	0.28-1.03	0.58	0.74
0.01-0.07	0.04	0.05	0.01-0.09	0.04	0.03	0.01-0.08	0.03	0.03
0.26-2.96	2.00	1.05	1.03-3.97	2.88	0.97	1.37-4.34	2.29	1.43
1.18-5.13	4.30	1.52	4.60-5.80	5.32	0.53	1.03-7.87	4.91	2.44
1.17-2.98	2.15	1.11	2.90-2.88	1.83	0.88	1.30-2.47	1.78	0.62
0.88-4.28	2.12	1.36	0.25-4.09	2.24	1.37	0.22-3.30	1.53	1.33
0.13-0.22	0.19	0.05	0.16-0.22	0.19	0.02	0.15-0.23	0.19	0.03
2.31-5.71	3.26	0.71	0.69-3.34	2.19	1.87	1.21-4.57	2.81	1.24
0.98-5.33	3.71	3.86	0.90-4.30	2.57	1.62	2.45-7.68	3.62	1.20
0.85-4.70	3.25	1.64	0.78-3.74	2.24	1.41	2.13-6.69	3.82	1.41
0.52-3.60	1.69	1.19	0.21-3.38	1.62	1.18	0.18-9.80	3.64	4.08

A, limits of variation; $\bar{x}$, arithmetical mean; s, standard deviation; n, number of the analyses.

accompanied by strong silicification and argillization. Within cracks the secondary quartz appears in fine aggregates with cloud-like extinction. The stage of argillic and alunitic alteration preceded the replacement of chlorite, carbonates, albite, adularia, biotite and other minerals by quartz, argillic minerals and alunite (Fig. 3). The alunitic alteration is, at least partially, of supergene origin.

On the vertical scale, the argillic, propylitic and phyllic alterations are very representative. In argillic altered rocks white, and white-grey fine-grained aggregates of clay minerals are represented by: hydromica, montmorillonite, illite, kaolinite, pyrophyllite and smectite identified by X-ray diffraction (Ianovici, Neacșu, 1989).

Chemical Data

The average chemical composition of fresh and altered rocks is given in Table 1, and the migration of elements during the hydrothermal alteration is shown in Figure 4. From the chemical analyses it may be inferred that during hydrothermal alteration the rocks were potassium enriched. This led to the formation of adular, biotite, sericite, illite etc. by metasomatic processes (Tab. 2, Fig. 4). The rocks were also enriched in H_2O and S. Increased amounts of K_2O have been remarked in propylitized, sericitized and feldspathized rocks (Figs. 5, 6, Tab. 1). Concomitantly the average contents of Na_2O , CaO , MgO decrease (Tabs. 1, 2, Fig. 5).

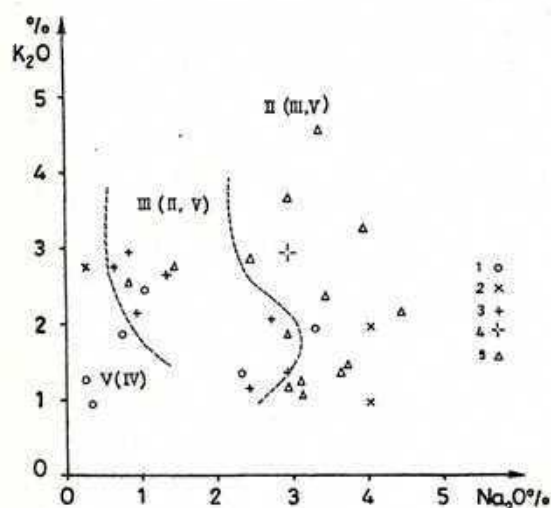


Fig. 5. K_2O - Na_2O diagram.

Altered rocks: 1, advanced argillic; 2, intermediate argillic; 3, phyllic±feldspathic; 4, feldspathic; 5, propylitic. (For II-V see Fig. 4.)

Quantitative data regarding the differences of average contents in fresh and altered rocks are given in Table 2. The difference is bigger for aluminium, calcium and sodium (Tab. 2). Therefore these elements were stronger removed. The higher Na_2O values in the propylitic assemblage, points to the replacement of plagioclases by albite, but generally the Na_2O content of altered rocks decreases gradually to the argillic

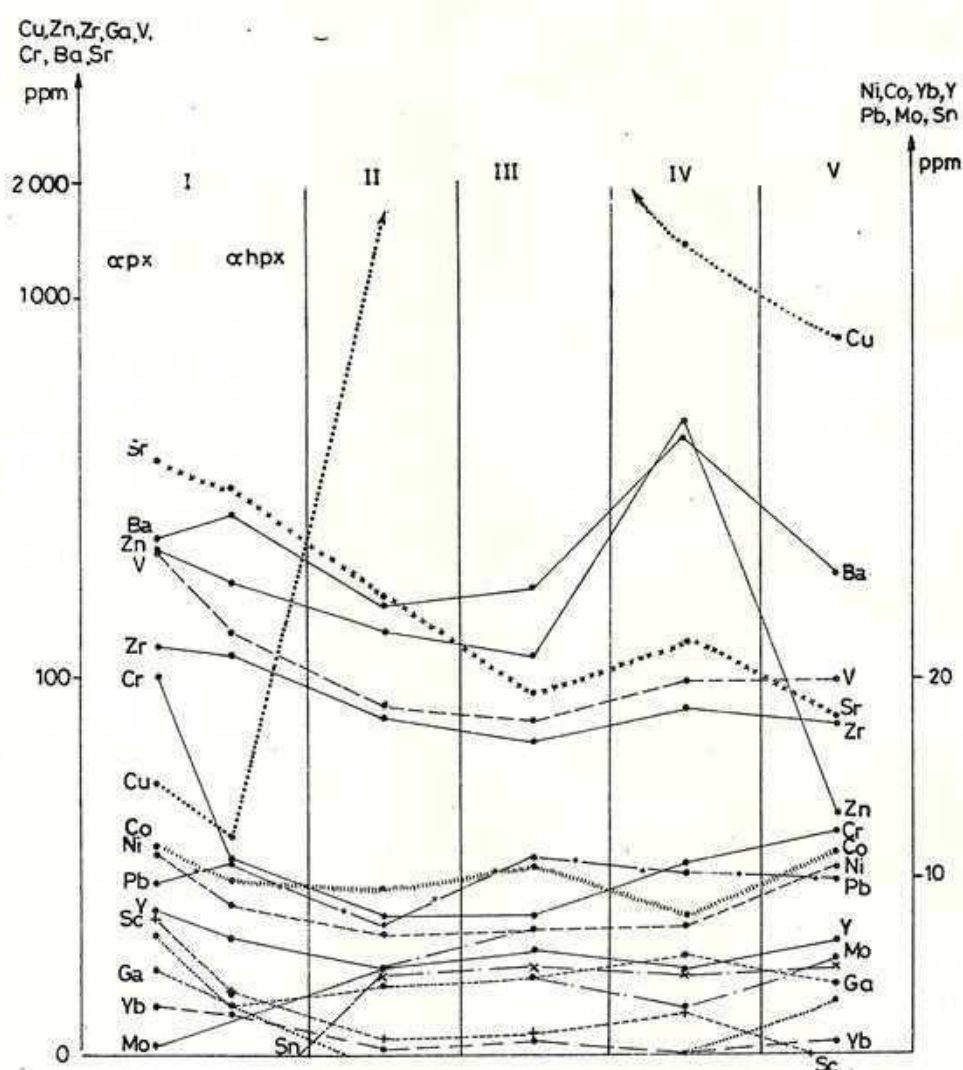


Fig. 6 – Variation of microelements in fresh and altered rocks.
For I–V, see Fig. 4.

Table 2
Supply and removal of elements

	I	II	III	IV	V
SiO ₂	59.53	-3.49	-3.72	-4.64	-0.02
Al ₂ O ₃	17.58	-10.98	-13.56	-6.03	-23.54
MgO	2.81	-26.00	-40.50	+2.43	-22.70
CaO	6.89	-49.45	-60.23	-29.51	-40.32
K ₂ O	1.09	+53.61	+49.30	+40.43	+38.76
Na ₂ O	3.02	-6.33	-42.45	-34.82	-97.38

+ enter; - removal; I, fresh rocks; Altered rocks: II, propylitic; III, phyllic-feldspathic; IV, intermediate argillic; V, advanced argillic.

assemblage. Magnesium released during the decomposition of ferrous minerals (pyroxenes, amphibole) is prevalently fixed in secondary chlorites, epidote and montmorillonite of the propylitic and argillic assemblages. Excepting the quartz-alunite assemblage, there is no significant change of the SiO₂ content, although abundant quartz filled fissures occur in the sericitic, propylitic and argillic assemblages. But sometimes in a more intensive stage of rock alteration a SiO₂ enrichment occurs in close connection with adularization, sericitization, propylitization and argillization. This SiO₂ increase implies a decrease of Al, Fe, Mg, Ca, K. It is due to the formation of secondary quartz at the expense of the secondary minerals previously formed. In the porphyry copper-gold mineralization the increased

SiO₂ contents are correlated with increased Cu and Au contents. In the advanced argillic assemblage the lowest contents of oxides were recorded excepting SO₃ and SiO₂.

A characteristic feature of the hydrothermal processes associated with the porphyry copper mineralization from the subvolcanic body, is the relative abundance of anhydrite at depth (350–1200 m) and of gypsum at the upper part of the structure. The SO₃ contents of altered rocks decrease from the argillic, through the phyllic-feldspathic and intermediate argillic to the propylitic alteration.

In comparison with the fresh hornblende-pyroxene andesites, trace elements in altered rocks associated with the porphyry copper-gold mineralization of the subvolcanic body show the following peculiarities: (Tab. 3, Fig. 6):

1. Cu, Mo, Sn and Ga show higher average values in all hydrothermally altered rocks, but the highest Cu and Mo contents are in propylitic (1808; 4.3 ppm) and phyllic (1319.5; 4.46 ppm) rocks. Sn contents are higher in the phyllic-feldspathic (5.45 ppm) and argillic (4.91 ppm) rocks and Ga in the intermediate argillic (18 ppm) and phyllic-feldspathic (16.0 ppm) rocks;

2. Zr, Y, Yb, Sc, V and Sr values are lower in all types of altered rocks. The highest contents for Y (20.6 ppm), Yb (1.38 ppm), Sc (13.66 ppm) and V (97.5 ppm) have been remarked in the advanced argillic rocks;

3. Cr (14.6 ppm), Ni (11.58 ppm) and Co (12.5 ppm) values only in advanced argillic rocks are higher than in fresh rocks;

4. Ba content (436.8 ppm) is higher in intermediate argillic rocks;

5. Pb contents in phyllic-feldspathic (11 ppm) and intermediate argillic (10.3 ppm) rocks show almost similar values to the fresh rocks (11.4 ppm). It is strange that the Zn average in intermediate argillic rocks is approximately 2.7 times higher (472.6 ppm) than in fresh andesites (178.2 ppm) and that the lowest values have been remarked in advanced argillic rocks (41.5 ppm).

It is worth to notice that immobile elements like Y, Yb (Fig. 7), Ti, V (Fig. 8) were removed by the hydrothermal alteration processes. The distribution of Y, Yb, Ti and V (Figs. 7, 8) on borehole sections and in fresh rocks, obviously shows a positive correlation. Another conclusion is that there is no significant correlation between Cu content and Pb, Zn and all the other trace elements. Only a positive Cu and Au correlation is possible.

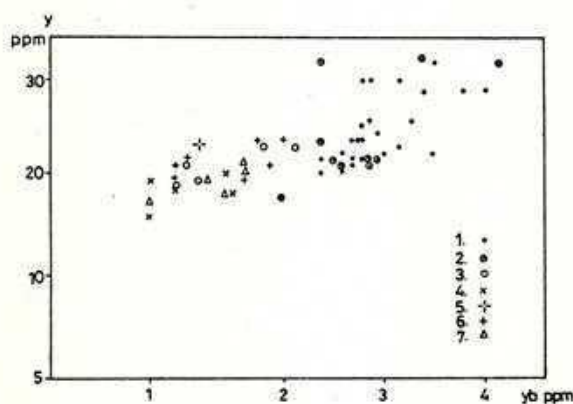


Fig. 7 - Y-Yb diagram.

Fresh rocks: 1, pyroxene andesite; 2, hornblende-pyroxene andesite; Altered rocks: 3, advanced and 4, intermediate argillic; 5, feldspathic; 6, phyllic-feldspathic (potassic); 7, propylitic.

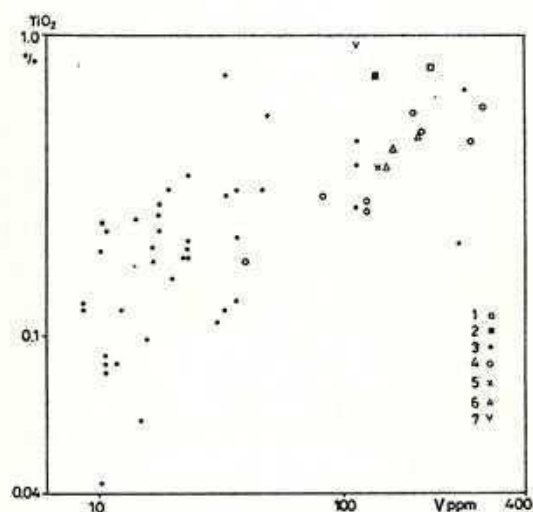


Fig. 8 - TiO₂-V diagram.

1, pyroxene andesite; 2, hornblende-pyroxene andesite; 3, pyrite; Altered rocks: 4, advanced argillic; 5, intermediate argillic; 6, propylitic; 7, quartz-alunitic.

Contents of trace elements in pyrites are listed in Table 4 (IV, III, IIa, II) for 34 samples from outcrops and in Table 4 (III 1) for 18 samples from drill cores.

The distribution of trace elements in pyrites shows a broad concentration interval (Tab. 4). According to the a reduced number of available analyses, the pyrites seem to be poor in microelements. The TiO₂ contents is higher in the pyrites from surface than at depth. With a few exceptions the Co:Ni ratio, is > 1; a simi-

Table
Trace elements contents (ppm) of fresh and

Type of rock	α px I; n=23			α hpx I; n=10			α hpx II; n=10		
	A	$\bar{x}$	s	A	$\bar{x}$	s	A	$\bar{x}$	s
Zr	82-140	105.10	19.11	52-130	104.70	27.60	55-90	76	11.65
Y	20-32	24.54	3.55	17-32.5	22.50	5.98	<10-20	16.3	5.48
Yb	2.3-3.4	2.84	3.57	2-4.20	2.69	1.25	<1-1.7	1.16	0.46
Ca	2.3-21	17.38	5.29		13.60	4.23	11-22	15.7	4.81
Sc	13-25.5	22.54	4.67		14.10	3.06	6.5-12	10.3	4.02
V	125-340	209.16	47.19	80-165	127.80	24.82	63-110	83.1	23.41
Cr	5-56	20.64	13.42	4.5-23	11.30	9.97	3.5-9.5	6.7	4.09
Ni	6-23	13.08	4.33	4.5-12	7.70	2.43	<2-7.5	5.5	1.97
Co	7-25	13.12	4.27	7-18	9.80	3.14	6-14	8.9	4.99
Mo	<1-4	<1	<1	<1-7	<1	<1	<2-14	4.3	5.64
Pb	4-28	9.54	5.05	4-43	11.40	11.20	2-17	6.0	9.01
Cu	16-120	51.43	27.93	15-60	34.40	14.88	150-10000	1808	2969
Zn	95-360	215.62	92.86	72-360	178.20	82.68	42-620	129	178.24
Sn	<1-9	<1	<1	<1-2.5	<1	<1	<2-7.5	3.4	2.7
Ba	130-370	222.30	58.90	135-360	275.50	59.90	40-300	156	158.87
Sr	275-450	364.60	49.26	230-400	309	48.40	15-270	160	61.37

Symbols: α px I, pyroxene andesite; α hpx I, hornblende-pyroxene andesite; Altered rocks: II, propylitic; III, phyllic-feldspathic (potassic); IIIa, intermediate argillic; IV, advanced argillic;

Table 4
Trace elements contents (ppm) of pyrites from Tălagiu

	Pb	Cu	Zn	Ti	Mn	Ni	Co	Cr	V
py+m.a. IV (n=25)									
A	27-135	34-1500	75-470	320-4400	7-300	12-145	43-125	<10-17	7.5-246
$\bar{x}$	65.38	290.56	176.80	1670.80	67.40	41.08	88.42	10	36.88
s	37.63	377.01	113.59	1003.98	84.81	25.23	23.18		52.70
py+m.a. III a (n=5)									
A	80-300	3.5-145	175-400	1200-3000	18-205	15.5-225	70-130	<10	16-110
$\bar{x}$	195	71.7	400	2330	82.5	89.1	100		45
s	106.3	59.33	141.69	799.69	82.15	92.41	27.61		37.69
py+m.a. III (n=2)									
A	80-430	160-370	270-300	5400-6000	66-610	16-60	60-140	<10	55-250
$\bar{x}$	255	265	285	5700	338	38	100		152.5
py+m.a. II (n=2)									
A	87-110	100-330	175-300	1200-3000	7-160	32-145	43-190	<10	7.5-54
$\bar{x}$	98.5	215	237.5	2100	83.5	88.5	116.5		30.75
py+ an $\pm$ gs, cp, mg, he III ₁									
A	<10-290	<10-4800	<100-100000	<30-380	<10-180	<10-16.5	<10-280	<10	

Symbols: py, pyrite; cp, chalcopyrite; mg, magnetite; he, hematite; an, anhydrite; gs, gyps; A, limit of contents; $\bar{x}$, arithmetical average; s, standard deviation; n, number of the samples; Type of alteration: II - propylitic; III a - intermediate argillitic (at the surface); III₁ - phyllic-feldspathic (in the boreholes); III - phyllic-feldspathic; IV - argillic.

lar ratio is shown by the fresh pyroxenic, hornblende-pyroxenic andesites and hydrothermally altered rocks (Fig. 9) collected from the surface and by the pyrites which proceed from depth (boreholes 2, 3, 4). The Co:Ni ratio in pyrites ranges within wide limits (0.29-11). According to Cambel and Jarkovsky's data (1967) the irregular distribution of Ni and Co in pyrites shows their hydrothermal origin.

The trace element content of pyrites seems to be influenced by the type of hydrothermal alteration. Thus, the Ti, Mn, V, Pb and Zn contents increase in pyrites from advanced argillic rocks through intermediate argillic rocks to phyllic-feldspathic rocks; Co in pyrites increases from argillic to propylitic rocks; Cu shows high values in pyrites from the advanced argillic rocks and phyllic-feldspathic rocks.

3

altered andesites from Tălagiu

α hpx III; n=10			α hpx IIIa; n=3			α hpx IV; n=6		
A	$\bar{x}$	s	A	$\bar{x}$	s	A	$\bar{x}$	s
42-85	67.2	13.73	58-120	81	23.20	47-90	75	16.18
<10-25	19	4.26	15-18	17	1.95	15-24	20.6	3.62
<1-2	1.3	0.37	<1-1.2	1.06	0.48	<1-2.1	1.38	0.42
9.5-23	16.0	3.97	15-21	18	3.77	6.5-24	15.25	6.44
6.5-17	11.0	3.58	12-15	13	3.32	6-21	13.66	4.68
47-125	77	26.95	85-110	96.6	25.96	28-135	97.5	38.76
2-14	6.5	3.06	7-15	10.6	4.10	7-13	14.25	11.96
<2-9	5.85	3.39	3-7.5	5.66	1.62	4.5-33	11.58	12.02
<2-6	10.4	3.90	7-8.5	6.66	8.13	11-15	12.5	2.51
<2-16	4.46	4.28	<2-7	3.6	2.24	<2-17	3.6	7.41
<2-17	11	6.24	<2-20	10.33	7.36	<2-27	9.66	6.84
105-2300	1319.5	2824	200-1900	1200	751.2	16-3600	898	1501.18
<30-210	112	63.28	98-1200	472.6	497.01	30-60	41.5	41.35
<2-12	5.45	3.61	<2-5	2.66	2.97	<2-9.5	4.91	3.25
70-570	166.1	94.21	80-1100	436.6	415.79	150-300	191.6	67.46
18-160	90.2	57.39	83-150	122.6	36.69	32-130	79	39.44

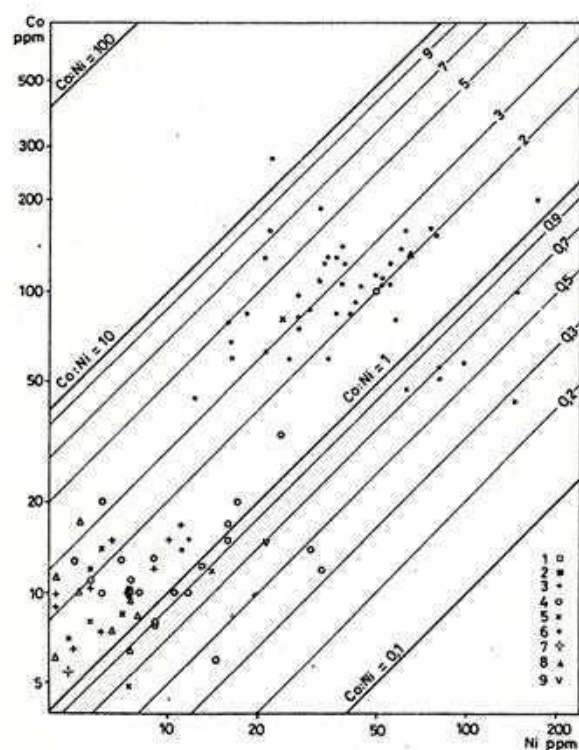
A, range of variation; $\bar{x}$, arithmetical means; s, standard deviation; n, number of the analyses.

Fig. 9 - Co:Ni ratio diagram.

1, pyroxene andesite; 2, hornblende-pyroxene andesite; 3, pyrite; Altered rocks: 4, advanced argillic; 5, intermediate argillic; 6, phyllic-feldspathic; 7, feldspathic; 8, propylitic; 9, quartz-alunitic.

Conclusions

Intensive hydrothermal alteration of rocks by significant migration of elements occurred in the Tertiary subvolcanic andesite-microdiorite body connected with metallogenetic process. Similarly as in other Tertiary subvolcanic structures (Voia, Valea Morii, Berbelec et al., 1981; Borcoş et al., 1980; Ştiavnicke, Harman, Forgač, 1988) Na, Ca and Mg were strongly removed from the rocks, while Al and Si were only slowly released. The altered rocks were enriched in K, H₂O and S.

A significant horizontal and vertical zonality has been remarked. It includes propylitic to advanced argillic stage in horizontal position and intermediate and advanced argillic through propylitic to phyllic-feldspathic (potassium) alteration towards depth. These zonalities are in direct connection with the subvolcanic body and the porphyry copper-gold mineralization. Associated with this structure the mineralization seems to exhibit also a horizontal and vertical zonality showing the following sequence from the border to the centre and from the surface to depth: py±Au(Ti,Co)→Pb-Zn-Cu-Au-Ag(Ti,Co)→Cu-Au(Co) (porphyry) (Figs. 1, 2). An obvious positive correlation is recognized between K and Au, Cu, Pb and Zn. Potassium and Au, Cu, Pb, Zn, Ti and Co may be considered as indicative elements for py-Au, Pb-Zn-Cu-Au-Ag (veins, stockworks, etc.) and Cu-Au (porphyry) prospecting in the Tălagiu region.

A characteristic feature is the abundance of anhydrite in the area of phyllic-feldspathic (potassium) altered rocks in the deep part of the porphyry copper-gold mineralization.

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ZĂCĂMINTELE DE SKARN CU MAGNETIT ȘI SULFURI DIN ZONA BĂIȘOARA (MUNȚII APUSENI)

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Key words: Mineralization. Skarn. Banatite. Magnetite. Sulfides. Lithologic controls. Apuseni Mts - Neocretaceous-Paleogene magmatites - Băișoara.

Abstract: *Magnetite and Sulphide Skarn Ore Deposits from Băișoara (Apuseni Mts).* Magnetite and sulphide ore deposits in the skarns from Băișoara (Apuseni Mts) have been identified and investigated mainly these last twenty years. They are related to the banatitic magmatism, represented by biotite±hornblende granodiorite intrusions, Maastrichtian-Paleocene in age, which generated a contact aureole, of complex structure, consisting of hornfelses, marbles, skarns and mineralisations. Skarns are classified according to the paleosome (exo- and endoskarns), chemistry (magnesian skarns, calcic skarns) and mineral composition. Exoskarns are widespread and result both from the substitution of a carbonate complex (crystalline limestones and dolomites) of Paleozoic age (Mașca-Băișoara and Cacova Ierii deposits) and from some flysch-like Senonian deposits (marls, sandstones) (Valea Lita deposit). According to their chemistry, the exoskarns are divided into magnesian skarns (spinel, forsterite, diopside, phlogopite±clinohumite) with MgO/CaO ratio > 1 and calcic skarns (salite-hedenbergite, garnets, epidote±wollastonite±vesuvianite±ilvaite) with MgO/CaO ratio < 1. The ore deposits are represented by several metasomatic bodies of complex shape and relatively small size, randomly spread among calcic or magnesian exoskarns. Four mineralizations types have been identified: the iron ore occurs in the Mașca-Băișoara and Cacova Ierii deposits and consists of oxides (magnetite±hematite±maghemite) and iron sulphides (pyrrhotite±pyrite±marcasite); the zinc mineralisation (sphalerite±galena±pyrite±chalcopyrite) is present in the Valea Lita deposit; the base metal ore (galena, sphalerite, pyrite, chalcopyrite±mispickel±molybdenite) occurs subordinately in peripheral areas; the boron mineralisation (ludwigite±szaibelyite) is sparsely related to magnesian skarns. The skarns and the related mineralisations formed during two successive stages: the magmatic stage, less developed, including the magnesian skarn phase bearing spinel±forsterite, generated by diffusion; the postmagmatic stage, largely developed, with four phases: the skarn phase, the borate phase, the magnetite phase and the hydrothermal phase including alterations and sulphides. The postmagmatic metasomatites were generated by infiltration±diffusion processes assigned to a temperature range of 620-150°C.

1. Introducere

Zăcămintele asociate skarnelor din regiunea Băișoara sînt situate pe rama estică a masivului Gilău, în apropierea comunelor Băișoara și Iara, județul Cluj. Lucrările de explorare efectuate de I.S.E.M. în perioada 1953-1958, reluate în anul 1961 și continuate de IGEX, apoi de I.P.E.G. Cluj, (galerii de coastă, foraje, patru puțuri și lucrări miniere subterane) au conturat trei zăcăminte: Mașca-Băișoara, Cacova Ierii și Valea Lita, primele două fiind de magnetit±sulfuri, iar ultimul preponderent zincifer. Zăcămintul Mașca-Băișoara, (în exploatare), cuprinde mineralizațiile din

sectorul Mașca (puțul I), cit și cele din perimetrul Dealul Grecului (puțul II), care în unele documentații au fost tratate ca un zăcămint separat. Zăcămintul Cacova Ierii a fost deschis pînă la adîncimi de 300-500 m, prin puțul IV, iar zăcămintul Valea Lita se află în stadiul final de explorare.

Dintre studiile anterioare menționăm pe cele referitoare la geologia regiunii (Borcoș, Borcoș, 1962; Mărza, 1969; Solomon et al., 1977, raport nepubl.); Hărtopan et al., 1982), la prospecțiunile magnetice (Romanescu, 1957, raport nepubl.; 1964; Cristescu, Trifulescu, 1965, raport nepubl.), la rocile eruptive ba-

natitice (Lazăr et al., 1972; Ștefan et al., 1985), la skarne și mineralizații asociate (Stoica, Iliescu, 1966, raport nepubl.; Lazăr, 1970, raport nepubl.; Intorsureanu, Popescu, 1970, raport nepubl.; 1973; Popescu et al., 1972, raport nepubl.; Stoicovici et al., 1973; Intorsureanu, 1976; Gheorghiescu et al., 1979; Lazăr, Intorsureanu, 1982; Pomârleanu et al., 1988). La acestea se adaugă documentațiile asupra lucrărilor de explorare elaborate de: Savu, 1957 (raport nepubl.); Harosa, Cucuietu, 1969 (raport nepubl.); Burz, Tibad, 1980 (raport nepubl.); Magyari, Burz, 1986 (raport nepubl.).

2. Cadrul geologic

Cele trei zăcămintе din zona Băișoara, dispuse aproximativ pe direcția N-S, sînt localizate în aria de contact morfostructural dintre două unități geologice majore reprezentate de Munții Apuseni, situați în partea vestică și Bazinul Transilvaniei, în partea estică. La structura geologică a zonei participă șisturi cristaline, formațiuni sedimentare și roci eruptive banatitice (pl. I).

Șisturile cristaline, aparțin masivului Gilău și au fost atribuite seriilor de Baia de Arieș, Biharia și Vulturese - Belioara (Hărtopanu et al., 1982; Lazăr et al., 1984 (raport nepubl.). Metamorfitele seriei de Baia de Arieș, atribuită Precambrianului, aflorăază pe arii restrinse (Valea Iara, Valea Ierții, Valea Vadului, Piriul Miei) și sînt reprezentate prin micașturi, șisturi cuarțitice micacee, cuarțite cu biotit, amfibolite, șisturi cu granați. Metamorfismul regional s-a desfășurat în condițiile faciesului amfibolitelor, după care a urmat un retromorfism în faciesul șisturilor verzi. Formațiunile seriei de Biharia atribuită precambrianului superior (Visarion, Dimitrescu, 1971) ocupă arii extinse din partea vestică. Sînt constituite din șisturi cuarțitice, plagiometavulcanite, gnaise albitice, șisturi amfibolice, șisturi cloritoase cu porfiroblaste de albit, șisturi tufogene bazice la care se asociază meta-granite. Șisturile cristaline au fost metamorfozate în condițiile faciesului șisturilor verzi. Seria de Vulturese - Belioara, de vîrstă paleozoică, ocupă arii reduse (Valea Vadului, Piriul Cacova, Piriul Miei), fiind alcătuită dintr-un termen bazal detritogen, cu metaconglomerate și cuarțite sericitoase și o formațiune carbonatică, situată la partea superioară, reprezentată prin calcare și dolomite cristaline. Anterior, această formațiune carbonatică a fost atribuită seriei de Baia de Arieș în (Lazăr et al., 1972; Mărza, 1969).

Formațiunile sedimentare aparțin Permianului, Senonianului, Terțiarului și Cuaternarului. Depozitele permiane apar în Valea Ierții și sînt constituite din conglomerate, microconglomerate și gresii roșii-violacee (Borcoș, Borcoș, 1962). Senonianul este reprezentat printr-un facies calcaros (Piatra Mare, Valea

Vadului) și un facies flișoid (Valea Lita, Valea Iara, Valea Vadului), alcătuit din microconglomerate, gresii, marne, marno-calcare, argile, atribuite Santonian-Maastrichtianului (M. Lupu, în Hărtopanu et al., 1982). Depozitele terțiare, preponderent eocene, dispuse transgresiv peste formațiunile mai vechi, ocupă arii importante, constituind unplutura Bazinului Iara și sînt alcătuite din argile roșii, argile nisipoase, nisipuri, conglomerate, tufuri, marne. Formațiunile cuaternare se dezvoltă în lungul rețelei hidrografice, formînd terase, aluviuni, conuri de dejecție.

Rocile eruptive banatitice (laramice) formează un complex intrusiv alcătuit din numeroase corpuri, apofize sau filoane orientate NNW-SSE, mai rar NE-SV sau N-S, care sugerează prezența în profunzime a unui pluton major cu caracter hipabisic. Banatitele sînt reprezentate prin granodiorite, granodiorite porfirice, porfire granodioritice, porfire microgranodioritice, diorite cuarțifere, diorite porfirice, granite, andezite cu hornblendă, dacite, riolite, aplite granitice, lamprofire (Lazăr et al., 1972; Ștefan et al., 1985). Granitele, aplitile granitice, lamprofirele nu sînt figurate pe harta alăturată (pl. I) intrucît au fost întîlnite numai în foraje. În general predomină granodiorite cu biotit±hornblendă, care formează cîteva corpuri mai mari, situate în partea centrală a zonei cercetate. Aceste roci prezintă frecvent structuri porfirice și conțin plagioclazi zonati, ceea ce denotă că s-au consolidat în condiții subvulcanice (Giușcă et al., 1966). Datele petrochimice indică proveniența din magme calco-alkaline de compoziție cuarț-dioritică-granodioritică (Lazăr et al., 1972; Ștefan et al., 1985). Din relațiile cu rocile înconjurătoare rezultă că s-au pus în loc în intervalul Maastrichtian-Paleocen. Intruderea corpurilor banatitice a generat o importantă aureolă de contact în care s-au produs intense recristalizări termice succedate de variate procese metasomatice și metalogenetice.

Structura tectonică a masivului Gilău, configurată în liniile ei esențiale în ciclurile tectonice prehercinic și hercinic, a fost desăvîrșită în tectogeneza alpină. Seria de Baia de Arieș prezintă contacte tectonice atît cu seria de Vulturese - Belioara (Valea Vadului, Piriul Miei), cît și cu depozitele senoniene (Valea Ierții, Valea Iara, Piriul Săcel etc.).

Tectonica disjunctivă a produs importante modificări în configurația regiunii. Datele geofizice (Airinei, 1980), evidențiază prezența unei fracturi crustale (G 10), situată aproximativ la limita de NE a masivului Gilău. În lungul acestei dislocații și a fracturilor sale adiacente, s-a produs în Cretacicul superior scufundarea Bazinului Transilvaniei și ridicarea masivului Gilău. Segmentul Băișoara - Păniceni al acestei fracturi crustale este marcat de numeroase intruziuni banatitice și probabil a avut un rol major

în evoluția magmatismului laramic (Mârza, 1982, p. 162). Existența fracturii menționate a fost confirmată și de datele unor foraje executate în bazinul văii Lita (Întorsureanu, Gheoghițescu, 1978, raport nepubl.). Pentru această dislocație regională, marcată și în aspectul morfostructural al zonei, propunem denumirea de "falia Băișoara - Păniceni".

În Paleogen, mișcarea de scufundare a Bazinului Transilvaniei s-a continuat, depunându-se formațiuni eocene cu dezvoltare regională, care acoperă în mare parte contactele tectonice menționate.

3. Metamorfismul de contact

Metamorfismul de contact generat de intruziunile banatitice a determinat apariția unei aureole de contact, cu structură complexă, alcătuită dintr-o gamă largă de corneene, marmure, skarne, mineralizații etc., care se dezvoltă pe distanțe de ordinul zecilor sau sutelor de metri, în rocile înconjurătoare.

Corneene, marmure, dolomite recristalizate. Metamorfismul termic cel mai intens s-a manifestat în jurul corpurilor granodioritice, în timp ce intruziunile mici (filoane, apofize) au produs transformări slabe. Prin recristalizarea metamorfitelor s-au format corneene cu biotit + hornblendă, corneene cu biotit + andaluzit. Calcarele cristaline au fost decolorate și transformate pe scară mare în marmure albe cu structuri granoblastice, inechigranulare, sau în calcare cu brucit (predazzite). Dolomitele au suferit, de asemenea, procese de decolorare și recristalizare, iar impuritățile au condus la formarea dolomitelor cu forsterit + minerale serpentinite (oficalcite). Pe seama rocilor sedimentare permieni sau senoniene au apărut corneene cu diopsid, corneene cu epidot + actinot, corneene cu biotit. Aceste produse arată că metamorfismul termic s-a realizat în faciesul corneenelor cu hornblendă și cel al corneelor cu albit și epidot.

Skarne. Produsele metamorfismului pirometamorfic sunt larg dezvoltate fiind reprezentate prin variate tipuri de skarne, formate în aureola de contact. Corpurile de skarne, interceptate cu numeroase foraje sau lucrări miniere subterane, au fost întâlnite până la adâncimea de 800 m (forajul 31783). Ele se caracterizează, în general, prin dimensiuni relativ mici și forme variate (lentile, cuiburi, stâlpi, pseudo-filoane, corpuri cu conture neregulate etc.). În cele ce urmează adoptăm clasificarea skarnelor în funcție de natura paleosomului (exoskarne, endoskarne), chimism (skarne magneziene, skarne calcice) și compoziția mineralogică.

Exoskarnele. Exoskarnele s-au format prin substituția rocilor înconjurătoare și au o largă răspândire. Paleosomul este reprezentat îndeosebi prin complexul carbonatic al seriei de Vulturese-Belioara, în cazul zăcămintelor Mașca-Băișoara și Cacova Ierii

și prin depozite senoniene, cu caracter flișoid, în perimetrul Valea Lita. După chimism, exoskarnele se divid în skarne magneziene în care raportul MgO/CaO este supraunitar și în skarne calcice, care au acest raport subunitar.

Skarnele magneziene apar în zăcămintele Mașca-Băișoara și Cacova Ierii, fiind formate la contactul direct dintre granodiorite și dolomite sau calcare dolomitice din complexul carbonatic. Aceste skarne au culori cenușii-negricioase cu tente verzui, textura masivă și structura fin granolepidoblastică sau heteroblastică. Observațiile microscopice au condus la identificarea următoarelor tipuri: skarne cu spinel, skarne cu forsterit + spinel, skarne cu diopsid + forsterit, skarne cu flogopit, între care se remarcă treceri gradate. Intrucit mineralele magneziene sunt deseori substituite de granați, se deduce că formarea skarnelor magneziene a precedat formarea skarnelor calcice. Probabil skarnele cu spinel + forsterit s-au format în stadiul inițial magmatic al intruziunilor banatice, stadiu în care se consideră că aluminiul a avut o mobilitate ridicată. Skarnelor magneziene li se asociază frecvent concentrații de magnetit, pirotină și, mai rar, de ludwigit + szaibelyit (ascharit). În faza hidrotermală aceste skarne au fost adesea serpentinizate și, uneori, flogopitizate.

Skarnele calcice alcătuiesc masa principală a pirometamorfitelor. S-au format îndeosebi, prin substituția marmurelor metamorfice (zăcămintele Mașca-Băișoara și Cacova Ierii) și a depozitelor senoniene, cu caracter flișoid reprezentate prin marne silicioase și gresii cu ciment marno-argilos, (conservate în proporții până la 40-50 % din volumul rocii; zăcămintul Valea Lita). În mod subordonat, skarne calcice s-au format și pe seama metaconglomeratelor cornificate sau a skarnelor magneziene. Skarnele calcice se caracterizează prin culori închise (maronii-cenușii-verzui), texturi masive și structuri granoblastice-heteromere, cu granulație de la fină la grosieră. Observațiile macro și microscopice, au permis separarea următoarelor tipuri, în funcție de mineralele dominante: skarne cu granați, skarne cu granați + piroxeni, skarne cu piroxeni + granați, skarne cu piroxeni, skarne cu granați + piroxeni + plagioclazi, skarne cu wollastonit, skarne cu epidot. Între aceste tipuri de skarne există frecvente combinații în care apar asociații mineralogice complexe. În exoskarnele calcice este localizată masa cea mai importantă a mineralizațiilor din regiune.

Endoskarnele. rezultate prin substituirea rocilor granodioritice, prezintă o răspândire relativ redusă. În unele cazuri (zăcămintul Mașca-Băișoara, puțul I, oriz. -80 m), skarnificarea s-a produs pe fisurile din granodiorite, până la distanțe de câțiva metri de contactul cu rocile carbonatice, roca eruptivă rămâne ca relict în masa endoskarnelor. La compoziția mineralogică participă piroxeni, granați, feldspați pla-

gioclazi (58-60 % An), tremolit, epidot, sfen±pirită. La contactul cu dolomite s-a remarcat și prezența flogopitului. Ca minerale relict s-au observat plagioclazi zonați, parțial substituiți de piroxeni sau granați și apatit. Chimismul endoskarnelor este caracterizat printr-un conținut ridicat de Al_2O_3 (16,83 %), foarte apropiat de cel al granodioritului (17,29 %), iar raportul MgO/CaO este subunitar, asemănător cu cel al exoskarnelor calcice. Aceste observații, împreună cu localizarea endoskarnelor la contactul dintre granodiorite cu roci carbonatice, sugerează că endoskarnele s-au format prin procese bimetasomice. În endoskarne nu s-au întâlnit mineralizații semnificative sub aspect cantitativ.

În general, skarnele din zona Băișoara nu reprezintă zonalități bine conturate. S-a observat uneori dispunerea skarnelor apocarbonatice cu piroxeni la contactul cu roca granodioritică, trecându-se, apoi, spre exterior, la skarne cu piroxeni + granați, skarne cu granați și calcare. O tendință de zonare mai bine exprimată se remarcă la skarnele din zăcămintul Valea Lita unde s-a întâlnit următoarea succesiune: corp eruptiv-skarne cu piroxeni-skarne cu granați-skarne cu wollastonit-skarne cu epidot. Limitele dintre tipurile menționate sînt confuze; se remarcă preponderența skarnelor cu epidot. Skarnele formate pe seama metaconglomeratelor cornificate prezintă următoarea dispoziție zonală: corneene cu biotit-skarne cu piroxeni±plagioclazi±granați-skarne cu piroxeni±granați-skarne cu granați-skarne cu granați±magnetit±pirotină-pirotină±magnetit (zăcămintul Cacova Ierii, orizontul -250 m).

Tabel 1

Compoziția moleculară a granaților din zăcămintul Mașca-Băișoara*

Minerale	Es.183	Es.1283	Es.776	Es.2233
Almandin	0,51	2,87	1,47	2,13
Pirop	0,40	5,11	8,10	10,50
Spessartin	0,51	1,86	2,66	3,17
Andradit	98,58	70,11	22,68	10,89
Grossular		20,05	65,39	73,31

* După Popescu et al. (1972)

Es. 183 - granat din skarne formate pe fisuri în calcare cristaline;

Es. 1283 - granat din skarne cu magnetit formate pe calcare cristaline;

Es. 776 - granat din endoskarn cu flogopit±amfibol;

Es. 2233 - granat din endoskarn cu granați.

3.1 Minerale de skarn

Granații sub formă de agregate mono- sau poliminerale, sînt foarte răspîndiți aproape în toate tipurile de skarne. Cristale bine dezvoltate, cu dimensiuni pînă

la 4-5 mm - întilnesc frecvent în skarne apocarbonatice și endoskarne, în timp ce skarnele din zăcămintul Valea Lita au granați cu dimensiuni submilimetrice. Formele criptocristaline frecvente sînt cele de dodecaedru romboidal (110), mai rar apar cele de tetra-trioctaedru (211). Culoarea este galben-maronie, mai rar verde-oliv. Granații din skarnele apocalcaroase sînt preponderent izotropi, spre deosebire de cei din skarnele formate pe alte roci (dolomite, marne, gresii, granodiorite), care au adesea efecte de anizotropie ce evidențiază macle sectoriale cu zone lamelare. După compoziția moleculară calculată pentru patru probe (tab. 1), granații din exoskarne se caracterizează prin dominarea moleculelor de andradit și participarea redusă a piralspilitelor, spre deosebire de granații din endoskarne care sînt preponderent grosularici și au un conținut mai ridicat în piralspite. În general, granații substituie piroxeni și pot fi înlocuiți de magnetit, pirotină, epidot, clorit etc.

Piroxeni din seria diopsid-hedenbergit se întilnesc atît în skarnele magneziene cit și sub formă de mase aproape monominerale în asociere cu alte minerale formate ulterior. Diopsidul este frecvent în skarnele magneziene putînd ajunge pînă la aproximativ 95 % din volumul rocii. A fost de asemenea întilnit și în skarnele cu piroxeni din zăcămintul Valea Lita. Mai răspîndiți sînt, piroxeni cu compoziție salit-hedenbergitică din skarnele apocarbonatice. Se prezintă sub formă de cristale prismatice cu lungimea pînă la 1-2 cm, de culoare verzui-cenușie, dispuse adesea în agregate radiare. În secțiuni subțiri sînt incolore sau verzui cu c:Ng de 42° - 45° și 2V de 56° - 63° . În endoskarne apar clinostatit sau salit substituind feldspații sau biotitul din granodiorite. Piroxeni sînt adesea substituiți de granați, magnetit, pirotină, tremolit, actinot etc.

Epidotul este mineralul de skarn predominant din zăcămintul Valea Lita. S-a format prin substituția componentilor din paleosom (cuarț, minerale argiloase, carbonați) sau pe seama piroxenilor și granaților formați anterior. Apare în agregate fine compacte, de culoare verzuie, adesea sub formă de cristale prismatice, cu dimensiuni submilimetrice, divers orientate. Este reprezentat printr-un termen ferifer, pistacit cu un pleocroism pronunțat (galben pal - galben verzui) și cu c:Ng de 4° și 2V de 65° C (Gheorghiușescu et al., 1979). Epidotul se asociază frecvent cu piroxeni, granați, zoiziți, tremolit, blendă, pirită etc. Întrucît este frecvent substituit de blenda feriferă formată aproximativ între 360° - 400° C (Gheorghiușescu et al., 1979), rezultă că epidotul din skarne s-a format la temperaturi ridicate, ceea ce este în acord cu date experimentale (Liou, 1973). Subordonat apare un epidot hidrotermal depus pe fisuri sau formînd pseudomorfoze după unele minerale din skarne (granați) și din banatite (biotit, hornblendă).

Tabelul 2
Compoziția mineralogică a zăcămintelor de skarn din zona Băișoara

Nr. crt.	Minerale metalice	Zăcămintele			Nr. crt.	Minerale nemetalice	Zăcămintele		
		MB	CI	VL			MB	CI	VL
1.	Magnetit	+++	+++	*	1.	Spinel	+	+	
2.	Hematit	+	+	*	2.	Forsterit	+	+	
3.	Maghemit	*	*		3.	Piroxeni	++	++	++
4.	Ludwigit	+	+		4.	Granați	+	+	++
5.	Pirotină	++	++	*	5.	Wollastonit	*		*
6.	Pirită	+	+	++	6.	Flogopit	+	+	
7.	Mispichel	*			7.	Clinohumit	*		
8.	Molibdenit	*			8.	Scapolit	*		
9.	Blendă	+	+	++	9.	Vezuvian	*		
10.	Calcopirită	+	+	+	10.	Ilvaît	*		
11.	Galenă	+	+	+	11.	Epidot	+	+	+
12.	Tetraedrit			*	12.	Tremolit-actinot	+	+	+
13.	Mackinawit			*	13.	Ferohastingsit	*		
14.	Boulangerit			*	14.	Zoizit-clinozoizit	*	*	+
15.	Cubanit			*	15.	Hercinit	*		
16.	Marcasită	+	+	+	16.	Albit	+	+	
17.	Bornit	*		*	17.	Sericit	+	+	+
18.	Covelină	*		*	18.	Magnezit	+	+	
19.	Goethit	*	*		19.	Dolomit	+	+	
20.	Hidrogoethit	*	*		20.	Brucit	+	+	
21.	Malachit	*		*	21.	Minerale serpentinite	++	++	*
22.	Azurit	*		*	22.	Sepiolit	*		
					23.	Palygorskit	*		
					24.	Minerale argiloase	+	+	+
					25.	Hisingerit	*	*	
					26.	Szaibelyit (ascharit)	*	*	
					27.	Cuarț	++	++	++
					28.	Anhidrit	*		
					29.	Calcit	++	++	++
					30.	Calcedonie	*	*	*
					31.	Zeoliți	+	+	+

Legenda: +++, mineral dominant; ++, mineral foarte răspândit; +, mineral răspândit; *, mineral rar sau foarte rar; MB, Mașca-Băișoara; CI, Cacova Ierii; VL, Valca Lita.

Spinelul s-a întâlnit exclusiv în skarnele magneziene, ca idioblaste sau relict, uneori asociat cu forsterit, diopsid, magnetit, pirotină. În secțiuni subțiri se remarcă fisuri pe care s-au dezvoltat minerale serpentinite.

Flogopitul este frecvent în skarnele magneziene și mai rar în endoskarne. Formează cuiburi sau lentile decimetrice, în care lamelele de flogopit verzui-argintii ajung până la dimensiunea de 4-5 cm. Analiza chimică a flogopitului din zăcămintul Mașca-Băișoara (puțul 1, suborizontal -50 m), arată un conținut relativ mic (5,49 %) de K_2O (Popescu et al. 1972, raport nepubl.).

Ilvaîtul a fost identificat în zăcămintul Mașca-Băișoara (puțul 1) sub formă de cuiburi sau în zone aproape monominerale cu grosimi până la 3 m, la contactul skarnului granato-piroxenitic cu rocile carbonatice (Popescu, 1973). Apare asociat cu piroxeni (salit-hedenbergit) granați, magnetit, pirotină, actinot.

Hercinitul s-a întâlnit într-un singur eșantion de skarn cu piroxeni prelevat din zăcămintul Mașca-Băișoara puțul 1 (pl. III, fig. 3).

4. Mineralizații

Mineralizațiile aparțin tipului genetic pirometamorfic-hidrotermal. Sunt localizate cel mai frecvent în exoskarnele calcice sau magneziene și subordonat în rocile înconjurătoare (calcare, dolomite, corneene) sau în banăite slab alterate hidrotermale. Corpurile metamorfice de minereu au morfologia foarte variată, cu dimensiuni relativ mici și sunt dispersate neuniform în aureola de contact. Predomină minereurile masive și cele de impregnație caracterizate prin variate texturi metamorfice, și o gamă largă de structuri relict formate prin substituții. Mineralizațiile au o compoziție mineralogică complexă și diferențiată

în cele trei zăcămintele (tab. 2). Se constată o mare asemănare între zăcămintele Mașca-Băișoara și Cacova Ierii, formate prin substituția aceluiași paleosom carbonatic, în timp ce zăcămintul Valea Lita, format pe seama marnelor și gresiilor marnoase, prezintă o mineralogie sensibil diferită. După compoziția chimică și mineralogică se deosebesc următoarele tipuri de mineralizații:

- mineralizația de fier, reprezentată prin oxizi de fier (magnetit $\pm$ hematit $\pm$ maghemit) și sulfuri de fier (pirotină $\pm$ pirită $\pm$ marcasită), larg dezvoltată atît în zăcămintul Mașca-Băișoara (Lazăr, Întorsureanu, 1982), cît și în zăcămintul Cacova Ierii.

- mineralizația de zinc (blendă $\pm$ galenă $\pm$ calcopirită $\pm$ pirită) este preponderentă în zăcămintul Valea Lita (Gheorghitescu et al., 1979);

- mineralizația polimetalică (galenă, blendă, pirită, calcopirită $\pm$ mispichel $\pm$ molibdenit), uneori asociată cu mineralizația de fier, apare mai ales în sectoare periferice ale aureolei de contact, afectate de alterații hidrotermale;

- mineralizația de bor (ludwigit $\pm$ szaibelyit) apare sporadic și este localizată în skarne magneziene, mai rar în dolomite. Inițial a fost identificată în zăcămintul Mașca-Băișoara (puțul I) (Întorsureanu, Popescu, 1973).

4.1 Minerale metalice

Mineralele metalice din zăcămintul Mașca-Băișoara (puțul I) și Valea Lita au fost descrise anterior de Lazăr, Întorsureanu, (1982); și Gheorghitescu et al., (1979).

Magnetitul este mineralul metalic dominant în zăcămintele Mașca-Băișoara și Cacova Ierii, în care formează numeroase corpuri metasomatice cu forme neregulate și cu dimensiuni relativ mici, de ordinul zecilor de metri, rar depășind 100 m. Acumulările de magnetit se prezintă adesea ca mase compacte, cu textura masivă, în care uneori se păstrează structuri relict. În zona marginală a corpurilor apar impregnații sau pseudofilonașe de magnetit în skarne ori în roci carbonatice. Rocile cu magnetit prezintă uneori aspecte tigrate, mai rar leopardine sau colormorfe, ultimele sugerind o depunere în goluri. Structura fin cristaloblastică este specifică pentru minereul compact, constituit din cristale anhedrale de magnetit cu dimensiuni submilimetrice. În zonele cu impregnații apar uneori porfiroblaste cu dimensiuni care pot ajunge pînă la 1-2 cm, în forme de octaedri (111) sau dodecaedri romboidali (110). Pe fețele cristalelor de magnetit se observă frecvent striații paralele cu diagonala lungă a romburilor sau urme de coroziune; de asemenea, s-a observat prezența macrelor după (111). Analiza chimică parțială efectuată pe patru probe de magnetit din zăcămintul Mașca-Băișoara (puțul I), arată următoarele conținuturi: $MgO = 0,65-$

$7,11 \%$, $MnO = 0,13-0,37 \%$. De asemenea, determinările spectrale pe 11 probe de magnetit (Popescu et al., 1972 (raport nepubl.); Lazăr et al., 1984 (raport nepubl.)), au evidențiat următoarele conținuturi medii (în ppm): Mg (6450), Mn (1180), Al (2600), Zn (730), Sn (120), Cu (47), Pb (< 5), Zr (< 30), Ti (50), Ni (< 10), Co (< 10), Cr (30), V (14). De remarcă că magnetitul format prin înlocuirea skarnelor magneziene se caracterizează prin conținuturile cele mai ridicate în magneziu, semnalate atît prin analize chimice ($Mg = 7,11 \%$), cît și prin analize spectrale ($Mg > 10000$ ppm), spre deosebire de magnetitul format prin substituția skarnelor calcice care au concentrații mai mici ($MgO = 0,65-1,64 \%$; $Mg = 2900$ ppm). Subliniem, de asemenea, conținuturile reduse de Ti, Ni, Co, Cr, V, ce caracterizează magnetitele formate prin procese pirometasomatice.

Observațiile microscopice au permis identificarea a trei generații de magnetit (Lazăr, Întorsureanu, 1982): magnetit de generația I, apare ca mici incluziuni în granați, reprezentînd probabil începutul cristalizării mineralelor metalice; magnetit II constituind faza principală de formare a mineralizației de fier; magnetit III, puțin răspîndit, legat de faza hidrotermală tardivă. Asociațiile mai frecvente ale magnetitului cuprind: magnetit $\pm$ granați andraditici $\pm$ piroxeni; magnetit + hematit $\pm$ maghemit; magnetit + pirotină; magnetit + ludwigit $\pm$ szaibelyit; magnetit + magnezit $\pm$ dolomit; magnetit $\pm$ blendă $\pm$ galenă $\pm$ calcopirită $\pm$ marcasită. Determinările decrepitometrice (Pomârleanu et al., 1988), indică temperaturi de formare cuprinse între $460-500^{\circ}C$, pentru magnetitul de generația II.

Pirotina, sub aspect cantitativ, este al doilea component metalic al mineralizației de fier. Apare frecvent asociată cu magnetitul și manifestă tendința de localizare în zonele marginale ale corpurilor de minereu. Pirotina formează adesea concentrații locale aproape monominerale cu textura masivă și structuri granoblastice sau sub formă de agregate lamelare. Se remarcă prezența dezamestecurilor de calcopirită în pirotină (Lazăr, 1970, raport nepubl.) și a pirotinei monoclinice alături de cea hexagonală (Popescu et al., 1972, raport nepubl.). Pirotina s-a format în cea mai mare parte, în faza hidrotermală, dar unele relații cu magnetitul arată că parțial a luat naștere și în condiții pirometasomatice.

Blendă este principalul mineral metalic din zăcămintul Valea Lita, fiind localizată preponderent în skarne cu epidot. Blendă formează uneori plaje compacte cu dimensiuni centimetrice și conture sinuoase în masa skarnului. Culoarea este neagră cu tinte cafenii și urma brună ceea ce sugerează o varietate bogată în fier. Granulele de blendă au conture allotriomorfe și dimensiuni pînă la 5 mm , iar la microscop

se observă dezamestecuri de calcopirită, sub formă de granule micronice, dispuse uneori după direcții cristalografice. Analizele spectrale efectuate pe 12 probe de blendă arată următoarele conținuturi medii (în ppm): Cd (4750), Mn (4680), Bi (695), Co (190), Ni (70), Ag (270), In (7,5). Blenda a fost întâlnită în următoarele asociații de minerale: blendă + pirită + galenă + marcăsită; blendă + pirită + calcopirită + cubanit + mackinawit; blendă + galenă + tetraedit.

Blenda împreună cu galena, pirita, calcopirita ± mispichel ± molibdenit, reprezintă principalii componente ai mineralizației polimetalice din zăcămintul Căcova Ierii (orizontul -250) și din sectoarele învecinate (forajele 31762, 2, 4, 7, 14, 17, 18, 24, 93, 94), galeria IV. Valea Vadului; galeria I Nergheș; aflorimente pe Valea Iara și fragmente pe piriul Fintinii, afluent drept al Văii Vadului). Mineralizația polimetalică se prezintă sub formă de cuiburi, filonase sau impregnații, cu dimensiuni relativ reduse, localizate în exoskarne și în banatite sau șisturi cristaline hidrotermalizate. Distribuția mineralizației polimetalice sugerează prezența unei zonalități periplutonice, cu aspect asimetric și discontinuu, vag conturată. Astfel în partea centrală a zonei predomină mineralizația de fier în timp ce sulfurile polimetalice sunt localizate, îndeosebi, în sectoare periferice afectate de procese hidrotermale.

Ludwigitul este componentul principal al mineralizației de bor care se asociază cu skarnele magneziene formind cuiburi, lentile, benzi, impregnații, în general cu dimensiuni de ordinul metrilor. Minerul de bor în general negricios, prezintă texturi compacte, uneori rubanate sau aproape sub formă de impregnație. Cristalele de ludwigit au habitusul fibros, cu luciu mat, rar sticlos, alcătuind agregate evisiparalele sau radiare. Ludwigitul este adesea transformat în szaibelyit, care formează microagregate aciculare alb-gălbui. Ludwigitul substituie minerale magneziene (forsterit, diopsid, clinohumit, dolomit), și este înlocuit de magnetit, pirotină, minerale serpentinite.

Produsele metalogenetice menționate mai sus, se caracterizează prin prezența în concentrații relativ ridicate a Sn (Popescu et al., 1972, raport nepubl.; Popescu, 1973; Lazăr et al., 1984, raport nepubl.; Ștefan et al., 1985), atât în unele tipuri de roci cit și în minerale (ppm): banatite (10-120), skarne (12-490), mineralizația de bor (3800), granați (90-1400), magnetit (20-900), ludwigit (10-30), ilvaît (500), flogopit (3-100), ferohastingsit (1600), turmalină neagră (150). De asemenea, au fost semnalate conținuturi relativ ridicate în W (ppm), în unele banatite (30-300), în skarne (300-800) și în mineralizația de bor (500). Aceste date sugerează eventuala prezență a unor minerale de Sn și de W, atât în skarne cit și în rocile turmalinizate din bazinul Văii Vadului, în aureola de contact

a plutonului granodioritic. Rocile turmalinizate au rezultat probabil prin aporturi de bor în faza pneumatică, în masa unor metamorfite cuarțo-feldspatice (gnaise, plagiometavulcanite) și se caracterizează prin asociația turmalină neagră + cuarț ± miche + pirită (Lazăr et al., 1984, raport nepubl.). După Nacovnic (fide Kurec, 1954), asemenea roci apar în faciesul cu turmalină + cuarț al gnaiselor, și pot fi gazda unor mineralizații de Sn ± W ± sulfuri metalice.

5. Considerații genetice

Geneza skarnelor și a mineralizațiilor asociate a fost controlată, pe lângă condițiile fizico-chimice respective, de factori magmatici, structurali și litologici, cu rol de metalotect.

Factorul magmatic (magmatismul banatic) a fost caracterizat, printr-un potențial metalogenetic ridicat determinat de fluidele mineralizate cu Fe, Zn ± Pb, Cu, S, B etc., separate din magnă.

Factorii structurali s-au manifestat la scară regională și locală. La scară regională sunt reprezentați de falia Băișoara-Păiceni și fracturile sale adiacente care au controlat evoluția și localizarea intruziunilor banatitice. Circulația ascendentă a fluidelor mineralizante a fost asigurată îndeosebi de structurile locale reprezentate de fracturi, zone de contact, diaclaze, pori, spații intergranulare etc.

Factorii litologici au fost reprezentați, în principal prin formațiunea carbonatică, din seria de Vulturese-Belioara și prin depozitele flișoide, senoniene.

Proprietățile fizice (grad ridicat de fisurare, spații intergranulare) și chimice (solubilitate accentuată pentru Ca, Mg, CO₂), specifice rocilor carbonatice, au favorizat desigur, în mod pregnant dezvoltarea largă a proceselor metasomatie. Influența rocilor carbonatice s-a manifestat, probabil, și prin: a) asimilarea acestora, în adâncime, de către magmele banatitice, rezultând astfel o îmbogățire în fier și o concentrare a acestuia în fluidele postmagmatice (Ovciniov, 1958) și b) eliminarea unor cantități însemnate de CO₂, prin procesul de skarnificare, controlind în acest fel, în aureola de contact mediul oxidant care a influențat depunerea magnetitului (Butler, 1923; Nokleberg, 1973). În acest sens, este concludent faptul că zăcămintul Valea Lita, dezvoltat pe seama unor mărne și gresii, se caracterizează, prin absența magnetitului.

Factorii fizico-chimici (temperatură, presiune, chimism, pH-ul fluidelor, mobilitatea componentelor etc.), au controlat, în mod direct, atât reacțiile chimice de substituție, cit și natura și succesiunea produselor. Din bilanțul metasomatic (tab. 3), întocmit după metoda Goroh (1964), pentru principalele tipuri de skarne ne-mineralizate, rezultă însemnate schimburi de materie.

Tabelul 3
Bilanțul metasomatic

Tip de skarn	Oxizi	K=60/M	Paleosom Dolomite (8) D=2.84		Skarne cu diopsid ± forsterit (3) D=3.36		Bilanț	
			c	x	c	x	Aport.	Levig.
Exoskarne magneziene	SiO ₂	1,00	0,96	2,73	37,03	124,42	121,69	
	Al ₂ O ₃	0,59	0,28	0,47	4,11	8,15	7,68	
	Fe ₂ O ₃	0,37	1,44	1,52	3,49	4,34	2,82	
	FeO	0,83	0,22	0,52	1,52	4,24	3,72	
	MgO	1,48	20,35	85,54	29,06	144,51	58,97	
	CaO	1,07	30,14	91,59	9,90	35,60		55,99
	MnO	0,85	0,43	1,04	0,24	0,69		0,35
	Na ₂ O	0,96	0,09	0,25	0,11	0,36	0,11	
	K ₂ O	0,63	0,08	0,15	0,83	1,76	1,61	
	TiO ₂	0,75	0,01	2,13	0,21	0,53		1,60
	P ₂ O ₅	0,42			0,02	0,03	0,03	
	CO ₂	1,36	45,57	176,01	10,43	47,66		128,35
	H ₂ O	3,34			2,90	32,55	32,55	
	Total		99,57		99,85			
Exoskarne calcice			Paleosom Calcare (3) D=2,74		Skarne cu granat (3) D=3,61		Aport.	Levig.
	SiO ₂	1,00	1,28	3,51	36,07	130,22	126,71	
	Al ₂ O ₃	0,59	0,40	0,65	1,56	3,33	2,68	
	Fe ₂ O ₃	0,37	0,22	0,23	26,68	35,51	35,28	
	FeO	0,83			0,63	1,89	1,89	
	MgO	1,48	1,22	4,95	1,86	9,94	4,99	
	CaO	1,07	53,09	155,85	28,53	110,21		45,44
	MnO	0,86	0,06	0,14	0,49	1,51	1,37	
	Na ₂ O	0,96	0,13	0,35	0,14	0,49	0,14	
	K ₂ O	0,63	0,08	0,14	0,05	0,12		0,02
	TiO ₂	0,75			0,13	0,36	0,36	
	P ₂ O ₅	0,42			0,02	0,03	0,03	
	CO ₂	1,36	42,69	159,08	2,79	13,70		145,38
	H ₂ O	3,34			0,48	5,79	5,79	
	Total		99,17		99,83			
			Paleosom Calcare (3) D=2,74		Skarne cu piroxeni (2) D=3,41		Aport.	Levig.
	SiO ₂	1,00	1,28	3,51	41,95	143,05	139,54	
	Al ₂ O ₃	0,59	0,40	0,65	1,55	3,12	2,47	
	Fe ₂ O ₃	0,37	0,22	0,23	5,40	6,82	6,59	
	FeO	0,83			5,09	14,41	14,41	
	MgO	1,48	1,22	4,95	9,68	48,85	43,90	
	CaO	1,07	53,09	155,85	25,04	91,37		64,28
	MnO	0,85	0,06	0,14	1,10	3,19	3,05	
	Na ₂ O	0,96	0,13	0,35	0,17	0,56	0,21	
	K ₂ O	0,63	0,08	0,14	0,02	0,05		0,09
	TiO ₂	0,75			0,11	0,29	0,29	
	P ₂ O ₅	0,42			0,04	0,06	0,06	
	CO ₂	1,36	42,69	159,08	8,45	39,19		119,89
	H ₂ O	3,34			1,22	13,90	13,90	
	Total		99,17		99,82			

Tabelul 3 (continuare)

		K=60/M	Paleosom Marne (1) D=2,42		Skarne cu epidot (1) D=3,08		Aport.	Levig.
Exoskarne calcice	SiO ₂	1,00	50,65	122,58	48,37	148,98	26,40	
	Al ₂ O ₃	0,59	15,78	22,53	11,65	21,17		1,46
	Fe ₂ O ₃	0,37	3,01	2,70	8,54	9,74	7,04	
	FeO	0,83	3,88	7,80	1,96	5,01		2,79
	MgO	1,48	1,53	5,48	1,82	8,30	2,82	
	CaO	1,07	9,77	25,30	19,06	62,82	37,52	
	MnO	0,85	0,08	0,17	0,61	1,76	1,59	
	Na ₂ O	0,96	1,85	4,30				4,30
	K ₂ O	0,63	2,83	4,32				4,32
	TiO ₂	0,75	0,52	0,95	0,40	0,93		0,02
	P ₂ O ₅	0,42	0,08	0,09	0,07	0,09		
	CO ₂	1,36	7,10	23,37	6,40	26,81	3,44	
	H ₂ O ⁺	3,34	2,51	20,29	1,42	14,61		5,68
	Total		99,59		100,36			
			Paleosom Granodiorit (4) D=2,78		Skarne cu pirox.+granați (7) D=3,42		Aport.	Levig.
Endoskarne	SiO ₂	1,00	58,98	163,97	43,18	147,68		16,29
	Al ₂ O ₃	0,59	17,29	28,36	16,83	33,96	5,60	
	Fe ₂ O ₃	0,37	1,36	1,40	3,82	4,84	3,44	
	FeO	0,83	4,06	9,37	2,05	6,82		3,55
	MgO	1,48	3,91	16,09	5,65	28,60	12,51	
	CaO	1,07	6,46	19,22	23,05	84,35	65,13	
	MnO	0,85	0,02	0,05	0,38	1,11	1,06	
	Na ₂ O	0,96	3,35	8,94	0,71	2,34		6,60
	K ₂ O	0,63	2,26	3,95	0,32	0,69		3,26
	TiO ₂	0,75	0,69	1,44	0,67	1,72	0,28	
	P ₂ O ₅	0,42	0,17	0,20	0,17	0,25	0,05	
	CO ₂	1,36	0,54	2,05	1,65	7,68	5,63	
	H ₂ O	3,34	0,47	4,37	1,16	13,25	8,88	
	Total		99,56		99,64			

- Date analitice după Lazăr et al. (1971, 1984, rap. nepubl.); Popescu et al. (1972, rap. nepubl.).

- Cifrele din paranteze indică numărul analizelor chimice utilizate.

- Formula utilizată: $x = DCK$ (x = numărul moleculelor dintr-un volum standard de 10 000 Å³; D = densitatea rocii;

C = media aritmetică a oxidului în procente greutate din rocă; K = coeficient de calcul; M = greutatea moleculară a oxidului.)

Formarea exoskarnelelor implică pe de o parte aporturi substanțiale de SiO₂, Fe₂O₃, FeO, și subordonat de Al₂O₃, MgO, iar pe de altă parte eliminarea unor cantități importante de CaO și CO₂. Endoskarnele implică levigarea parțială a SiO₂, FeO, Na₂O, K₂O și adausuri de CaO, MgO, Al₂O₃, CO₂.

Formarea acumulărilor de magnetit sau de sulfuri s-a produs prin aporturi de metale și sulf și levigarea componentilor din mineralele substituie. Sursa metalelor o presupunem în magnele banatitice, din care s-au separat prin diferențiere. Cantitatea mare de fier transportată ascendent de fluidele postmagmatice ar putea proveni din diferențierea unor magne banatitice, bogate în fier, la care s-a adăugat și fierul remobilizat din roci preexistente, de către aceleași fluide postmagmatice. Conținutul ridicat în fier al magnelelor s-ar putea explica atât prin chimismul lor inițial, cât și printr-o îmbogățire ulterioară, datorită asimilării parțiale a unor roci din formațiunea carbonatică de

Belioara (Intorsureanu, 1976), care foarte probabil a conținut și roci ferifere (paraankerite, dolomite ferifere), așa cum s-a menționat în zona Pleșa Runcului (Marza, 1969).

Modelele clasice privind succesiunea de formare a skarnelor și mineralizațiilor asociate (Korjinski, 1965; Zharikov, 1970; Pertsev, 1974) sunt în acord cu observațiile din regiunea cercetată și cu rezultatul studiului incluziunilor fluide (Pomârleanu et al., 1988). În zona Băișoara au fost recunoscute două stadii succesive, alcătuite din mai multe faze și subfaze.

Stadiul magmatic este reprezentat prin faza skarnelor magneziene cu spinel + forsterit, localizate la contactul nemijlocit dintre granodiorite și dolomite. Aceste skarne par a avea o dezvoltare subordonată. Ele au luat naștere prin difuzie și implică o mobilitate ridicată a aluminiului.

Stadiul postmagmatic a generat, aproape întreaga masă a metasomatitelor. Acestea au rezultat prin

procese de infiltrație și difuzie, după cum sugerează modul lor de localizare, relațiile structural-texturale și caracterele mineralogice. Metasomatitele postmagmatice s-au format după consolidarea, cel puțin periferică, a intruziunilor granodioritice și într-un interval de temperaturi cuprins aproximativ între 620° și 150° C (Pomârleanu et al., 1988). După natura produselor se disting patru faze:

a) Faza de skarn (620°-400° C) este caracterizată prin aporturi de SiO_2 , Fe_2O_3 și levigarea CaO , CO_2 etc. Se remarcă trei subfaze, primele două sint bine reprezentate în zăcămintele Mașca-Băișoara și Cacova Ierii, iar ultima în zăcămintul Valea Lita.

- Subfaza skarnelor magneziene (~620° C) cu forsterit, diopsid, flogopit + clinohumit.

- Subfaza skarnelor calcice (620°-400° C), cu granați, piroxeni + vezuvian + wollastonit + ilvait + magnetit I.

- Subfaza skarnelor cu epidot (> 400° C).

b) Faza cu borați (~530° C) este determinată de metasomatoza borului și formarea ludwigitului (Ionescu et al., 1971). Prin aportul de bor a rezultat, de asemenea, turmalinizarea metamorfitelor cuarțofeldspatice (Valea Vadului).

c) Faza cu magnetit (500°-460° C) este cea mai importantă din punct de vedere metalogenetic. Se distinge prin aport de fier care s-a concentrat în aureola metasomatică, unde fugacitatea oxigenului este relativ ridicată, determinând astfel formarea magnetitului II.

d) Faza hidrotermală (400°-150° C) este larg dezvoltată și cuprinde trei subfaze intim asociate:

- Subfaza alterațiilor hidrotermale a generat variate transformări dintre care mai semnificative sint: biotitizarea, propilitizarea, sericitizarea, albitizarea, argilizarea (illit, montmorillonit, caolinit) + anhidritizarea - dezvoltate în special pe seama rocilor banatitice; serpentinizarea și flogopitizarea - afectează skarnele magneziene; actinolitizarea, epidotizarea, cloritizarea - substituie skarnele calcice. Dintre numeroasele neoformațiuni amintim prezența ferohastingsitului și sepiolitului (Popescu et al., 1972, raport nepubl.), a hisingeritului (Marza, Marza, 1974) și a palygorskiteului (Lazăr et al., 1980, raport nepubl.).

- Subfaza cu sulfuri se remarcă prin aporturile de S și metale (Fe, Zn, Pb, Cu etc) și creșterea acidității soluțiilor, ceea ce a determinat depunerea sulfurilor + magnetitul III, ultimul implicând apariția unui mediu slab oxidant.

- Subfaza cu calcit și zeoliți, marchează încheierea proceselor afiliate magmatismului banatic.

În stadiul *crogen*, procesele de eroziune la nivelul Eocenului, au deschis parțial zonele mineralizate. Produsele sint constituite din depozite detritice și de oxidație cu blocuri și fragmente de marmure, skarne + mineralizații, opalite feruginoase etc., prinse într-o ma-

trice argiloasă-limonitică de culoare brun-cărămizie. Dintre mineralele metalice s-au întâlnit goethit, hidrogoethit, bornit, covellină, marcasită, malachit, azurit.

Din datele expuse rezultă că zăcămintele de skarn (sau metasomatice de contact) de la Băișoara alcătuiesc un cîmp metalogenetic cu mineralizații de fier, zinc, polimetalice și bor. Dispunerea pe direcția N-S a zăcămintelor sugerează prezența unui aliniament metalogenetic, care coincide aproximativ cu un segment de 6 km al faliei Băișoara-Pănceni.

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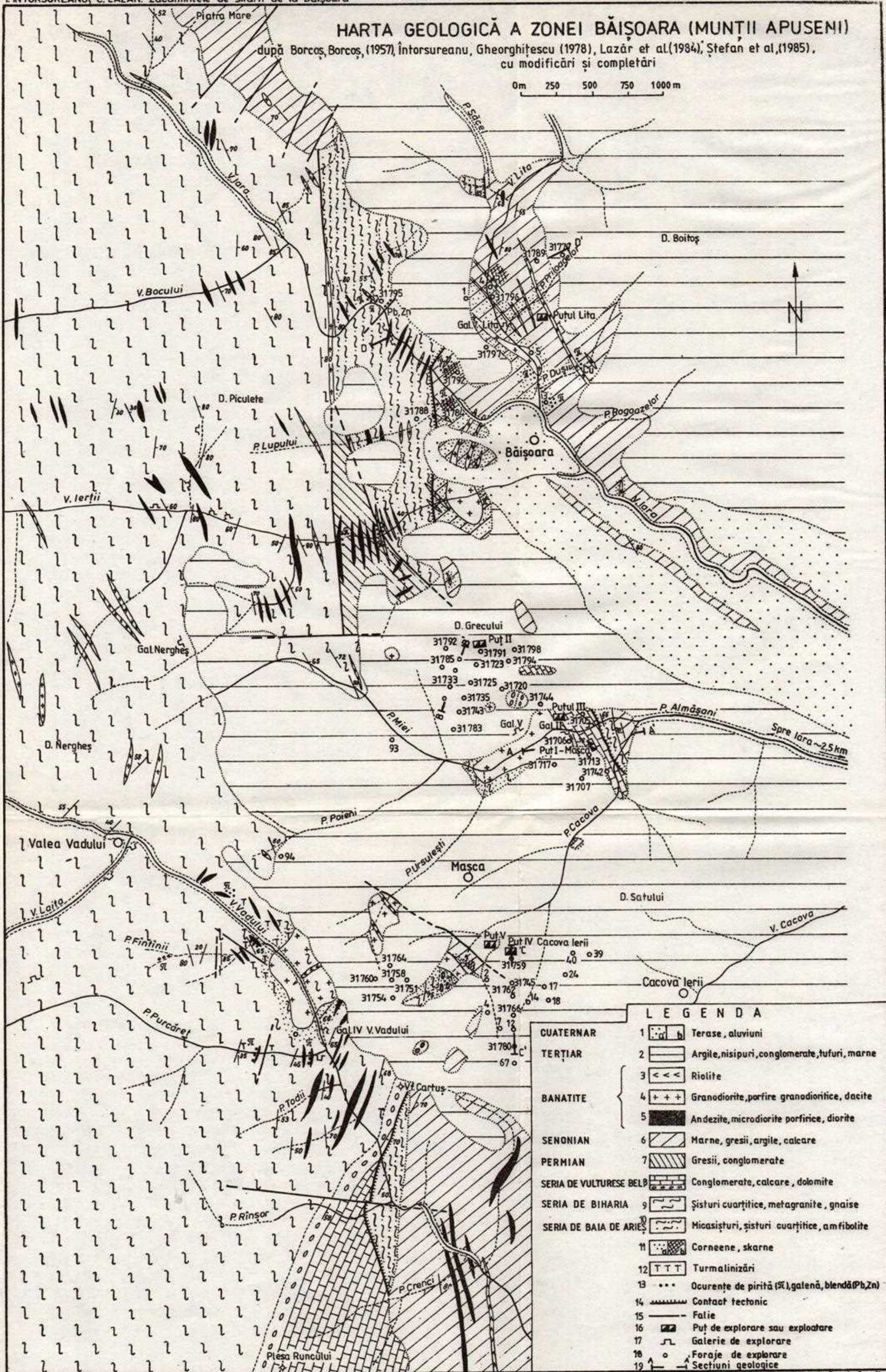
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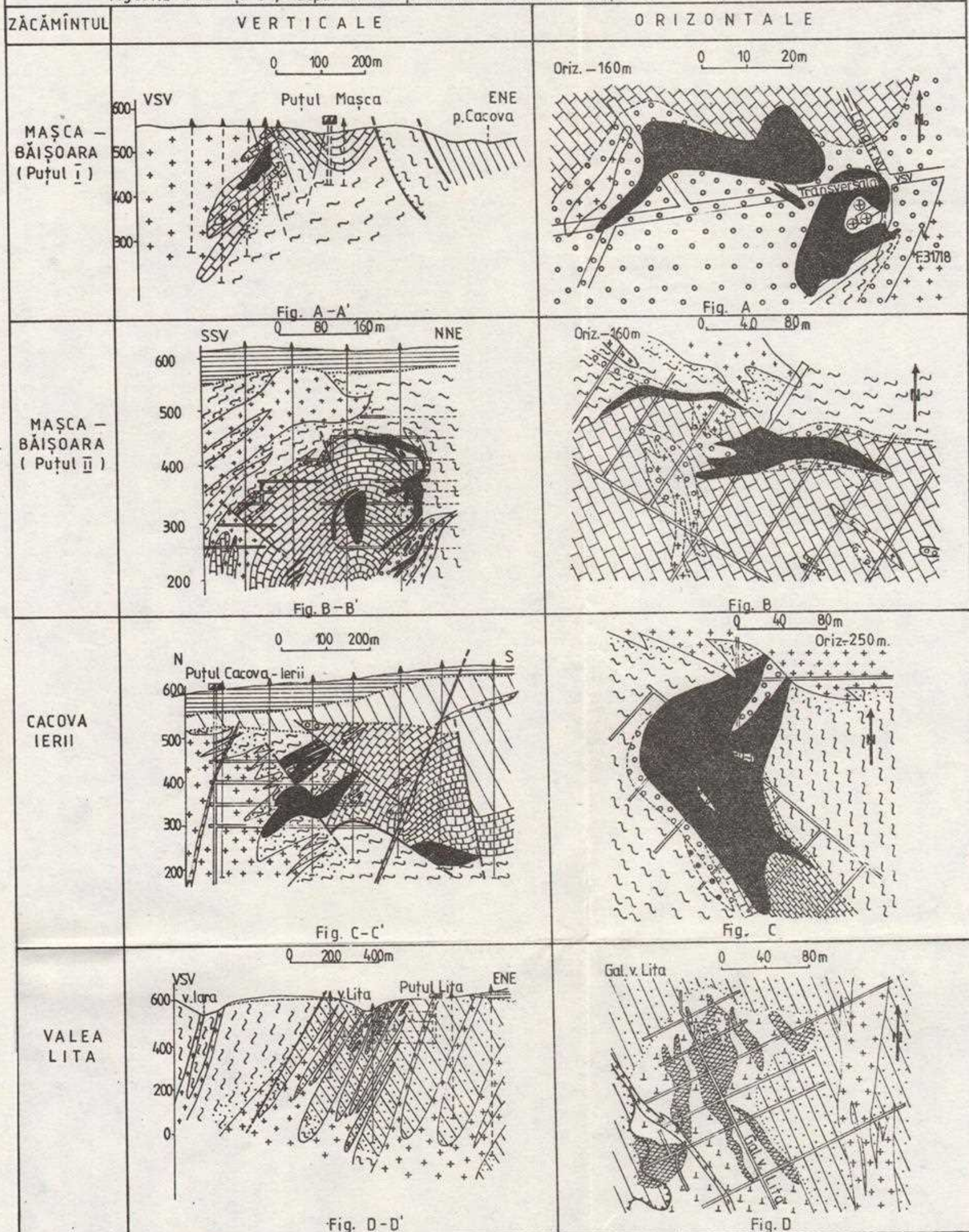
după Borcoș, Borcoș, (1957), Întorsureanu, Gheorghițescu (1978), Lazăr et al. (1984), Ștefan et al. (1985),
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Figurile B-B' și B, după Burz și Tibad (1980) cu simplificări



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THE CIOCLOVINA ORE OCCURRENCE : MINERALOGICAL DATA AND SOME REMARKS ON ITS GENESIS

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Key words: Mineralization. Sulfides. Ore Microscopy. Minor Elements. Shear Zone Processes. South Carpathians – Getic and Supragetic Crystalline – Sebeș Mts.

Abstract: *The Cioclovina Occurrence: Mineralogical Data and Some Remarks on Its Genesis.* Although of small size and situated in an isolated area, the Cioclovina ore occurrence is interesting due to its contrasting mineral assemblages and its geological setting. Both concordant and discordant ore bodies are present exhibiting quite distinct mineral assemblages, i.e. lenses and beds (sometimes folded) in gneisses, containing sphalerite, galena and pyrite as well as veins or veinlets and impregnations in brecciated gneisses with nickeliferous pyrite, jamesonite and arsenopyrite. Greigite globular aggregates are present too, showing advanced transformations into pyrite and marcasite intergrowths. Sulfur isotope analyses show a great variation interval, i.e. from -4.64 to $+12.76$ ‰ $\delta^{34}\text{S}$. The sulfide pairs are in isotopic disequilibrium. Overlapping parageneses, the lack of hydrothermal-like alteration and the relationships between ore bodies, host rocks and S–planes suggest that the Cioclovina ore occurrence belongs to the shear-zone related mineralizations.

Although seemingly unimportant, the Cioclovina ore occurrence is particularly of interest due to both its contrasting mineralogical features and its geological setting and genetical affiliation. The present study is based on the data yielded by numerous (ca 100) polished and thin sections and available reports. The mineralogical composition has proved to be more complex than previously known, while the location of the ore bodies is quasiconcordant to the metamorphic foliation. The data newly inferred and the apparently contradictory aspects justify this study, aiming at arguing a new hypothesis on the genesis of this ore occurrence.

Previous Investigations

Fragments of mineralized rocks were identified by Pavelescu L. and Constantino D. (1955, unpubl. report) on the waste dump of an old gallery privately dug in 1940–1942. Other ore occurrences are mentioned later by Teodoru L. (1963, unpubl. report), as veins of decimetric thickness located at the top and base of a fault. Benea Gh. (1963, unpubl. report) draws up some geochemical anomalies for Zn and Pb of relatively high value and reduced extent. A thorough report of the mining works from this area is presented by Harosa S. (1964, unpubl. report). Șeclăman M. (1981, unpubl. report), Pitropov O. et al. (1983, unpubl. report) and Hărtopanu I. et al. (1984, unpubl.

report) cite other mineralized places and put forward global analytical data on the ore occurrences, informing on the epigenetic character of the mineralizing process associated with a deep-seated intrusive body.

Geological Setting

The Cioclovina ore occurrence is located in the western part of the Sebeș Mts, north of the well-known Cioclovina cave. Ore occurrences are located along the Cioclovina brook, within the metamorphites of the Sebeș-Lotru Series (Group) (Precambrian), unconformably overlain by Permian sedimentary deposits (Fig. 1). The tectonic contact between the sedimentary rocks and the metamorphites is due to two important structural elements, out of which the reverse fault west of Cioclovina brook represents here the boundary between the lower formation (plagiogneisses) of the Sebeș-Lotru Series and the upper formation (plagiogneisses and micaschists). The metamorphic rock pile on the Cioclovina brook is cut, according to Pitropov et al. (1983), by faults of reduced extent, along which the mineralizing hydrothermal fluids did flow. Igneous (non-metamorphosed) rocks occur sparsely, as metric bodies represented by rhyodacites (Fig. 1). The radiogenic age of biotite contained by these rocks is of 90.5 Ma (Hărtopanu, in Pop et al., 1985).

Ore Bodies Morphology

All the previous studies mention mainly vein-like concentrations located in metamorphites with scarce gangue minerals (quartz, calcite). M. Șeclăman (oral communication, 1988) points out ore occurrences within Liassic sandstones. It is worth noting that Harosa (1964) mentions the occurrence of some mylonites associated with sulfides, as well as lens-like ore bodies, conformable to the metamorphite foliation, accompanied by unconformable bodies (Fig. 2). The ore is massive, exhibiting sometimes oriented texture (mainly compact sphalerite fragments), which under the microscope is proved to be due to lamination.

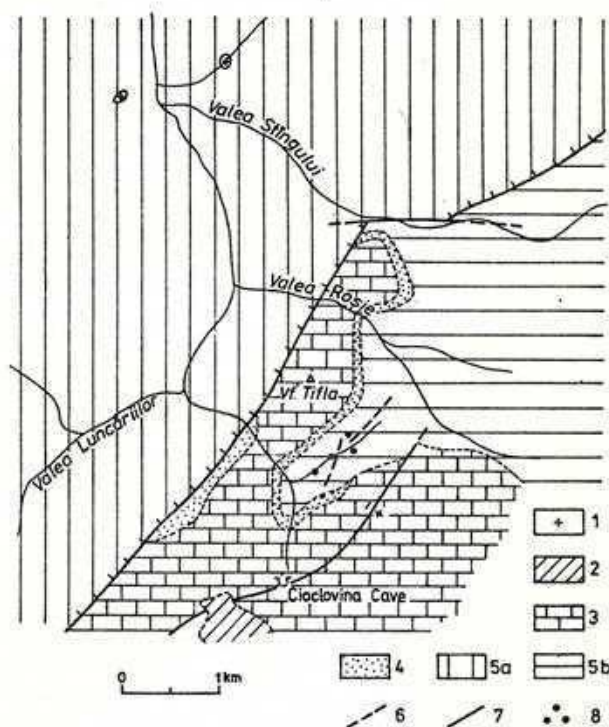


Fig. 1 - Geological sketch of the Cioclovina area (acc. to Pop et al., 1985).

1, rhyodacites (Mesozoic ?); 2, Cenomanian marly deposits; 3, mainly carbonate deposits (Lower Jurassic-Aptian); 4, Permian gritty deposits; 5, Sebeș-Lotru Series (Precambrian metamorphites): (a) plagiogneisses and micaschists formation; (b) paragneisses formation; 6, reverse fault; 7, normal fault; 8, ore occurrences.

Ore Structures and Textures

Mesoscopically, one notices deformation (lamination) structures, compact and breccious textures, with gneiss fragments looking like sulfides-cemented. Microfolds or parts of them, parallel sphalerite and galena strips or laminated sphalerite strips crossed by parallel

or sheaf-like pyrite and marcasite veinlets. Particularly interesting are the globular aggregates 1-3 mm in size consisting of pyrite and marcasite, isolated, attached to or intermingled with compact strips (Fig. 3). Unfortunately the contrasting aspects mentioned cannot be surely reported to the main morphological types illustrated in Figure 2.

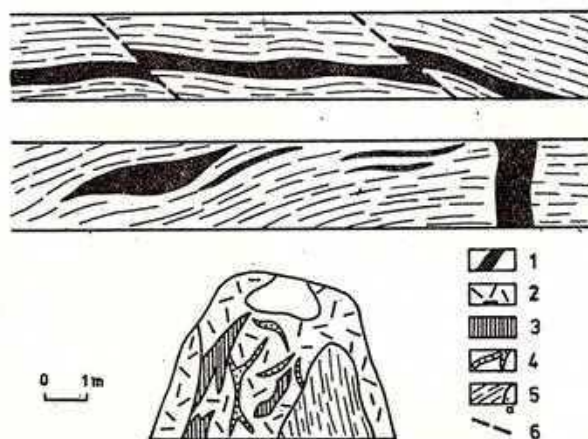


Fig. 2 - Mesoscopic features of the ore occurrence (sketches drawn acc. to mining works) (acc. to Harosa, 1964).

1, marcasite veinlets; 2, breccias; 3, mylonites; 4, conformable and unconformable massive ore (sphalerite and galena); 5, micaschists and paragneisses; (a) ocellar migmatites; 6, faults.

Mineralogical Composition

Excepting the data presented by P. Hărtopanu et al., 1984), all the previous studies mentioned the following minerals: sphalerite, galena, pyrite, chalcopryrite, marcasite, gold, silver, quartz, calcite. However, the number of mineral species contained by the Cioclovina ore occurrence is higher (Table 1). Sphalerite is the prevailing mineral; galena and pyrite occur subordinately, while the other minerals are components observed only under the microscope; jamesonite forms dense aggregates of centimetric size.

Iron sulfides. Although quantitatively subordinate, the four iron sulfides (pyrite, marcasite, greigite and pyrrhotite) together with bravoite or nickeliferous pyrite mostly inform on the ore genesis. Excepting the common intergrowths with sphalerite and galena, pyrite also forms monomineral aggregates of different shapes, out of which the "lamellar" aggregates are worth mentioning (Pl. I, Figs 1-3), which are in fact pyrite/silicates intergrowths; pyrite veinlets (local remobilisations ?) pierce the lamellar structures (Fig. 3c). The features illustrated in Pl. I, Fig. 4 are also

characteristic ones, prismatic pyrite aggregates being surrounded by or "floating" within filigree-like pyrite and marcasite groundmass.

in diameter)(Fig. 3e) which under the microscope exhibit lamellar-radial structure, the lamellae consisting of pyrite and marcasite converging into a pyrite nu-

Table 1
Mineralogical Composition of the Cioclovina Ore Occurrence

Major components:	sphalerite galena pyrite	Observed with the naked eye
Minor components:	chalcopryrite arsenopyrite bravoite (Ni-pyrite) jamesonite greigite tetrahedrite bournonite ? cobaltite ? pyrrhotite ^x magnetite ^x hematite ^x gold rutile ^x graphite ^{xx}	Observed only under the microscope, encountered in several polished sections "Minor minerals" occurring in some polished sections or as isolated grains

^x Occurring exclusively as inclusions in pyrite

^{xx} "Petrogenic" minerals

? Single grains of reduced size (preliminary diagnosis)

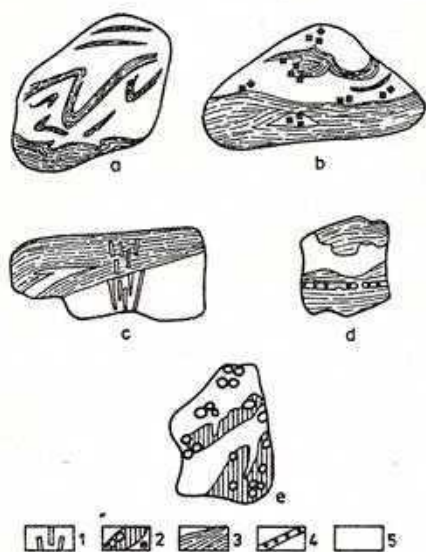


Fig. 3 - Mesoscopical features of the ore components (drawings acc.to polished sections, natural size).

1, marcasite veinlets; 2, compact pyrite strips containing globular pyrite-marcasite formations; 3, microfolded and/or laminated ore (prevailing sphalerite); 4, galena-rich strips; 5, pyrrhotite.

Pyrite usually occurs as globular aggregates (1-2 mm

cus (Pl. I, Figs. 5, 6; Pl. II, Fig. 1). These aggregates are supposed to be the final product of greigite evolution, a metastable mineral, usually forming spheroidal or ellipsoidal aggregates (Pl. II, Fig. 2). Greigite is preserved only sparsely and exhibits pyrite or marcasite rims; its colour resembles the colour of pyrrhotite, its hardness is lower and it is completely isotropic. Marcasite is more abundant than pyrite, with which it is frequently associated either in globular "melnicovite pyrite" structures or in lamellar structures (probably a pseudomorph after a silicate). Pyrrhotite has been sparsely noted as minute inclusions in pyrite which suggest a pre-existing iron-poor mineralizing stage preserved by massive pyrite. Pyrrhotite is associated in places with magnetite which occurs also as inclusions in pyrite arguing for the hypothesis according to which part of pyrite was formed at the expense of early pyrrhotite.

Sphalerite is the main mineral, often forming monomineral aggregates, massive or laminated, exhibiting deformed strips resembling locally microfolds (Fig. 3 a, b). Macroscopically *galena* is very sparse, constituting bands in the sphalerite groundmass (Fig. 3 d); in spite of its small amounts, galena is frequently observed under the microscope, intergrown with sphalerite; worth mentioning are the structures based on "hesitating" relationships between the two sulfides (Pl.

II, Fig. 3), marked by mutual insertion and quasi-isometrical grains, which account for structures typical of regionally metamorphosed ore. Sphalerite is relatively homogeneous, of dark brown colour, with orange-brown or red-orange internal reflections. Extremely fine pyrite veinlets which mould or pierce the sphalerite aggregates (Pl. II, Fig. 4) are of interest. These features suggest the deferrization of sphalerite, pyrite being a "residual" product of (Zn, Fe)S solid solution destabilization under pressure.

Arsenopyrite is a minor component; it occurs as isolated, euhedral grains included in sphalerite, but it often associates with nickeliferous pyrite/bravoite-jamesonite, usually as inclusions in pyrite. The bravoite-jamesonite-arsenopyrite assemblage is typical of the Cioclovina ore occurrence, but unfortunately the relationships to the other sulphides have not been defined. The nickeliferous pyrite or bravoite zoned grains often show uneven contours (Fig. 4) and are cemented by prismatic to acicular crystals of jamesonite. The grain zoning is not always obvious, (Pl. II Fig. 5). Other details of the structure of these grains are presented in Figure 4.

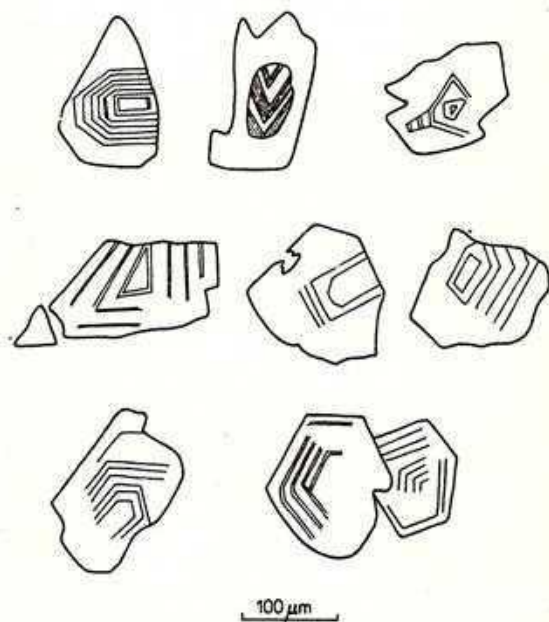


Fig. 4 - Microscopic features of zoned bravoite-like pyrite grains (drawings acc. to polished sections). The pyrite grains are euhedral or anhedral and always moulded by compact jamesonite aggregates.

The prismatic *jamesonite* aggregates often moulds subhedral or anhedral bravoite grains: jamesonite inclusions in pyrite or bravoite are frequent, pointing to local zoned arrangement. Acicular jamesonite aggregates form reticulate structures in quartz. The "spatial

arrangement" of these aggregates can be seen under the microscope by crossed nicols (Pl. II, Figs 6).

The Cioclovina ore contains also some minor minerals which occur mainly as inclusions. Tetrahedite and bournonite (?) form fine inclusions in galena. Subhedral grains of a mineral resembling cobaltite and chalcopryite grains and laths have been observed in sphalerite. The latter mineral contains also small inclusions of gold (?) (RNAA analyses of sphalerite gave 0.1 ppm Au). Small hematite inclusions are locally present in pyrite. Rutile prisms and graphite lamellae occur associated with quartz and micas, respectively.

Two still unidentified minerals appear intimately associated with jamesonite, i.e. the mineral A - a sulphosalt optically related with it but with different color shades and birefractance intensity and the mineral B - a product of the jamesonite decomposition.

Supergene alteration involves scarce development of goethite and cerussite at the expense of pyrite and galena, respectively.

Analytical Data

Quantitative emission spectrographic analyses (analyst Alla Zămircă, I.G.G.) show for pyrite (Tab. 2) high Sb, As and Ni contents in accordance with the numerous jamesonite and arsenopyrite inclusions and the composition zoning imposed by nickel. Ti and Ca amounts are rather interesting, as far as they are usually immobile during geological processes. The Ni:Co ratio is oscillating, the nickel amount usually exceeding the cobalt one. Sphalerite (Tab. 3) stands out due to its high and relatively constant cadmium and silver contents, partly the antimony ones, due to the numerous inclusions of other minerals. A single galena sample (Tab. 4) has been subject to the monomineral analysis; the Sb:Ag ratio and the lack of Bi eliminate the problem of the ore assignment to the banatitic metallogeny.

The analyses of bulk ore samples (Tab. 5) yield similar high contents of the same minor elements identified on monomineral samples. Worth mentioning are the high Cr and Ti contents and Mn ones which account for a "syngenetic support" of ores.

The chemical data reported by Pitropov et al. (1983) and the spectrographic ones from Table 5 were plotted on the diagram of Figure 5, which suggests the zinciferous character of the ore occurrence.

The sulfur isotopes analyses are presented in Table 6. Due to the sulfide intergrowths, only a single sample exhibiting coexistent sulfide pairs was obtained. The variation of the sulfide isotope composition analysed is worth noting. The heaviest sulfide is the globular pyrite, supposedly formed at the expense of greigite. The lack of mineralogical equilibrium, noticed under

Table 2
Minor Elements in Pyrite (ppm)

Sample No.	1	2	3	4	5	6	7	8	9	10	11
Cu	34	*	*	50	85	170	80	65	270	70	50
Pb	3200	240	420	9000	120	160	360	400	> 3%	> 1%	< 30
Zn	4500	130	< 100	16500	< 100	< 100	190	< 100	2.2%	< 100	< 100
Ag	16	34	58	90	15	12.5	24	180	240	65	15
Sb	2200	300	580	800	1700	3200	1400	> 1%	2300	1350	< 300
As	5400	< 1000	< 1000	< 1000	10500	< 1000	8500	< 1000	400	11500	10000
Ni	40	140	240	300	75	410	27	110	740	30	30
Co	11	17	36	55	*	55	5	210	120	19	*
Ti	*	170	150	190	*	460	170	*	1200	55	55
Mn	*	29	40	145	*	*	11	125	360	*	*
Cr	200	*	*	*	*	*	280	*	230	*	*

(*) Below the detection limit: Ga (10), Cd (100), Sn (10), Bi (10), Mo (10), V (10), Cr (30), Co (10), Ti (30), Cu (30).
Isolated contents: 200 ppm Mo (sample 6), 160 ppm Ti (sample 33), 33 ppm V (sample 9), 90 ppm Cd (sample 9).

Table 3
Minor Elements in Sphalerite (ppm)

Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cu	170	160	170	280	180	260	160	160	240	460	180	260	180	210
Pb	>3 %	3 %	750	>3 %	>3%	1.5 %	2100	1 %	>3 %	1%	>3 %	1.5 %	>3 %	2.2 %
Cd	1500	1400	1500	1750	2200	1300	1500	1700	1900	2300	1800	1800	1900	1600
Ag	>100	100	37	>100	>100	>100	56	64	>100	160	650	>100	>100	>100
Ga	30	22	12	37	39	22	16	26	52	42	34	56	25	38
Ge	50	46	12	65	50	65	52	52	77	52	26	80	70	55
Sb	800	600	380	750	750	420	<300	<300	900	170	650	550	550	480
Ni	52	*	10	*	*	*	*	23	*	11	31	*	*	30
Co	135	100	65	125	135	105	95	96	95	95	120	135	75	155
Ti	120	145	*	100	105	300	*	170	*	600	480	*	140	140
Mn	46	55	48	115	58	180	35	39	54	750	65	100	64	48

The iron content exceeds 3 %. (*) Below the detection limit: Sn(10), Tl (30), In (10), Bi (10), As (1000), Mo (10), Ni (10), Ti (30). Isolated contents: 31 ppm Sn (sample 3); 11.5 ppm In (sample 9); 16 ppm In (sample 11).

Table 4
Minor Elements in Galena (ppm)

Cu	46	Sb	2800
Zn	>3 %	As	<1000
Cd	340	Co	26
Ag	1200	Mn	200

Below the detection limit: Ga (10), Sn (30), Tl (30), As (1000), Ni (10), Bi (10).

the microscope, is also confirmed by the sulphur isotopic composition. The isotopic geothermometer is not possible to apply, not even by averaging the individual values to the global values of +6.48 ‰ for pyrite and +3.48 ‰ for sphalerite.

Genetic Remarks

The Cioclovina occurrence cannot be considered as being formed by syngenetic or epigenetic processes in the classical sense. Its syngenetic character is difficult to harmonize with the relatively monotonous nature of the host rocks (migmatic gneisses) in which the lithologic unconformity (elements typical of most of the regionally metamorphosed syngenetic ores) are absent. The conformity of some ore strips (see Fig. 2) to the host rocks as well as the obviously unconformable ore bodies, the ores located in breccias or associated with mylonites prove the relationship with a postmagmatic epigenetic process difficult. The absence of hydrothermal changes is also obvious: the host rocks of ores are laminated, cataclased, brecciated and mylonitized resulting in nests or lenses (sometimes noticed only

Table 5
Minor Elements in Bulk Ore Sample (ppm)

A. Slightly mineralized samples					
Sample No	1	2	3	4	5
Pb	55	480	9000	130	100
Zn	140	420	520	320	170
Cu	47	24	100	100	7
Ag	10	7	100	1	1
Sb	<100	230	8600	<100	<100
As	<300	4400	8600	<300	3200
Zr	30	7	<5	34	16
Ga	14	5	7	17	8
Ni	34	13	20	28	6
Co	24	4	10	25	6
Cr	160	3	4	160	3
V	160	11	14	124	6
Ti	5000	210	72	4600	92
Mn	4200	<30	40	880	1600

Below detection limit: Cd (30 ppm), Ge (10), In (3),
Sn (5), Bi (3).

B. Highly mineralized samples											
Sample No	6	7	8	9	10	11	12	13	14	15	16
Cu	62	50	420	290	130	40	76	<30	52	30	72
Ag	240	340	480	230	200	44	280	14	170	10	80
Cd	450	380	1050	1100	350	220	90	54	200	160	600
Ge	14	14	40	34	10	<10	<10	<10	<10	<10	20
In	3.5	<3	5.5	9	3	<3	<3	<3	<3	<3	<3
Sb	300	380	600	270	900	>100	700	>100	400	600	>100
As	<300	<300	<300	<300	<300	<300	<300	<300	<300	1.1 %	<300
Sn	<5	<5	13	7	6.5	<5	<5	18	7	<5	<5
Zr	34	50	32	15	36	30	64	56	76	15	84
Ga	17	22	34	43	23	13	11	23	24	3	28
Ni	21	10	9	8	62	26	400	<3	250	36	15
Co	36	25	115	115	55	32	60	13	44	28	48
V	42	85	30	46	34	60	76	36	92	<5	68
Ti	400	1100	300	480	370	380	700	600	1000	44	1200
Mn	480	70	620	160	105	300	92	760	42	44	280

Not found: Cr (30), Bi (3).

under the microscope) consisting of quartz and carbonates, with subordinate amounts of sulfides. The relationships between sulfides are contrasting, and characterized by a general lack of mineralogical and isotopic equilibrium. The sulfides contain minor elements (Cr, Mn, Ti) which account for a syngenetic or rather "petrogenic" support of sulfide crystallisation process or processes.

The presence of pyrrhotite (as relicts within pyrite) associated with greigite, of cobaltite with jamesonite, of hematite with pyrrhotite, etc. point to a complex assemblage, yielding incompatible minerals and superposed parageneses (Udubașa, 1986) which suggest the polygenetic character of the ore occurrence. By the very detailed analysis of the relationships between sul-

fides it is still difficult to get a unitary image of the normal crystallization sequence, thus a mosaic-like image of the heterochronous parageneses is inferred instead (Fig. 6).

In spite of the numerous data on the Cioclovina ore occurrences, a thorough reconstruction of the mineralogical process is difficult, mainly because of the lack of a connection between mesoscopic, microscopic and analytical data. Therefore, the genetic model presented below is only a tentative one.

The metamorphic pile of the Sebeș-Lotru Series (Group) is supposed to have contained rocks yielding Zn, Pb, Ni contents exceeding the characteristic average values of gneisses and micaschists. The migmatization processes were probably a former stage of metal

Table 6
Sulfur Isotope Analyses ($\delta^{34}\text{S}$, ‰)

	Pyrite	Sphalerite	Galena	Remarks
1	+ 2.02			Compact pyrite with fine inclusions of sphalerite, pyrrhotite and jamesonite
2	+ 2.38			Compact pyrite, partly euhedral, with filigree-like pyrite envelopes; compact pyrite is locally marcasitized and exhibits fine pyrrhotite and magnetite inclusions
3	+ 5.95	+ 6.62	- 2.42	The three sulfides are finely intergrown; pyrite also occurs on the micas cleavages, being partly marcasitized
4	+ 9.28			Pyrite associated with marcasite forming globular aggregates (Fig. 4) with greigite relics
5	+12.76			Compact pyrite, slightly brecciated, exhibiting bravoite appearance
6		+ 7.59		Massive sphalerite, exhibiting galena veinlets or undulated bands
7		+ 4.29		Compact sphalerite, slightly laminated, within graphite-bearing gneissic rock
8		- 4.64		Breccia containing feldspar fragments cemented by sphalerite, galena and pyrite

Analyst: Filofteia Gaftoi, I.G.G., Bucharest.

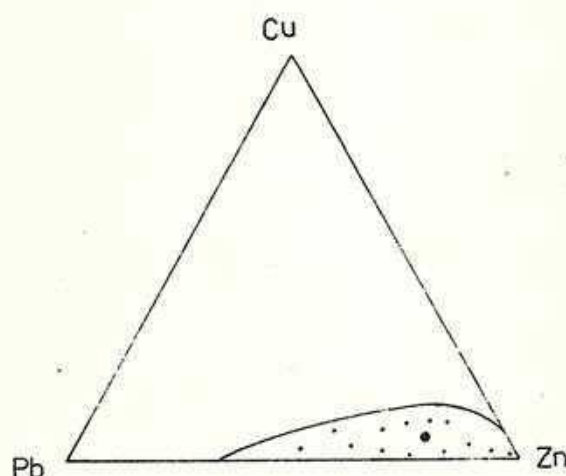


Fig. 5 - Cu-Pb-Zn diagram of ore (chemical and spectrographic data).

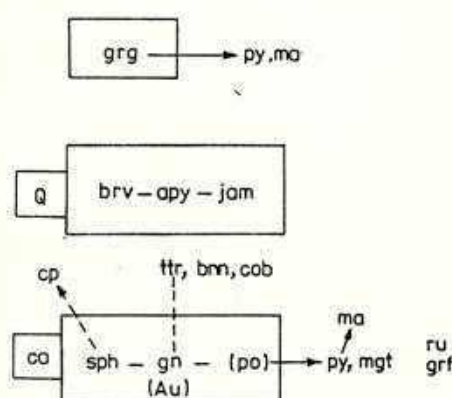


Fig. 6 - Sketch of the mineralizing process.

Continuous arrows suggest mineral transformation and dotted ones exsolution and/or quasi-simultaneous crystallization. Abbreviations: apy, arsenopyrite; bnn, bournonite; brv, bravoite; ca, calcite; cp, chalcopryite; cob, cobaltite; jam, jamesonite; gn, galena; grf, graphite; grg, greigite; mgt, magnetite; po, pyrrhotite; py, pyrite; Q, quartz; sph, sphalerite; ttr, tetrahedrite; ru, rutile; ma, marcasite. Rectangles suggest the main ore parageneses.

concentration, viewed as an indirect "residual" process imposed by the volume reduction of restites. Therefore, a protore partly transformed during regional metamorphism is supposed. The ore bands or lenses, slightly folded, mainly consisting of sphalerite (probably pyrrhotite, too), unconformable to the main S-plane of gneisses, might account for this stage of metal concentration. Alpine or older structural elements (mainly intrafolial shearings) allowed the continuity of the mineralizing processes, by the presence of PT gradients and the volume increase of interstitial fluids which carried the metals to dilatant zones and fixed them as sulfides. The destabilization of pre-existing sulfides in rocks

reaching high PT zones was a process which ensured an additional source of sulfur. Pyrrhotite was thus altered to pyrite, concomitantly with the appearance of pseudexsolution phenomena mainly imposed by pressure: chalcopryite in sphalerite, tetrahedrite and bournonite in galena. The distension areas (open fractures)

offered the favorable environment for the concentration of low temperature iron sulphides (greigite, pyrite and marcasite as spheroidal aggregates), probably also related to a moderate flow of fluids (or only heat), associated with Mesozoic magmatites (small-size bodies scattered in the area).

The Cioclovina ore occurrences could be thus assigned to the "tectogenetic" group (shear-zone related) of ores; a poorly individualized protore was processed during several stages, leading to contrasting morphological features of orebodies. According to the classification proposed by Udubaşa (in press), the Cioclovina ore occurrences occupy an intermediate position between those of Leaota-Rimeşti type (small dispersion of negative $\delta^{34}\text{S}$ values, prevalence of carbonates over quartz) and those of Valea lui Stan type (wide range of $\delta^{34}\text{S}$ values, prevalence of quartz over carbonates).

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Planșa I



Fig. 1 – Parallel bands of pyrite (white) and silicates (black) crossed by pyrite veinlets, probably representing local regenerations. Reflected light (RL), x 150.



Fig. 2 – Lamellar pyrite (white); silicates (black) intergrowth surrounded by subhedral pyrite grains. RL, x 150.



Fig. 3 – Fine silicate (black) inclusions in almost compact pyrite (white). RL, x 100.

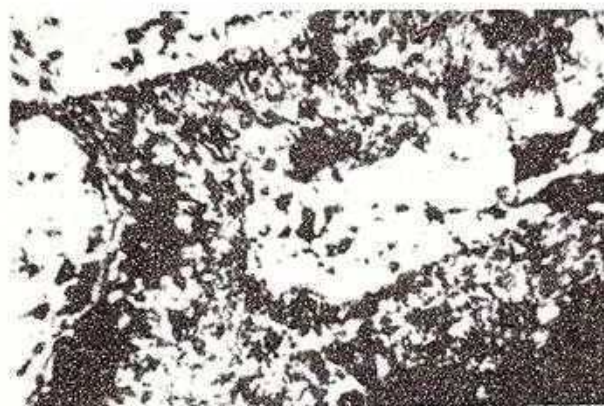


Fig. 4 – Massive pyrite aggregate enveloped by fine-grained pyrite. RL, x 150.



Fig. 5 – Mushroom-like marcasite±pyrite aggregate; nearby, subhedral pyrite. RL, x 100.



Fig. 6 – The same image with crossed nicols; the lamellar structure of the aggregate is noticed.

Planşa II



Fig. 1 - Globular aggregate of lamellar marcasite radially disposed, exhibiting pyrite nucleus. RL, N +, x 75.



Fig. 2 - Ellipsoidal greigite aggregate (grey-white), with pyrite aureole (white), partially included in sphalerite (grey) and galena (white). RL, x 150.



Fig. 3 - Sphalerite (grey) intergrown with galena (white); galena also occurs as subhedral inclusions, similar to the sphalerite ones in galena (see Fig. 1). RL, x 100.

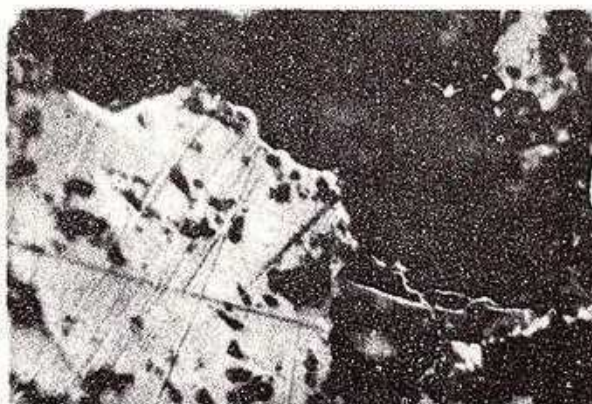


Fig. 4 - Sphalerite (grey) enveloped by "filmy" pyrite (white). RL, oil immersion, x 250.

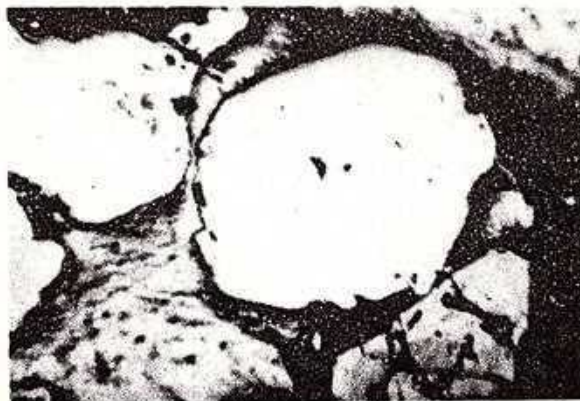


Fig. 5 - Subhedral pyrite grains exhibiting zoning of bravoite type cemented with prismatic-acicular jamesonite (grey). RL, x 150.



Fig. 6 - Needle-like jamesonite in quartz, Crossed nicols, x 150.

OBSERVAȚII ASUPRA SKARNELOR ȘI MINERALIZAȚIILOR DIN ZONA ȘOPOT (BANATUL DE SUD)

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Key words: Mineralization. Skarn. Iron Oxides. Magnetite. Sulfides. Lithologic Controls. South Carpathians - Neocretaceous Palaeogene Magmatites - Șopot-Semenic.

Abstract: *Remarks on the Skarns and Mineralization in the Șopot Area (Southern Banat).* The products of the contact metamorphism generated by the (Laramian) banatitic subvolcanic bodies from the Șopot area are represented by hornfelses, marbles, skarnoids, carbonate metasomatites, skarns and Cu $\pm$ Fe ores. They resulted mainly from the transformation of Upper Cretaceous carbonatic sediments and subordinately at the expense of crystalline schists. The metasomatites are particularly represented by calcic exoskarns exhibiting CaO/MgO ratio >1 . According to the mineralogic composition they are garnet skarns, pyroxene skarns, thremolite skarns and epidote skarns. The mineralization was pyrometasomatic (hematite $\pm$ magnetite) and hydrometasomatic (pyrite + chalcopyrite $\pm$ pyrrhotite $\pm$ sphalerite $\pm$ galena). Significant metasomatic supplies and levigations generated the garnet and pyroxene skarns. The evolution of the processes and the associated mineralization implies a pyrometasomatic stage (skarns and iron oxides) and a hydrometasomatic stage (hydrothermal alteration; sulphide mineralization and carbonates $\pm$ zeolites deposition).

Introducere

Skarnele din zona Șopot sunt situate în partea vestică a munților Almaș, între localitățile Șopotu Vechi și Liubcova. Aceste produse s-au format în aureola de contact a intruziunilor de banatite ce află în bazinele văilor (ogașelor) Lilieci, Purcaru, Nasovăț, și după Giuscă et al., 1966, aparțin aliniamentului central de magmatite laramice.

În prezent există puține informații asupra skarnelor și mineralizațiilor din zonă. Înainte de anul 1948 skarnele au fost cercetate cu câteva galerii de coastă cu lungimi metrice, despre care nu deținem alte date. Prospekțiunile geologice (Ilanomolo et al., 1961, raport nepublicat) au dus la identificarea unor tipuri de skarne și mineralizații de Cu $\pm$ Fe, iar prospekțiunile geochimice (Buracu, 1962, raport nepublicat), efectuate în sectoarele Lilieci și Purcaru, au evidențiat câteva anomalii de cupru în sol, cu concentrații ce ajung până la 0,2 %. Mineralizațiile din zonă au constituit obiectul unor lucrări de prospekțiuni și explorări, efectuate de I.S.E.M. (Neguț, Popa, 1965, raport nepublicat; Neguț, 1970, raport nepublicat). Cercetările ulterioare (Gunnesh et al., 1973, raport nepublicat; 1975) au arătat prezența exoskarnelor (granat, diopsid, epidot, wollastonit) și a unei mineralizații de tip porphyry

copper, slab dezvoltată (Intorsureanu et al., 1980, raport nepublicat).

Cadrul geologic

Zona cercetată aparține domeniului getic și este situată în apropierea contactului tectonic cu unitățile danubiene (fig. 1).

Șisturile cristaline aparțin seriei de Sebeș-Lotru și sunt reprezentate preponderent prin paragneise cu biotit, în care se află intercalate micașisturi cu biotit și muscovit, micașisturi cu granați, amfibolite, șisturi amfibolice și numeroase filoane sau lentile de pegmatite cuarț-feldspatice. Paragenezele principale (cuarț-plagioclaz-muscovit-biotit-hornblendă-almandin $\pm$ staurolit) arată că metamorfismul regional, atribuit Precambrianului superior A s-a produs în condițiile faciesului amfibolitic zona cu almandin (Săvu et al., 1977, raport nepublicat).

Formațiunile sedimentare se atribuie Cretacului superior, Badenianului și Cuaternarului. Depozitele cretaceice se dezvoltă în culmea Sichevița, alcătuind o structură sinclinală orientată NNE-SSV și la Tilva Toronița sub forma unei zone mai restrinse. Codareea și Pop (1963) au separat patru unități litostratigrafice:

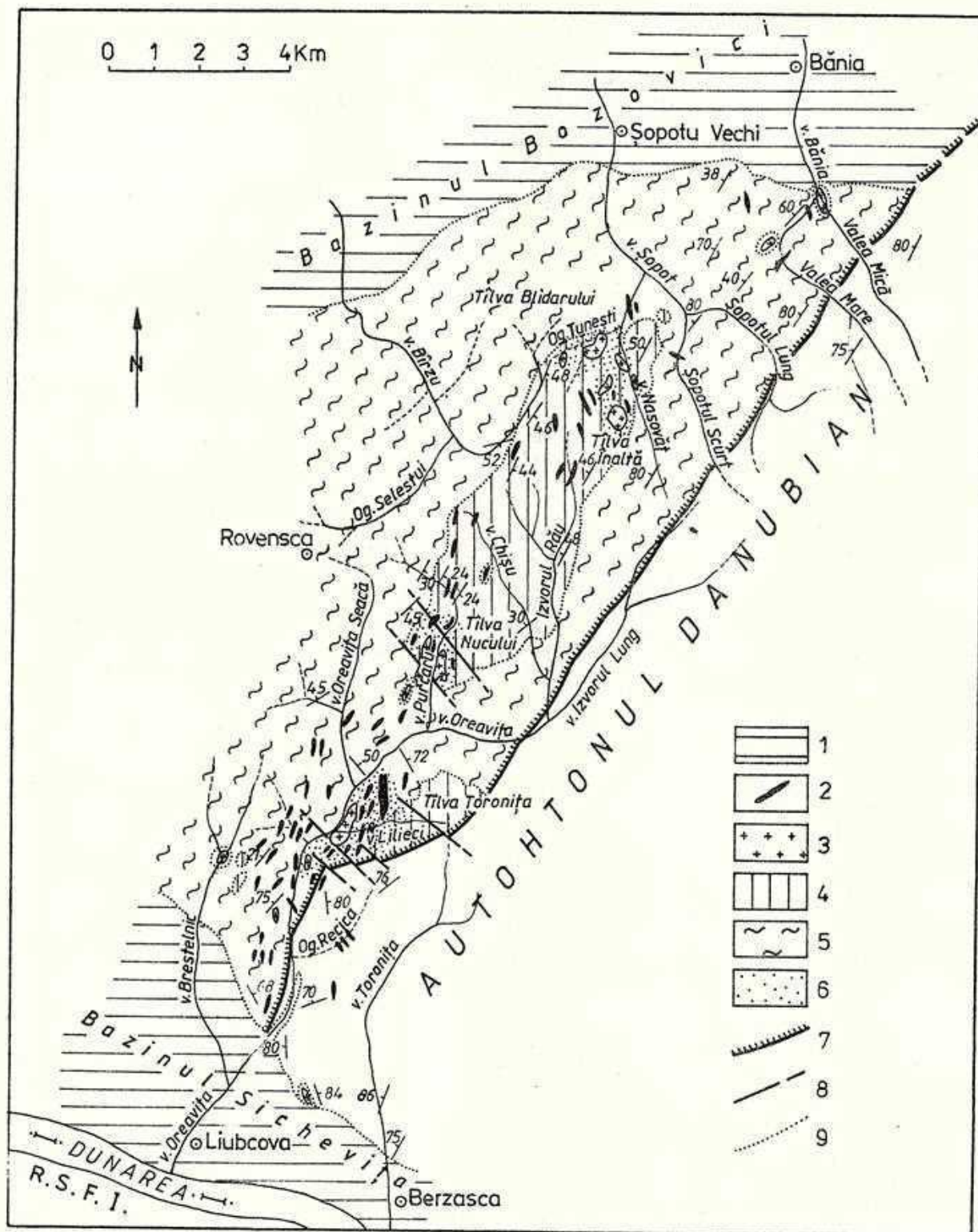


Fig. 1. Schiță geologică a zonei Șopot.

1. terțiar: conglomerate, pietrișuri, nisipuri, gresii, marne, argile; 2. andezite; 3. monzoniorite cuarțifere±porfirice; granodiorite±porfirice; 4. cretacic: calcare, gresii, marne, conglomerate; 5. seria de Sebeș Lotru: paragneise, micașturi, amfibolite, pegmatite; 6. aureole de contact: corneene, marmure, skarnoide, skarne mineralizate; 7. contact tectonic; 8. falie; 9. limită de transgresiune.

orizontul calcarelor grezoase organogene și al gresilor calcaroase, cu grosimi de ordinul zecilor de metri, probabil de vîrstă cenomaniană, transgresiv pe fundamentul cristalin; complexul de gresii marnoase, marne grezoase și marno-calcare, de vîrstă turoniană; orizontul conglomeratic, cu grosimi reduse; complexul de marno-calcare, marne grezoase și gresii de vîrstă santonian-campaniană, în partea superioară a succesiunii. Depozitele badeniene formează umplutura bazinului Sichevița, la sud, și a bazinului Bozovici, la nord. Acestea sînt constituite din conglomerate, pietrișuri, nisipuri, gresii, marne argile, cărbuni, tu-furi etc. (Năstăsescu et al., 1981). Cuaternarul este reprezentat prin depozite de terasă, aluviuni și conuri de dejecție.

Rocile banatitice (laramice) sînt reprezentate prin numeroase intruziuni sub formă de filoane, apofize sau alte corpuri subvulcanice care străpung șisturile cristaline și depozitele cretacice. Dintre numeroasele intruziuni, dispersate neuniform în aria cercetată, mai dezvoltate, dar fără a depăși 1 km în zona de aflorare, sînt corpurile subvulcanice situate în sectoarele Liliaci, Purcaru, Nasovăț, alcătuite din monzodiorite cuarțifere, porfire monzodioritice cuarțifere, granodiorite și porfire granodioritice (Întorsureanu, 1986). La compoziția mineralogică a acestora participă plagioclaz (44,4-61,8 %) cu 32-48 % An, feldspat potasic (11-18,1 %), cuarț (12,3-16,3 %), hornblendă verde (7-21,7 %), biotit (0,2-2,3 %) și minerale accesorii (magnetit, apatit, sfen). Datele petrochimice arată că rocile banatitice au derivat din magme calco-alkaline, cu ușoare tendințe shoshonitice (Întorsureanu, 1986).

Metamorfismul de contact

Metamorfismul de contact determinat de intruziunile banatitice a dat naștere unor aureole de contact, alcătuite din corneene, marmure, skarnoide, metasomatite carbonatice, skarne ± mineralizații. Aureole de contact mai importante au fost întîlnite în jurul corpurilor subvulcanice din perimetrele Liliaci, Purcaru, Nasovăț, atît în depozitele cretacice cît și în formațiunile cristaline. Au putut fi remarcate toate stadiile de tranziție de la roci integral transformate la roci neafectate. Gradul ridicat de acoperire a terenului nu a permis stabilirea exactă a extinderii produselor de transformare. În cele ce urmează acestea vor fi descrise aproximativ în ordinea de formare.

Corneene, marmure

Corneenele apărute prin recrystalizări în depozitele cretacice se caracterizează prin culori cenușii-verzui, textura masivă și structuri fin granoblastice. În zona internă a aureolei de contact se disting corneene cu diopsid + cuarț + calcit ± granați; corneene cu tremolit + calcit + cuarț ± granați, iar în zona externă corneene cu epidot + calcit + albit ± tremolit ±

cuarț, de la care se trece gradat spre roci slab afectate, cu aspect de șisturi pătate. Corneenele formate pe seama metamorfitelor au fost întîlnite în ogașele Liliaci, Praznici, Tuncuș. Caracterele textural-structurale ale rocii inițiale sînt bine conservate, macroscopic deosebindu-se cu greu de paragneisele neafectate. Mineralele formate prin metamorfismul de contact sînt reprezentate prin biotit brun cu structură decusată, cuarț poligonal ± epidot ± albit. Aceste asociații arată că metamorfismul termic s-a desfășurat în condițiile faciesului corneenelor cu albit-epidot.

Marmure, formate prin recrystalizarea calcarelor grezoase organogene, aflorază în bazinele ogașelor Liliaci, Puciosul, Tuncuș, Bobot și pe culmea Cracul Liliaci. În vecinătatea contactului cu intruziunile banatitice, calcarele sînt larg recrystalizate, au structuri granoblastice și culoarea albă.

Spre exteriorul aureolei, se trece treptat la marmure cenușii, cu granulația mai fină și urme de cochilii. Decolorarea calcarelor, pe scară largă, sugerează prezența unui fenomen de oxidare a materiei organice sub acțiunea fluxului termic și/sau a unor fluide de origine magmatică, proces asemănător cu cel descris de Fontelles și Machairas (1968), în zăcămintul Salau (Ariege).

Skarnoide

Skarnoide, în accepțiunea lui Korjinski (1948), s-au identificat în aureolele de contact din sectoarele Purcaru și Nasovăț. După tipul de transformare și paragenesele acestor roci par a se situa între corneene și skarne, dezvoltându-se indeosebi pe seama gresurilor calcaroase sau a marnelor. Macroscopic se caracterizează prin culori cenușii, cu tente maronii, duritate ridicată, granulație fină și păstrarea stratificației inițiale. În secțiuni subțiri se observă structuri microgranoblastice. Ca minerale de neoformație apar granați, epidot, tremolit, ce sînt dispersate relativ uniform într-o matrice recrystalizată, alcătuită preponderent din calcit și/sau cuarț, cu numeroase incluziuni de epidot, și/sau minerale argiloase.

Granații au dimensiuni mici (0,02-0,4 mm), ocupă pînă la 30-35 % din volumul rocii și conțin adesea numeroase incluziuni solide primare. Frecvent se observă cristale embrionare de granați la care s-au dezvoltat doar zonele marginale cu forme poligonale, în interiorul cărora se păstrează resturi din mineralele rocii inițiale. Cristalele embrionare sînt, de obicei, anizotrope și zonate. Ele cresc transversal peste minerale din roca primară (carbonați, cuarț, feldspat), ceea ce presupune o slabă metasomatoză de difuzie (fig. 2). Aceste observații sugerează că dezvoltarea cristalelor de granați s-a produs de la exterior spre interior, fapt ce pledează pentru prezența unui mecanism de creștere diferit de cel de nucleație, așa cum a descris și Holoie (1971) la granați din zona Montagne Noire.

Epidotul, de culoare verzuie, apare subordonat, în cristale prismatice izolate sau în cuiburi. Tremolitul apare sporadic, alcătuind agregate prismatic-radiare. În faza hidrotermală granații au fost uneori parțial substituiți de clorite, iar pe fisuri s-au depus pirită + calcit + zeoliți.

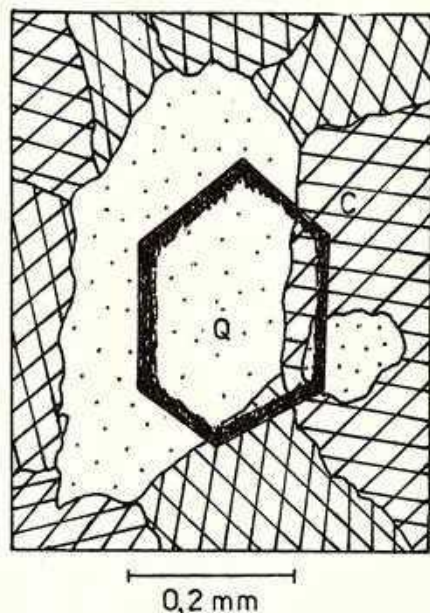


Fig. 2 Cristal embrionar de granat, în skarnoide, substituind calcit (C) și cuarț (Q).

Aspectele menționate sugerează că aceste roci s-au format prin recrystalizare, în condițiile unei slabe metasomatoze de difuzie. Skarnoide asemănătoare au fost descrise de Fontcilles și Machairas (1968) în zăcămintul Salau (Ariège) și de Harris și Einaudi (1982) în districtul Yerington (Nevada).

Metasomatite carbonatice.

Pe halda galeriei Lileci și în câteva aflorimente din bazinul ogașului Lileci s-au întâlnit frecvent roci albicioase, carbonatice, formate în mod evident prin substituția paragneiselor micacee. Aceste metasomatite carbonatice formează cuiburi, lentile și pseudofiloane cu dimensiuni decimetrice. Se caracterizează prin textura masivă și structura fină. Uneori se recunosc resturi netransformate din paragneisele primare. La microscop se remarcă o structură heterogranoblastică, roca fiind alcătuită din calcit (85-90 % din volum) și numerale relict (cuarț cu extincție ondulatorie, feldspați, muce) în proporții reduse.

Skarne

Produsele metamorfismului pirometasomatic sînt reprezentate prin variate tipuri de exoskarne. Substituțiile metasomatice au variat în limite largi, fiind controlate indeosebi de natura paleosomului și de căile de acces pentru fluidele skarnizante. Rocile cele mai favorabile pentru formarea skarnelor au fost calcarele gresoase organogene, situate în baza depozitelor cretacee. Rocile din celelalte orizonturi ale cretacului au fost mai puțin afectate. De asemenea sînt reduse în extindere skarnele formate prin substituția paragneiselor din seria de Sebeș-Lotru. Skarnele formate pe seama gresiilor calcaroase sau a marelui gresoase, prezintă adesea treceri gradate spre skarnoide. În general, skarnele sînt eterogene și au o dezvoltare discontinuă, formînd lentile, benzi, cuiburi, pseudofiloane, corpuri neregulate, cu dimensiuni relativ reduse. După chimism, skarnele sînt reprezentate indeosebi prin varietăți calcice, caracterizate prin raportul CaO/MgO supraunitar. După compoziția mineralogică se disting skarne cu granați, skarne cu piroxeni, skarne cu tremolit și skarne cu epidot.

Skarnele cu granați sînt larg răspîndite în cele trei sectoare cercetate (Lileci, Purcaru, Nasovăț), fiind formate, în special, prin substituția calcarelor gresoase organogene, pe distanțe ce pot ajunge pînă la zeci de metri.

Gresiile calcaroase, situate deasupra calcarelor, au fost de asemenea frecvent transformate în skarne cu granați, însă la scară mai redusă. Macroscopic, skarnele sînt reprezentate prin roci maronii-cenușii, cu texture masive și structuri granoblastice, mai groasere la skarnele formate prin substituția calcarelor și mai fine la cele rezultate pe seama altor roci. La microscop se remarcă transformări gradate de la stadii incipiente, caracterizate prin prezența granaților embrionari, pînă la substituții totale.

Granații au dimensiuni variate alcătuind adesea agregate compacte, monominerale, în care uneori se conservă resturi din paleosomă (pl. I, fig. 1). Frecvent prezintă fenomene de anizotropie și macle sectoriale (pl. I, fig. 2) sau lamele de macle paralele cu fața de dodecaedru romboidal (pl. I, fig. 3). Creșterea granaților din skarne, pare a fi avansat, cel puțin în unele cazuri, de la marginea mineralului spre interior, cînd se formează mai întîi zona externă a cristalului (pl. I, fig. 4), așa cum s-a menționat și la granații din skarnoide. Compoziția chimică (tab. 1) determinată pentru două probe de granați din skarne arată că aceștia sînt preponderenți andraditici, cu proporții reduse de pirop, almandin, spessartin și grossular.

Scapolitul (dipir) apare rar în skarnele cu granați. A fost identificat microscopic în câteva eșantioane din sectorul Purcaru sub formă de cristale prismatice bine dezvoltate, cu clivaj bun după (100); este uniax nega-

tiv și are birefrință scăzută.

Skarnele cu piroxeni au fost întâlnite sub formă de blocuri pe halda galeriei I amplasată în versantul drept al ogașului Liliaci. Paleosomul acestor skarne este reprezentat prin paragnais. Galeria menționată este inaccesibilă, dar din examinarea materialului de pe haldă se poate deduce că skarnele cu piroxeni apar sub formă de cuiburi sau pseudofiloane cu grosimi ce depășesc ordinul decimetrilor. Rocile au culoarea verde închis-cenușie, duritate ridicată, și conțin cristale prismatice de piroxeni verzi, cu lungimea pînă la 1 cm, dispuse în agregate radiare și cuiburi. Mineralul dominant este piroxenul, la care se asociază în cantități reduse, epidot, amfiboli aciculari, cuarț, carbonați ± oxizi de fier.

TABELUL 1
Compoziția granaților din skarne

Nr. crt.	COMPOZIȚIA CHIMICĂ			COMPOZIȚIA MOLARĂ		
	Oxizi, %	E. 1488 (Og. Liliaci)	E. 1500 (Og. Purcaru)	Minerale	E. 1488	E. 1500
1	SiO ₂	35,14	34,40	Androdit	90,68	81,90
2	Al ₂ O ₃	1,80	5,37			
3	Fe ₂ O ₃	27,66	26,80	Grossular	—	3,04
4	FeO	0,57	0,57			
5	MnO	0,22	0,41	Pirrop	7,40	12,65
6	MgO	3,20	5,40			
7	CaO	28,84	24,92	Spessartin	0,52	1,01
8	Na ₂ O	0,20	0,10			
9	P ₂ O ₅	0,08	0,08	Almandin	1,40	1,40
10	H ₂ O ⁺	2,28	1,68			
11	H ₂ O ⁻	0,34	0,46			
12	S	—	0,03			
Total		100,32	99,77		100,00	100,00

Analiză: C. Popescu, E. Clirciumaru

Piroxenul, reprezentat printr-un termen al seriei diopsid-hedenbergit, se prezintă în cristale prismatice (pl. I, fig. 5), uneori cu aspecte embrionare, cu fețe bine conturate (fig. 3), substituind granule de calcit. Frecvent se remarcă incluziuni relict (carbonați, cuarț) sau secundare, (fibroblaste de tremolit-actinot). Pleocroismul este slab (Ng-verde, Np-verde gălbui), clivajul bun (110), apar macles după (100), și unghiul de extincție cuprins între 40-48°. Datele optice, coroborate cu analiza chimică pe roca globală (tab. 2) arată că piroxenul este de compoziție hedenbergitică.

Epidotul, de culoare verzuie, formează cuiburi cu dimensiuni milimetrice sau cristale izolate, care substituie piroxenul. Amfiboli aciculari, incolori sau slab verzi, din seria tremolit-actinolit apar în mod subordonat.

Dintre mineralele paleosomului se mai păstrează cuarț, uneori cu extincție ondulatorie sau feldspati ce conțin frecvent numeroase cristale fibroase de amfiboli. Prezența calcitului, pe scama cărnia s-au format piroxenii (pl. I, fig. 6), arată că într-o primă etapă paleosomul a fost substituit parțial de calcit.

Skarnele cu tremolit apar în bazinul superior al ogașului Liliaci la exteriorul zonei skarnelor cu granați. Aflorază pe distanțe de zeci de metri și în sectorul

Purcaru (ogașul Puciosul și forajul 61527, m. 37,70-71,10). Sînt roci dure, de culoare cenușiu deschis cu tente verzi, textura masivă și granulație fină. Compoziția mineralogică este dominată de prezența tremolitului la care se pot asocia granați, piroxeni, epidot, cuarț, feldspati.

Tremolitul se prezintă sub formă de cristale prismatic-aciculare, dispuse adesea în agregate radiare ce ocupă uneori aproape tot volumul rocii (pl. II, fig. 1). Este incolor, și are unghiul de extincție cuprins între 18-20°. Tremolitul substituie granații sau piroxenii, care au fost întâlniți doar în câteva secțiuni.

Epidotul apare subordonat, și formează cristale idiomorfe, cuiburi, mai rar vinișoare, depus în faza hidrotermală. Dintre mineralele paleosomului se păstrează adesea cuarțul și feldspatul. Din observațiile microscopice și cele de teren se deduce că aceste skarne s-au format prin substituția gresilor cu ciment carbonatic și mai rar pe scama gnaiselor. Prezența tremolitului implică un chimism ușor magnezian al acestor skarne, însă nu dispunem de date analitice în acest sens.

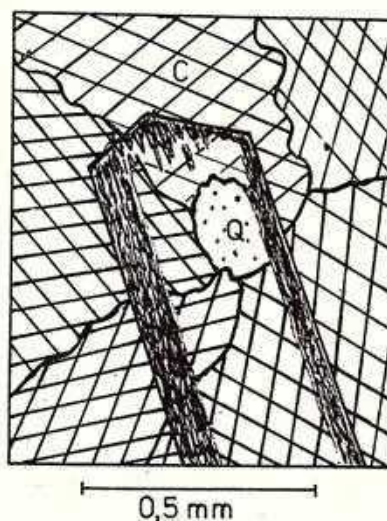


Fig. 3. Cristal embrionar de piroxen, substituind calcit (C) și cuarț (Q).

Skarnele cu epidot s-au întâlnit sub formă de blocuri pe haldele unor galerii din sectoarele Liliaci și Purcaru, avînd o răspîndire redusă. Sînt roci de culoare galben-verzuie și se asociază uneori cu skarnele piroxenice, de unde rezultă că s-au format, cel puțin în parte, prin substituția paragnaiselor. Studiul secțiunilor subțiri arată o participare largă a epidotului verzu (pl. II, fig. 2) la care se adaugă în cantități reduse cuarț, clorit, apatit, calcit, minerale opace, formate în stadiul hidrometasomatic.

Tabel 2 Bilanțul metasomatic

Oxizi	$K = \frac{60}{M}$	Calcare		Sk cu gran.		Bilanț		Calcare		Sk cu gran.		Bilanț		Paragneise		Sk cu pirax.		Bilanț
		E. 1482 D=2.697	C	E. 1488 D=3.380	C	+	-	E. 1498 D=2.678	C	E. 1500 D=3.387	C	+	-	E. 1476 D=2.691	C	E. 1475 D=3.167	+	
SiO ₂	1	1,22	3,29	31,61	106,84	103,55		1,00	2,68	45,73	154,89	152,21		68,50	184,33	42,93	135,96	48,37
TiO ₂	0,75									0,22	0,56	0,56		0,44	0,89	0,55	1,30	0,41
Al ₂ O ₃	0,59	0,60	0,95	0,86	1,72	0,77		0,20	0,32	2,63	5,26	4,94		13,87	22,02	4,32	8,07	
Fe ₂ O ₃	0,37	0,32	0,32	23,60	29,51	29,19		0,35	0,35	14,84	18,60	18,25		1,02	1,02	10,83	12,69	11,67
FeO	0,83	0,07	0,16	0,70	1,96	1,80		0,14	0,31	1,93	5,43	5,12		2,74	6,12	11,17	29,36	23,24
MnO	0,85	0,03	0,07	0,20	0,57	0,50		0,08	0,18	0,42	1,21	1,03		0,04	0,09	0,36	0,97	0,88
CaO	1,07	55,03	158,80	33,74	122,02	36,78		55,36	158,63	26,04	94,37	64,26		3,52	10,14	20,68	70,08	59,94
MgO	1,48	0,60	2,40	0,72	3,60	1,20		0,62	2,49	1,15	5,76	3,27		1,51	6,01	1,30	6,09	10,90
Na ₂ O	0,96							0,08	0,21					4,22	10,90			4,34
K ₂ O	0,63													2,56	4,34			0,14
P ₂ O ₅	0,42									0,03	0,04	0,04		0,16	0,18	0,03	0,04	
H ₂ O*	3,34	0,02	0,18	0,09	1,02	0,84		0,03	0,27	0,73	8,26	7,99		0,73	6,56	0,51	3,28	3,28
CO ₂	1,36	42,41	155,56	7,46	34,30	12,126		41,88	152,53	5,60	25,80	126,73		1,13	4,14	7,54	32,48	28,34
S		0,07								1,09								
PC																		
Total		100,37		99,00				99,74		100,40				100,44		100,02		

1) Formula de calcul este: $X = DCK$, unde: X = cantitatea de molecule din volumul standard D = densitatea C = procentul în greutate al componentilor K = coeficient de calcul egal cu $\frac{60}{M}$, unde M = greutatea moleculară a componentului

2) Localizarea probelor

a) Og Lileci: 1482; 1488; 1475; 1476

b) Og Purcaru: 1498; 1500

c) Og Tunesi: 1710; 1711

Analist: Aurelia Movileanu

Mineralizații

Metalogeneza asociată magmatismului banatitic din regiune se caracterizează prin două tipuri de mineralizații: mineralizații de tip porphyry copper, localizate în banatite, la Lăpușnicu Mare și sporadic în sectoarele Liliaci-Purcaru-Nasovăț și mineralizații metasomatice (oxizi de fier $\pm$ sulfuri), asociate skarnelor. Întrucât primul tip de mineralizație a constituit obiectul unor studii recente (Intorsurcanu et al. 1980, raport nepublicat; Pomarleanu, Intorsurcanu, 1985), vom prezenta în cele ce urmează doar concentrațiile de minereu metasomatic asociate skarnelor.

Mineralizații metasomatice au fost întâlnite în sectoarele Liliaci-Purcaru-Nasovăț, la suprafață (aflorimente, fragmente) și în unele foraje sau lucrări miniere de explorare (Neguț, Popa, 1965, raport nepublicat; Neguț, 1970, raport nepublicat).

Din coroborarea datelor de la suprafață cu cele din foraje și lucrări miniere, rezultă că mineralizația metasomatică este asociată, de regulă, skarnelor cu granați. Celelalte tipuri de skarne, skarnoidale și corneenele găzduiesc uneori doar impregnații de pirita $\pm$ hematit, lipsite de importanță.

Concentrațiile metalifere apar sub formă de cuiburi, lentile, pseudofiloane, impregnații neregulate, în general cu dimensiuni modeste. După compoziția mineralogică se disting mineralizații de oxizi de fier (hematit + magnetit) și mineralizații de sulfuri (pirita + calcopirita $\pm$ pirotină $\pm$ blendă $\pm$ galenă) care se suprapun peste primele.

Hematitul a fost întâlnit în galeria veche situată în versantul drept al ogașului Liliaci, pe haldele unor lucrări executate de I. S. E. M. (galeria I Liliaci, galeria XIV Purcaru, galeria Tuncuști etc.) și în câteva aflorimente, sub formă de impregnații sau cuiburi cu dimensiuni reduse. Se asociază frecvent cu granatul pe care-l substituie și se prezintă adesea în formă de agregate aciculare, (specularit) (pl. II, fig. 3). Hematitul de pe halda galeriei I Liliaci, asociat skarnelor cu piroxen, este în cea mai mare parte muschetovizitat. În stadiul hidrotermal hematitul este uneori substituit de epidot, clorit, calcit.

Magnetitul se prezintă sub formă de pseudomorfoze după hematit (pl. II, fig. 4) și este asociat skarnelor cu piroxen sau cu granați. Observațiile microscopice au arătat că muschetovizarea a afectat îndeosebi hematitul asociat skarnelor cu piroxen (halda galeriei I Liliaci) și mai puțin hematitul din skarnele cu granați. Inegala răspundere a muschetovizării arată că potențialul oxidant, care a determinat acest proces, a scăzut în skarnele cu piroxen (unde concentrația CO_2 a fost mai redusă) comparativ cu skarnele cu granați. Această concluzie rezultă și din interpretarea bilanțului metasomatic (tab. 2).

Pirita este componentul principal al mineralizației de sulfuri. Apare sub formă de impregnații, cuiburi, filonașe etc., în skarne și mai rar în skarnoidale sau corneene. La microscop se observă forme idiomorfe sau hipidiomorfe care mulează sau substituie granați și oxizi de fier. Uneori pirita este brecifiată, iar pe fisuri s-au depus hidroxizi de fier (pl. II, fig. 6).

Calcopirita este frecvent asociată cu pirita formând cuiburi sau impregnații. La microscop apare în granule allotriomorfe sau plaje cu dimensiuni reduse (pl. II, fig. 5) și poate substitui pirita sau hematitul. Din documentațiile anterioare (Neguț, Popa, 1965, raport nepublicat) rezultă că cele mai interesante mineralizații de calcopirita au fost întâlnite în lucrările de explorare (în prezent inaccesibile) din sectorul Purcaru (galeria XIV, m 56-64; forajul 27502, m 271,08-273,96) și Nasovăț (puțul 4, m 6-12). Cel mai ridicat conținut de cupru a fost de 2,25 %, întâlnit în forajul 27502.

Pirotină a fost rar observată (Liliaci, Purcaru), apărind sub forme de granule xenomorfe, plaje sau cuiburi, asociate cu pirita sau cu oxizi de fier.

Blendă și galenă apar cu totul sporadic, sub formă de impregnații în skarnele din ogașele Tuncuști, Subtuncuști și se asociază cu calcopirita sau pirita.

Stibina a fost menționată de Hanomolo (1966, raport nepublicat) la Liliaci în forajul 27518 (m 233,33-234,03 și 255,53-256,60) sub formă de cristale fin aciculare, în asociație cu calcopirita.

În stadiul exogen pe seama skarnelor granatiferă cu impregnații de sulfuri se dezvoltă uneori zone de alterații ("pălării de fier"), cu dimensiuni ce pot ajunge pînă la ordinul zecilor de metri, ca cele din versantul stîng al ogașului Puciosul (sectorul Purcaru) sau ogașul Tuncuști (Nasovăț). Zonele de oxidație au culoarea maroniu-cărămizie și sunt alcătuite predominant din limonit în care apar, cu totul subordonat, mici cuiburi de azurit sau malachit.

Considerații genetice

Geneza skarnelor și a mineralizațiilor legate de magmatismul banatitic, caracterizat printr-un potențial metalogenetic ridicat, a fost controlată de prezența calcarelor grezoase organogene care au favorizat substituțiile metasomatice și de căile de acces pentru fluidele postmagmatice.

Factorii fizico-chimici (temperatură, chimism, presiune, mobilitatea componentelor) au controlat atât natura produselor, cât și succesiunea acestora. Bilanțul metasomatic (tab. 2), întocmit după metoda indicată de Goroh (1964), arată că pentru formarea skarnelor cu granați prin substituția calcarelor sedimentare, au fost necesare aporturi substanțiale de SiO_2 , Fe_2O_3 , FeO , Al_2O_3 și eliminarea CaO și CO_2 . De asemenea, apariția skarnelor cu piroxen, pe seama paragneisurilor,

implică adausuri însemnate de FeO , Fe_2O_3 , CaO , CO_2 și levigarea SiO_2 , Al_2O_3 , Na_2O , K_2O (alcaliile în totalitate). Schimbul acestor componente, coroborat cu observațiile de teren, sugerează că skarnele s-au format preponderent prin procese metasomatice de infiltrație.

Zonalitatea metasomatitelor este slab exprimată, iar absența aflorimentelor sau a lucrărilor miniere accesibile, nu a permis efectuarea unor observații detaliate pentru stabilirea acesteia. Se remarcă, totuși, că în zona internă s-au format fie skarne cu granați prin substituția calcarelor sau a gresiilor calcaroase, fie skarne cu piroxeni, pe seama paragnaiselor. În zona mediană par a predomină skarnele cu tremolit ± skarne cu epidot, iar spre exterior, apar adesea skarnoide.

În succesiunea de formare a metasomatitelor se disting două stadii postmagmatice:

- stadiul pirometasomatic cu două faze: faza de skarn și faza cu oxizi de fier (hematit ± magnetit);
- stadiul hidrometasomatic ce cuprinde trei faze: faza alterațiilor hidrotermale (epidot, clorit, cuarț, sericit), faza cu sulfuri (pirită ± calcopirită ± pirotină ± blendă ± galenă) și faza cu carbonați ± zeoliți.

Concluzii

Din datele expuse rezultă că produsele metamorfismului de contact, generat de intruziunile banatitice din zona Șopot, sunt reprezentate prin corneene, marmure, skarnoide, metasomatite carbonatice, skarne și mineralizații de $\text{Cu} \pm \text{Fe}$. Acestea s-au format, indeosebi, prin transformarea depozitelor cretacic superioare și, subordonat, pe seama metamorfitelor seriei de Sebeș-Lotru.

Skarnele cu granați mineralizate s-au format pe seama calcarelor grezoase organogene situate în baza depozitelor cretactice, care alcătuiesc o structură sinclinală ce include sectoarele Purcaru și Nasovăț. Astfel este foarte probabil ca la baza sinclinalului, în zona de contact dintre calcare și intruziunile banatitice, skarnele și mineralizațiile să fie mai larg dezvoltate.

Mulțumiri. Mulțumim dr. A. Ștefan pentru observațiile și sugestiile date în faza de manuscris, care au contribuit la îmbunătățirea lucrării. De asemenea, mulțumim următorilor analiști: Aurelia Movileanu, pentru analizele chimice efectuate pe skarne, calcare și paragnaise și C. Popescu și E. Circumaru, pentru analiza chimică a granaților.

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Planșa I

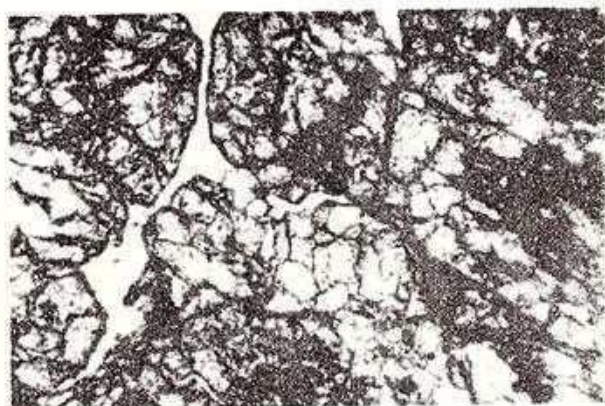


Fig. 1 - Skarn cu granăți. Ogașul Lilieci; N II, x 42.

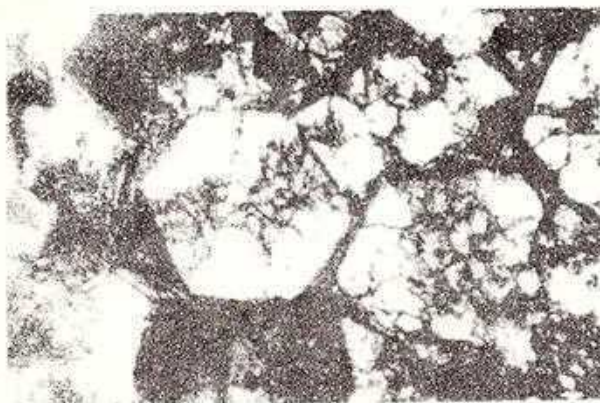


Fig. 2 - Skarn cu granăți maciați sectorial. Ogașul Purcaru; N +, x 32.



Fig. 3 - Granăți cu macle sectoriale anisotrope. Ogașul Purcaru; N +, x 64.

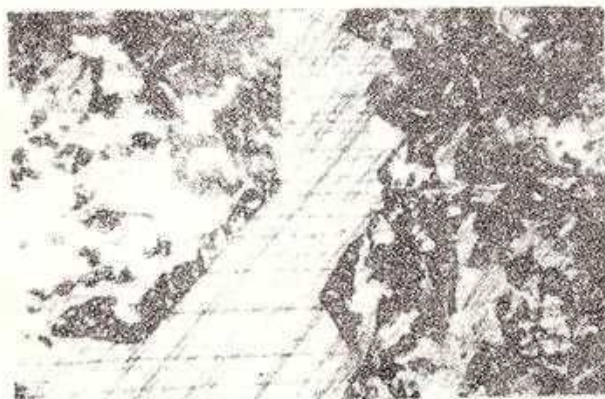


Fig. 4 - Cristal de calcit substituit parțial de granăți embrionari. Ogașul Tuncăști; N II, x 42.



Fig. 5 - Skarn cu piroxeni. Halda galeriei Lilieci; N +, x 24.



Fig. 6 - Cristal de calcit substituit parțial de piroxeni embrionari. Halda galeriei I Lilieci; N +, x 24.

Plasa II



Fig. 1 – Textură colomorfă (detaliu); negru=magnetit, alb=piroxeni; N II, x 24.

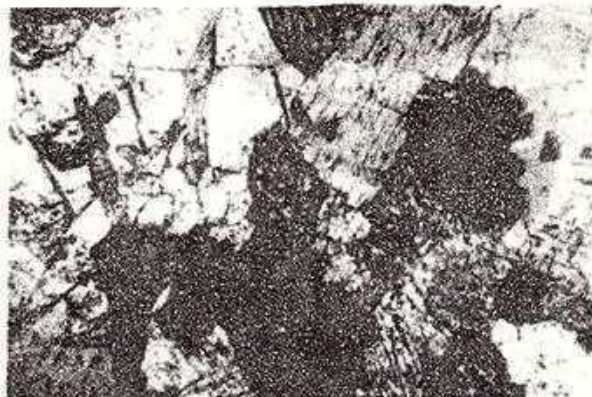


Fig. 2 – Magnetit cu textură xenoblastică. Zăcămintul Mașca-Băișoara, puțul I; N +, x 80.



Fig. 3 – Cristale embrionare de magnetit (negru) substituind piroxenul (cenușiu). Zăcămintul Mașca-Băișoara, puțul II; N II, x 72.

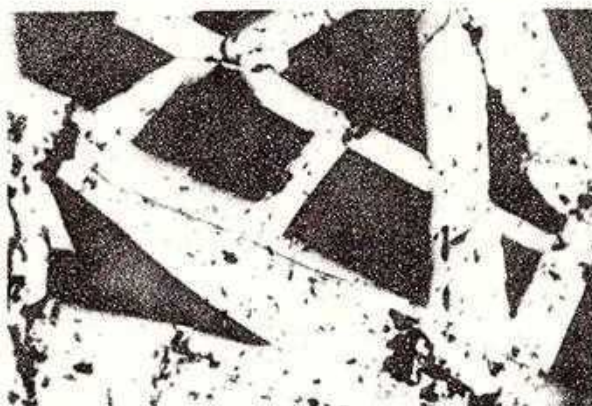


Fig.4 – Ludwigit (cenușiu) sub formă de cristale prismatic aciculare, cu rare cristale de piroxină (alb). Zăcămintul Căcova Ierii; N +, x 80.



Fig. 5 – Ludwigit (negru) transformat în saibelyit (alb). Zăcămintul Mașca-Băișoara, puțul II.

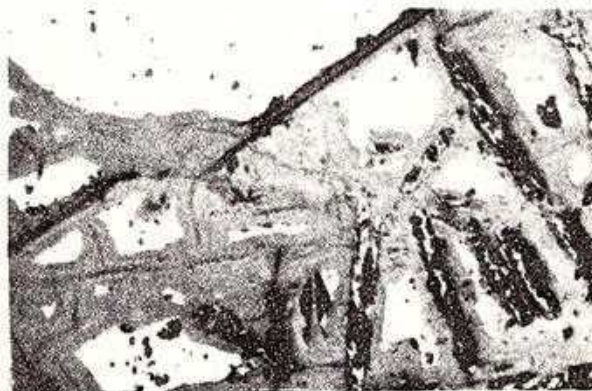


Fig. 6 – Gnais cu turmalină (negru) în cuiburi. Valea Vadului.

DETERMINĂRI CRIOMETRICE ASUPRA INCLUZIUNILOR FLUIDE DIN CUARȚUL FILONIAN ASOCIAT MINERALIZAȚIEI DE BARITINĂ DE LA MARCA-MALCOCI (DOBROGEA DE NORD)

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Key words: Quartz. Fluid inclusions. Geologic thermometry. Dobrogea - Northern Dobrogea - Tulcea and Consul-Niculițel Zones.

Abstract: *Cryometric Determinations of the Fluid Inclusions in the Vein Quartz Associated with the Marca-Malcoci Barite Mineralization (Northern Dobrogea).* The vein quartz from barite occurrences in the Triassic limestones of the Marca-Malcoci district (Northern Dobrogea) formed at temperatures between 139° and 165° C, from hydrothermal solutions of low concentration (2.49-2.48 % NaCl) and with density ranging from 0.919 to 0.949 g/cm³.

Introducere

Determinările criometrice au fost efectuate asupra incluziunilor fluide din probe de cuarț, colectate din filoane care traversează mineralizația de baritină localizată în calcarele triasice de pe aliniamentul Marca-Malcoci. Filoanele menționate se inscriu în două sisteme cu orientare diferită: un sistem N50W constituit din filoane de cuarț și baritină și un sistem NE-SW reprezentat prin filoane cuarțifere.

Metoda aplicată (Gatter, 1980) se bazează pe principiul răcirii incluziunilor fluide până la atingerea punctului de congelare a soluțiilor. Printr-o ușoară încălzire se determină temperatura punctului eutectic T_e al componentilor (primul punct de topire, cînd alături de particolele de gheață apare prima picătură de lichid) și temperatura de dispariție a ultimului cristal de gheață T_m (al doilea punct de topire). Transformările de fază dintr-o incluziune fluidă la temperaturi negative sînt ilustrate în figura 1.

Cu ajutorul valorilor obținute pentru primul punct de topire, se determină tipurile de componente existenți în incluziuni (Borisenko, 1982), iar cu ajutorul valorilor celui de-al doilea punct de topire, se poate calcula concentrația soluțiilor după o metodă inițiată de Potter II et al. (1978). De asemenea se pot face aprecieri asupra concentrației după diagrama T-X al sistemului H₂O - NaCl (Roedder, 1962).

Pentru obținerea datelor criometrice s-a folosit un aparat de răcire/încălzire elaborat de Poty et al. (1976) și comercializat de firma Chaixmeca de la Nancy.

Rezultate experimentale

În tabelul următor sînt prezentate date criometrice asupra incluziunilor fluide din cristalele de cuarț dintr-un filon de cuarț și baritină, orientat N50W (proba 4111/a) și din alt filon ce intersectează pe primul (proba 4111/b). Soluțiile din incluziunile fluide aparținînd cuarțului asociat cu baritină din proba 4111/a se caracterizează prin limite relativ joase ale punctului eutectic T_e (-17,5 -19,5° C), iar în cele provenind dintr-un cuarț filonian mai nou (proba 4111/b), cu puține excepții, T_e are limitele relativ ridicate (-25,0 -26,5° C).

După limitele acestor puncte eutectice, soluțiile hidrotermale din care au rezultat cristalele de cuarț din aceste două filoane, pot fi atribuite, conform datelor experimentale ale lui Borisenko (1977, 1982), la două sisteme: sistemul NaCl-H₂O cu punctul eutectic T_e de -21,2° C (în cazul nostru -19,5° C) și sistemul NaCl-KCl-H₂O cu punctul eutectic T_e de -23,5° C (media în cazul nostru este de -23,2° C).

Cele două sisteme de soluții, menționate, se deosebesc și printr-o ușoară scădere a valorilor medii de concentrație, determinate după metoda Potter et

al. (1978). Pentru primul sistem valoarea medie de concentrație corespunde la 2,49 echivalenți greutate % NaCl, iar pentru al doilea sistem, concentrația este de 2,48 echivalenți greutate % NaCl (fig. 2). Cit privește densitatea soluțiilor, calculată din volumul fazei de gaz, T_m și T_h (metoda Bodnar, 1983), se caracterizează prin valori de la 0,924 g/cm³ la 0,940 g/cm³ pentru soluțiile aparținând primului sistem și prin valori de 0,919-0,949 g/cm³ pentru soluțiile celui de-al doilea sistem (fig. 3).

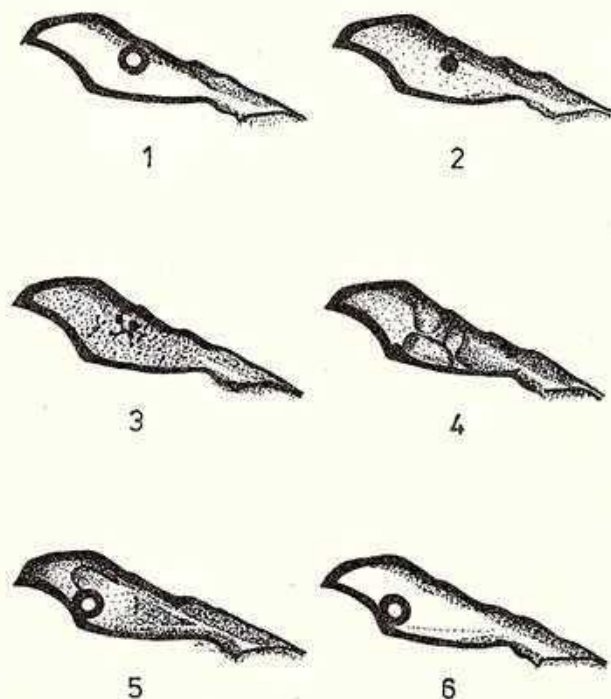


Fig. 1 - Transformările de fază într-o incluziune bifazică dintr-un cristal de cuarț filonian asociat cu baritină de la Marca (Dobrogea de nord).

1-Incluziunea bifazică lichid-gaz la +18⁰ C; 2-Aceeași incluziune la -52⁰ C. Bula de gaz s-a micșorat, iar mediul lichid din incluziune (gheața) a devenit ușor opac; 3-La -16,5⁰ C are loc prima fuziune a gheții care se grupează în cristale izolate; 4-La -4,7⁰ C apare bula de gaz printre cristalele de gheață și lichid; 5-La -2,0⁰ C se observă ultimul cristal de gheață; 6-La -1,6⁰ C dispare ultimul cristal de gheață și mediul din incluziune devine bifazic ca în figura 1.

Histograma generală a concentrației în săruri, pentru toate incluziunile supuse cercetărilor criometrice arată un maximum de concentrație de 2,5 - 2,7 % NaCl (fig. 4).

Din examinarea datelor prezentate în tabelul 1 se evidențiază unele corelații între temperatura de omogenizare T_h și parametrii criometrici.

Acest lucru se remarcă în special între valorile temperaturilor de omogenizare (T_h) și cele ale punctelor eutectice. Sub acest aspect proiecțiile punctelor eutectice (T_e) și ale temperaturilor de omogenizare (T_h) se distribuie în două cimpuri bine distincte (fig. 4).

În cîmpul I, la o ușoară creștere a lui T_h , corespunde o creștere bruscă a lui T_e . În cîmpul II la o ușoară creștere a lui T_h corespunde, de asemenea, o ușoară creștere a lui T_e .

Tabel

Date criometrice pentru incluziunile fluide din cuarțul hidrotermal de la Marca-Malcoci

Nr.	T_h °C	T_e °C	T_m °C	NaCl %	densitate g/cm ³
4111/a	146	-19,5	-1,4	2,39	0,940
	157	-19,5	-1,4	2,39	0,930
		-18,5			
	158	-19,1	-1,4	2,39	0,929
	143	-19,2	-1,3	2,22	0,942
	162	-18,5	-1,5	2,56	0,927
		-17,5			
	159	-18,5	-1,5	2,56	0,929
		-17,5			
	158	-18,5	-1,6	2,72	0,931
		-17,5			
	162	-17,5	-1,5	2,56	0,926
	165	-18,0	-1,5	2,56	0,924
	158	-19,3	-1,5	2,56	0,931
4111/b		-25,0	-1,4	2,39	
		-25,5	-1,4	2,39	
	167	-18,5	-1,3	2,22	0,919
	147	?	-1,6	2,72	0,942
	153	-26,0	-1,5	2,56	0,935
	139	?	-1,7	2,88	0,949

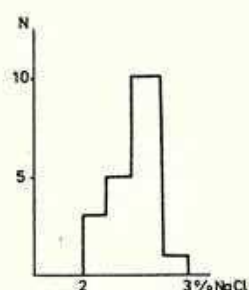


Fig. 2 - Histograma salinității soluțiilor din incluziunile fluide din cuarțul de la Marca.

Concluzii

Datele criometrice arată că: filoanele de cuarț cu baritină de ultima generație, s-au format din soluții cu concentrații joase, soluții atribuite sistemului NaCl-H₂O caracterizat printr-o valoare medie de temperatură eutectică de -18,5⁰ C, salinitate de 2,49% NaCl.

densitate de $0,924 - 0,940 \text{ g/cm}^3$ și temperatură de $145-165^\circ \text{C}$.

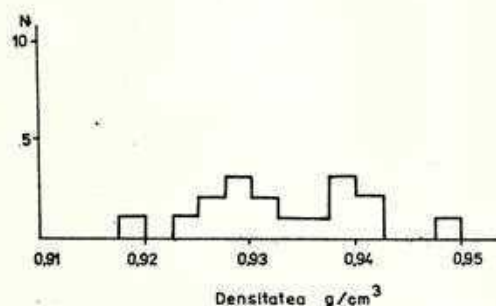


Fig. 3 - Histograma densității soluțiilor din incluziunile fluide din cuarțul filonian de la Marca.

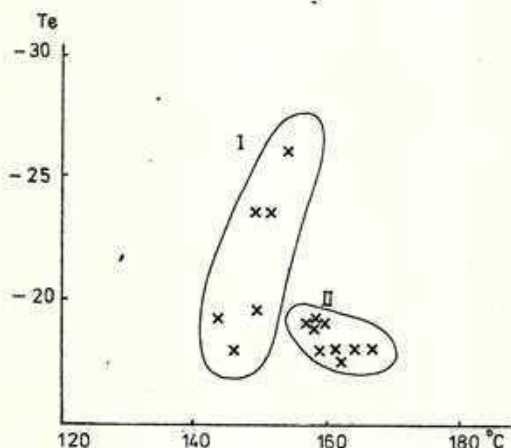


Fig. 4 - Corelații între temperaturile punctelor eutectice (T_e) ale soluțiilor și temperaturile de omogenizare ale incluziunilor fluide din cuarțul de la Marca.

Cuarțul steril din filoanele mai noi, care traversează primul sistem de filoane, s-a format din soluții hidrotermale aparținând, probabil, sistemului $\text{NaCl-KCl-H}_2\text{O}$, caracterizat printr-o temperatură eutectică medie de $-23,2^\circ \text{C}$. Salinitatea soluțiilor a fost în medie de 2,48% NaCl , iar densitatea a variat în limite mai largi ($0,919-0,949 \text{ g/cm}^3$).

Din datele și corelațiile prezentate rezultă că soluțiile hidrotermale din care s-au format cristalele de cuarț asociate cu baritină, au fost supuse unor variații slabe de concentrație, densitate și temperatură.

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MINÉRALISATIONS POLYMÉTALLIQUES ASSOCIÉES AUX MAGMATITES BANATITIQUES DE LA RÉGION GROPI – CĂPRIȘOARA (MONTS DE POIANA RUSCĂ D'OUEST)

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Key words: Mineralization. Skarn. Metasomatism. Hydrothermal Processes. Zoning. Sulfides. Banatite. South Carpathians – Getic and Supragetic Realms – Poiana Ruscă Mts.

Abstract: *Base Metal Ores Related to Banatitic Magmatites in the Gropi – Căprișoara Area (Western Poiana Ruscă Mts).* The banatitic magmatites represented by dacites, rhyodacites, porphyric granodiorites and andesites show petrochemical features slightly different from those of the same rocks occurring in the Ruschița area. Skarns and concentric hydrothermal alteration zones point to the presence of an intrusive pluton in the depth. The copper-bearing, subordinately lead-zinc mineralisations, are spatially related to the Tincova-Nădrag line. They differ qualitatively and quantitatively from the lead-zinc ores of in the Ruschița area.

Court historique des investigations géologiques

Des anciens travaux miniers exécutés dès le dix-huitième siècle jusqu'aux premières décennies de notre siècle prouvent l'intérêt suscité par cette région. Parmi les premières informations scientifiques on peut citer L. Loczy (1982), Fr. Schafarzik (1900) et K. V. Papp (1919), le dernier réalisant une monographie d'ensemble sur la région des monts de Poiana Ruscă. Les travaux de Giușcă et al. (1956), Codarcea et Pavelescu (1954), Pavelescu (1958), Dimitrescu (1956) ont aussi contribué à la connaissance de cette région.

Importantes pour élucider les problèmes structuraux de détail et d'ensemble de la région sont les travaux de Papiu et al. (1963; 1964) et Popescu (1964), qui ont démontré la nature récifale-récifogène de la dolomie de Luncani et qui ont fait un premier essai de séparation lithostratigraphique des épimétamorphites. Les investigations effectuées par Mureșan (1973) et Kräutner et al. (1969; 1973) ont clarifié la plupart des problèmes lithostratigraphiques, d'âge, de structure et de magmatisme de la région, et ont formé la base dans l'élaboration des cartes géologiques à 1:50000.

Cadre géologique

Les formations cristallophylliennes des monts de Poiana Ruscă sont représentées par des épimétamorphites d'âge paléozoïque (Cristallin de Poiana Ruscă) et par des mésométamorphites précambriens (Cristallin de

Lotru-Sebeș). Les deux unités sont séparées par le plan de chevauchement Cinciș-Vadu Dobrii-Tincova et partiellement par le décrochement de Ruschița-Cherghes. La région qui est le sujet de cet article comporte des épimétamorphites attribués à la série de Padeș (Kräutner et al., 1973; Mureșan, 1973). Cette série représente la partie supérieure de la succession épimétamorphique. Elle a été attribuée au carbonifère inférieure et comporte des dépôts terrigènes, organogènes et volcanogènes, métamorphisés au niveau du faciès à schistes verts.

Caractérisation pétrographique

Les roches métamorphiques.

Le périmètre investigué comporte des épimétamorphites appartenant à la Formation de Luncani, représentées par des roches carbonatées (dolomies, dolomies calcaires, calcaires), schistes séricito-chlorito-quartzeux±biotite et quartzites blancs ou noirâtres.

Les roches carbonatées, ayant en général une composition dolomitique, occupent la plupart du périmètre et représentent des digitations terminales orientales de la masse principale des dolomies de Luncani. Elles sont des roches à texture massive ou vaguement orientée, à réseau épais de fissures et comportent: dolomie (80-90 %), calcite (10-15 %) et quantités réduites d'ankérite, quartz et phyllosilicates du groupe des chlorites. Dans des divers endroits apparaissent des variétés à teneur

plus élevé en calcite du type des calcaires dolomitiques et des calcaires blancs à peu près purs. Dans le bassin supérieur de la vallée de Feru on a trouvé une petite lentille de roche magnésiennes issue des processus métasomatiques post-métamorphiques. Autour des petits corps d'andésite et porphyrite granodioritique du versant gauche de la vallée de Căprișoara, les dolomies et les calcaires dolomitiques sont partiellement recristallisés (marbres dolomitiques) et skarnifiés.

Les *schistes séricito-chlorito-quartzeux* représentent des anciens dépôts terrigènes de type pélito-psamitique, endentés avec les roches carbonatées. La paragenèse commune comporte: quartz-muscovite-chlorite ($\pm$ biotite) et subordonnément tourmaline, apatite, minéraux opaques et en quelques variétés graphite.

Les *quartzites* apparaissent seulement dans la colline de Gruul Lung sous forme de deux corps lenticulaires, allongés. Ils sont représentés par des quartzites jaunâtres ferrugineux englobant des petites lentilles de minerai limonitique.

Les roches magmatiques laramiennes

Le magmatisme laramien est représenté par des divers produits assez variés appartenant aux stades principal et final du cycle paléogène des intrusions banatitiques. Ils sont représentés par des dacites, rhyodacites, andésites quartzeuses, porphyrites granodioritiques et par des andésites à amphiboles, andésites basaltoïdes, lamprophyres.

Les *dacites* et les *rhyodacites* forment un corps à contour à peu près isométrique, à un diamètre de presque 400 m, situé dans le bassin supérieur de la vallée de Gropi. Le contour, est reproduit, assez exacte, par les anomalies pédogéochimiques de Cu, Pb, Zn et Mo. Le côté septentrional du corps est traversé par un filon de lamprophyres. Vers les extrémités orientale et occidentale les roches dacitiques passe à des roches andésitiques. La partie centrale du corps éruptif est imprégnée par des sulfures finement disséminées, principalement la pyrite. Des corps plus petits de dacites ont été contournés dans le bassin du ruisseau d'Aramei. Dans le bassin supérieur de la vallée de Vilcan des andésites quartzifères forment un corps lenticulaire à allongement SW-NE, localisé sur un plan de fracture. Contraire aux dacites les andésites quartzeuses n'ont pas subi des transformations hydrothermales, fait qui suggère leur mise en place plus récente. Les dacites et rhyolites comportent des fénocrystaux de quartz, orthose, plagioclase acide et biotite. En général, les feldspaths sont kaolinisés ou séricitisés. La pyrite et subordonnément la chalcoppyrite sont disséminées dans la masse de la roche d'une manière inégale ou se présente dans des petits filons.

Les *porphyrites granodioritiques* ont été identifiées en quelques corps petits à contour irrégulier, dans

la vallée de Căprișoara, vallée d'Aramei et vallée de Tirsu. Les corps d'andésites affectés par des altérations hydrothermales et les porphyrites granodioritiques représentent des apophyses d'un plutonite granodioritique situé probablement au-dessous de la zone des affleurements.

Les *roches andésitiques* sont plus fréquentes que les dacites et se trouvent surtout sous forme de filons à épaisseurs et longueurs variables, en quelques endroits localisés sur des plans de failles. On peut séparer trois variétés de roches andésitiques: andésites à amphibole, andésites à amphibole et biotite et andésites à biotite. En quelques filons la teneur plus élevée en mélano-crates imprime à la roche une couleur noirâtre-verdâtre, faisant le passage vers l'andésite basaltoïde. L'aspect de la matrice varie de hyalin jusqu'à microcristallin ou même phanéritique. Les phénocrystaux sont représentés par plagioclase andésine-labrador ou labrador-bitownite, amphibole et/ou biotite. Les amphiboles, fréquemment maclés, sont du type hastingsite ou hornblende titanifère et, par altération hydrothermale sont transformées, en quartzine, chlorite, rutile et minéraux opaques. Généralement les roches andésitiques, excepté celles quartzifères, sont fortement transformées du point de vue hydrothermal (kaolinisation, silicification, propylitisation et pyritisation).

Les *lamprophyres* apparaissent tout à fait isolées dans la vallée du ruisseau de Gropi, la colline de Gruul Lung et la vallée du ruisseau de Feru. Ils représentent une étape finale du magmatisme laramien. Dans la vallée de Gropi un filon de lamprophyre du type spessartitique à direction N-S perce le corps de roches dacitiques sans déclencher aucune transformation au contact. Les lamprophyres de la vallée du ruisseau de Feru et de Gruul Lung, du type odionitique, percent des schistes séricito-chlorito-quartzeux. Les lamprophyres ne sont pas affectés par les transformations hydrothermales et la minéralisation.

Pour une caractérisation pétrochimique des magmatites banatitiques on présente dans le tableau 1 la composition chimique de six échantillons d'andésite, dacite, porphyrite granodioritique, lamprophyre et pour la comparaison, le chimisme de neuf échantillons de roches similaires prélevées d'un périmètre adjacent (Piriul cu Raci-Ruschița). On remarque le caractère acide plus accentué des andésites du périmètre de Riul cu Raci-Ruschița (SiO_2 varie de 57 à 69 %, tab. 1). Les valeurs Niggli situent la majorité des roches andésitiques et dacitiques dans le domaine des magmas dioritiques (quartzeux-dioritique normal dioritique) et granodioritique. Les lamprophyres correspondent au domaine des magmas gabbrodioritiques. Dans le diagramme QLM (fig. 1) les lamprophyres du périmètre de Piriul cu Raci-Ruschița se placent au-dessous du

segment PF. Le caractère moins alcalin des banatites du ruisseau de Gropi-ruisseau de Căprișoara résulte du diagramme al-alk (fig. 2), la plupart des échantillons étant placés sous le segment $\text{alk}=1/2\text{al}$. Le même caractère résulte aussi des diagrammes Pecerillo-Taylor (fig. 3) et $\text{Na}_2\text{O}+\text{K}_2\text{O}-\text{SiO}_2$ (fig. 4). Le diagramme $\text{Al}_2\text{O}_3-\text{SiO}_2$ (fig. 5) relève le contenu plus haut en aluminium de la même catégorie des roches. Dans le diagramme QAP (Streckeisen)(fig. 6) les roches sont projetées dans le champ des dacites et celui d'andésites.

On remarque de nouveau la tendance vers une acidité plus prononcée des roches du périmètre de Căprișoara.

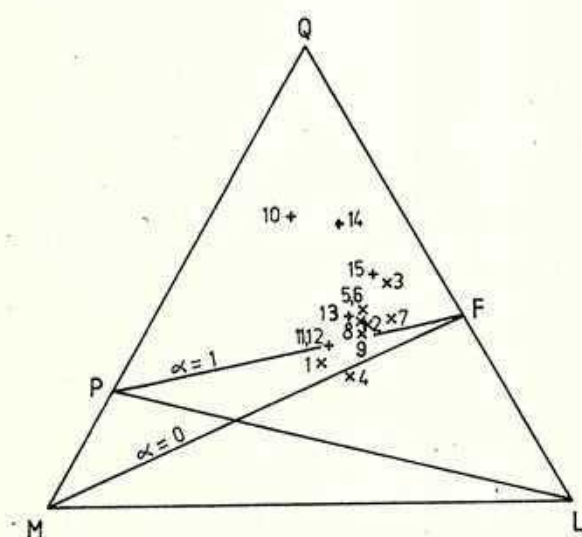


Fig. 1 Diagramme QLM

x, roches banatitiques du périmètre Ruschița; + roches banatitiques du périmètre Gropi Căprișoara.

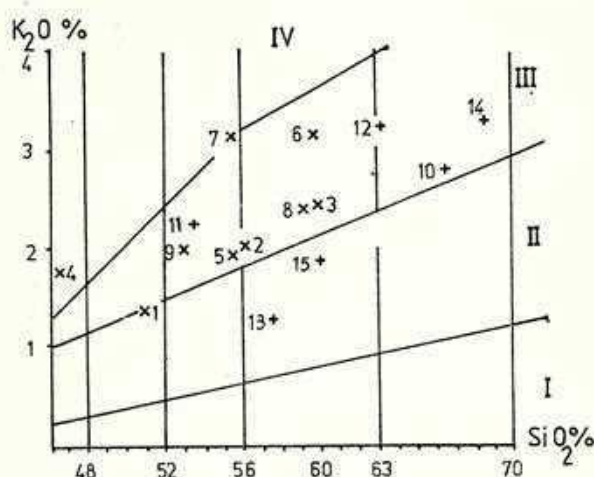


Fig. 3 Diagramme $K_2O - SiO_2$ (Peceryllo-Taylor)

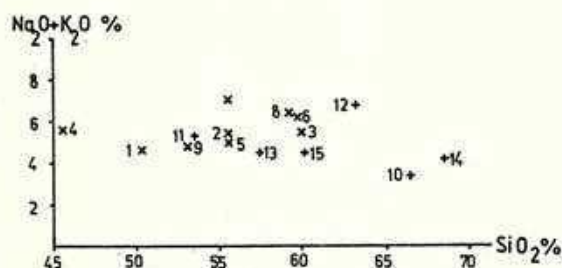


Fig. 4 Diagramme $\text{Na}_2\text{O} + \text{K}_2\text{O} - \text{SiO}_2$

Elements structuraux

Pendant l'étape du métamorphisme hercinien les déformations plastiques sont succédées dans plusieurs stades, et ont affecté toute la succession de roches carbonatées et détritogènes. Les plans axiaux des plis sont verticaux ou inclinés et les axes structuraux ont des faibles enfouissements accidentels. Dans le périmètre investigué les axes de ces plis ont été régénérés probablement sous forme de dômes larges pendant la phase laramienne, par subpressions dues à l'ascension des magmas banatitiques.

Les déformations plus importantes de la tectogenèse alpine sont liées à deux systèmes principaux de fractures. Le système à direction NNE-SSW, a constitué la principale voie d'accès des magmas andésitiques, dacitiques et des fluides hydrothermaux associés au

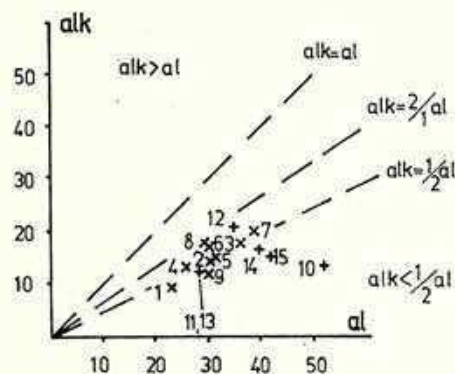


Fig. 2 - Diagramme al-alk

Tableau
Composition chimique des

No. échant.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	P ₂ O ₅	TiO ₂	CaO
1	51,00	16,60	3,50	3,15	0,20	0,24	1,45	8,50
2	56,20	17,35	3,40	2,55	0,14	0,19	1,25	7,90
3	60,00	15,95	3,00	1,15	0,09	0,36	0,70	4,90
4	46,60	16,75	3,20	4,15	0,14	0,45	1,85	8,40
5	55,65	15,15	2,55	2,20	0,10	0,70	1,10	6,80
6	59,84	15,25	4,00	2,52	0,12	0,19	0,65	4,80
7	55,60	18,99	5,60	1,08	0,17	0,45	0,95	4,68
8	59,20	15,40	3,80	2,15	0,13	0,23	1,05	6,00
9	53,25	17,35	5,55	3,24	0,25	0,18	1,40	7,70
10	66,45	16,50	5,60	0,09		0,07	0,68	0,40
11	53,60	17,70	4,75	2,40	0,09	0,13	0,83	7,50
12	63,25	16,20	2,90	1,85	0,19	0,08	0,62	3,45
13	57,48	15,64	3,91	1,87	0,04	0,18	1,40	6,58
14	68,48	12,80	3,00	0,40		0,10	1,20	2,52
15	60,10	18,00	4,30	1,00		0,04	1,30	4,97

1-9, banatites de la zone de Ruschița: 1, lamprophyre, Piriul Cracul Lung; 2, andésite, Piriul Turcului; 3, andésite, Piriul cu Raci Mare; 4, lamprophyre, Piriul cu Raci Mare; 5, andésite, Piriul cu Raci Mic; 6, andésite, Piriul Stuller; 7, andésite, Dealul Boul-sud; 8, porphyrite granodioritique, Piriul Cracul Lung; 9, lamprophyre,

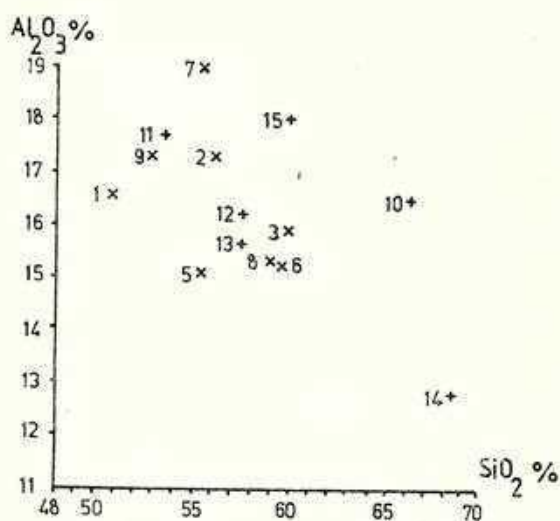


Fig. 5 - Diagramme Al₂O₃ - SiO₂

magmatisme banatitique. La plupart des filons de roches andésitiques sont associés à ce système de fractures qui a été actif probablement dès une étape préaramienne. Le deuxième système, à orientation WNW-ESE, moins représenté dans la région, comporte des failles qui ont actionné pendant et après la phase laramienne.

On connaît plusieurs failles pareilles dans la zone de Piriul cu Raci au nord de Ruschița, le long desquelles se sont emplacé des andésites "stériles" sans des transformations hydrothermales.

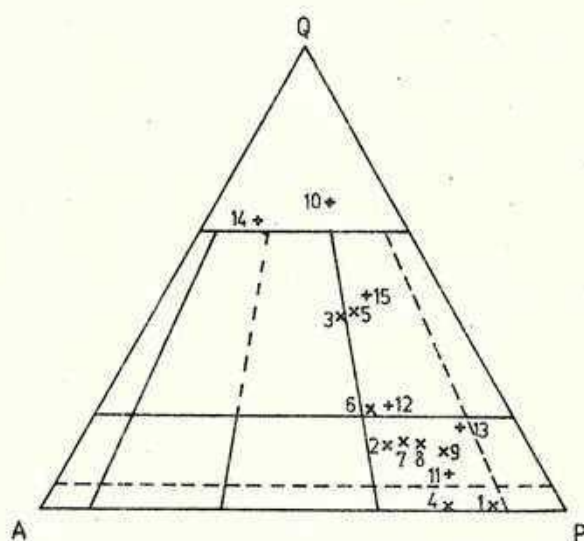


Fig. 6 - Diagramme QAPF

Métamorphisme magmatique et hydrothermal

Les transformations déterminées par le métamorphisme thermique et metasomatique exercé par le magmatisme banatitique se manifestent surtout en deux secteurs qui coïncident avec les aires de concentration des minéralisations polymétalliques et d'affleurement des roches banatitiques: secteur du

1

roches banatitiques (%)

MgO	Na ₂ O	K ₂ O	H ₂ O ⁺	H ₂ O ⁻	Co ₂	SO ₂	S	Total
8,80	3,00	1,30	1,55	0,85	0,45		0,65	99,69
3,30	3,40	2,05	0,70	0,95	1,85		0,09	100,62
2,00	3,05	2,45	2,60	0,90	3,80		0,17	98,52
5,00	3,85	1,80	2,80	1,25	3,75		0,75	98,44
2,80	3,05	1,95	3,05	0,65	5,10		0,35	98,15
3,35	2,90	3,15	2,12	0,40	0,35			99,64
0,97	3,87	3,12	2,67	0,92	0,53			99,60
3,50	4,00	2,40	0,53	0,97	0,90		0,04	100,44
2,90	2,80	2,00	0,45	2,50	0,70		0,09	100,36
1,00	0,75	2,80	0,60	2,60		0,17	3,00	100,71
5,05	3,05	2,25	1,36	0,78	1,20		0,01	100,70
2,95	3,60	3,25	0,74	1,30	0,30			100,68
5,30	3,28	1,25			0,18	0,12		97,23
2,00	0,90	3,33	1,00	0,17	2,80		0,20	98,90
1,00	2,70	1,77	0,56	0,14	3,00		0,30	99,18

Piriul Cracul Lung; 10-15, banatites de la zone de Piriul Gropilor-Piriul Căprișoara; 10, dacite, Piriul Gropilor; 11, lamprophyre, Piriul Gropilor; 12, andésite, Dealul Piciorul Moșiuței; 13, andésite, Piriul Gropilor; 14, porphyre granodioritique, Piriul Aramei; 15, granodiorite, Piriul Căprișoara.

ruisseau de Gropi au nord et le secteur d'Albota-Căprișoara, au sud.

Selon leur composition initiale les roches épimétamorphiques ont agi des manières différentes au métamorphisme thermique. Les schistes d'origine terrigène, se sont transformés progressivement en cornéennes caractérisées par la disparition graduelle de la schistosité, des modifications de structure et la formation progressive de la biotite. Les roches carbonatées magnésiennes ont recristallisé, résultant les marbres dolomitiques.

Le métamorphisme thermique est suivi du processus de métasomatose à de différentes intensités. Parallèlement a lieu le remplissage des cavités, fissures et interstices des plans de foliation. Les réactions métasomatiques ont affecté non seulement les cornéennes et les roches cristallines mais aussi les roches éruptives. Les pyrométasomatites représentent les premiers produits du processus de métasomatose. Ainsi, dans le versant gauche du ruisseau de Căprișoara, aux environs d'un corps d'andésite biotitique affleure une zone de skarn magnésien épaisse de 30 m, qui se développe sur une distance de 250 m, passant latéralement à un marbre dolomitique. Le skarn comporte forstérite remplacé presque en totalité par antigorite, brucite et talc, grenat du type andradite partiellement chloritisé, spinelle à grains petits à contours idiomorphes, trémolite en prismes bien développées et plages très développées de calcite et pyrite. Dans les zones à calcite on a remarqué aussi la présence de la hydromagnésite. La formation de l'antigorite et brucite au compte de forstérite, tout

comme la présence du talc, du chlorite et de la hydromagnésite sont dues à une altération hydrothermale ultérieure à la formation du skarn. Les hydrométasomatites sont largement développées dans l'aurole du plutonite banatitique, ayant des manifestations variées, déterminées par la nature des différents types de paléosomes soumis à des réactions métasomatiques avec les solutions hydrothermales.

Selon le mode de répartition des processus d'altération hydrothermale on remarque une disposition presque concentrique de zones comparables avec celles connues dans la littérature de spécialités: potassique, phyllique et propylitisée.

La zone potassique à un diamètre d'environ 300 m est située entre le ruisseau Arama et le ruisseau Feru. Les andésites, les dacites et les épimétamorphites y présentes sont fortement séricitisées, ont une couleur blanchâtre et comportent de la biotite de néoformation.

La zone phyllique à position extérieure et partiellement superposée à la zone potassique, se trouve entre le ruisseau Tirsu et le ruisseau de Feru et dans la zone du ruisseau de Vilcan. Une forte silicification a transformé les schistes séricito-quartzueux dans des schistes siliceux blancs à séricite. Les néoformations sont représentées par quartz, séricite et chlorite. De même on remarque une pyritisation intense des roches.

La zone propylitisée est situé à l'extérieur de la zone phyllique sur une largeur de 100 à 200 m. Les andésites et les schistes sont partiellement épidotisés et chloritisés. Dans cette zone se trouvent les principales occurrences de roches minéralisées à pyrite, chalcop-

rite (malachite, azurite), blende, galène etc. La propylitisation a des influences aussi sur le skarn du versant gauche du ruisseau de Căprișoara. Les dacites du ruisseau de Gropi présentent une forte altération hydrothermal (caolinisations, séricitisations, pyritisations).

Minéralisations polymétalliques associées aux banatites

Des minéralisations ont été identifiées dans les deux secteurs d'affleurement des roches banatitiques, respectivement le secteur du ruisseau de Gropi et le secteur du ruisseau de Căprișoara - colline d'Albota. Le degré de connaissance actuel des paragenèses minérales est limité au niveau de la zone d'oxydation et de la zone de cimentation basé sur des blocs provenant des anciens travaux miniers.

A. Secteur de Căprișoara-Albota. Les minéralisations hydrothermales métasomatiques se trouvent surtout au contact ou dans la proximité des corps andésitiques, de quelques failles orientées NE-SW et le plus souvent dans la zone des roches propylitisées. Les occurrences de roches minéralisées sont concentrées en quatre zones: ruisseau de Tîrsu, ruisseau de Căprișoara-Gruul Lung, Piciorul Mosta-colline de Vilcan, ruisseau de Feru-sources.

La zone du ruisseau de Tîrsu englobe six occurrences de roches minéralisées dans les calcaires dolomitiques grisâtres et dans les schistes séricito-chlorito-quartzeux situés dans la partie occidentale d'une faille à direction SW-NE. La roche minéralisée est formée d'une masse quartzreuse à quartz de type hydrothermal sous forme de petits cristaux bipyramidaux. Le liant des grains de quartz comporte goethite, malachite et azurite; parfois en des sections polies on observe des restes de pyrite, chalcoppyrite et arsénopyrite. La malachite est présente parfois en des petits filons qui percent la roche.

La zone du ruisseau de Căprișoara-Gruul Lung est constituée de trois occurrences principales situées dans les calcaires dolomitiques du versant gauche du ruisseau de Căprișoara. La roche minéralisée est soit une brèche siliceuse-carbonatée à quartz hydrothermal et goethite, malachite et azurite, soit un minerai goethitique compact qui garde encore des restes de pyrite. La localisation des occurrences est contrôlée par deux failles qui traversent le ruisseau de Căprișoara. Dans la même zone il y a le skarn déjà décrit et dans le terril d'une ancienne galerie on trouve des blocs de minerai de fer comportant magnétite, sidérite et subordonnellement pyrite et gangue quartzreuse.

La zone de Piciorul Mosta-colline de Vilsan renferme deux occurrences de roches minéralisées sur la crête de Piciorul Mosta et Vilsan, localisées tant dans les dolomies calcaires aussi bien que dans les schistes siliceux blancs. La roche minéralisée est une brèche

à éléments anguleux de dolomie calcaire, et matrice formée de limonite, goethite et malachite. La malachite apparaît aussi sous forme de petits filons qui traversent la brèche. Dans la crête de Vilsan, sur le terril d'une ancienne galerie il y a des blocs de minerai comportant pyrite et melnicovite (80 %), grains rares de chalcoppyrite et arsénopyrite, tous en gangue quartzreuse.

La zone des sources du ruisseau de Feru, située sous la crête de la colline d'Albota, porte deux occurrences de roches minéralisées localisées en des calcaires dolomitiques. Du point de vue pétrographique et minéralogique, la minéralisation se rapproche de celle de la zone antérieurement décrite. Dans les terrils des anciennes galeries on trouve des blocs de minerai comportant presque en totalité de la pyrite à granulation millimétrique et chalcoppyrite en quantité réduite (3 à 4 %).

Les minéralisations du secteur de Căprișoara-Albota peuvent être caractérisées comme des "minerais pauvres" à une teneur en éléments utiles de: Cu-0,10 à 2,12 %; Pb-0,06 à 0,36 %; Zn-0,10 à 0,84 %; Bi-40 à 350 ppm; Ni-20 à 180 ppm; Sb-100 à 600 ppm; Sn-25 à 1000 ppm; As-300 à 3000 ppm. La minéralisation est donc principalement cuprifère. Dans la zone d'altération potassique on remarque des teneurs anormales en Cu et Mo, accompagnant les impregnations de pyrite dans les schistes silicifiés et séricitisés.

Prospection géochimique et géophysique. Les auréoles de dispersion secondaire pour le cuivre (Cu 132 ppm) du secteur d'Albota-Căprișoara se superposent en partie aux zones à "chapeaux de fer" connues mais aussi aux autres possibles zones d'accumulation de la chalcoppyrite, (fig. 7). On remarque la tendance des anomalies de cuivre de se grouper près des failles qui traversent le secteur surtout dans les zones d'altération phyllique et potassique.

Les anomalies de plomb (Pb 180 ppm) et celles de zinc (Zn 266 ppm) occupent des aires plus larges et n'ont pas des liaisons évidentes avec les zones de faille ou avec le fond pétrographique. Les valeurs des anomalies de Mo coïncident en grande partie avec celles de Cu; se détachent quelques points à Mo 15 ppm situés dans la zone d'altération potassique. La disposition des anomalies indique une zonalité des éléments. Ainsi, au centre, superposées aux zones d'altération potassique, phyllique et partiellement propylitique, apparaissent des anomalies de Cu et Mo. Les anomalies de Pb et Zn se superposent à la zone propylitique. On observe une tendance de superposition des anomalies de Pb et Zn aux niveaux des roches carbonatées.

Les anomalies électrométriques de polarisation induite (fig. 8) ont des valeurs entre 30 et 80 ms, les plus significatives anomalies ayant des valeurs de 40 ms. La plupart des anomalies sont déterminées par la

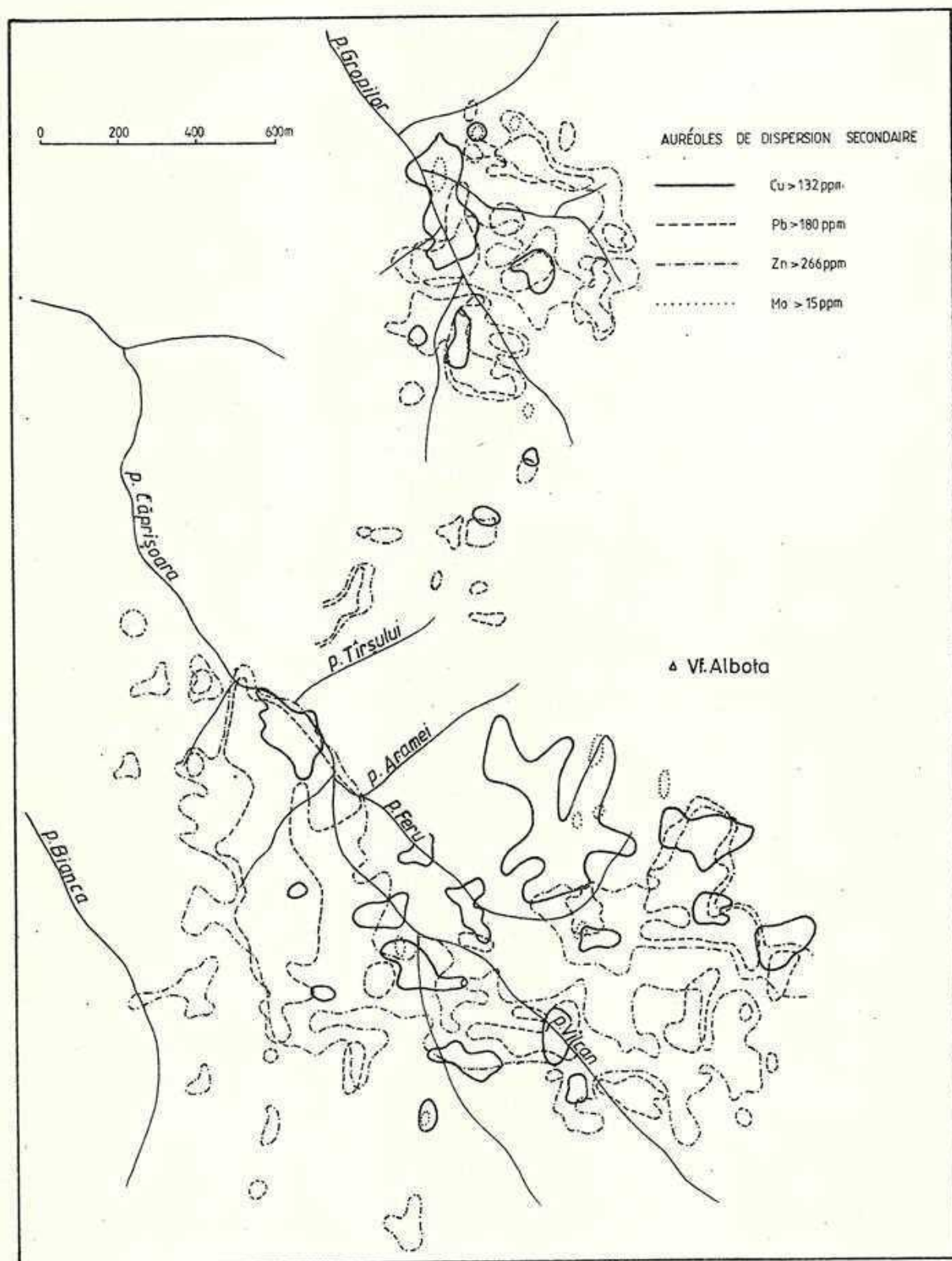


Fig. 7 - Carte géochimique du secteur Albota-Căprișoara (d'après I. Șchiopu, 1986).

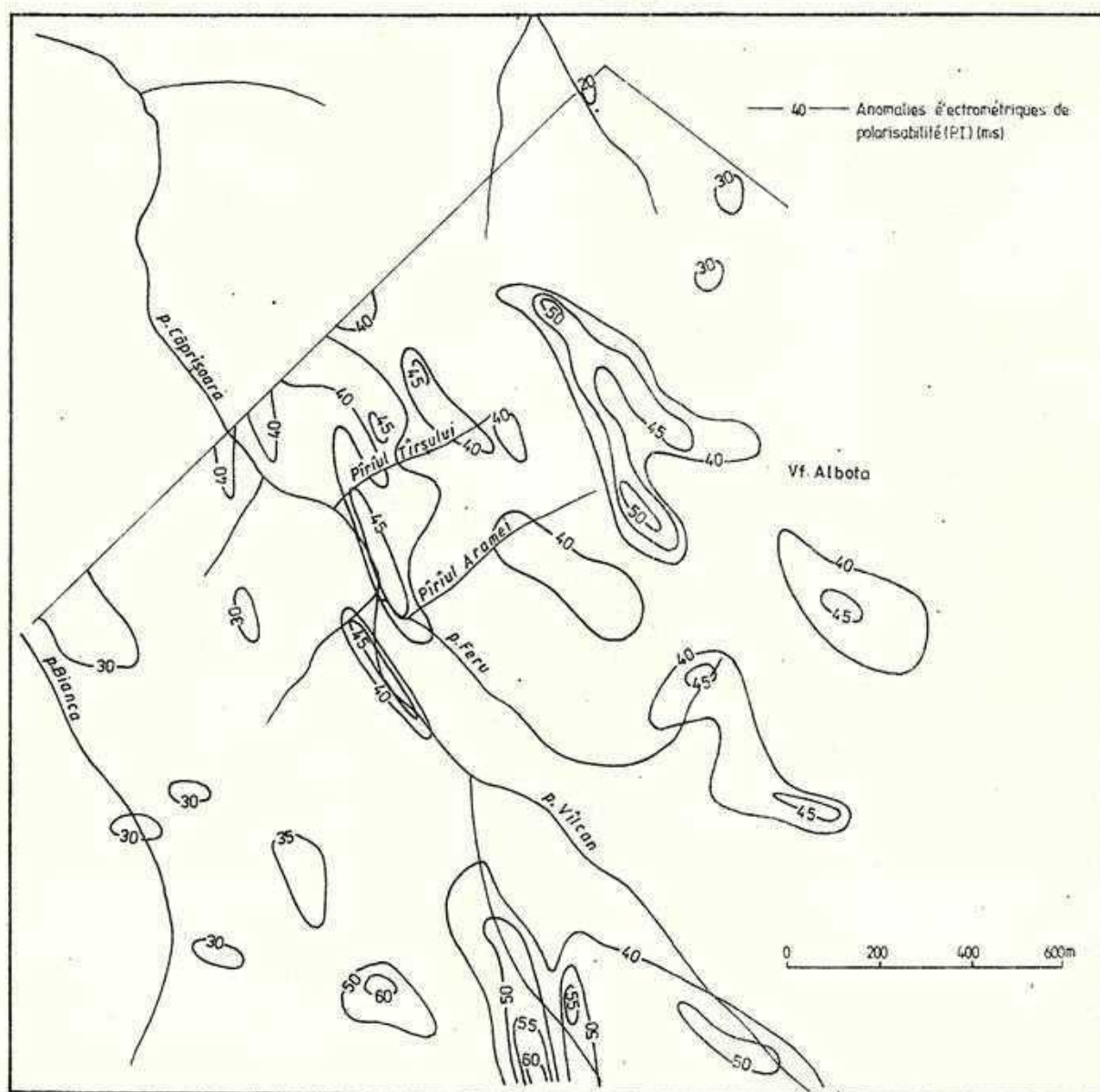


Fig. 8 — Carte des isolignes de polarisabilité du secteur Albota-Căprișoara (d'après I. Balint, 1985)

présence de la pyrite dans les schistes siliceux, séricitisés, dans les dolomies et les andésites altérées hydrothermal. Quelques apex coïncident aux zones pyritisées à chalcopryrite (zones à malachite et azurite). Dans la partie occidentale de la crête d'Albota et dans le versant gauche de la vallée de Mostă, les anomalies électrométriques se superposent aux zones anomalies géochimiques (Pb, Cu, Zn). On soupçonne donc la présence de certaines minéralisations de Cu, Zn, et Pb, en profondeur.

B. Secteur du ruisseau de Gropi. Dans le bassin du ruisseau de Gropi, dans une zone dépressionnaire, apparaît un corps de roches éruptive à contour isométrique et un diamètre d'environ 400 m. Il comporte principalement dacites à biotite qui vers l'ouest et l'est passent à rhyodacites et andésites à biotite. Le corps dacitique est traversé par un filon de lamprophyres à une épaisseur moyenne de 14 m. Vers le nord apparaît un autre corps petit de porphyrite granodioritique.

La minéralisation comporte spécialement pyrite et subordonnement chalcopryrite, arsénopyrite, galène et blende distribués sous forme d'impregnation diffuse, hétérogène, aussi que dans des filons submillimétriques en des dacites et rhyodacites fortement altérées hydrothermal. Des observations chalcographiques résulte la présence de la pyrite en grains à contours xénomorphes, corodés, associé avec des petits grains de chalcopryrite. La blende forme des petites plages pas associées avec des autres sulfures. Dans l'andésite de la partie ouest du corps éruptif on constate aussi la présence de la magnétite qui renferme un réseau lamellaire d'hématite.

Les analyses spectrographiques sur les échantillons prélevés des roches minéralisées ont indiqué des contenus très faibles: Cu, 200 à 2500 ppm, Zn, 100 à 3000 ppm.

Prospection géochimique. Il y a une remarquable superposition des auréoles de dispersion secondaire du Cu (132 ppm) et Mo (15 ppm) d'une part, et du Pb (180 ppm) et Zn (266 ppm) d'autre part. Si les anomalies de Pb et Zn recouvrent toute la surface du corps dacitique et se diffusent plus vers l'ouest et vers le sud, les anomalies de Cu et Mo suivent le contour du corps, manifestant seulement une faible tendance d'extension vers le sud.

Facteurs de contrôle sur la métallogénèse

La répartition spatiale des minéralisations polymétalliques associées à la métallogénèse laramienne indique trois facteurs principaux qui ont contrôlé les processus métallogéniques: magmatique, tectonique et lithologique.

Le facteur magmatique, le plus important, a contrôlé tant la qualité, aussi bien que la quantité des minéralisations. Toutes ces minéralisations se disposent au contact ou très proche des corps de roches banatitiques (granodiorites, porphyrites granodioritiques, andésites et dacites). Une autre série d'andésites, mises en place probablement plus tard, ne sont pas accompagnées d'une métallogénèse. Les lamprophyres aussi n'ont pas joué aucun rôle métallogénique. En ce qui concerne le chimisme des magmas on peut remarquer que les magmas moins alcalinisés et plus acides du périmètre Gropi-Căprișoara ont engendré des minéralisations principalement cuprifères, tandis que les magmas de la région de Ruschița ont généré des minéralisations plombo-zincifères.

Le facteur tectonique. Le système de dislocation à direction NNE-SSW présente une importance métallogénique particulière, formant la principale voie d'accès des magmas impliqués dans le processus métallogéniques et des fluides hydrothermaux. Ce fait est confirmé aussi par la disposition des anomalies

pédogéochimiques de Cu, Mo, Pb et Zn du secteur de Căprișoara-Albota qui suivent en général les zones proches de ce système de dislocations.

Le facteur lithologique, est impliqué surtout dans l'aspect quantitatif des minéralisations. On remarque, dans tout le périmètre, la tendance des roches carbonatées de favoriser les processus métasomatiques qui ont déterminé la formation des accumulations de sulfures. Les dolomies, par leur réseau dense de fissures et clivages et les calcaires par leur solubilité ont facilité la circulation des fluides minéralisés et les processus métasomatiques. Une disposition préférentielle des zones d'oxydation du type "chapeau de fer", des anomalies chimiques dans les aires de développement des roches carbonatées est très évidente.

Dans les schistes séricito-quartzeux, les schistes siliceux et les quartzites ont trouvé seulement quelques minéralisations diffuses de type impregnation.

Conclusions

Les roches éruptives de la région de Gropi-Căprișoara sont situées dans l'extrémité nord-est de l'alignement laramien de Tincova-Nădrag. Elles percent les roches épimétamorphiques du cristallin de Poiana Ruscă.

Les transformations déterminées par le métamorphisme thermique et métasomatique exercé par le magmatisme laramien sont évidentes dans une zone en quelque sorte elliptique où on sépare des subzones d'altération potassique, phyllique et propylitique. Cette région (secteur d'Albota-Căprișoara) correspond probablement à la zone apicale d'une plutonite banatitique.

Les minéralisations afférentes sont du type pyrométasomatique et hydrothermal (filonien et d'impregnation). L'activité métallogénique a débuté pendant la phase subséquente du métamorphisme de contact avec la formation des concentrations de magnétite et hématite. La diminution de la température, corrélée avec la diminution de la teneur en fer, a conduit vers la déposition des sulfures de Fe, Cu, Pb, Zn par substitutions métasomatiques. Ultérieurement des fluides hydrothermaux ont déposé une nouvelle génération de sulfures le long des fissures et sous forme d'impregnations.

Le caractère principalement cuprifère et subordonnement plombo-zincifère des minéralisations de tout le périmètre constitue une permanence des minéralisations associées aux magmatites laramiennes de l'alignement de Tincova-Nădrag.

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**CARTE GÉOLOGIQUE DU SECTEUR
 ALBOTA - CĂPRIŞOARA**

MONTS POIANA RUSCĂ D'OUEST

0 200 400 600 m

LÉGENDE

**PALÉOGÈNE
 ROCHES MAGMATIQUES**

-  Lamprophyres
-  Dacites
-  Andésites: à biotite (x bi); a amphiboles (x h); quartzifères (x q)
-  Porphyrites granodioritiques
-  Skarns
-  Alterations hydrothermales: potassique (a); phyllique (b); propylitique (c)
-  Pyritisations

**PALÉOZOÏQUE
 ROCHES METAMORPHIQUES**

-  Zones d'oxidation (limonite ± malachite ± azurite)
-  Brèches
-  Dalomies
-  Quartzites
-  Schistes séricito-quartzeux

--- Limite géologique

— Faille

⊕ Axe synclinal

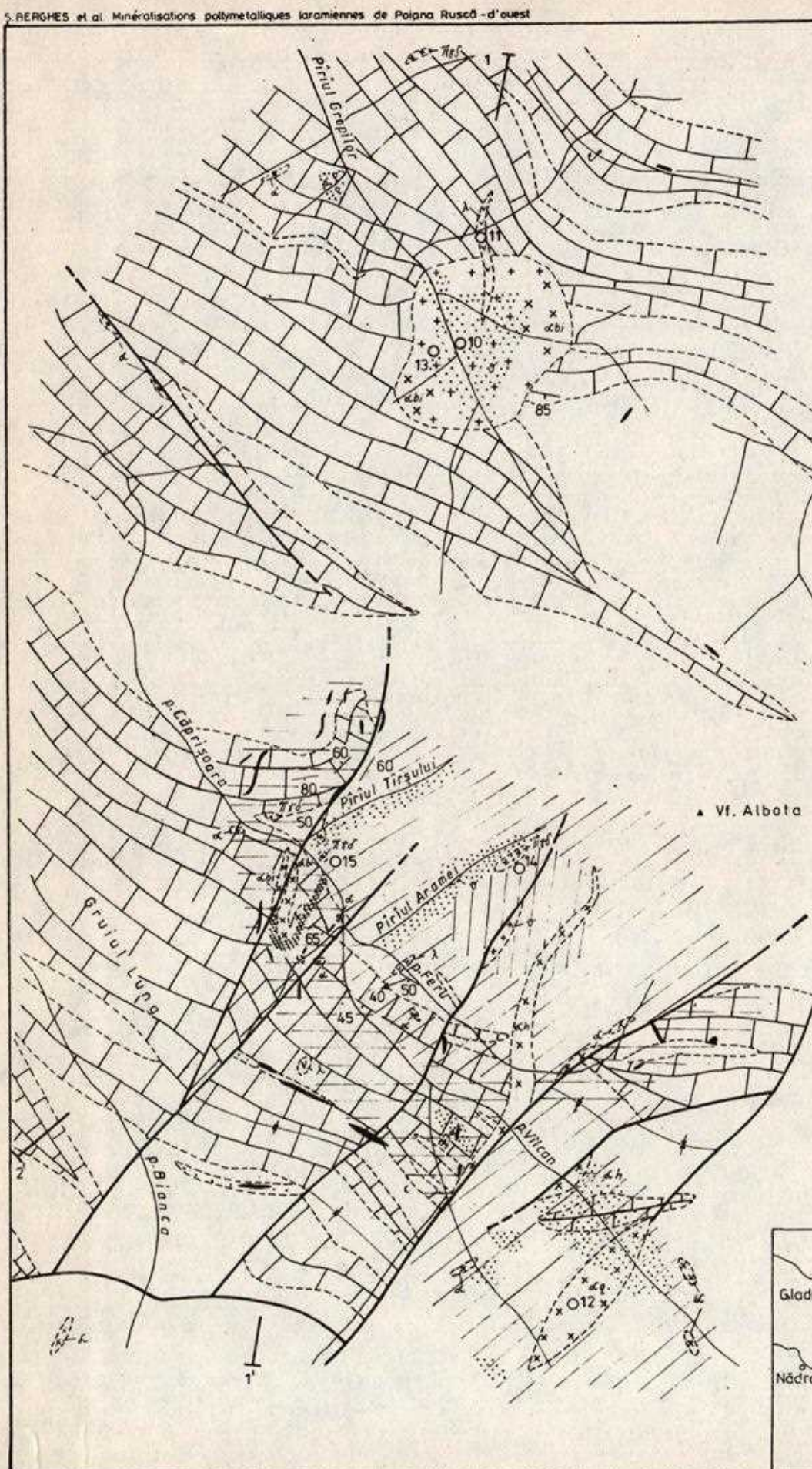
⊖ Axe anticlinal déversé

65 Schistosité

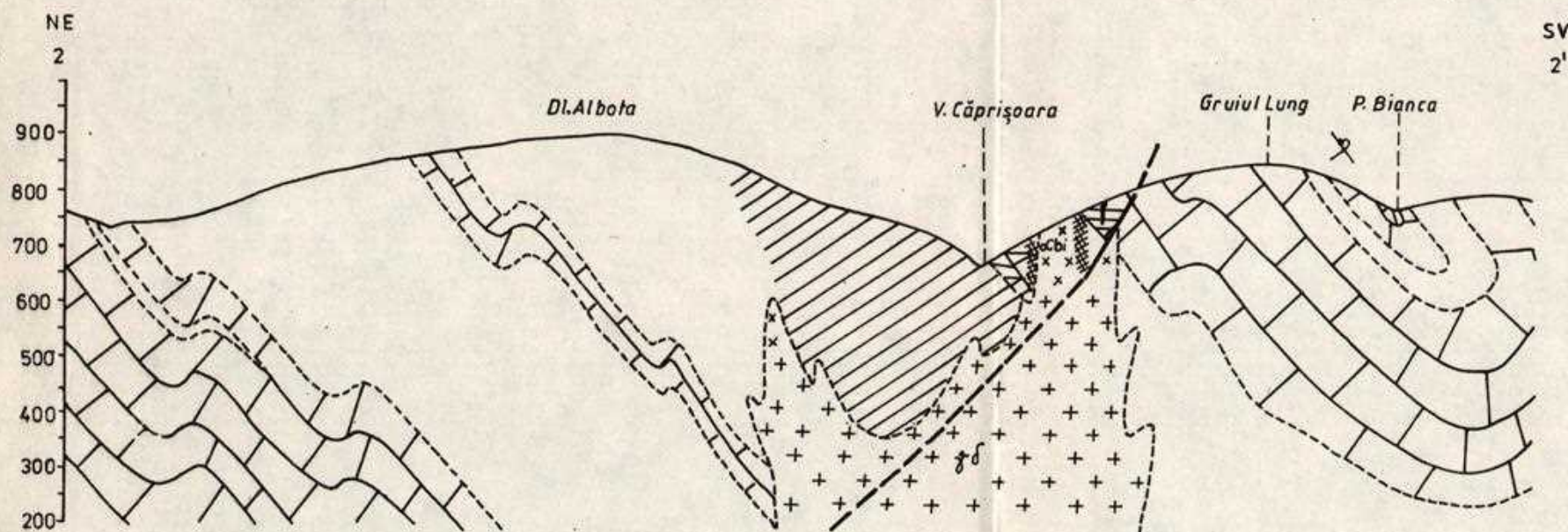
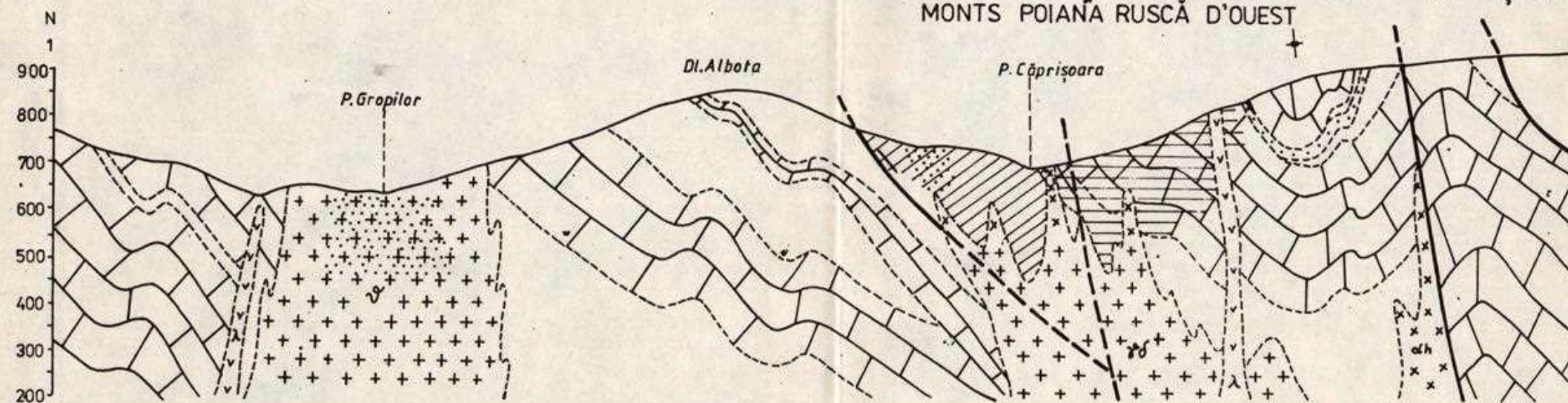
40 Linéations

1 1' Position des coupes géologiques

○ 12 Echantillons silicates



S. BERGHES, M. BERGHES, G. TUDOR

COUPES GÉOLOGIQUES DANS LE SECTEUR ALBOTA-CĂPRIȘOARA
MONTS POIÂNĂ RUSCĂ D'OUEST

LÉGENDE

- PALÉOGÈNE**
ROCHES MAGMATIQUES
- Lamprophyres
 - Dacites
 - Andésites (α); à biotite (αbi); à amphiboles (αh)
 - Granodiorites
 - Skarns
 - Altérations hydrothermales: phyllique (a); propylitique (b)
 - Pyritisations
- PALÉOZOÏQUE**
ROCHES MÉTAMORPHIQUES
- Zone d'oxidation (limonite $\pm$ malachite $\pm$ azurite)
 - Dolomies
 - Quartzites
 - Schistes sericito-quartzeux
 - Limite géologique
 - Faille
 - Axe synclinal
 - Axe synclinal déversé
 - Schistosité

PÉTROGRAPHIE ET PROPRIÉTÉS PHYSICO-CHIMIQUES DES CHARBONS PLIOCÈNES DU SECTEUR JIU-DANUBE

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Key words: Coal. Pliocene. Petrography. Macerals. Physico-chemical properties. Getic Plateau - Strehaia Platform.

Abstract: *Contributions to the Knowledge of the Petrography of and Physico-Chemical Characteristics of the Pliocene Coals Between the Jiu and the Danube.* Four main lithotypes originating in different coaly facies have been distinguished. They differ one from another by their petrographic composition, physico-chemical features and the yield of low-temperature products. Xylite, mostly constituted of textinite, displays the lowest ash content among the lithotypes, a high thermal power and an yield of tar from low-temperature carbonization up to 28.5 per cent. The detrital coal, mostly consisting of humodetrinite, is the predominating lithotype. Its high content of ash points to a palustrine depositional environment of the flooded plains separated by fluvial channels. The xylitic coal is the most frequently found lithotype. Its petrographic composition and the physico-chemical properties depend on the content of xylite. The low-xylite coal is an intermediary lithotype. Due to the wide variation domains of the contents of humic acid and cellulose, xylite occurs in different stages of transformation (carbonification): from weakly altered, close to wood, up to close to the dull brown coal. On the basis of the primary composition and of the content of volatiles these coals have been assigned to the lignite group (=soft brown coal).

1. Introduction

Les investigations concernant la pétrographie et les propriétés physico-chimiques des charbons de l'Olténie débutent approximativement en 1954, une fois avec l'ouverture des travaux de prospection et exploration. Les premières données sur la composition pétrographique des charbons de la zone de Motru ont été publiées par Bițoianu et Ilie (1967), qui ont publié aussi une autre étude concernant les charbons de Rovinari (1967).

Les recherches paléobotaniques corroborées avec celles du domaine de la pétrographie des charbons ont fourni de nouvelles données concernant les conditions génétiques des gisements de charbon (Țicleanu et al., 1982; 1985; Țicleanu, Bițoianu, 1988), la reconstitution des principales associations végétales carbogénératrices (Țicleanu, 1986), ainsi que la séparation de sept faciès charbonneux qui ont engendré des charbons de l'Olténie (Țicleanu, Bițoianu, 1990).

Récemment, Țicleanu et Bițoianu (in Țicleanu et al., 1989, rapport nonpubl.) ont indiqué l'existence de quelques différences entre les principales propriétés physico-chimiques des lithotypes des charbons du secteur de Jiu-Amaradia.

Selon les nouvelles investigations (Andreescu et al., 1985) les plus de 20 couches de charbon d'âge dacien inférieur-romain moyen connues dans le secteur du Jiu-Danube peuvent être groupées, sur base de critères lithologiques et géologiques, en trois complexes charbonneux: le complexe de Valea Vișenilor comportant les couches de charbon A-B et I-IV; le complexe de Motru, le plus important renfermant les couches V à XIII et le complexe de Bălcești formé par les couches XIV à XVIII.

Les couches du complexe de Valea Vișenilor affleurent entre la vallée de Coșuștea et le Danube et ont été investiguées dans les affleurements des vallées de Spulba, Dedovița, Blahnița, le long des affluents de celles-ci, dans les mines de Prunișor et Livezile, ainsi

que dans de nombreux autres forages.

Le complexe de Motru est bien développé entre le Jiu et le Motru, notamment dans les carrières de Tismana, Pinoasa, Roşia de Jiu, Peşteana Nord, Peşteana Sud, Jilţ Sud, Roşiuţa et Lupoaia.

Les couches de charbon du complexe de Bălceşti sont relativement bien développées dans la zone de colline, entre le Jiu et le Motru et affleurent (couches XIV et XV) dans la carrière de Miculeşti.

2. Caractéristiques pétrographiques des lithotypes

On a identifié les suivants lithotypes: xylite, charbon xylitique, charbon faiblement xylitique, charbon détritique, charbon fibreux, charbon argileux et associée à ceux-ci argile charbonneuse et argile.

2.1 Analyse macroscopique

La xylite (=xylain, bois fossile) résulte des parties ligneuses des arbres et arbustes (racines, troncs et rameaux) et est présente dans les charbons sous forme de bandes, lentilles ou fragments de bois fossile (plus de 5 cm d'épaisseur) plus ou moins transformé.

Selon la couleur de la xylite, dans les charbons investigués nous avons identifié trois types principaux de xylite. Assez souvent y apparaît une xylite jaune, faiblement transformée, comportant des fibres élastiques. La xylite brune, un autre type, est prédominante. Elle est plus métamorphisée que celle jaune et apparaît intercalée soit dans le charbon xylitique, soit dans celui faiblement xylitique. La xylite noire est rare et se présente sous forme de lentilles petites, étant gélifiée. Par dessiccation elle acquiert un éclat intense, elle est très friable, en résultant de petites morceaux à cassure conchoïdale.

Les types de xylite décrits sont compris dans les trois catégories connues dans la littérature de spécialité comme Faser-Xylit, Bruch-Xylit et Gel-Xylit. Les différences entre celles-ci consistent non seulement dans la couleur, mais aussi en d'autres propriétés physiques et chimiques (Abell, 1965). L'élasticité de la xylite jaune et jaune-brune lui imprime une résistance avancée au broyage, ce qui détermine l'usure prématurée des moulins et une grande consommation d'énergie. Au contraire, le charbon détritique est facilement à broyer, ce qui détermine l'accumulation de la xylite en des grandes quantités dans les fractions lourdes. Selon Mocanu et al. (1973, rapport nonpubl.) la fraction de 1 mm comporte 15 à 32 % xylite.

Le charbon xylitique (charbon ligneux) comporte une masse humique, fine à plus de 15% intercalations xylitiques, de couleur brun, brun-noirâtre, il est faiblement stratifié et s'exfolie au contact avec l'air.

Le charbon xylitique est un des principaux lithotypes des charbons de l'Olténie, le caractère xylitique

très prononcé de ceux-ci étant souligné aussi par Lisner et Thau (1956).

Le charbon faiblement xylitique est un lithotype de transition vers le charbon détritique et apparaît plus rarement dans la composition des charbons de l'Olténie, ayant en général les mêmes caractéristiques que le charbon xylitique. Seulement la teneur en xylite varie entre 5 et 10 %.

Le charbon détritique prédomine dans la composition des lignites analysés, touchant même 60 %. Il comporte une masse détritique fine, brun-noirâtre, homogène, où on observe, notamment dans cassure récente, des différents débris végétaux carbonifiés, même de petits fragments de bois fossile.

Le charbon détritique est mat, stratifié, se présente sous forme de bandes et bancs qui dépassent 1 m d'épaisseur et constitue parfois plus de 80 % de la composition des couches de charbon y apparaissant associés à ce lithotype.

Le charbon fibreux, plus rare, a une couleur noire, il est soyeux (fin) et dépourvu de stratification. Il se présente sous forme d'aiguille, lentilles petites et nids renfermés dans le lignite ou même dans l'argile.

Le charbon argileux a une couleur brun-grisâtre à cassure terreuse et aspect stratifié-feuillu. Assez souvent il comporte des aiguilles de fusain, des os de poissons, concrétions calcaires et apparaît comme des intercalations dans quelques couches de lignite, parfois formant même des bancs décimétriques indépendants.

Associées aux lithotypes qui forment les charbons apparaissent les argiles charbonneuses intercalées surtout dans le charbon détritique. Dans toutes les couches de charbon il y a des intercalations, à épaisseurs variables, d'argiles noirâtres, grisâtres, gris-vertâtres et même gris-blanchâtre, comportant souvent des restes végétaux fossiles et des restes de faune. Parfois les intercalations argileuses sont très denses conférant à la couche un aspect rayé, tel le cas de la couche VI de l'exploitation de Gîrla. Rarement nous avons rencontré aussi des intercalations centimétriques d'argiles diatomitiques et même diatomites, comme par exemple celles de la couche VI de charbon de la carrière de Tismana.

Les recherches ont relevé que dans le secteur de Jiu-Danube, les charbons sont formés surtout de charbons détritiques et charbons xylitiques, ce dernier constituant parfois des niveaux très développés. La plupart des couches de charbon comportent, avec prépondérance, du charbon détritique et les couches I, IV, V, VII, VIII et XII ont un prononcé caractère xylitique.

2.2 Analyse microscopique

On constate, dans la composition des lithotypes, une élévation graduelle du contenu moyen en masse organique de 72 % dans le charbon détritique à 95 % à la xylite. Cette masse organique comporte des macéraux

appartenant aux groupes : huminite et inertinite.

En ce qui concerne la composition des lithotypes (tab. 1) par groupes de macéraux, on constate une diminution graduelle du contenu moyen dans les macéraux huminitiques, de la xylite (94,83 %), au charbon détritique (68,42 %). Les teneurs relativement basses en macéraux liptinitiques et inertinitiques de la xylite, par rapport aux autres lithotypes, s'expliquent par la nature variée de la matière végétale originaire.

Tableau 1

Composition en groupes de macéraux des lithotypes

Groupes de macéraux Lithotypes	Huminite %	Liptinite %	Inertinite %
Xylite	94,83	0,15	0,31
Charbon xylitique	81,80	1,30	2,40
Charbon faiblement xylitique	76,70	1,80	4,40
Charbon détritique	68,42	1,10	2,07

Excepté la xylite, dans les autres lithotypes les macéraux liptinitiques se maintiennent à des valeurs petites (1,01-1,8 %). Les macéraux du groupe de l'inertinite arrivent à la valeur maximum (4,4 %) dans le charbon faiblement xylitique, fait qui contribue à la formation de ce lithotype dans les zones inondées périodiquement et où dominaient des conditions aérobie-anaérobies favorables à l'extension des incendies naturels, cause principale de la genèse des macéraux inertinitiques (Cope, Chaloner, 1980).

La teneur en macéraux huminitiques varie d'un lithotype à un autre (tab. 2), fait qui facilite l'identification exacte des lithotypes par des analyses microscopiques. Aussi dans le cadre du même lithotype, le contenu en macéraux huminitiques présente des limites de variation assez larges. Ainsi l'humotélinite participe en grande quantité à la formation de la xylite (75,6-92,9 %) et du charbon xylitique (43,3-68,7 %), pendant que l'humodétrinite prédomine dans le charbon détritique (43,5-75,9 %); le taux en humocollinite est très réduit dans tous les lithotypes (0,2-2,7 %).

La xylite, le lithotype représentant 12-15% dans les charbons situés entre le Jiu et le Danube, comporte dans toutes les couches plus de 75 % humotélinite, la teneur plus grande étant enregistrée dans les couches V, X et XII. L'humotélinite est représentée par le textinite qui correspond à la xylite jaune et brune et moins par l'ulminite de la composition de la xylite noire. Dans toutes les couches l'humotélinite englobe

dans sa structure cellulaire une substance rougeâtre, résin probablement, des substances minérales, corpohuminites et/ou phlobaphinites.

Tableau 2

Composition moyenne en macéraux huminitiques des lithotypes

Macéraux Lithotypes	Humotélinite %	Humodétrinite %	Humocollinite %
Xylite	87	8	0,13
Charbon xylitique	49	32	0,60
Charbon faiblement xylitique	22	54	0,30
Charbon détritique	8	59	0,20

L'humodétrinite est présent en des quantités très réduites dans la xylite (3 à 6 %, rarement 10 %). On constate un taux plus élevé en attrinite non gélifié et très impure dans les couches XIV et XV de l'exploitation de Miculesti. Dans l'humodétrinite on a identifié des restes de microspores (couche VII de l'exploitation de Gîrla, sclérotites du type *Sclerotites brandenianus* (couche VI de la carrière de Tismana) et beaucoup d'aiguilles de fusinite (couche X de la carrière de Peșteana Sud).

Dans la xylite l'humocollinite est presque inexistant et se présente sous forme de corpocollinites isolés. Le liptinite et l'inertinite sont aussi faiblement représentés.

Les composants minéraux représentés surtout par des grains de pyrite et oxydes de fer, apparaissent en des quantités réduites dans la xylite, sans dépasser 7%. On a observé des quantités très réduites de composants minéraux dans la xylite de la couche V de charbon et plus élevées dans les couches III et VIII.

Le charbon xylitique comporte les mêmes macéraux que la xylite. L'humotélinite présente les mêmes valeurs élevées (43-68%), étant représentée par textinite et ulminite dans des quantités presque égales; rarement on enregistre une prédominance du dernier, sous forme de texto-ulminite (couche VIII de la carrière de Roșia de Jiu). Ces macéraux présentent une structure cellulaire bien conservée, imprégnée soit avec résine, soit avec des substances minérales. L'eulminite correspond en partie à la xylite noire et apparaît sous forme de lentilles, ayant un degré avancé de gélification.

La plus grande teneur en humotélinite pour le charbon xylitique est enregistrée dans la couche III et la plus basse dans la couche XII.

Dans la composition du charbon xylitique l'humodétrinite est représentée surtout par attrinite et moins par densinite, variant entre 29 et 37 %.

L'humocollinite apparaît plus souvent dans le charbon xylitique dans la plupart des couches investiguées mais ne dépasse pas 2,7 %, étant représenté par corpohuminites existants dans les structures du textinite (couche V, carrière de Poiana).

Le groupe du liptinite est moins abondante dans le charbon xylitique que dans la xylite (3,7 %) et comporte des restes de spores minéralisés (couche VI de la carrière de Peșteana Nord et couche XI de la carrière de Lupoia) et cuticules, tout comme mésophyle en grande quantité (couches VI de la carrière de Poiana, VIII de la carrière de Lupoia et VIII de la carrière de Roșia de Jiu).

Le groupe de l'inertinite est présent par des lambeaux et bandes de fusinite (couche XII de la carrière de Pinoasa) tout comme par de nombreuses colonies de sclérotés (couche IV de la carrière de Husnicioara).

Les composants minéraux sont en quantités qui varient de 12 à 16 % dans l'humodétrinite, sous forme de nids de pyrite (couche VI de la carrière de Lupoia).

Le charbon faiblement xylitique comporte humotélinite (16 à 30%) et humodétrinite (46 à 63 %). L'humocollinite et le liptinite sont presque inexistantes dans la composition du charbon faiblement xylitique. En échange, l'inertinite est plus abondante (1 à 10 %) que dans les autres lithotypes, étant représenté surtout par fusinite.

Les substances minérales varient entre 16 et 20 % et sont présentes le long des fissures des macéraux comme minéraux argileux, ou comme oxydes de fer.

Le charbon détritique, le lithotype prédominant du charbon de l'Olténie comporte en grande partie humodétrinite et subordonné humotélinite.

L'humodétrinite représente plus de 53 % des couches investiguées, comporte attrinite et densinite en des quantités presque égales, étant fortement impurifié par les minéraux argileux. On y rencontre parfois des cuticules minces (couche VI de Poiana), fragments de spores minéralisés (couche VII de Peșteana Nord), lambeaux de fusinite (couche V de Poiana) et sclérotés pluricellulaires (couches X de Pinoasa).

L'humotélinite, représenté par ulminite, apparaît en des quantités plus réduites (inférieure à 10 %) par rapport aux autres lithotypes, étant parfois imprégné par résine (couche VII de la carrière de Tismana).

L'humocollinite comportant de rares corpohuminites apparaît seulement dans quelques couches de charbon (VI de Poiana, couche X de Roșiuța et couche XI de Lupoia).

Les substances minérales apparaissent dans de grandes quantités dans le charbon détritique, plus de 20 % et sont représentées en majorité par des minéraux argileux épigénétiques, pyrite épigénétique et singénétique et par carbonate de calcium épigénétique.

3. Genèse des lithotypes

L'analyse microscopique a évincé des particularités qualitatives et quantitatives significatives entre les principaux lithotypes des charbons investigués. On a remarqué aussi, dans le cadre des lithotypes, des limites larges de variabilité des contenus en des différents macéraux, surtout ceux huminitiques. Ces faits s'expliquent par la grande diversité des conditions de milieu des marécages carbogénérateurs, chaque lithotype résultant d'une certaine association de plantes dont la phytomasse s'accumule en des différentes conditions, en résultant plusieurs faciès charbonneux parcellaires à ceux définis par Teichmüller et Thomson (1958) pour les charbons miocène inférieurs de la vallée du Rhin.

Ayant en vue les reconstitutions des principales collectivités de plantes carbogénératrices (Ticleanu, 1992) et les résultats des études pétrographiques effectuées par Bițoiu, Ticleanu et Bițoiu (1988, 1989) on a individualisé plusieurs faciès charbonneux dont ont résulté 1 à 2 lithotypes (tab. 3).

4. Analyse physico-chimique des lithotypes

Les investigations dans le secteur situé entre le Jiu et le Danube ont confirmé les résultats antérieurs (Ticleanu et al., 1989) et ont relevé d'autres particularités concernant la composition élémentaire des lithotypes, les teneurs en acides humiques, cellulose et produits de sémicarbonisation.

4.1 Analyse technique

Pour l'analyse technique on a prélevé 135 échantillons des couches de charbon I à XV, la plupart provenant des lithotypes xylite et charbon détritique. Les résultats de ces analyses sont présentés dans le tableau 4.

4.1.1 Teneur en cendre. Les valeurs du tableau 4 indiquent que les contenus moyens en cendre ($\Lambda_{anh.}$) se développent peu à peu de la xylite (4,73 %) jusqu'au charbon détritique (28,69 %). Ces différences s'expliquent tant par la quantité réduite de la cendre dans le matériel originnaire de la xylite et du charbon xylitique, dont la formation ont contribué des forêts de *Glyptostrobus*, aussi bien que par la participation plus active des minéraux argileux à la formation du charbon faiblement xylitique et notamment à celui détritique.

On connaît que le bois a en général peu de cendre. Ainsi, selon Simionescu et al. (1964) la teneur en cendre des essences ligneuses de la flore actuelle de la Roumanie varie entre 0,11 et 0,83 % pour la plupart des conifères et angiospermes herbacées.

Les angiospermes herbacées comportent du cendre en des quantités plus grandes de 2,41 % à 6 %, c'est-à-dire jusqu'à 54 fois de plus que les arbres (Simionescu, Rozmarin, 1966).

Tableau 3
Faciès charbonneux et les lithotypes qui en résultent

Faciès charbonneux	Conditions du dépôt	Lithotype résulté
Forêt à Sequoia	aérobie	charbon détritique ± charbon xylitique
Marais de forêt à feuillus ± <i>Glyptostrobus</i>	aérobie-anaérobie	charbon détritique charbon faiblement xylitique
Marais de forêt à <i>Glyptostrobus</i>	anaérobie	xylite charbon xylitique
Marais à <i>Phragmites</i>	anaérobie	charbon détritique charbon argileux ± charbon détritique
Formation végétale flottante à <i>Phragmites</i> (île flottante)	aérobie-anaérobie	
Zones à végétation aquatique	anaérobie	charbon argileux argiles charbonneuses

Tableau 4

Valeurs moyennes des principales propriétés
physico-chimiques des lithotypes (rapportées à l'anhydre)

Lithotype propriété	Xylite	Charbon xylitique	Charbon faiblement xylitique	Charbon détritique
A %	4,73	15,3	17,7	29,69
V %	61,10	49,2	46,9	41,30
C _{fix} %	33,40	36,5	36,8	29,50
S _{comb} %	2,50	2,7	2,6	2,00
Q _{inf} %	6020	5159	4877	4202

Etant donné que dans la majorité des cas (54 %) les teneurs en cendre de la xylite ne dépassent pas 3 %, résulte que le bois de *Glyptostrobus* a été conservé et puis transformé dans un milieu isolé par les eaux de percolation, ce qui signifie un enfouissement rapide dans la tourbe et une période relativement courte de compactage de cette dernière.

De l'analyse de la répartition par couches des contenus en cendre (A_{anh}) de la xylite, résultent des valeurs plus élevées dans les couches III, IV et VIII de charbon. Ces valeurs ont été déterminées par l'instabilité du milieu carbogénérateur manifestée par: le développement lenticulaire de la couche III, la présence fréquente des intercalations argileuses dans la couche IV, accompagnée d'une accentuée variation de l'épaisseur de celle-ci et l'épaisseur et les caractéristiques morphologiques de la couche VIII.

Le charbon détritique provient surtout de deux faciès charbonneux: marécage de forêt à arbres feuillus et marécages à roseau (*Phragmites*, *Typha* etc.) Bien que la teneur en cendre des plantes herbacées soit assez élevée, jusqu'à 6 % (*Typha*) dans le matériel original, nous considérons que par enrichissement résiduel il ne peut pas dépasser 10 %. Etant donné que les charbons détritiques du secteur investigué comportent souvent 20 % cendre, on doit accepter que dans la plupart

des cas ce composant provient du matériel argileux fin, accumulé une fois avec la phytomasse carbogénatrice. A titre de comparaison nous mentionnons qu'aucun des cinq faciès charbonneux séparés par Teichmüller et Thomson (1958) pour les charbons miocène inférieurs de la vallée du Rhin ne comporte plus de 11,1 % cendre (A_{anh}).

Donc, une caractéristique du milieu du dépôt des charbons étudiés la constituait la présence, dans les eaux des marécages, notamment dans ceux des zones inondées périodiquement ou dans les zones recouvertes en permanence par des eaux, d'un riche matériel terrigène en suspension qui s'accumulait une fois avec la tourbe. Ce fait corrobore avec les résultats des études sédimentologiques effectuées par Jipa et Ungureanu (in Ticleanu et al., 1985) indique un milieu de dépôt palustre installé dans les plaines d'inondation étendues entre canaux fluviaux.

4.1.2 Matières volatiles (V). La teneur en matières volatiles est une caractéristique très importante pour la connaissance du degré de carbonification, l'établissement des domaines d'utilisation et de la classification des charbons.

Selon le tableau 4, la teneur en V_{anh} diminue de la xylite (61,1 %) vers le charbon détritique (41,3 %). Patteisky et Teichmüller (selon Francis, 1961) considèrent un $V^{mc} = 53$ % comme limite entre le lignite (soft lignite) et charbon brun mat. Les analyses effectuées sur le lithotype xylite indiquent que les teneurs entre 55 et 60 % V^{mc} sont les plus fréquentes. Donc, selon la teneur en V^{mc} les charbons de l'Olténie se situent dans le groupe du lignite (charbon brun ligneux = Weichbraunkohle = soft lignite).

4.1.3 Pouvoir calorifique. Une caractéristique physique très importante dans la détermination du domaine d'utilisation des charbons est le pouvoir calorifique. Les valeurs moyennes du

pouvoir calorifique des charbons étudiés présente des différences évidentes entre la xylite ($Q_{anh,inf}^{anh} = 6020$ Kcal/kg) et le charbon détritique ($Q_{anh,inf}^{anh} = 4204$ Kcal/kg), les autres lithotypes ayant des pouvoirs calorifiques d'autant plus grandes la teneur en xylite est plus élevée. Le pouvoir calorifique d'une couche de charbon est en rapport avec le contenu de celle-ci en xylite; donc, pour une utilisation plus judicieuse du point de vue énergétique il est nécessaire de valorifier au maximum l'énergie thermique de la xylite.

4.2 Analyse élémentaire

C'est une des plus importantes analyses pour la connaissance complexe des combustibles solides. Le tableau 5 présente les limites de variabilité des teneurs en: C, O, H et N pour la xylite, ainsi que la moyenne de quelques échantillons de lignite.

Tableau 5

Limites de variabilité pour les principaux éléments chimiques du lignite et la xylite de l'Olténie

Éléments Lithotypes	C %	H %	O %	N %
Xylite	58,1-67,1	5,4-6,3	23,2-33,7	0,17-1,76
Lignite	62,4-65,5	5,5-6,6	25,1-27,4	1,05-1,70

Les teneurs inférieures à 60 % C^{mc} enregistrées pour quelques échantillons de xylite et charbon xylitique sont caractéristiques aux bois et tourbes, indiquant la faible carbonification d'une partie des xylites de l'Olténie. Cependant les teneurs plus grandes en carbone (67,66 %) sont enregistrées aussi pour la xylite, mais plus rare en indiquent une grande variété des conditions d'accumulation et diagenèses des charbons investigués. Les teneurs très élevées en oxygène (jusqu'à 33,67 %) de quelques xylites prouvent aussi la faible carbonification de celles-ci.

Pour établir le degré de carbonification des charbons et des principaux lithotypes nous avons représenté, sur un diagramme, avec les rapports entre les rations atomiques O/C et H/C, quelques-uns des résultats de l'analyse élémentaire (fig. 1). Du diagramme résulte la grande variabilité de la xylite, de faiblement carbonifié (proche de la tourbe) jusqu'à une carbonification plus avancée, proche de la limite avec le charbon brun. Dans un diagramme similaire (fig. 2) nous avons projeté les valeurs pour des différents charbons de la Roumanie. En comparaison avec les valeurs moyennes fournies par deux échantillons de lignite de l'Olténie on observe la situation de ces derniers dans le domaine du lignite, vers la limite avec le charbon brun.

L'analyse élémentaire des lithotypes qui forment les charbons de l'Olténie justifie l'encadrement de ceux-ci dans la catégorie des charbons bruns ligneux "Weichbraunkohle" selon la classification allemande qui corresponde au type "Soft Lignite" (selon Patteisky et

Teichmüller, in Francis, 1961) et à celui "unconsolidated lignitous coals" conformément à la classification américaine. La teneur relativement réduite en C^{mc} explique en partie les propriétés thermiques du charbon détritique et du lignite de l'Olténie en général.

4.3 Teneur en acides humiques (AH) et cellulose

On a effectué des analyses pour les acides humiques et pour la cellulose en vue de déterminer le degré de carbonification et pour reconstituer le milieu où a eu lieu l'accumulation de la phytomasse carbogénératrice.

On a déterminé en général les teneurs en acides humiques et cellulose pour la xylite et moins pour le charbon détritique. La teneur en AH de la xylite varie de 2,13 % à 41,45 %, mais prédominent les valeurs inférieures à 15 % (fig. 3); en échange pour les autres lithotypes ces valeurs se situent à plus de 12 %, notamment à plus de 20 % indiquant une transformation plus intense de ceux-ci par rapport à une grande partie des échantillons de xylite.

Les limites larges de variabilité des teneurs en AH de la xylite sont dues particulièrement à la diversité des conditions dans lesquelles a eu lieu l'accumulation et puis à la carbonification du matériel végétal.

En ce qui concerne la teneur en cellulose, rapportée à la masse combustible, celle-ci varie entre 6,8 % et 31,06 % pour la xylite et entre 9,68 % et 30,44 % pour les autres lithotypes.

Comparativement aux autres lithotypes, la teneur élevée en cellulose de la xylite indique aussi la faible transformation de celle-ci. Par contre, dans le cas du charbon xylitique et détritique, la cellulose s'est transformée rapidement en acides humiques. La présence de la cellulose en des quantités relativement élevées (10,62-11,78 %) dans les charbons xylitiques et dans ceux détritiques (12,59 à 30,44 %) indique une accumulation de la phytomasse en des conditions d'isolation rapide de celle-ci contre l'action des facteurs biodégradeurs. La présence de la cellulose tant dans la xylite que dans les autres lithotypes aussi, atteste son rôle, près de la lignine, dans la formation des charbons.

La grande variabilité des teneurs en acides humiques et cellulose (fig. 3) indique des différences notables entre les conditions carbogénératrices d'une zone à une autre.

Les teneurs élevées en acides humiques, des substances colloïdales ayant des propriétés hygroscopiques remarquables dans les principaux lithotypes des charbons de l'Olténie expliquent d'une manière satisfaisant le grand contenu en eau de ceux-ci et leurs grandes propriétés hygroscopiques même après un dessèchement partiel.

4.4 Semicarbonisation des lithotypes

Les premiers essais de semicarbonisation des charbons pliocènes de Roumanie a été intenté par Blum

Tableau 6
Limites de variabilité pour les produits de semicarbonisation
des principaux lithotypes

Produit Lithotype	Goudron %	semicoke %	Gaz Nm ³ /t	Eau de pyro- généation 1/T
Xylite	6,03-28,51	36,39-51,90	130,00-234,96	95,37-233,57
Charbon xylitique	3,22-9,11	45,60-59,48	140,20-240,86	70,01-153,90
Charbon faiblement xylitique	3,76-7,09	48,02-53,80	190,70-266,68	92,80-120,06
Charbon détritique	2,70-7,33	48,40-65,78	136,18-257,20	35,92-68,78

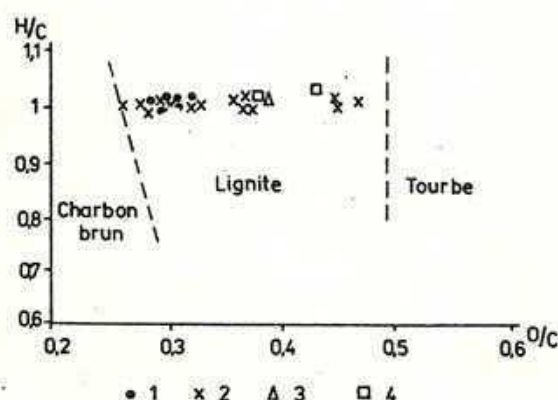


Fig. 1 - Représentation sur le diagramme des rapports O/C et H/C de quelques échantillons de lignite de l'Olténie par rapport aux échantillons des lithotypes.
1, lignite; 2, xylite; 3, charbon xylitique; 4, charbon détritique.

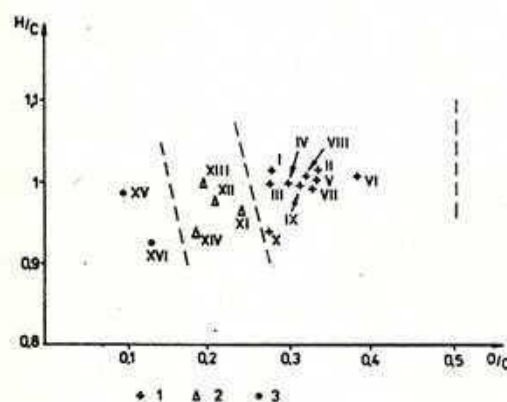


Fig. 2 - Représentation sur le diagramme des rapports O/C et H/C de quelques échantillons de lignite de l'Olténie, par rapport à d'autres types de charbons de la Roumanie.
1, lignite: I-Rovinari, II-Albeni, III-Ceptura, IV-Filipești de Pădure, V-Schitu Golești, VI-Virghiș, VII-Șotînga, VIII-Căpeni, IX-Bahna, X-Negrești; 2, charbon brun: XI-Tebea-Brad, XII-Mehadia, XIII-Comănești, XIV-Ticu; 3, houille: XV-Lupeni et XVI-Uricani.

(1926) sur quelques lignites du Pontien de Jidava-Pescăreasa, ainsi que sur les lignites du Romanien de Pralea. Ultérieurement cet essai a été repris par Dănilă et Blum (1939).

Quant à la semicarbonisation de la xylite, on mentionne dans le Lexique (1971) que le contenu élevé en cellulose et/ou résines font que le textinite ait un pourcentage élevé en goudron, 15 à 20 % environ, et beaucoup du gaz, rapporté à l'échantillon séché.

Nos investigations concernant la semicarbonisation des lithotypes des lignites du secteur entre le Jiu et le Danube ont comme résultats les valeurs du tableau 6.

L'analyse des limites de variabilité pour les contenus obtenus par la semicarbonisation des principaux lithotypes indique des valeurs élevées pour le goudron de la xylite, jusqu'à 28,5 %, plus que les données de la littérature de spécialité.

5. Conclusions

Selon leur genèse dans des faciès charbonneux différents, les principaux lithotypes qui forment les charbons pliocènes du secteur situé entre le Jiu et le Danube, diffèrent entre eux par : la composition pétrographique, la teneur en cendre et matières volatiles, le pouvoir calorifique, les propriétés mécaniques et contenus en produits de semicarbonisation.

La composition élémentaire et la teneur en matières volatiles situent les charbons de l'Olténie dans le groupe des lignites (=charbon brun ligneux). La teneur élevée indique un milieu de dépôt palustre installé dans des plaines d'inondation délimitées par des

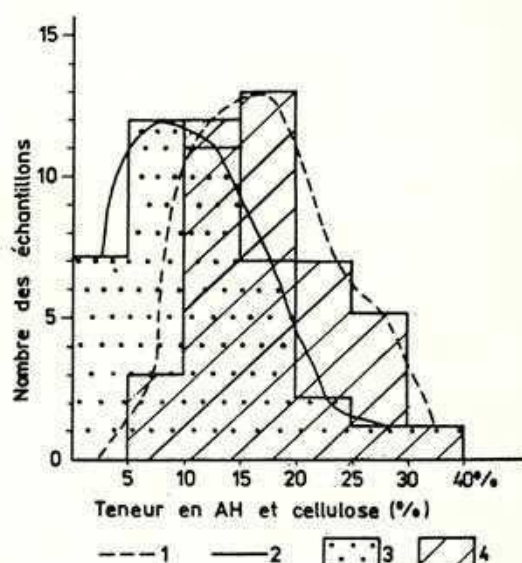


Fig. 3 - Histogrammes et courbes cumulatives avec la distribution par catégories des contenus en acides humiques et cellulose de quelques échantillons de xylite. 1, courbe cumulative pour la cellulose; 2, courbe cumulative pour les acides humiques; 3, histogramme pour la cellulose; 4, histogramme pour les acides humiques.

canaux fluviaux. La grande variabilité des contenus en acides humiques et cellulose indique une riche diversité des conditions de dépôt, tout comme des différents degrés de carbonification, surtout pour la xylite.

La connaissance en détail des causes qui ont déterminé la différenciation des lithotypes permet la détermination des conditions génétiques des charbons et de la manière de distribution dans l'espace des couches et complexes charbonneux et contribue en même temps à la valorisation supérieure des charbons.

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