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Editorial Office:
Geological Institute of Romania
Str. Caransebeş Nr. 1
RO - 79 678 Bucureşti - 32
Tel. (+40) 1 665 66 25, 665 75 30
Fax (+40) 1 312 84 44
e-mail GEOL@IGR.RO

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THE REGIONALLY METAMORPHOSED Mn-Fe DEPOSIT AT RĂZOARE, PRELUCA MTS, ROMANIA

Gheorghe UDUBAȘA, Paulina HÂRTOPANU, Gheorghe ILINCA

Geological Institute of Romania Str. Caransebeș, nr. 1, 79678 București 32.

Ștefan VALDMAN

S.C. "CUART" S.A., Str. Victoriei, nr. 146, 4800 Baia Mare.



Key words: Manganese deposit. Metamorphosed (regionally). Manganese minerals (silicates, carbonates, oxides). Geochemistry. Black quartzites. Layered protolith.

Abstract: The manganese-iron deposit at Răzoare, Preluca Mts, Romania, is a stratiform concentration of manganese-iron and iron minerals showing evidences of regional metamorphism in the upper amphibolite facies. The ores consist of silicates, carbonates and oxydes, forming lenses up to 60 m thick, which are invariably enveloped by nearly continuous bands of blackish quartzites reaching a maximum thickness of about 2 m. The deposit is enclosed in a sequence of kyanite-bearing micaschists, paragneisses, pegmatites, carbonate rocks and amphibolites interpreted to be of Precambrian age. At least three metamorphic events have been recognized in the host metamorphic rocks and in the ores as well. The ores contain about 60 mineral species, of which nearly half represent primary minerals. The typical minerals of the Răzoare deposit are: manganoan fayalite, dannemorite, rhodochrosite, pyroxmangite, magnetite and jacobsite. The manganese humite minerals (sonolite, alleghanyite, leucophenicitite and jerrygibbsite), tephroite, carbonate-fluorapatite and a scarcely developed orthopyroxene, are here for the first time described. Three mineral assemblages have been recognized to display different positions within the ore-bearing sequence. The bottom is defined by the rhodochrosite-rich assemblage, containing also jacobsite, manganoan fayalite and apatite. It is followed by an assemblage composed of tephroite and manganese humite minerals, with which jacobsite associates. The upper part of the ore sequence is clearly amphibole dominated, typically containing dannemorite, spessartine, magnetite, pyrrhotite, with a definite enrichment in quartz towards the hanging wall. The Fe:Mn ratio seems to characterize both the lower parts ($Mn > Fe$) and the upper part ($Mn < Fe$) of the ore-bearing sequence. The available, but still incomplete data, suggest a polyphase metamorphism of the ores and support the idea of the pre-existence of a slightly "layered" primary protolith of sedimentary origin.

Introduction

The regionally metamorphosed Mn-Fe deposit at Răzoare, Romania, is located in the Preluca Mts, an "island" of Precambrian metamorphic rocks in a Tertiary sedimentary environment (Fig. 1 A). The ores contain 18–20% Mn, 17–20% Fe, 8–13 SiO₂ and 0.5% P₂O₅, showing a nearly constant Mn:Fe ratio. The mining activity in the area goes back to 1776 (Kossmat and von John, 1905) and it has continued with some interruptions till now. Near an open pit in the upper part of the deposit, drillings have shown the continuity of the ore-bearing rock sequence over a total length of 2–3 Km, partly located under the sedimentary cover at depths reaching 300–400 m.

The Răzoare deposit (Macskameso in the older papers) was originally described by Kossmat and von John (1905), who reported the general geology and the relationships of the ores minerals with the host rocks, concluding that the deposit was undoubtedly regionally metamorphosed. Kossmat and von John also recognized the knebelite and dannemorite as the main minerals occurring together with variable amounts of magnetite (partly manganoan), spessartine, apatite and pyrite. Subsequent studies have shown the presence of pyroxmangite, rhodonite, pyrite and of many secondary minerals. Giuscă (1962) reported the presence of the manganoan hisingerite. Kalmár (1972) made a general approach concerning the "crystalline islands" of North Romania including an overview on the associated mineral deposits. In an unpublished paper, Götz *et al.* (1977) gave important data on mineralogy and geochemistry of the ores, mainly from the point of view of ore beneficiation. Kalmár and Lelkes-Felvári (1991) summarized old and new data about the Preluca Mts and gave also a list of minerals so far identified in the Răzoare deposit. A hydrothermal submarine origin of the ore-bearing solutions is postulated, but with no specific arguments.

Three distinct assemblage have been recognized to exist at Răzoare, all having a constant position within the ore lenses. At the bottom there is a rhodochrosite-rich assemblage, followed by an assemblage consisting mainly of tephroite and manganese humite minerals (MHM). At the top of the sequence there is a dannemorite-dominated assemblage with a definite enrichment in quartz towards the hanging wall. During our investigations no rhodonite was found here. Other Ca-richer pyroxenoids (bustamite, wollastonite), which were previously described at Răzoare, seem also to be lacking. However, some other minerals have been identified, i.e. tephroite, MHM, carbonate-fluorapatite, orthopyroxene, pyrophanite, suggesting a very complex mineralogical composition and metamorphic evolution of the ore. This is a preliminary report on the Răzoare Mn-Fe deposit which is the biggest of this kind in Romania, showing evidences of medium (-high) grade metamorphism.

Geological setting

The crystalline "island" of the Preluca Mts is made up of medium grade metamorphics belonging to the Precambrian Baia de Arieș (or Rebra) Group (Balintoni, in Rusu *et al.*, 1983). The Mn-Fe-bearing rock sequence develops in the lower formation of the group and is located in the south-eastern part of the crystalline "island" (Fig. 1 B). The lower Răzoare Formation includes widely developed micaschists and paragneisses with relatively thin beds of carbonate rocks and amphibolites. A thick, quite monotonous dolomite-dominated carbonate rock sequence of the Măgureni Formation overlies the ore-bearing metamorphics. Interesting vein-like massive sepiolite aggregates are sometimes encountered within this formation (Pop, Angelescu, 1981). The following Preluca Nouă Formation is petrographically more complex and consists of paragneisses and micaschists (matrix rocks) as well as of bands of variable thickness represented by white gneisses, amphibolites, carbonate

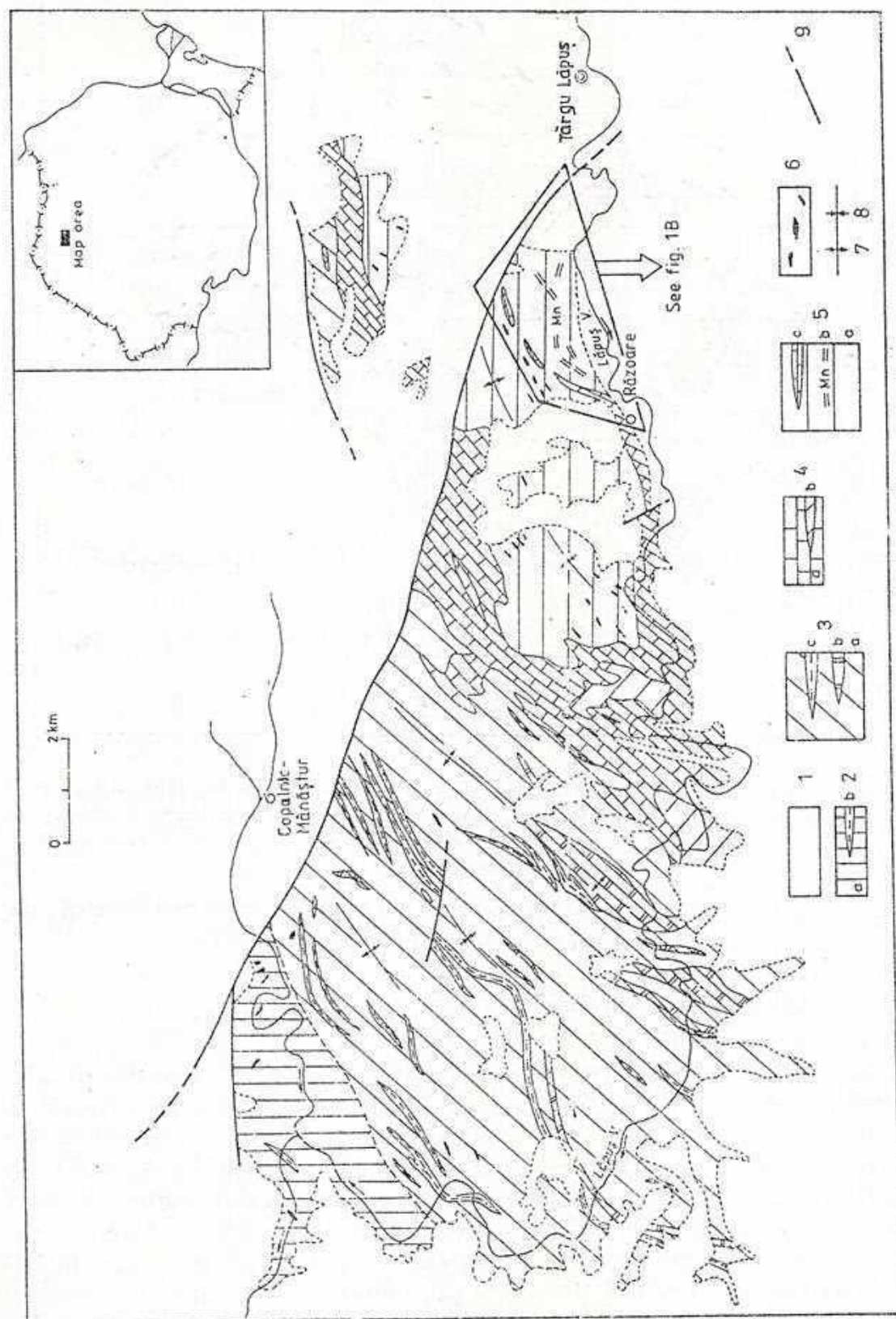


Fig. 1 A - Geological map of the Preluca Massif (acc. to Kossmat and v. John, 1905, Rusu et al., 1983 and Kalnár, 1972, simplified). 1, Tertiary and Quaternary sedimentary cover; 2, Valea Cavnicului Formation (a, gneisses and micaschists; b, marbles; c, amphibolites); 3, Preluca Nouă Formation (a, gneisses and micaschists; b, marbles; c, amphibolites); 4, Măgureni Formation (a, marbles; b, gneisses and micaschists; c, amphibolites); 5, Răzoare Formation (a, gneisses and micaschists; b, marbles; c, amphibolites); 6, Pegmatites; 7, Antiforms; 8, Synforms; 9, Faults; 10, Open pit; 11, Old mining workings; 12, Shafts.

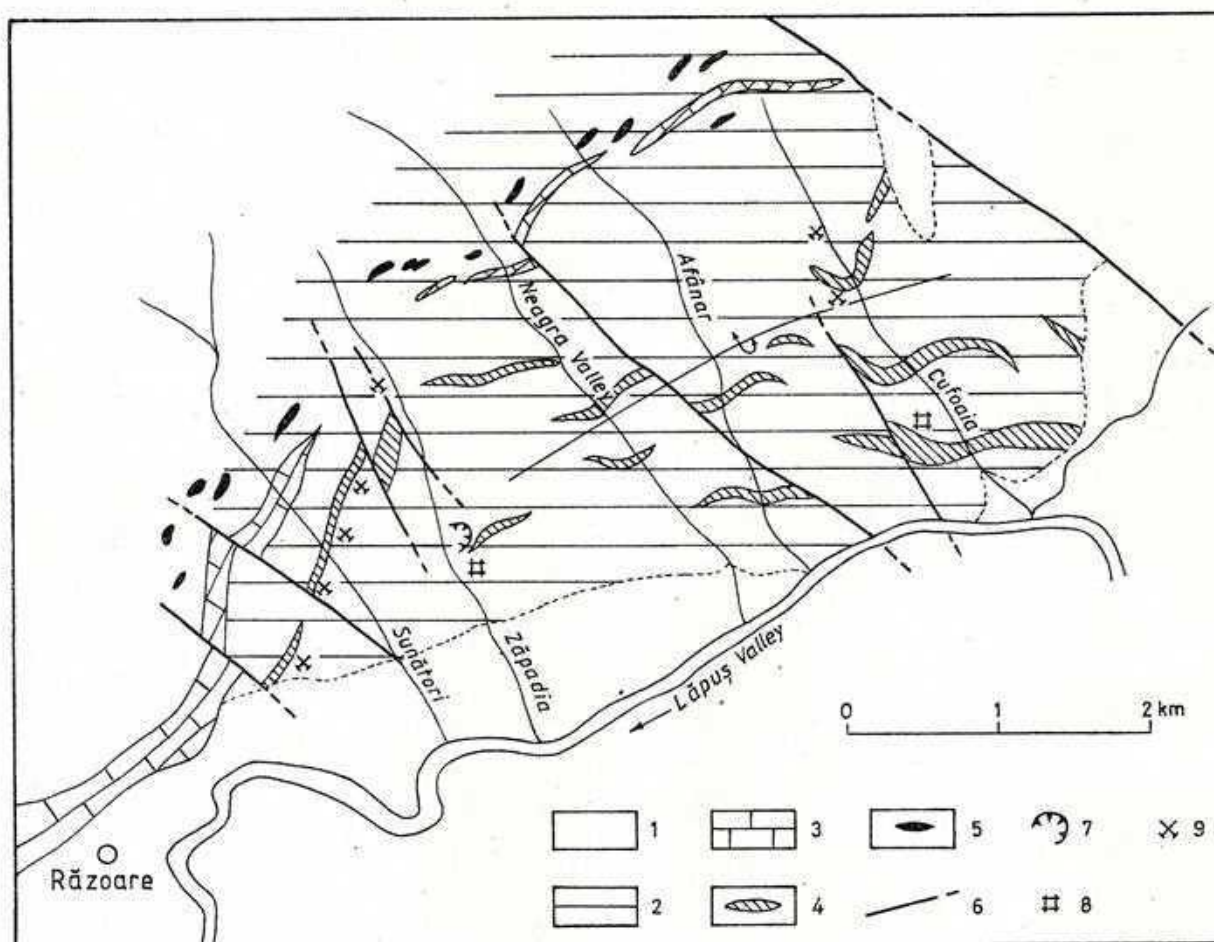


Fig. 1 B – Geological map of the Răzoare area (mainly acc. to Kossmat and von John, 1905, with some authors' data). 1, Sedimentary cover; 2-5, Răzoare Formation (2, gneisses and micaschists; 3, marbles; 4, manganiferous sequence (black quartzites and Fe-Mn ores; 5, pegmatites); 6, faults; 7, open pit; 8, shafts; 9, old mining workings.

rocks, augen-gneisses, etc. The uppermost rock sequence (Valea Capnicului Formation) includes quartz-rich rocks, mostly paragneisses and covers a quite limited area. Abundant metamorphic pegmatites develop within the Preluca Nouă Formation; their supergene decomposition locally results in kaolinite bodies of industrial interest.

The general trend of the metamorphic rocks is east-west with a gentle southward dip. Some faults of minor importance are known in the mining field. The northern margin of the Preluca Mts is marked by an important E-W fault.

The sedimentary cover begins with Eocene continental deposits. It has been presumed that the supergene alteration of the Mn-Fe

area has already commenced during the Eocene time (Kalmar, 1972).

Host rocks

The rock sequence directly hosting the Mn-Fe ore includes kyanite-bearing micaschists, paragneisses and quartzites. Numerous pegmatite bodies are known North of the ore field. They contain green apatite and black tourmaline crystals reaching 10 cm in size, in a medium-grained matrix of quartz and feldspars. Stanciu (1955) has also identified here beryl, danburite and baddeleyite (?). The micaschists show sometimes a local development of small pegmatite or pegmatite-like

Table 1
Chemical analyses of foot-wall (FW) and hanging-wall (HW) quartzites
from the Răzoare ore deposit

Sample no.	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	K ₂ O
1B(FW)	59.59	0.17	1.49	1.73	1.78	2.19	1.42	14.71	0.05
7A(HW)	86.99	0.30	5.73	0.76	1.29	0.14	0.41	0.53	1.49
18*	84.44	0.39	5.98	0.62	1.34	0.16	1.05	1.61	0.49
20(HW)	87.06	0.23	5.53	0.68	1.21	0.03	0.57	0.66	1.62
120(HW)	83.71	0.30	7.00	0.79	1.43	0.09	1.10	1.39	1.48
157(FW)	82.85	0.39	7.98	0.56	1.93	0.04	0.98	0.24	2.63
168B(HW)	83.13	0.06	1.25	0.61	1.40	0.52	1.36	4.49	0.08
188(FW)	86.35	0.14	5.63	0.30	1.72	0.11	1.02	0.81	1.31
195(HW)	85.62	0.24	1.74	1.08	0.78	1.26	1.65	2.38	0.35

Sample no.	Na ₂ O	P ₂ O ₅	H ₂ O ⁺	CO ₂	S	Fe(S)	Fe ₂ O ₃	Sum
1B(FW)	-	0.16	1.02	9.41	3.09	2.69	7.56	99.50
7A(HW)	0.13	0.07	0.85	0.65	0.19	-	2.19	99.53
18*	1.17	0.21	0.16	1.14	0.33	-	2.11	99.54
20(HW)	0.38	0.12	0.23	0.79	0.39	-	2.02	99.50
120(HW)	0.52	0.14	0.66	0.86	0.30	-	2.38	99.77
157(FW)	0.02	0.12	0.68	0.73	0.35	-	2.70	99.50
168B(HW)	-	1.47	0.73	4.23	0.21	-	2.16	99.54
188(FW)	0.36	0.04	1.33	0.17	0.27	-	2.21	99.56
195(HW)	-	1.01	0.30	2.72	0.38	-	1.95	99.51

* sample from the middle part of an ore lens

Analysts: D. Necşulescu, I. Năstase (wet chemical analyses)
(Prospecţiuni S.A., Bucureşti).

bodies. Balintoni (in Rusu et al., 1983) has recognized there metamorphic events in the Preluca crystalline schists, i.e. (1) an initial Barrovian type metamorphism of almandine amphibolite facies-staurolite-kyanite zones, (2) a second event (presumably Caledonian) of almandine-amphibolite facies - sillimanite zone and (3) a greenschists facies metamorphism - chlorite zone (presumably Hercynian). Due to the strong lithology differences between the host metapelites and the Mn-Fe ore sequence, it is difficult to correlate directly the metamorphic events in the two environments. However, the Mn-Fe ores exhibit also a polymetamorphic character as it will be further shown.

The ore beds or lenses invariably exhibit

rather continuously developed envelopes of black quartzites of varying compositions (Fig. 2). They consist of biotite- and garnet-bearing quartz-carbonate schists, magnetite-bearing microblastic quartzites, plagioclase- and biotite-bearing quartzites; amphibole-bearing quartzites were also recognized. The mangan contents of such rocks is generally low (Tab. 1) and it is presumed that they acted as geochemical barriers. Two groups of minor elements show significant variation, i.e. Cu, Zn, Ni and Mo with increasing contents and Ba, Sc and Zr with decreasing ones as compared to each other and with the increasing contents of some major elements (Fe₂O₃, P₂O₅ and MnO (Tab. 2).

Table 2
Quantitative spectrographic data on quartzite sample from Răzoare

Sample no.	Pb	Cu	Zn	Ga	Ni	Co	Cr	V	Sc
1B	10	95	310	2	115	48	16	44	5
7A	2	8.5	30	5	24	12	30	41	9
18	17	44	30	5.5	65	15	41	57	9
20	7	4.5	30	5	16	9.5	24	32	8.5
120	9.5	4	30	5	18	8	30	28	8.5
157	2	8	30	6.5	22	14	38	48	10
168 B	2	4.5	60	2	90	13	80	130	10
188	5	13	30	5	17	9	23	31	7.5
195	2	130	155	2	230	48	60	75	9

Sample no.	Nb	Zr	Y	Yb	Mo	La	Sr	Ba
1B	18	230	41	2.8	50	55	310	10
7A	26	600	32	2.9	8.5	55	150	500
18	36	1000	41	3.6	9	30	67	600
20	25	220	24	2.1	7.5	44	15	360
120	25	320	32	3.4	7	65	95	370
157	25	480	31	3	6	33	95	480
168B	25	65	50	4.2	12	44	28	330
188	25	190	25	1.8	6.5	44	12	500
195	23	100	53	3.8	17	55	10	34

Analyst: Carmen Fărăianu (Inst. Geology and Geophysics, Bucharest)

Ore mineralogy

The mineralogical composition of the Răzoare ores is quite complex, including about 60 mineral species (Tab. 3). The main manganese minerals are: olivines (manganoan fayalite and tephroite), dannemorite, manganese humite minerals (MHM), pyroxmangite, rhodochrosite, jacobsonite and spessartine. Special mention deserve the MHM, the calderite-rich garnet, the carbonate-fluorapatite and the tephroite, minerals which have not been previously reported from this locality. The scarcely developed orthopyroxene (presumably a manganoan ferrosilite) has to be especially emphasized as it suggests a higher grade of the main metamorphic event.

The minerals are medium-grained but locally pegmatoid-like aggregates especially of

pyroxmangite and manganoan fayalite grains up to 5–6 cm were found. Generally the ore is massive, sometimes with a well-expressed banding which is presumed to be mainly of metamorphic origin. It occurs at the mesoscopic scale and under the microscope as well (Plate, Figs. 1–5).

In the oxydation zone there appear bementite, neotokite, manganoan hisingerite as well as manganese ochres (now under study). However such ochres host some small geodes which are lined with needle-like pyrolusite crystals forming also rosetes, limpid microcrystals of quartz of common habit and small barite crystals. Such geodes were also reported by Kossmat and von John (1905).

The primary minerals show preferential association that generally could be interpreted as a result of primary deposition and of differ-

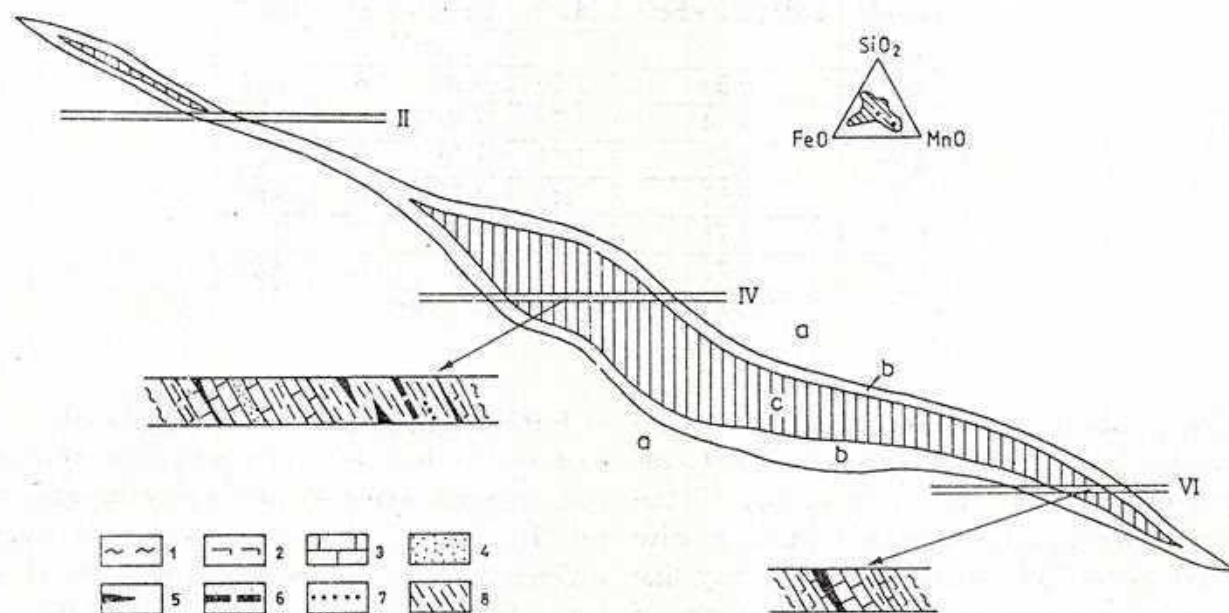


Fig. 2. - Cross section through an ore lens (Augustin lens) with details of ore sequence at two different mine levels. a, gneisses and micaschists; b, quartzites; c, Mn ores. 1, gneisses and micaschists; 2, black quartzites; 3, carbonate (rhodochrosite) - rich part; 4, tephroite and manganese humite minerals with disseminated jacobite; 5, massive manganiferous fayalite; 6, magnetite beds or lenses; 7, pyrrhotite beds or disseminations. 8, dannemorite-rich rocks; The ternary compositional diagram ($\text{SiO}_2\text{:FeO:MnO}$) (taken from Ianovici et al., 1968) refers to the Răzoare ore as a whole.

ent stages of metamorphic evolution. In a carbonate dominated fine-grained matrix there are beds or lenses of different compositions in which the leading minerals are the Mn-Fe-silicates. Jacobite and magnetite may occur everywhere in the stratigraphic sequence, but the preference of jacobite for the MHM is obvious, whereas the magnetite associates mainly with the dannemorite-rich aggregates; the pyrrhotite is also frequently centered on the amphibole-rich parts.

The passing from the lower carbonate-rich part to the upper amphibole dominated part is a common feature of the ore beds or lenses. Thinning of the carbonate beds as well as the merging of all the beds into a quasiuniform

mass of varying composition may be observed at the ends of lenses.

Minerals assemblages of the ore

The carbonate dominated assemblage. The carbonate rich assemblage forms the lowest part of the Mn-bearing sequence. It has rather sharp boundary to the host quartzites and/or paragneisses and micaschists (Figs. 2, 4). The fine-grained carbonates consist mainly of rhodochrosite and constitute the matrix of the olivine rich patches or alternate with fayalite dominated assemblages. Sometimes, the bottom of a lens begins with a pure rhodochrosite sequence (usually, no more than 1 m thick) in

Table 3
Chemical features of the Răzoare dannemorites

Sample no.	Fe ²⁺ /Mg+Fe ²⁺	Mn ²⁺	Fe ²⁺	Mg ²⁺	Ca ²⁺
		at %			
130	0.50	1.59	3.15	1.68	0.07
56	0.53	1.72	3.60	2.26	0.02
32A	0.61	1.75	3.00	1.86	0.08
47	0.65	1.48	3.15	1.68	0.06
128*	0.71	3.04	2.62	1.11	0.22
198*	0.77	3.06	2.34	0.67	0.33

* from pegmatoid-like-aggregates

which jacobsonite aggregates gradually develop as well as fayalite dominated lenses. The banding is present everywhere (Plate, Fig. 1); the most frequent are the bands of fayalite, apatite or carbonate-fluorapatite and more rarely, fine bands of dannemorite+quartz. Analyses of fine-grained carbonate matrix indicate compositions near the rhodochrosite, i.e. Mn²⁺ 0.76, Ca²⁺ 0.10, Fe²⁺ 0.09 and Mg²⁺ 0.05 at %.

The dannemorite dominated assemblage. Generally of secondary nature, the dannemorite forms the upper part of the Mn-bearing sequence and by adding quartz, it passes to the host quartzites or paragneisses ("hanging wall"). The dannemorite represents frequently 50 percent of the whole mineral aggregate. Here the banding is present, too. The Mn-amphibole alternates with bands of varying thickness of magnetite, magnetite+apatite+carbonate, spessartine and fayalite+apatite (Plate, Figs. 2 and 3). Fine bands and/or veinlets of pyrrhotite have here their typical development. At least three dannemorite generations have been depicted. Dannemorite I is typically twinned and forms at the expense of the manganoan fayalite (fayalite I). Pegmatoid aggregates consisting of dannemorite II, pyroxmangite and spessartine may locally disturb the obvious banding of dannemorite I. Statically grown dannemorite III exhibits no banding and sometimes it is partly bleached and/

or further transformed in an asbestos-like amphibole. Such features are related to the last metamorphic event(s) of retrograde character. The Răzoare dannemorites show chemical differences largely corresponding to the three generations of the mineral. The dannemorite II belonging to the pegmatoid-like aggregates shows the highest Mn content and also the highest Fe²⁺/Mg+Fe²⁺ ratios (Tab. 3), which places it close to the dannemorite end-member of the dannemorite-tirodite series. It contains also the highest Ca-amount. The fine-grained dannemorite I (samples 56 and 130) has the lowest Fe²⁺/Mg+Fe²⁺ ratios and also low Ca contents (Tab. 3).

The fayalite dominated assemblages. The manganoan fayalite occurs especially as beds and lenses within the lower, carbonate dominated assemblage and within the upper parts of the ore sequence. Usually, the banding of the fayalite-bearing beds is well expressed due to layers of fayalite in alternation with bands of carbonate-apatite-magnetite-dannemorite-carbonate-fluorapatite, all together or as simple associations of magnetite-carbonate, dannemorite-apatite, etc. (Plate, Figs. 4 and 5). Although scarcely developed, the paragenesis manganoan fayalite-orthopyroxene-garnet (a calderite-rich spessartine) is of special importance; seemingly, it represents the oldest and the highest grade assemblage of the Răzoare ores. Unfortunately, the orthopyro-

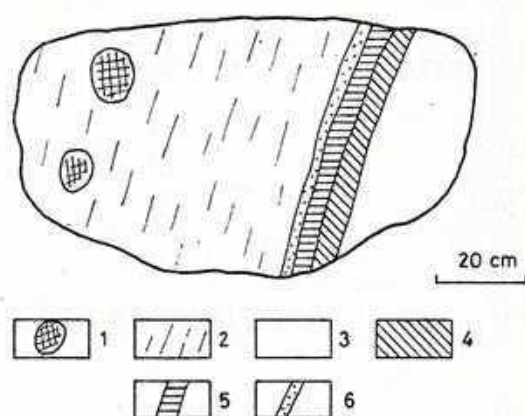


Fig. 3. – Ball-like relics of manganoan fayalite (1) in a slightly oriented aggregate of tephroite + MHM (2). 3, MHM and jacobsite aggregate, slightly brecciated and altered (calcite, bementite, chlorite, etc.). 4, MHM + jacobsite more strongly deformed and altered; 5, Late deposition of quartz, calcite and chlorite; 6, Calcite and chalcedony.

xene grains are very small and have been only rarely encountered.

Within the banded MHM-carbonate, lens-shaped aggregates of pegmatoid appearance with fayalite prisms up to 8 cm in length and ball-shaped aggregates occur (Fig. 3). This fayalite II represents a second metamorphic peak of somewhat lower grade consisting of fayalite II, pyroxmangite, spessartine and dannemorite II. The fayalite shows gradual transformation to dannemorite. The first stage is marked by fine intergrowths of dannemorite and magnetite, forming fine veinlets within the fayalite grains. Further evolution of the replacement leads to a quasitotal conversion of fayalite in dannemorite; the former is preserved as relics sharing the same optical orientation within the dannemorite aggregates.

Wet chemical analyses carried out on four fayalite samples show the dominance of iron over manganese; thus justifying the name of

manganoan fayalite; the same is shown by the end-members percentage (Tab. 4) and by cell parameters (Hârtopan et al., 1992). The larger-grained olivines of pegmatoid appearance are richer in fayalite as compared with the olivines of normal grain size. All the analysed fayalites have a nearly constant percentage of the tephroite component. The Ca content is generally low (0.01–0.09 at.-%). If the conclusions of Simkin and Smith (1970) regarding the Ca behaviour in magmatic olivines are to be accepted for the metamorphic ones as well, then the low Ca-contents would suggest a deep-seated origin of the Răzoare olivines.

The garnets assemblages. Although relatively frequent, the garnets rarely form significant amounts within the Răzoare ores. However, two different garnet types have been depicted i.e. (1) a calderite-rich garnet associated with the manganoan fayalite I forming an early, high-grade paragenesis of the Răzoare ores and (2) a spessartine garnet, commonly intergrown with dannemorite and forming alternating bands with magnetite and/or quartz. The composition of the analysed garnet samples is given in the Table 5.

The assemblage tephroite+manganese humite minerals (MHM). Beside the manganoan fayalite, these minerals are the most typical ones of the Răzoare ores. However, none of them have been previously reported from this locality. Both the tephroite and the MHM have a wide distribution forming the middle part of the ore-bearing sequence. As a rule, such assemblages contain jacobsite, thus having a typical appearance of a pink-brown-black medium-grained rock and resembling the pyroxmangite-bearing rocks. The tephroite is intimately associated with the MHM, rhodochrosite, carbonate-fluorapatite and jacobsite. The most conspicuous feature of the Răzoare MHM is the constant presence of boron which seems to play the role of stabilizing element. Further details are given in the paper of Hârtopan et al. (1993).

The associated jacobsite generally tends

Table 4
Chemical features of the Răzoare fayalite

Sample no.	Fe ²⁺	Mn ²⁺	Mg ²⁺	End-members	percentage	mole %
	at%			fay	teph	fors
45	1.05	0.66	0.66	55.14	34.66	10.20
63	0.93	0.71	0.71	50.66	38.70	10.64
88*	1.08	0.64	0.64	59.64	35.58	4.88
101**	1.09	0.70	0.70	58.48	37.39	4.13

* pegmatoid aggregates forming lenses

** ball-shaped aggregates of large grains within the MHM

Table 5
Chemical features of the Răzoare garnets (mole %)

Sample no	pyr	alm	spess	andr	gross	cald
32A*	3.62	27.43	39.17	9.06	-	20.72
60*	1.38	13.87	64.63	7.05	-	13.08
29**	3.27	11.68	63.80	17.83	3.42	-
194**	2.54	18.86	57.17	7.63	13.80	-

* associated with manganoan fayalite

** associated with dannemorite

to cement the MHM. Retrograde changes of tephroite result in bementite, pennantite, holdawayite and neotokite, but they do not seem to affect the MHM.

The pyroxmangite dominated assemblages. Pyroxmangite is closely associated with dannemorite, sometimes in mixed aggregates gradually passing to the host garnet-bearing quartzites. Beside dannemorite, the associated minerals include small amounts of rhodochrosite, apatite, garnet, carbonate-fluorapatite and quartz. The pyroxmangite is largely replaced by dannemorite and apparently forms, in its turn, at the expense of spessartine. The banding is mainly due to alternating bands of varying compositions and especially to the presence of apatite-rich bands. Rarely, the pyroxmangite alters to chlorite.

At least three generations of pyroxmangite have been observed to exhibit either different

grain size and colour or specific relationships with other minerals. Pyroxmangite crystals up to 5–6 cm in size form sometimes small bodies of pegmatoid appearance, highly probably of the same age as the apatite and tourmaline-bearing pegmatites in the host metapelites. Worth mentioning is the lack of rhodonite, all the samples initially presumed to represent rhodonite or pyroxmangite proved to be pyroxmangites with relatively high Fe content. The iron content is relatively high as shown by the wet chemical analyses (Tab. 6).

Emission spectrographic analyses of the Răzoare pyroxmangites (13 samples) showed significant zinc contents with a variation range of 150–400 ppm. The pyroxmangite belonging to the pegmatoid lenses contains also higher Be contents (up to 7 ppm) as compared to the normal, fine-grained pyroxmangite (2–4 ppm).

The opaque minerals. Jacobsite and mag-

Table 6
Chemical features of pyroxmangites from
Răzoare

Sample no.	Fe ²⁺	Mn ²⁺	Mg	Ca
20R	1.19	1.98	0.19	0.17
44	0.57	3.17	0.12	0.08
60*	1.36	2.18	0.20	0.14
60C*	1.34	2.11	0.21	0.16
70	0.81	2.65	0.31	0.14

* pegmatoid aggregates

netite are the most frequently encountered opaque minerals. They are preferentially associated with the MHM and dannemorite, respectively. Thus, they rarely occur together; if this is the case, magnetite seems to be later formed. However, some grains were observed to have an intermediate colour between magnetite and jacobsite, probably ascribable to the mineral iwakiite.

Generally, the jacobsite grains are euhedral but sometimes, anhedral grains tend to cement the silicates. It is locally substituted by carbonates along S-planes or alters to secondary Mn-hydroxydes which develop either along grain boundaries or within the grains themselves. Usually, the magnetite forms fine interlocked grains intergrown with silicates, mainly dannemorite. Three generations have been identified, i.e. magnetite I, associated with dannemorite I and presumably of primary origin; magnetite II, forming small euhedral grains intergrown with dannemorite II on fine veinlets within the grains of manganoan fayalite; magnetite III appears as a product of pyrrhotite decomposition and it is closely intergrown with secondary pyrite.

The pyrrhotite is the next frequent opaque mineral and it is at the same time the most frequent sulfide. Unlike magnetite, it prefers the dannemorite dominated assemblage. The pyrrhotite is always accompanied by chalcopyrite and accidentally it contains minute grains

of gold. Locally, it is completely altered to a lamellar intermediate product and/or fine aggregates of pyrite magnetite $\pm$ marcasite. Globular grains of pyrrhotite enclosed in silicates have been observed as well. Certain microstructures such as mirmekitoides intergrowths with magnetite and fine veinlets of pyrrhotite, lining the triple junctions of the magnetite grains are present, too (Plate, Fig. 6).

The chalcopyrite forms also small swarms of rounded grains within carbonates and, as a rule, it associates with pyrrhotite.

Small amounts of graphite are always present either in the host quartzites or in the ores. Rounded graphite aggregates, sometimes with radially disposed lamellae enclosed either in silicates or in sulfides (pyrrhotite and pyrite), are very typical of the Răzoare ores.

Accessory pyrophanite has been observed in some sulfide-rich samples but without direct boundaries with other opaque minerals. It forms subhedral, twinned grains exhibiting a lower reflectivity (as compared to ilmenite) and red internal reflections.

Randomly distributed grains of molybdenite (within the dannemorite-rich aggregates) and gold (fine inclusions in pyrrhotite) have been observed, too.

Pyrite aggregates or crystals up to 4 cm in size, were formed either by substitution of pyrrhotite or by direct deposition in some breccias surrounding fractures. The pyrrhotite alteration develops gradually: first by formation of the intermediate product which lately evolves to fine aggregates of pyrite + magnetite $\pm$ marcasite. Apparently, the transformation is related to the introduction of water in the system which seems to cause also the transformation of magnetite into maghemite (Plate, Fig. 7). It is presumed that the pyritization of pyrrhotite and the maghemitization of magnetite represent simultaneous processes. No equivalent process has been depicted to affect jacobsite excepting perhaps its strong substitution by carbonates.

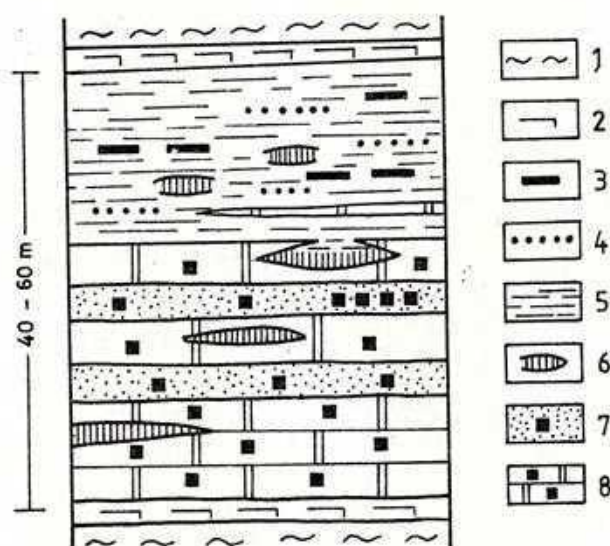


Fig. 4 - A generalized column of lithologies of the ore lenses. 1, gneisses and micaschists; 2, black quartzites; 3, magnetite beds or lenses; 4, manganoan fayalite; 7, massive aggregates of tephroite + MHM with disseminated jacobsite; 8, massive rhodochrosite with disseminated jacobsite.

	SiO ₂	MnO	FeO %	
1	85	1-2	3-4	Zn, Ni, Cu, Zr, Ba, Mo
2			Mn < Fe	dann, fay, spss, pxm, mgt, po, ap, Zn, Be
3	15-20	20	20	Mn >> Fe, teph, MHM, jac, B
4			Mn > Fe	rdc, fay, jac, ap
1	85	1-2	3-4	Zn, Ni, Cu, Zr, Ba, Mo

Fig. 5 - The layered protholith of the Răzoare deposit. The whole sequence is Ca (and Mg) - low (black quartzites - 0.5-4.5% CaO; ores-about 1% CaO) with variable Mn:Fe ratios. The mineralogy is quite contrasting and the minor element distribution is mineralogically controlled (e.g. B in MHM, Zn and Be in pyroxmangite, Au in jacobsite and pyrrhotite, etc.). 1, black quartzites; 2, silicate (dannemorite)-rich part. 3, tephroite and manganese humite minerals; 4, carbonate (rhodochrosite)-rich part;

Abbreviations: ap-apatite; dann-dannemorite; fay-manganoan fayalite; jac-jacobsite; mgt-magnetite; MHM-manganese humite minerals; pxm-pyroxmangite; po-pyrrhotite; rdc-rhodochrosite; sp-spessartine; teph-tephroite.

By entering the oxydation zone, the ores become first blackish due to the appearance of Mn hydroxides masses and of neotokite nests and veinlets. Further inflow of meteoritic water produces the mixing of Mn and Fe hydroxydes, generating large masses of coloured ochres (blackish, brown, yellow, reddish) with small geodes inlaid with quartz, pyrolusite and barite.

Discussion

The Răzoare Mn-Fe ore deposit underwent a medium (-high) grade metamorphism (upper almandine amphibole facies) together with the whole pile of surrounding metapelites. The retrograde metamorphic evolution during the Caledonian and the Hercynian events led to a much more complicated mineralogy. Due to the different behaviour of the micaschists and of the Mn-Fe ores it becomes difficult to draw a perfect parallel between the metamorphic events depicted in the two environments with contrasting lithologies.

There are numerous typical interlocking metamorphic textures in the ores at Răzoare (Plate, Fig. 8). Triple junction points could be seen on magnetite, jacobsite, olivines and even rhodochrosite grain boundaries. No evidence inconsistent with a premetamorphic sedimentary origin of the Răzoare deposit was found. The ore banding is frequent and presumably it was produced mostly during regional metamorphism.

The Răzoare protolith seems to have had a complex composition, which is revealed at first glance by the three contrasting, somehow well separated lithologies (Fig. 4). The lower lithology is carbonate-rich with small silica-rich pods, now represented by fayalite bed or lenses. The next lithology contains Mn-rich, carbonate poor assemblages from which the tephroite and MHM have derived. Both lithologies contain mainly jacobsite and are silica-undersaturated. The upper lithology is Fe-richer and silica-saturated;

they consist of pyroxmangite, dannemorite and spessartine with prevailing magnetite and pyrrhotite. Both the hanging and foot wall of the ore sequence include nearly continuous beds of quartzites which acted as lithological-geochemical barriers (Fig. 5). Outside the barriers, the manganese-bearing assemblages are scarcely developed or even lacking.

The metamorphic evolution of the Răzoare ores is quite complicated and the geological environment could not be precisely reconstructed. However, it can be assumed that the "layered protolith" approached a composition roughly corresponding to a mixture of manganese carbonate, iron oxide and silicate, with variable amounts of calcium phosphate, graphite and locally silica.

The first metamorphic event corresponds to the formation of paragenesis including manganoan fayalite, a calderite-rich garnet and a seldom occurring orthopyroxene. A slight lowering of the metamorphic grade allowed the formation of a first generation of dannemorite. The next metamorphic event (of the first, polyphasic event?) includes a second generation of manganoan fayalite (slightly depleted in Mn), pyroxmangite II, spessartine and dannemorite II. This assemblages prevail at the upper part of the Mn-bearing sequence, whereas the middle and partly the lower parts contain the nearly synchronous formed assemblage of tephroite, MHM and jacobsite.

Closely related to this second metamorphic peak there is a peculiar pegmatoid-like development of pyroxmangite, fayalite and dannemorite under conditions of increasing fluid activity in the system. This corresponds to the abundant pegmatite development (numerous bodies rich in green apatite and black tourmaline) within the host metapelites.

Further retrograde changes are accompanied by the development of a partly bleached, asbestos-like amphibole. The abundant formation of maghemite on magnetite, of pyrite at the expense of pyrrhotite and probably the substitution of jacobsite by carbonates seem to

be contemporaneous events; they are accompanied and/or followed by rather abundant chlorites, calcite and pyrite crystals mainly linked to the fault-related subsequent transformation.

As regard some previously reported minerals (Tab. 7) which have not been found during our investigation, certain remarks seem to be necessary. Bustamite is unlikely to occur at Răzoare because of the low Ca content of the ore in general. Moreover, the Mn:Fe ratio of about 1:1 suggests that the pyroxmangite has to be the stable phase in the $\text{MnSiO}_3\text{-FeSiO}_3\text{-CaSiO}_3$ system as shown by the diagram proposed by Brown *et al.* (1980) and Winter *et al.* (1981). In addition, the higher-pressure pyroxmangite (Maresch, Mot-tana, 1976) matches better the mineral assemblages of the surrounding micaschists in which the kyanite is the leading mineral. For the same chemical reason the existence of wollastonite in the Răzoare ores seems to be improbable, too. Further on, no evidences exist for the presence of forsterite excepting its mole participation in the manganoan fayalite (especially in fayalite II) composition.

Conclusions

The Răzoare deposit contains manganese and iron minerals weakly separated within the ore-bearing sequence. The minerals have formed during repeated metamorphic events at the expense of a primary protolith of presumably sedimentary origin (Udubaşa, Hârtoşanu, 1992). The initial composition of the ore protolith largely corresponds to a mixture of manganese carbonate, iron oxide and silicate, zonally developed, with variable amounts of calcium phosphate, graphite and silica, showing an irregular distribution within the ore sequence.

The ore sequence is accompanied in both the footwall and hanging wall by black quartzites which acted as lithological barriers. The whole metamorphic pile under-

went an initial regional metamorphism under conditions of the upper almandine amphibolite facies: manganoan fayalite-calderite-rich, spessartine-orthopyroxene. Later metamorphic events of essentially retrograde character involving high activity of water and other volatile components led to the formation of several parageneses showing a slight separation in space. The most important are: (1) fayalite II-pyroxmangite-dannemorite II-spessartine and (2) tephroite-manganese humite minerals (MHM)-jacobsonite. From the lower carbonate-rich assemblage which is undersaturated in silica and has a Mn:Fe ratio greater than unity, the ore sequence passes through a Mn-dominated assemblage with tephroite and MHM to an upper silicate-rich part, now represented by dannemorite in which the Mn:Fe ratio becomes subunitary; this upper part is silica-saturated (the association spessartine + quartz is more frequently encountered towards the boundary with the hanging wall quartzites) and shows a marked increase in sulphur.

The whole mineral association of the Răzoare ores is rather complex, consisting of about 60 species (including secondary minerals not completely studied). The mineralogical composition seems not to be very common and bears some peculiarities which can be expressed as follows:

- the lack of rhodonite; instead, pyroxmangite develops quite abundantly;
- the presence of two olivines (manganoan fayalite and tephroite) forming rather distinct assemblages and occupying different position in the ore sequence;
- the presence of nearly the whole morphotropic series of the manganese-humites (sonolite, alleghanite, leucophenite, jerrygibbsite) formed at the expense of their "start"-member, i.e. tephroite as well as their constant boron content;
- the pegmatoid development of pyroxmangite, dannemorite and manganoan fayalite, suggesting an "ore equivalent" of the peg-

matites (apatite, beril, tourmaline) known in the host metapelites;

- the abundant apatite and the presence of the carbonate-fluorapatite;

- the slight separation of Mn and Fe as related to fayalite vs. tephroite and magnetite vs. jacobsonite different distribution within the ore sequence;

- the slight depletion in Mn of the successive generations of some minerals such as fayalite, pyroxmangite and dannemorite.

The main minerals of the ores are now under study and have been or will be later published in separate papers. Their exact nature will help in elucidating the metamorphic evolution

of the ore-bearing sequence and will also allow more documented comparison with other deposits in the world. However, it is likely that the Răzoare ore deposit bears some similar features (metamorphic grade, main minerals present, etc.) with the Bald Knob, North Carolina (Simmons et al., 1981). The peculiarity of the Răzoare ores consists in being iron-richer. The ratio Mn:Fe is here near unity. Correspondingly, there exist both Mn-Fe minerals with varying Mn:Fe ratios induced by repeated metamorphic events and Fe minerals (magnetite, siderite, pyrrhotite) or Mn minerals (tephroite, MHM, rhodochrosite), the presence of which seems to reflect the primary "layering" of the protolith.

Table 7
Mineral species and varieties described so far
in the Răzoare area

Minerals		Sources						
1.	Actinolite*						(6)	
2.	Adularia**	(1)						
3.	Allegghanite						(6)	
4.	Anatase**	(1)						
5.	Apatite***	(1)	(2)	(3)	(4)	(5)	(6)	(7)
6.	Barite****	(1)		(3)			(6)	
7.	Bementite						(6)	
8.	Braunite				(4)			(7)
9.	Bustamite!					(5)		
10.	Calcite						(6)	(7)
11.	Carbonate-fluorapatite						(6)	
12.	Chalcantite							(7)
13.	Chalcedony				(4)			(7)
14.	Chalcocite							(7)
15.	Chalcopyrite				(4)	(5)	(6)	(7)
16.	Clinocllore						(6)	
17.	Covellite							(7)
18.	Dannemorite	(1)	(2)	(3)	(4)	(5)	(6)	(7)
19.	Fayalite, manganoan ⁺						(6)	
20.	Forsterite!					(5)		
21.	Franklinite!					(5)		
22.	Galena				(4)			(7)
23.	Goethite ⁺⁺	(1)	(2)		(4)	(5)	(6)	(7)
24.	Gold						(6)	
25.	Graphite ⁺⁺⁺						(6)	
26.	Greenalite					(5)		
27.	Gypsum							(7)

Minerals		Sources					
			(3)		(5)		(7)
28.	Hematite						
29.	Hisingerite		(2)				
30.	Holdawayite (?)					(6)	
31.	Iwakiite (?)					(6)	
32.	Jacobsite	(1)		(4)		(6)	(7)
33.	Jerrygibbsite					(6)	
34.	Kutnahorite						(7)
35.	Leucophoenicite					(6)	
36.	Maghemite					(6)	
37.	Magnetite	(1)	(2)	(3)	(4)	(5)	(6) (7)
38.	Manganite	(1)		(3)			
39.	Manganophyllite (manganoan biotite)					(6)	
40.	Marcasite				(5)	(6)	(7)
41.	Melanterite			(4)			
42.	Molybdenite					(6)	
43.	Neotokite			(4)		(6)	(7)
44.	Opal						(7)
45.	Orthopyroxene					(6)	
46.	Pennantite					(6)	
47.	Piemontite						(7)
48.	Psilomelane	(1)		(3)	(4)	(5)	(7)
49.	Pyrite	(1)		(3)	(4)	(5)	(6) (7)
50.	Pyrolusite	(1)		(3)	(4)	(5)	(6) (7)
51.	Pyrophanite					(6)	
52.	Pyroxmangite			(3)	(4)	(5)	(6) (7)
53.	Pyrrhotite				(4)	(5)	(6) (7)
54.	Quartz					(6)	(7)
55.	Rhodochrosite	(1)	(2)	(3)	(4)	(5)	(6) (7)
56.	Rhodonite !		(2)	(3)	(4)		(7)
57.	Siderite			(3)	(4)	(5)	(6) (7)
58.	Sonolite					(6)	
59.	Spessartine	(1)		(3)	(4)	(5)	(6) (7)
60.	Spessartine-calderite					(6)	
61.	Sphalerite					(5)	(7)
62.	Staurolite * !	(1)					
63.	Szinkite				(4)		(7)
64.	Tephroite					(6)	
65.	Tourmaline (red)*					(6)	
66.	Triplite !				(5)		
67.	Vivianite						(7)
68.	Wad						(7)
69.	Wolfeite !				(5)		
70.	Wollastonite !			(3)	(5)		
71.	"Zwischenprodukt"					(6)	
72.	Ni-Co-minerals++++						

* From rocks near or within the ores.

** From Alpine-veins near the ore field.

*** Chlorapatite; a manganoan apatite has been also reported (5).

**** In geodes within oxydized ores with quartz and pyrolusite.

+ Labelled knebelite in the previous papers.

++ "Ochreous limonite" in the previous papers.

+++ Graphite forms sometimes rounded aggregates included in both silicates and oxides.

++++ Very small blebs irregularly distributed.

! Minerals unlikely to occur (see text)

(?) Incompletely described

Sources: (1) Kossmat and von John (1905)

(2) Giuşcă (1962)

(3) Rădulescu, Dimitrescu (1966)

(4) Kalmár (1972)

(5) Götz *et al.* (1977, unpubl. report)

(6) Udubaşa, Hărtopanu, Ilinca (1990, unpubl. report)

(7) Kalmár, Lelkes-Felvári (1991)

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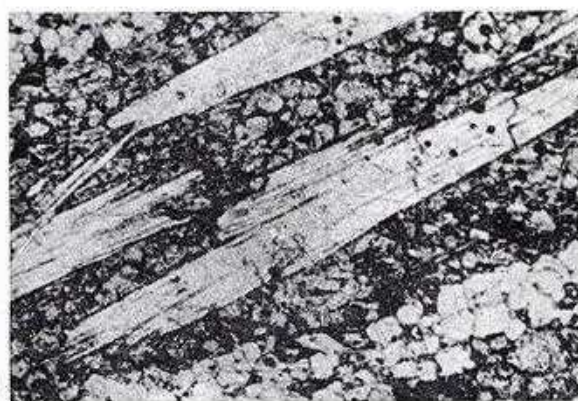
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Plate

Photomicrographs of typical banded ores as seen in thin sections (Fig. 1-5) and some features of the oxide grains (Fig. 6-8). Fig. 1 - Fine-grained manganoan fayalite, rhodochrosite and jacobsite (black). Sample 86, main quarry; x 40. Fig. 2 - Alternating bands of manganoan fayalite (grey), apatite (whitish) and late dannemorite. Small jacobsite grains are also present. Sample 80, main quarry; x 40. Fig. 3 - Secondary banding of apatite + magnetite with slightly altered dannemorite + rhodochrosite. Level VI/Shaft 1 x 40; Fig. 4 - Alternating bands of manganoan fayalite + magnetite and rhodochrosite (partly recrystallized). Waste dump of shaft 1; x 40; Fig. 5 - Oriented intergrowth of manganoan fayalite and dannemorite, with euhedral apatite. Waste dump of shaft 1; x 40. Fig. 6 - Magnetite grains with triple junctions lined with pyrrhotite. The grey grains without scratches represent magnetite transformed into maghemite. Level VI/Shaft 1. Reflected light, oil immersion, x 250. Fig. 7 - Partly maghemitized magnetite grains cemented with pyrite; black - siderite; Level VI/Shaft 1. RL, oil immersion, x 250. Fig. 8 - Triple junctions of jacobsite grains. Level VI/Shaft 1. RL, oil immersion, x 250.



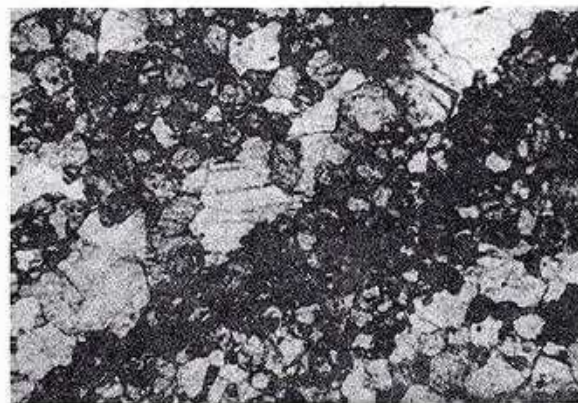
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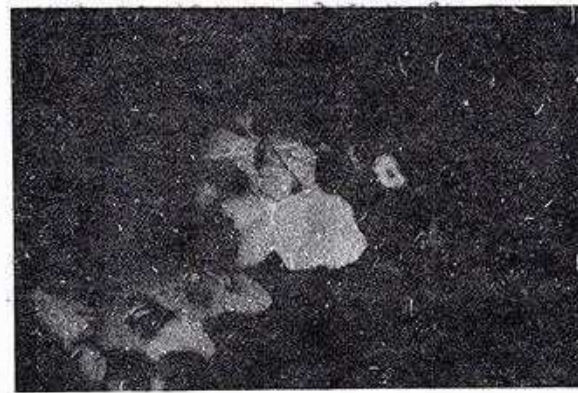
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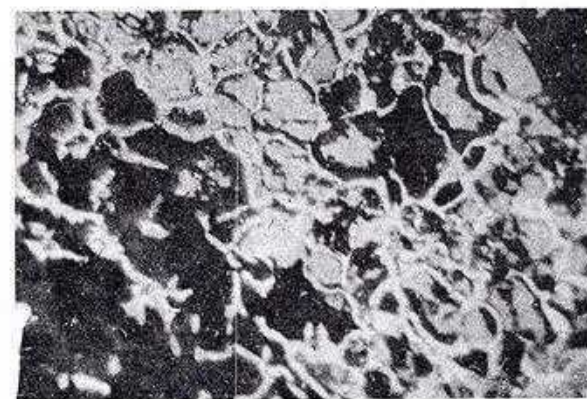
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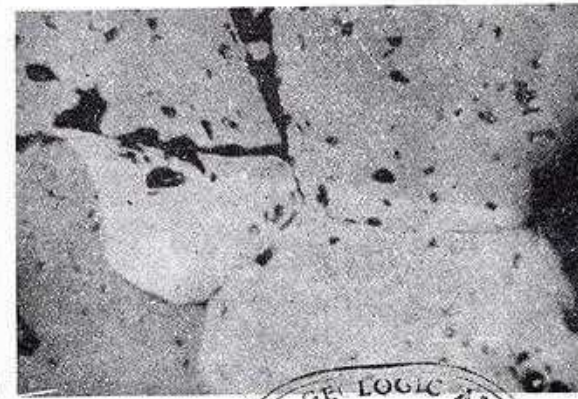
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NATIVE GOLD-BEARING MINERAL ASSEMBLAGES IN THE MĂGURA-FĂERAG HYDROTHERMAL VEIN DEPOSIT (METALIFERI MOUNTAINS)

Eugen ORLANDEA, Gheorghe VELCIOV

MINEXFOR S.A. Deva, Str. Minerului, nr. 2, 2700 Deva.



Key words: Native gold. Hydrothermal veins. Porphyry copper. Au:Ag ratio. Alterations. Neogene magmatism. Metaliferi Mountains.

Abstract: At least two mineralization stages contain native gold at Măgura-Făerag; the first one consists of pyrite, rutile, arsenopyrite, chalcopyrite and the other one is represented by pyrite, Pb-Cu sulphosalts, quartz and barite. The ore veins are located in Neogene andesites showing pervasive phyllic-argillic alterations. The propylitization forms marginal parts of the alteration zones. Locally, the potassic alteration (secondary biotite) is also developed and occupies a proximal position against the ore veins. It is indicative of the gold presence (positive metalotect). Taking into account the subvolcanic character of the andesite bodies and the major structural setting defined as island arc, it is presumed that a porphyry copper system develops at depth. Skorodite is described in the area for the first time.

The Măgura-Făerag eruptive structure is situated in the south-eastern part of the Brad-Săcărâmb post-tectonic basin, a unit which preserves a subsequent Neogene volcanic complex, the result of an andesitic volcanism related to an "island arc" major tectonic structure. The Neogene volcanics are associated with intramontane molasse formations, locally overlying the Mesozoic ophiolitic and/or calcareous flysch basement.

MINEXFOR S.A. DEVA began the systematic exploration of this deposit in 1980; in the period 1957-1959 and 1965-1967 several enterprises and institutes carried out sporadic research in this area. The experts' interest in this deposit increased concomitantly with the

starting of the exploration works. In this respect it is to note the studies effectuated by Cioflică et al. (1966), Udubaşa et al. (1982, 1984), Bordea, Pop (1989). The porphyry copper structures in the Metaliferi Mts, similar in some respects to the Măgura-Făerag zone, were described by Borcoş et al. (1980, 1984), Boştinescu (1981, 1984) and Vlad (1983).

The known gold-silver, subordinately lead-zinc, vein mineralization located in the Măgura, Măcieşul, Custura andesitic bodies and related lavas is grouped into six vein systems generally trending NNW-SSE or N-S. Among them, important in economic respect is West Măgura vein group, as most of the native gold occurrences have been identified here (Fig.1).

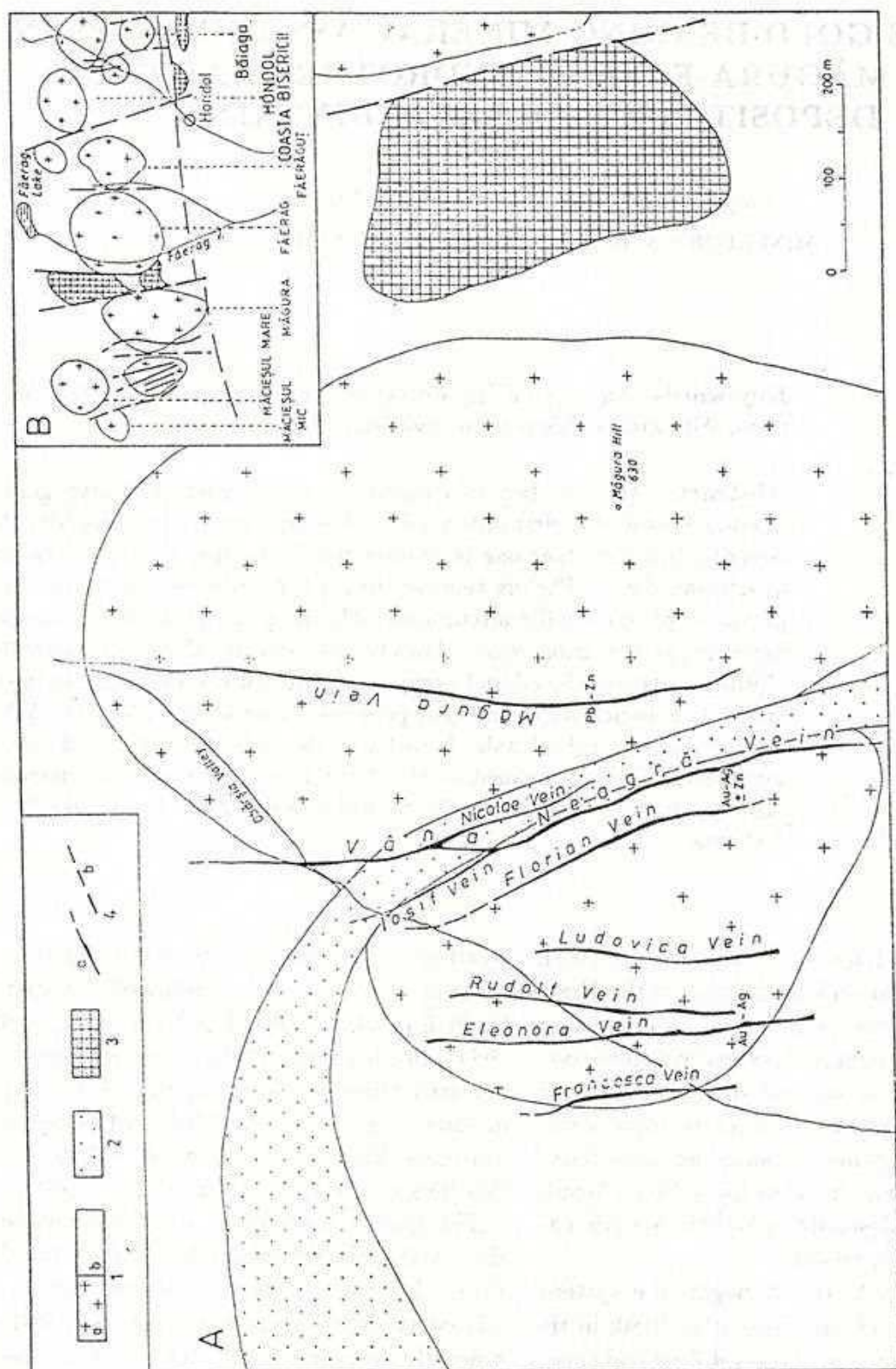


Fig. 1 - Geological map of the Măgura Zone (A) and tectonic sketch of the Măcișu-Măgura-Hondol Zone (B); according to M. Ioan, 1991, unpublished data, and Udubăș, 1983, unpublished data. 1, Barza-type quartz andesites (Sarmatian-Pannonian) (a, body; b, lava); 2, sedimentary rocks - marls, sandstones (Lower Miocene); 3, Mesozoic ophiolitic rocks; 4 a, veins, 4 b faults.

The exploration of this vein group has been achieved at five horizons, summing up on the vertical 180 m.

The evaluation of the results outlines both a zonality of deposition of the metallic elements from the source geothermal system and a hypogene alteration of the hornblende andesite rocks of Barza type, which hosts almost exclusively the vein mineralizations.

Native gold assemblages and parageneses

The mineralogical, textural, geochemical and field evidence pointed out the presence of at least two mineralization stages: the *gold-silver stage*, especially characterizes the western part (Francisca, Eleonora, Rudolf, Iosif, Ludovica veins) and the *lead-zinc stage*, dominantly occurs in the eastern part of the Măgura structure (Măgura vein) (Fig. 1, 2 A, 2 B). In our opinion, the median zone (Florian, Vâna Neagră veins) with a gold-silver, subordinately zinc character, corresponds to the overlapping of the two mineralization cycles. It is also possible that this assemblage might have a distinct position in the general evolution trend of the postmagmatic solutions (Fig. 2 A).

Gold-silver stage

In the upper horizon (Tina Neagră - absolute height 443 m) the metallic mineral assemblage is defined by the succession: pyrite-arsenopyrite-native gold-chalcopryrite±sphalerite in a quartz and clay minerals gangue. Significant parageneses for native gold are, as follows: quartz-native gold, quartz-arsenopyrite-chalcopryrite-native gold, quartz-arsenopyrite-native gold (Fig. 2 C).

At depth the identified metallic mineral assemblage consists of: rutile±ilmenite-pyrite-arsenopyrite-native gold, the parageneses quartz-native gold and quartz-pyrite-arsenopyrite-native gold being of great importance.

In the lower horizon (-140 m, absolute height 263 m) occur rutile-pyrite-chalcopryrite-native gold±sphalerite, the paragenesis pyrite-chalcopryrite-native gold being significant for gold. The presence of sphalerite and chalcopryrite is subordinate from the quantitative point of view.

Gold. Two generations of gold are present. The first generation was identified as lamellae, contorted plates, dendritoid forms, flattened crystals with trigonal outlines deposited on crusts or in microvoids of white-milky or grey bipyramidal quartz of first generation. Gold crystals display always well-developed octahedron faces, whereas the tetrahedron faces can be presumed only in few cases. It is to note the dendritoid forms in the marginal zones of the native gold foils constituted undoubtedly of several crystalline individuals. The quasiparallel trend of the extremely flattened crystals which form foils points to a oneway hydrothermal flux and a rapid growth of the crystals in a dynamic system controlled by the tectonic factor.

Native gold of the second generation occurs either as dendrites, a moss covering the translucent grey-violaceous quartz crystals with long prismatic habit and short rhombohedron faces, or as rounded inclusions in arsenopyrite or more rarely chalcopryrite.

Generally, all gold crystals described so far are typical of the gold deposits found at a shallow or medium depth, similar or identical forms occurring in the Musariu, Valea Morii (Berbelec, 1985) ore deposits as well as in ore deposits in NW Russia (e.g. Balei ore deposit - Petrovskaya, 1973).

Pyrite occurs as idiomorphic-idiomorphic single crystals (pentagonal dodecahedron forms prevailing) or as small crystal clusters which, in the vein influence zones, are found on the contour or inside the melanocrate crystals, associated with rutile, arsenopyrite, iron oxides and hydroxides (hematite?). Pyrite-sphalerite, pyrite-arsenopyrite intergrowths with a concentric zonal aspect

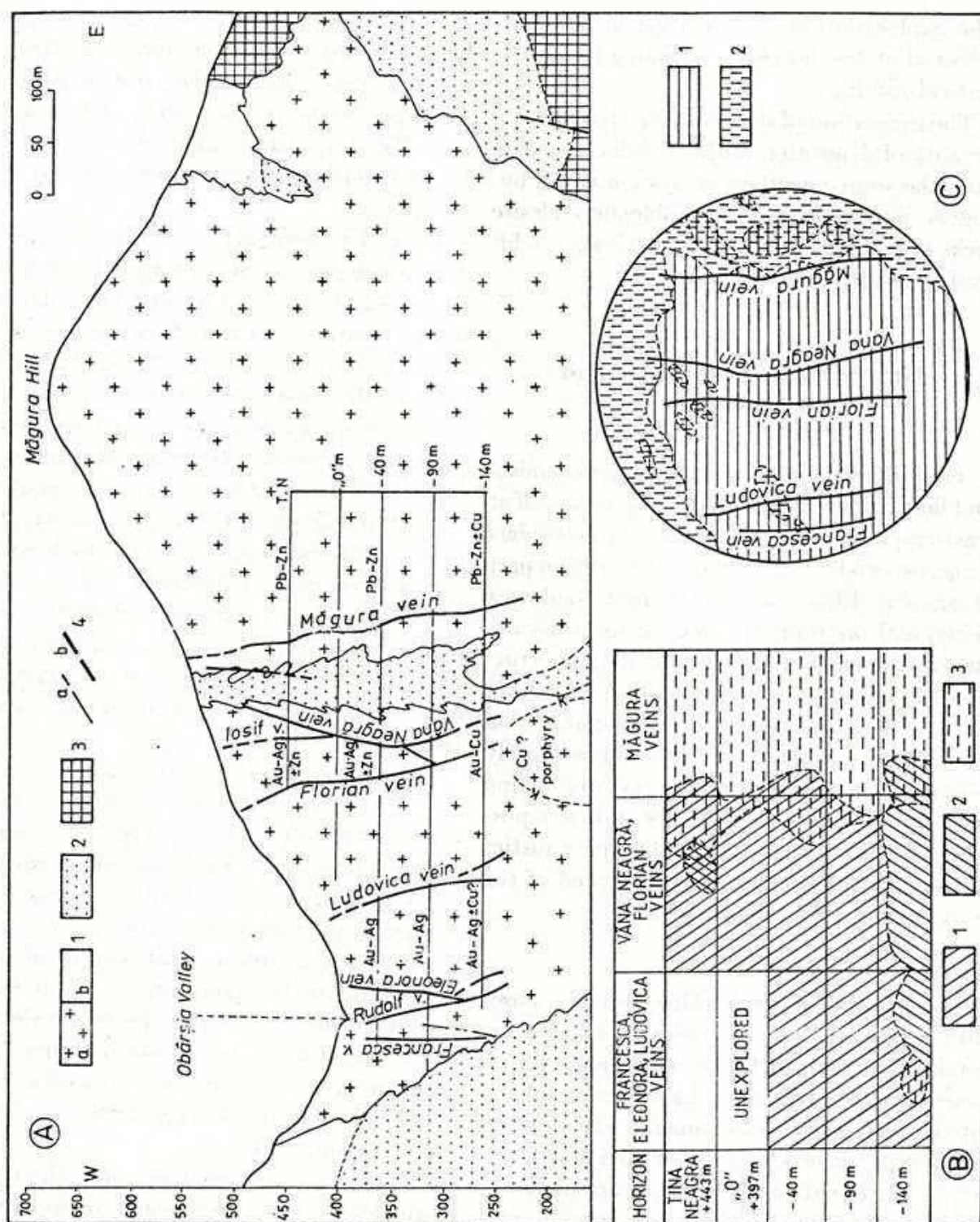


Fig. 2 A - Geological cross-section through the Măgura-Făerag ore deposit with the vertical distribution of the major elements (Legend: see Fig. 1).

Fig. 2 B - Sketch with the distribution of the mineral assemblages.

1, quartz-native gold-arsenopyrite; 2, pyrite-chalcopryrite-native gold; 3, common sulphides-native gold.

Fig. 2 C - Sketch with the distribution of the alteration facies (horizontal section); 1, phyllic-argillic zone; 2, propylitic zone.

of "atolls" are locally noticed.

Chalcopyrite is frequently intergrown with pyrite or occurs as fine-grained crystals, alone or associated with pyrite which is corroded by it.

Arsenopyrite is almost always found in association with native gold, as small crystals with an elongated rhombic, more rarely isometric habit, in places grouped in polycrystalline aggregates, locally grouped in small swarm-like clusters; frequently, it contains native gold inclusions of micron sizes.

Sphalerite, in this assemblage, is iron-rich and forms xenomorphic masses subsequent to pyrite. Generally, it does not show calcopyrite exsolutions, being often brecciated and cemented by quartz. Locally, sphalerite is associated with arsenopyrite, occurring as impregnations in rock where it substitutes or corrodes the amphibole phenocrysts.

Silver minerals (native silver, silver sulphides and sulphosalts) have not been found in the parageneses described by us in this mineralization phase. The high value of the Au/Ag ratio resulting from the chemical analyses carried out on samples from gold-silver veins points out that silver might form solid solutions with gold in pyrite and arsenopyrite.

The assemblage and parageneses described above, the shape of the ore minerals and the relationships between them and the gangue minerals (quartz $\pm$ clay minerals), the geothermometric measurements (Bordea and Pop, 1989) indicate a formation temperature of about 300°C, corresponding to the final hypothermal and hypomesothermal phase. The gold-arsenopyrite and gold-quartz assemblage is, in this case, of a higher temperature. It is to note the presence of graphite (Bordea and Pop, 1989) within the ore mineral assemblages in the gold veins, which, together with rutile, suggests the deposition of gold from high-temperature fluid systems.

Lead-zinc ($\pm$ Au, Ag) stage

The ore mineral assemblage specific to this

stage is characteristic of the veins in the eastern part of the structure (Măgura vein, Figs. 2 A, B). Generally, the succession of minerals is: pyrite, chalcopyrite, marcasite, sphalerite, arsenopyrite, tetrahedrite, galena, bournonite, jamesonite, plumosite, native gold, native silver. The gangue is constituted of quartz (deposited within a wide range of temperature), barite, clay minerals, gypsum, zeolites (natrolite group).

Pyrite occurs as two distinct generations, often forming idiomorphic or hypidiomorphic crystals with cubic or rhombododecahedron habit, usually grouped as aggregates corroded by subsequently deposited minerals.

Chalcopyrite generally corrodes pyrite and locally sphalerite, galena and tetrahedrite; covellite, chalcocite and bornite form at its expense. At least two generations can be distinguished in case of this mineral on the basis of the mutual microscopic relationships.

Arsenopyrite occurs frequently as idiomorphic crystals with a rhombic symmetry, as double and triple interpenetrating twins after (230) or as aggregates with a characteristic indented contour. As a mineralogical novelty for the Măgura structure it is to note the secondary formation on arsenopyrite crystals of yellow-greenish and/or brown scorodite crusts associated to iron hydroxides.

Sphalerite is frequently represented by the iron-poor variety (cleiophane), usually in association with galena (subsequently deposited), tetrahedrite and chalcopyrite (exsolutions structures).

Marcasite shows at least two distinct generations:

- nests or isolated crystals with a rhombic habit (faces 110, $\bar{1}\bar{1}0$, 014 are well developed) which frequently corrode pyrite of first generation;

- reniform-collomorphic aggregates constituted of micro- or cryptocrystalline prismatic crystals with a radiary disposition.

Gold, probably deposited at the end of the

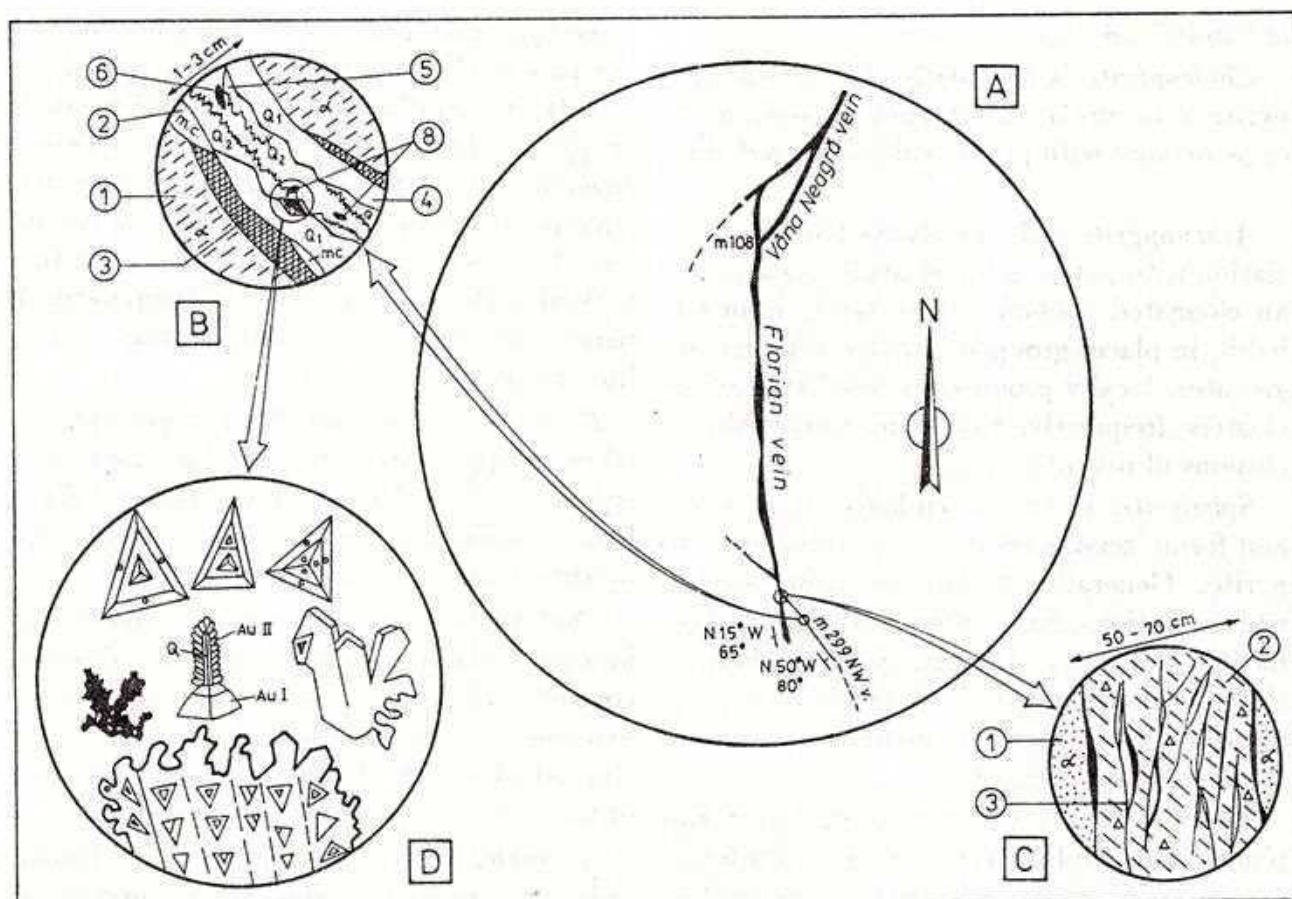


Fig. 3 - Distribution of the veins in the Tina Neagră horizon (A) with details on the position of the alteration zones and of the metallic mineral assemblages (B, C, D);

B: 1, potassic alteration (biotite, hydromica, sericite); 2, clay minerals (illite, kaolinite) and carbonates; 3, silica and hematite bands; 4, white quartz (bipyramidal crystals); 5, grey or violet quartz (prismatic habit); 6, marcasite-sphalerite-galena; 7, native gold I (plates, blades and flattened crystals)-arsenopyrite; 8, pyrite-arsenopyrite-chalcopryite-native gold II (dendrites);

C: 1, phyllic-argillic±pyrite alteration; 2, silicified andesite, hydrothermal breccias with pyrite, arsenopyrite, sphalerite, galena±chalcopryite; 3, fissures and mineralized veins with pyrite, marcasite, sphalerite, galena, quartz, clay minerals, carbonates;

D: Frequent shapes of the native gold grains.

activity corresponding to the second stage of mineralization, occurs as spangles, crystalloids, or included within the sulphides and sulphosalts network. The local association of native gold with iron oxihydroxides of goethite-hydrogoethite type suggests the secondary origin by mobilization and deposition from fluids with meteoric supply. It is possible that native silver, which occurs usually in

small quartz geodes, might be of secondary origin considering its strong sulphophile character.

Taking into account the results of earlier mineralogical-petrographical studies (Bordea & Pop, 1989) this association is considered to characterize a wider temperature interval corresponding to the meso-epithermal phase, being deposited from colloidal or almost colloidal

solutions.

The two stages of mineralization are delimited in time and space by ample disjunctive phenomena which determined brecciations of veins especially in the middle part of the structure. It is possible that Măgura vein might correspond to a protofissure during the first mineralization stage and the Florian and Vâna Neagră veins might be partially reactivated at the level of the second mineralization stage. A special situation occurs at the Tina Neagră upper horizon in case of vein m. 299 which includes the native gold-arsenopyrite-quartz association, and which is offset by the Florian vein fracture (Fig. 3). Pb-Zn sulphides $\pm$ sulphosalts have been identified especially on the Florian fracture and less on fracture m. 299 with native gold, generally in the axial zones of the veins. However, it is to emphasize the independence or weak negative correlation between the presence of native gold and that of Pb-Zn sulphosalts. The situation is changed in case of the Măgura vein, where the gold contents correlate with the Pb-Zn ones.

Hypogene Alteration Facies

The hypogene alteration phenomena display a pervasive character, at least in the western part of the structure, with different intensities and superpositions of facies according to the distance from the vein walls. Thus, it is to note a wall rock alteration type found in the influence zone of the vein fracture, as well as a regional zonality at the level of the andesitic body (Fig. 2 C).

The neomineral assemblage identified in the vicinity of the gold-silver veins made possible to establish a zonality of alteration facies.

The potassic facies occurring in the proximal zones (less than 1 m in thickness) of the native gold veins is characterized by the assemblage formed of: Ti-bearing, biotite, hydromica, ferrikerolite (phengite), quartz, albite.

In the lower horizons this facies is usually intensely overprinted by subsequent alterations

(argillization, carbonation, silicification), in places the sericite-hydromica assemblage indicating relics of a potassic metasomatism. However, the potassic facies is confirmed by the higher contents of K_2O , SiO_2 , Fe_2O_3 and the lower contents of CaO and S than those of the argillized rock.

In case of the m. 299 vein, an asymmetric and discontinuous band of silicified dark-coloured rock, about 3–7 cm thick, accompanying the mineralized fracture, can be correlated with the native gold occurrence. The lack of this silicified zone, relatively clearly delimited outwards, can be correlated with the deposition of the Pb-Zn sulfides. The coexistence of these two situations on the prolongation of the same vein points out the presence of two distinct mineralization stages.

The argillic and phyllic neof ormation frequently superposed and with a distal position displays maximum intensities in the zones close to the vein fractures where, as already mentioned, can completely overprint the potassic alteration.

The argillic facies is characterized by the neomineral assemblage made up of clay minerals (illite-kaolinite), quartz, carbonate $\pm$ sericite, gypsum, zeolites (natrolite), iron oxides and hydroxides (hematite, goethite, hydrogoethite). The phyllic facies is constituted of sericite, quartz, clay minerals, carbonates. One can notice the decrease of the intensity of the phyllic alteration with sericite downward to the lower exploration horizon, where the argillic association with clay minerals, carbonates $\pm$ zeolites, iron oxide/hydroxides is prevailing.

Silicification is more obvious in the upper levels in the argillic-phyllic associations with argillaceous minerals, microgranular quartz, sericite $\pm$ carbonates, gypsum, iron oxide/hydroxides.

In places, the texture of the clay minerals association (felt, fibrous aggregates) suggests their formation as a result of chlorite alteration. In some thin sections, cryptocryst-

talline aggregates of clay minerals, which preserve relict islands of fibrous chlorite, have been identified. As a matter of fact, chlorite, subordinately associated with carbonates and iron oxide/hydroxides, was formed at the expense of amphibole. In this case, minor albite can be found at the expense of feldspars and in the matrix sericite.

The neomineral assemblage described corresponds to a *chloritization-propylitization* almost entirely overprinted by the effects of subsequent alterations.

Considering the whole enrooted structure, the phyllic-argillic zone is widely developed in the western intrusion where the Au-Ag veins occur, symmetrically bordered by the propylitization-chloritization zone with chlorite, carbonates, albite, clay minerals, iron oxide/hydroxides especially developed in the Măgura vein area, as well as the westernmost part of the structure. In this alteration stage the fluids from the geothermal system had a reduced metallogene supply, at least in case of the metallic elements: gold, silver, lead, zinc.

Pyrite is present as disseminations-impregnations and nests in all the identified neomineral assemblages. Sphalerite, galena and arsenopyrite usually display an impregnation texture in rocks in the vicinity of the vein fractures. However, it is to note the constant presence of chalcopyrite in the argillic facies associations at the level of the lower horizon (-140 m).

Significance of the Au-Ag ratio. Behaviour of the minor and trace elements

The variation of the gold-silver ratio is significant in case of the Măgura structure, as it represents an argument in favour of the deposition of the mineralization during two main stages. Thus, in case of the eastern veins from the West Măgura vein group, the Au:Ag ratio shows values generally ranging between 1/10 and 1/100, whereas in the western veins it

displays a value between 1/2 and 1/20. The smaller values of the ratio, recorded especially in the Măgura vein, correspond in our opinion to a lower-temperature mineralization deposited during a secondary phase from less alkaline solutions. The high values of the ratio recorded in the Au-Ag veins stress out the mineralization deposition during a primary higher temperature phase from high alkaline solutions. Some of the high values of the gold-silver ratio in the Măgura vein are due to a primary circulation, with the deposition of a high temperature quartz-gold-arsenopyrite paragenesis. It is also obvious the direct correlation of the gold content and the value of the gold-silver ratio. This situation suggests that a large amount of native gold is associated to the first mineralization stage.

As regards the minor and trace elements occurring in the vein mineralizations and in the influence zones of the fractures, the number of spectral analyses effectuated so far does not make possible a general view on their behaviour. However, it is to mention high values for arsenic (1500–3000 ppm), which are generally correlated with the reduced presence of antimony and the absence of bismuth in the native gold veins. In this case the Au-Ag assemblage indicates a higher temperature of the hydrothermal fluids, as it is well known the larger temperature interval within which arsenic can occur in the magmatic rocks. High values (more than 50 ppm) are also observed for V, Ti, B, Mn, Ba.

Structural and genetic conditions of the mineralization

In order to understand the Tertiary metallogenesis in the Măgura ore deposit, several specifications are necessary regarding the general structural framework, the shape and depth of emplacement of the Măgura andesitic body.

As already mentioned the host rock of the mineralizations is represented by the am-

phibole ($\pm$ quartz) andesite of Barza type with phenocrysts/matrix ratio ranging from 5/3 to 3/5. The phenocrysts of plagioclase (An_{36-39}), amphibole (green hornblende) and sparsely quartz as well as the microcrystalline groundmass of randomly orientated plagioclase ($\pm$ quartz) are characteristic of these rocks. Generally the rocks present an incipient autometamorphic alteration of propylitic type which consists especially in the chloritization of amphibole and the albitization of plagioclase.

Both at the surface and at all the five mining levels two intrusions within the same structures can be delimited by the presence, in the median zone, of a pile of clayey-sandy-marly sedimentary rocks, intensely tectonized and transposed to the vertical. These Badenian (ante-Badenian ?) deposits underwent obvious hydrothermal alterations (carbonation, argillization, sericitization), impregnations with ore minerals, recrystallizations. Injections of andesitic material into sedimentary rocks at the contact zone are present, too.

The hypogene alteration shows an obvious and pervasive character in the western intrusion which encompasses the Au-Ag veins. It is worth mentioning the northern enrootment of this intrusion revealed by descendent vertical drillings from the lower horizon.

All structural data made us consider the subvolcanic character for the amphibole-bearing andesite-body in the West Măgura ore deposit. The subvolcanic body intruded rocks of the ophiolitic basement s.l. (Jurassic-Middle Cretaceous island arc volcanics), Miocene sedimentary deposits and previous Neogene volcanic sequence. It is to note the almost exclusive presence at the erosion level of the sedimentary rocks intruded by the subvolcanic body, in this situation the absence of the breccia pipe typical of structures of this type can be explained.

There are several observations of importance in the deciphering of the metallogenetic evolution associated to the Măgura subvol-

canic structure, e.g.:

- zonality of the hypogene alteration facies, represented by a central phillic-argillic zone encompassing the Au-Ag mineralizations bordered by a propylitized-chloritized zone with a variable degree of intensity;

- constant presence of chalcopyrite as disseminations-impregnations at the level of the lower horizon, as well as of the native gold-pyrite-chalcopyrite paragenesis. The copper minerals (chalcopyrite, tetrahedrite more frequently occur also in the vein fractures intercepted at this level, particularly in the Măgura vein;

- pinching out of the Au-Ag veins (Vâna Neagră, Florian) in the depth against the background of a more intense fissuration and argillic alterations;

- constant presence of the titanium oxides (rutile-ilmenite) in the determined associations, which point to the origin of the generating solutions in partially oxidated magmas;

- control of the mineralization and emplacement of the subvolcanic body (Fig. 1 B) by the local and regional tectonic elements.

All this stresses out the existence of a porphyry-copper system which would correspond to a primary mineralization stage overlapped, at the upper part of the subvolcano (dome zone), by Au-Ag mineralizations and subordinately by base-metal mineralizations corresponding to the two mineralization stages separated by us. Within this context, we estimate that beneath the lower research level of the western intrusion there are theoretical premises of development of copper concentrations in porphyry system, probably associated to the potassic zone.

The development of the mineralization processes is discontinuous, at least as regards the Au-Ag stage and base metal one. The two pulsatory stages strictly delimited temporally are stressed out by the effects of the marked syntectonism in the deposition of the mineralizations closely connected with the spatial delimitation of the two mineralization types.

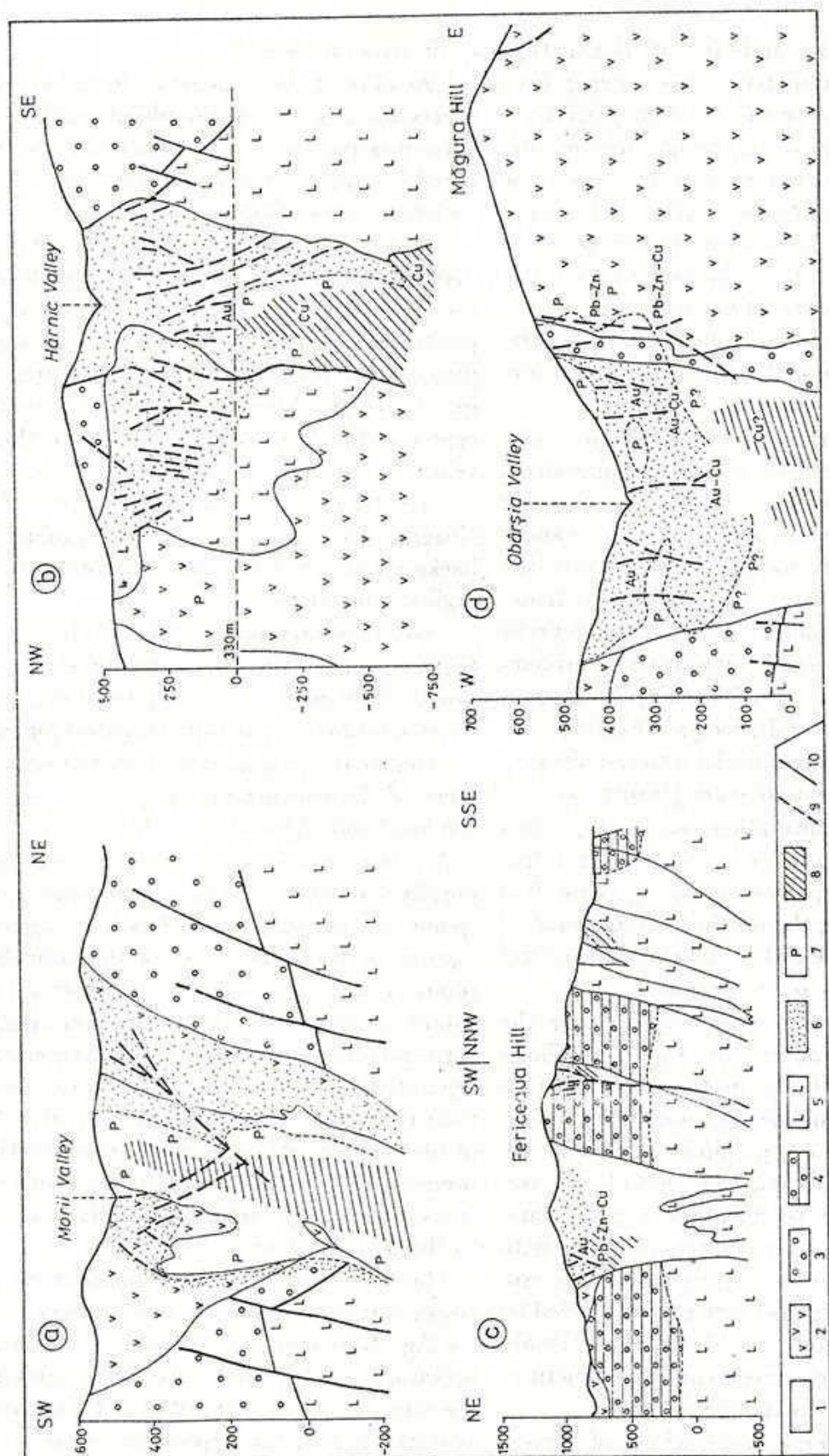


Fig. 4 - Geological sections through the porphyry copper-gold ore deposits (a, Vala Morii; b, Musariu; Muncăscas-Valea Ionului), according to Borcoș et al., 1984; Boștinescu, 1984, compared to the Măgura-Făerag structure (d). 1, quartz andesites and diorites (Sarmatian-Pannonian); 2, quartz andesites (Sarmatian-Pannonian); 3, Miocene sedimentary rocks; 4, Mesozoic sedimentary rocks; 5, Jurassic-Cretaceous ophiolitic rocks; 6-8, hydrothermal alterations (6, argillic; 7, propylitic; 8, potassic); 9, Au-Ag and base metal mineralizations; 10, faults.

As regards the continuity or discontinuity of the evolution from a porphyry type system to a vein type one, the discussion might be about the presence in the geothermal associations of some relatively "exotic" but frequent minerals, such as graphite. In this case there are two variants:

a. In the geothermal fluid the chemical reactions which led to carbon precipitation, stop the other chemical reactions specific to the porphyry-copper system; the evolution of the metallogenetic process can be continuous but the porphyry system is incompletely developed.

b. Graphite is not a "buffer" mineral, the process is probably discontinuous and the porphyry-copper system is well developed.

Coming back to the general framework of the mineralizations of the Măgura ore deposits, several similarities with other porphyry-copper subvolcanic structures, such as Valea Morii, Musariu Nou (Barza zone) and Muncăceasca-Podul Ionului (Zlatna zone) structures (Fig. 4) can be noted. In all cases the subvolcano occupies a central position within a complex volcanic structure. In case of the Măgura structure the subvolcano has also a relatively central position, marginally bordered by the andesite and quartz andesite necks (Teascu, Măcieșul Mic, Măcieșul Mare and Făerag hills) and the associated lavas (Fig. 1 B).

In the Musariu Nou structure (Fig. 4 b) there are Au-Ag vein mineralizations, dominated by the gold-pyrite-arsenic assemblage, and subordinately common sulphides and tellurides. They are mainly hosted by the subvolcanic andesitic rocks with hypogene alteration in phyllic-argillic and, marginally, propylitic facies. The porphyry-copper mineralization related to a potassic alteration zone is known in the mining works beneath the "0" m absolute height. The recent identification of the tellurides in the lower horizons of the Măgura subvolcano stresses out the existing similarities.

In the andesitic dome of the Valea Morii structure (Fig. 4 a), the Au-Ag and base metal vein mineralizations are formed subsequently to the porphyry-copper system. The phyllic-argillic alteration related to the vein mineralizations is superposed to a propylitic zone which occurs around the potassic central zone. The metallic minerals assemblage of the porphyry type is characterized by the presence of pyrite and chalcopyrite; titanium oxides (rutile) and free gold as inclusions in chalcopyrite occur as well.

Fericeaua subvolcano in the Muncăceasca-Podul Ionului structure (Fig. 4 c) probably represents an apophysis of the central body which especially penetrates the ophiolitic basement and Cretaceous sedimentary deposits, in some cases intensely altered in the thermal contact zone. Gold and base metal vein mineralizations with pyrite, chalcopyrite, bornite, sphalerite, native gold are subsequent to the porphyry copper mineralization probably developed at depth.

Conclusions

The synthesis of the available mineralogical, petrographical, metallogenetic and structural data concerning the Măgura ore deposit leads to several general conclusions, as follows:

a. The mineral assemblages and parageneses, their occurrence throughout the vein system as well as the relationships observed among the ore minerals, and between the ore minerals and the gangue ones, indicate a multistage and polyascendent circulation regime of the geothermal fluids. Thus, native gold was deposited during at least two stages stressed out by the assemblages:

- quartz, rutile, pyrite, arsenopyrite, native gold, chalcopyrite±sphalerite, with characteristic high-temperature parageneses, quartz-native gold and quartz-native gold-arsenopyrite, corresponding to the hypomesothermal deposition domain; the most important economic concentrations of native

gold, located in the veins in the western part of the structure, are related to this stage;

- pyrite, Pb, Zn, Cu sulphides, Pb, Cu sulphosalts, native gold, native silver, quartz, baryte; this stage is less significant in economic respect for gold, the metallic and gangue minerals constituting the filling of the veins in the eastern part of the structure. The described association was formed from meso-epithermal solutions which generated a mineral complex characterised by superposed parageneses and telescoping phenomena. Native gold was deposited during this stage at the end of the hydrothermal activity from low-temperature colloidal solutions.

The evolution of the metallogenic process was probably discontinuous, the two mineralization stages being delimited in time and space by complex disjunctive tectonic phenomena.

The host rock of the Au-Ag vein mineralizations is altered in phyllic-argillic facies, the neomineral association being constituted of clay minerals, quartz, carbonates, sericite, pyrite. Propylitic alterations, represented by chlorite, carbonates, albite, clay minerals, iron oxides and hydroxides, occur marginally.

b. Native gold associated to the first stage of mineralization was deposited from high-alkali solutions. In this context, potassium is a metallotherm, stressed out by the presence of this facies in a proximal position versus the vein opening. The neomineral assemblage characteristic of the potassic facies is represented by: Ti-bearing biotite, Fe-micas, hydromica, sericite, quartz. In the lower horizons this facies is partially or totally overprinted by subsequent alterations, and it can only be detected by chemical methods.

c. Barza-type amphibole andesite which hosts Au-Ag minerals is consolidated in sub-volcanic body facies. This body penetrates rocks of the ophiolitic basement, Miocene deposits and Neogene andesitic sequences, and occupies a relatively central position in the structure axis.

d. Structural, mineralogical metallogenetic data point out the existence of a gold porphyry-copper system (dioritic model) in the West Măgura subvolcano. At depth, beneath the lowermost level of the present research there might exist concentrations of economic interest of this type, probably related to a potassic zone. The similarities with the porphyry-copper type structures, little exposed by erosion, e.g. those at Valea Morii, Muncăceasca, and especially Musariu Nou, are in favour of this idea.

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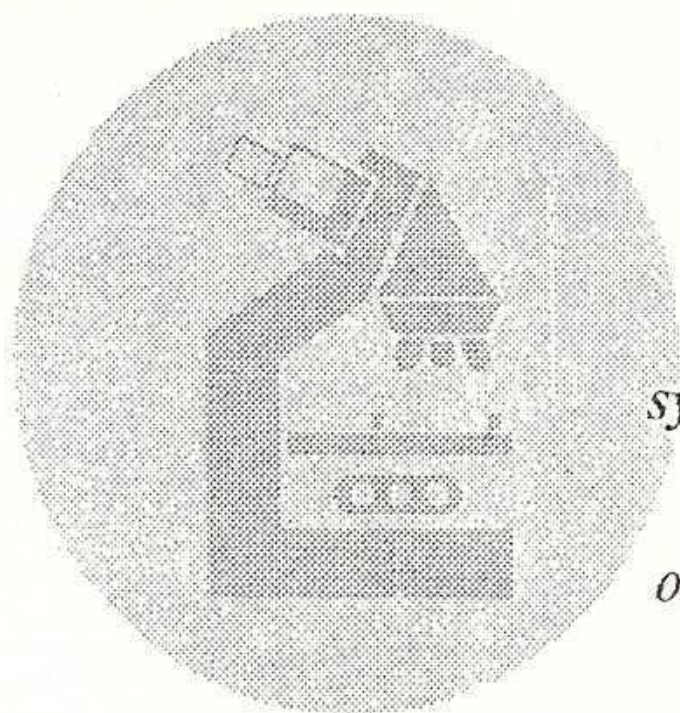
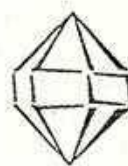
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NEW DATA ON THE MN-FE DELINEȘTI DEPOSIT, SEMENIC MOUNTAINS

Paulina HÂRTOPANU, Ion HÂRTOPANU

Institutul Geologic al României, Str. Caransebeș, nr. 1, 79678 București 32.



Key words: Gonditic ore. Quelusitic ore. Hybrid ore (=Koduritic). Metasomatism (Na, Fe⁺³, K, B, Cl, F). Hydrothermal.

Abstract: The Fe-Mn Delinești deposit (Semenic Mountains) is situated in the Sebeș-Lotru Series, which is metamorphosed in the almandine amphibolite facies and is often crossed by granite, pegmatite and hydrothermal quartz intrusions. These intrusions determined changes in the mineralogical composition of the gonditic and quelusitic ore, through temperature increase, pressure decrease, and especially metasomatism and hydrothermal phenomena. 45 minerals (7 metamorphic, 20 metasomatic and 18 hydrothermal) were described, of which 33 are new described in this deposit.

Historical Background

The first data on the Mn-Fe deposit at Delinești are mentioned by Schroeckenstein (1870, cf. Savu, 1962), who shows that the fresh ore consists of fowlerite, rhodonite and tephroite. Papp (1919, cf. Savu, 1962) deals with the oxidation zone of this deposit which, in the author's opinion, consists of pyrolusite, psilomelane and limonite. Schneiderhöhn (1955, cf. Savu, 1962) mentions the Delinești deposit, considering it similar to those from Bucovina and Czechoslovakia. The zone in which the deposit is situated was investigated from geological point of view by Roșca (1954), Savu et al. (1964). A geochemical study of this deposit was made by Ianovici (1956) and by Savu and Ianovici (1958). Mineralogical, chemical and structural data on the Delinești deposit (namely on the Valea Fieru-

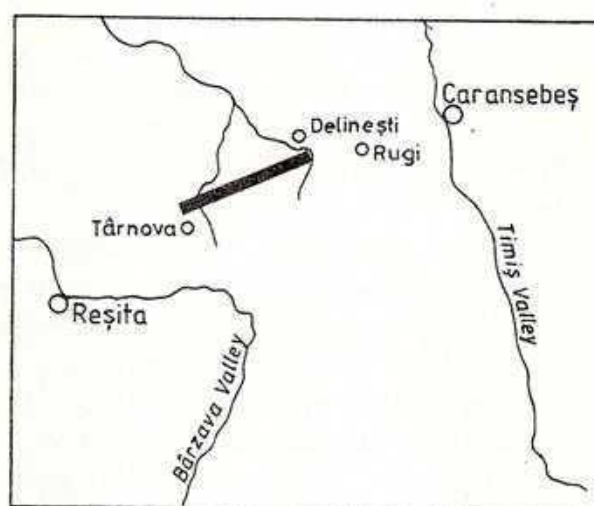


Fig. - Emplacement sketch of the Delinești deposit

lui, Tâlva Bobului and Măgura Mică sectors) are presented in a study made by Drăghici et al. (1967). Also, several sections are achieved through the deposit, whose images are based on the mining and drilling works carried out

by Special Enterprise of Mining Explorations (ISEM), between 1956–1959. Complete mineralogical, petrographic and chemical studies were made by Savu (1962). From the petrographic point of view the author establishes the following types of manganese rocks: spessartine quartzites with more than 50% quartz; spessartinite with more than 50% spessartine; carbonate with more than 50% rhodochrosite; rhodonite with more than 50% rhodonite; manganese schist with magnetite, with up to 30% magnetite; complex manganese schist; ferrimuscovite and piemontite schist; rocks bearing hydrothermal and contact minerals; oxidation zone.

From the mineralogical point of view the author describes the following minerals: *primary minerals*, formed of premetamorphic deposits as follows: magnetite, spessartine, rhodochrosite, rhodonite, pyroxmangite, dannemorite, piemontite, ferrimuscovite; *minerals connected with hydrothermal phenomena or contact minerals*, such as: shefferite, pistazite, green epidote, orthite, hematite pyrite, green hornblende, quartz; *accessory non-manganese minerals*: plagioclase, biotite, apatite, actinolite, tourmaline, clinozoisite, titanite, zircon, rutile, siderite, hematite, ilmenite, leucosene, pyrite and chalcopryrite; *minerals from the oxidation zone*: pyrolusite, psilomelane and limonite.

Dimitrescu and Popa (1973) establish a primary ore (carbonates and manganese silicates) and a secondary ore (oxides, especially psilomelane) for the Delinești deposit. Parageneses with spessartite, rhodonite-pyroxmangite, dannemorite, and carbonate are given for the primary ore. The authors propose for the minerals described the name of manganese skarnoids, comprising carbonatic and silicate rocks formed by regional metamorphism. They established the crystallochemical formulae for rhodochrosite, rhodonite-pyroxmangite, dannemorite, spessartine. Recent data on the Delinești deposit are presented by Pomârjanschi (1990). The

authors, petrographically separate tephroitic rocks, spessartitic rocks, and secondary oxidic rocks. We consider, regrettably, that the separation of the tephroitic rocks with the tephroitic, rhodonitic, dannemoritic and carbonatic subtypes (as they were separated in the Sebeș Mountains by Hârtopan, 1981) constitutes an error made by the above-mentioned authors because tephroite, as constituent mineral of the Delinești deposit, was reported as an extremely rare mineral by some authors (Savu, 1962), being not found at all by most of researchers of this deposit. Nor is the separation of the tephroitic ore type justified by our researches, which establishes improper conditions for the tephroite stability within the Mn-Fe Delinești deposit. Consequently the petrographic, geochemical and genetic remarks made by the above-mentioned authors on the "tephroitic rocks", which do not exist in fact within the deposit, are not longer valid. Complex mineralogical, petrographic, geochemical and genetic investigations were presented by Hârtopan et al. (1993).

Geological data

The metamorphics in the northern part of the Semenik Mountains which contain the manganese mineralizations at Delinești belong to the Sebeș-Lotru Series from the Getic Crystalline. They were integrated in the lithostratigraphic succession following two rather different patterns. According to the first pattern belonging to Savu (1970), the crystalline schists of the Sebeș-Lotru Series from the Semenik Mountains would consist of five complexes beginning in the base with the complex of the sillimanite paragneisses and of the carbonatic rocks (C₁), and ending at the upper part with the micaschist complex (C₄), the most developed one, from which the complex of orthoamphibolites and of the manganese formation (C₅) laterally differentiates and develops northwards. According to Savu (1962,

1964, 1970), this complex is 1,500 m thick, consisting of "banded orthoamphibolites associated with serpentinites, fine, greyish biotite quartzitic schists, as well as with Mn and Fe silicates and carbonate schists". Savu (1970) does not use here the "formation" notion in a lithostratigraphic sense but rather from the lithological and petrographical points of view.

Recently Hann et al. (1992), in agreement with Hârtopan's opinion (1982), considers that the Sebeș-Lotru Series consists of three major complexes: the *gneiss* complex, the *paragneiss* (*plagiogneiss*) complex, and the *micaschist* complex. In the framework of this lithogeometric pattern the above-mentioned authors consider that the manganese formation occupies an upper position within the median complex of the paragneisses towards the boundary with the upper micaschist complex.

Săbău (in Hann et al., 1992) states, however, that the manganese rocks constitute a marker level at the quartz-feldspar gneiss boundary (Delinești level). From the structural point of view the above-mentioned authors, but also Pomârjanschi and Pomârjanschi (1990) accept the hosting of the manganese rocks in north-eastwards trending synform.

The metamorphism of the adjacent rocks to the manganese ones as well as of the entire northern ending zone of the Semenic Mountains is conceived by Savu (1970) as being prograde, of Barrovian type, monostadial, at the level of the zone with staurolite and kyanite. The Poiana Granitoid determines thermal contact phenomena especially on the eastern flank of the body. Hann et al. (1992) support the idea of a polystadial metamorphism with two important moments, M_1 and M_2 , of similar intensities, in agreement with the pattern elaborated by Hârtopan (1981).

General data on the deposit

The Mn-Fe deposit at Delinești, situated between Valea Fierului to the northeast and

Poiana Finetului to the southwest, develops as some lenses, generally conformable with the host rocks (micaschists, gneisses or paragneisses) showing great variations in size. Thus, the thicknesses of these lenses range from some centimetres to maximum 30 m, and their extension along the strike and dip ranges from some decimetres-hundreds of metres. Based on some tectonic elements (mainly faults) checked by mining works, the Fe-Mn deposit at Delinești was divided into the following sectors (Drăghici, 1967): a) Valea Fierului, reaching 450 m in length; it comprises 10 lenses ranging between 0.70–20 m in thickness and dipping up to 200 m; b) Tâlva Bobului, with two compartments separated by a fault: an uplifted compartment situated to the east, where the ore extends along 400 m and comprises six lenses varying between 0.3–3 m in thickness, reaching up to ca. 130 m in depth, and a western compartment comprising 10 lenses which are 0.70–7.70 m thick; c) Măgura Mică, extending along 1.3 Km, including at least 20 lenses which reach 0.3–6.3 m in thickness; d) Măgura Mare about 700 m long, comprising six lenses that reach 0.6–8.3 m in thickness; e) Tâlva Socului, which is 1.3 Km long and comprises small and sporadic lenses which are 1–10 m thick; f) Poiana Finetului extending along 1.4 Km and comprising small lenses.

The structure of the ore is mainly banded as a result of the regional metamorphism massive due to a thermal metamorphism, and porphyroblastic, as a result of the great development of magnetite (Pl. II, Fig. 1) or albite (on a former banded structure). It is to note the presence of numerous veins (millimetre to centimetre, more rarely decimetre-sized) that cross the banded metamorphic ore (Pl. I, Figs. 3, 4). The ore is compact and hard. The colour differs depending on the prevailing minerals: yellow when acmite or spessartite-calderite prevail; pink when pyroxmangite or rhodonite dominate; black when hematite is prevalent; grey, when the manganese carbonate prevails, etc.

Mineralogy and petrography of the deposit

The Mn-Fe Delinești deposit is of silicate type (60%), less carbonatic (30%) and oxidic (10%). Known so far as a Mn deposit, the Delinești deposit, following the recent mineralogical investigations (HârtoBANU et al., 1992), turned out to be a Mn-Fe deposit, a composition justified by the presence in a relatively high amount of hematite, magnetite but also of trivalent iron within the composition of some minerals such as: acmite, spessartine-calderite, Mn-phlogopite, ferrimuscovite, piemontite, etc.

According to the mineralogical composition, which reflects the composition of the premetamorphic material, the ore at Delinești belongs to two important petrographic types: 1) the silicate or gondite type, consisting mainly of spessartine, quartz, magnetite, apatite, hematite; 2) silicate-carbonatic or quelusitic type formed of rhodochrosite, pyroxmangite, rhodonite, tephroite (?), Mn-humite, apatite. In the gonditic ore, the quartz is excessive, while the quelusitic ore is subsaturated in silica. These two types of metamorphic ore, both the spessartitic and the silicate-carbonatic one, underwent metasomatic, thermal, or even hydrothermal modifications, determining the appearance of a third ore type; (3) the hybrid (koduritic) ore. Thus the thermal metamorphism determined the occurrence of the magnetite porphyroblasts (Pl. II, Fig. 1), the Mn-anthophyllite, the Mn-tremolite, etc. as well as of the grossular and epidote within the rocks in the immediate vicinity of the ore. The Fe^{3+} metasomatism (accompanied by a pressure decrease and an increase in the oxygen fugacity) determined the appearance of the following minerals: spessartine-calderite, acmite, hisingerite, hematite, etc. The Na metasomatism led to the formation of the following minerals: acmite (Na Na^+ and Fe^+ metasomatism), yellow alkali amphiboles (Na metasomatism), dravite (Na, B, K metasomatism),

etc. The fluorine and boron metasomatism is reflected by the following newly formed minerals: Mn-humite, apatite, phlogopite, fluorine-tremolite, etc. The chlorine metasomatism led to the manganpyrosmalite, friedelite formation, etc. The last category of hydrothermal type minerals occurs as veins (unoriented) or clusters in the former ore, constituting together with the metasomatic ones the hybrid ore.

Therefore we shall further describe three genetic mineral categories which also reflect the order of formation and the percentage of quantitative participation in the ore composition:

A. Metamorphic minerals, formed as a result of regional metamorphism, show the highest (cca. 70%) participation in the deposit composition;

B. Metasomatic minerals, generated by a thermal metamorphism with a lower percentage (cca. 20%);

C. Minerals of hydrothermal type with a lower participation (cca. 10 %), but present within the ore.

A. Metamorphic minerals

Spessartine

It is the most widespread mineral from the Mn-Fe Delinești deposit, constituting the principal mineral of the gondite type ore. The mineral parageneses, chemical composition and genesis of this mineral were described in another paper (HârtoBANU et al., in press).

Pyroxmangite

Pyroxmangite is a main constituent of the quelusitic type manganese ore. It is associated with the old rhodochrosite, rhodonite, magnetite, dannemorite, apatite (all of them metamorphic minerals). From the chemical point of view the pyroxmangite at Delinești (Tab. 1) differs from the pyroxmangite at Răzoare by much lower FeO contents. The FeO, Fe_2O_3 , MgO, CaO contents of the pyroxmangite at Delinești are close to those at Dadu, Oița (Bistrița Mountains). The difference among

these pyroxmangites is given by subsequent evolution, although they had almost identical compositions: the pyroxmangite within the manganese deposits from the Bistrița Mountains evolved towards dannemorite, while that at Delinești underwent an obvious baritization process. The baritization process shows two aspects: (1) a corrosion of pyroxmangite by barite (Pl. 1, Fig. 5) and (2) pyroxmangite remnants within barite (Pl. 1, Fig. 6). Because of the baritization process, there occur high Ba contents in the spectral analyses of the pyroxmangites at Delinești (Ba=1000 ppm), as is shown in Table 2. The relatively high Ti

contents of some pyroxmangites can be explained by the presence of pyrophanite as fine, microscopic inclusions; the same explanation is valid for rhodonite, too.

Rhodonite

Rhodonite is less frequent than pyroxmangite and much less frequent than its later vein-like variety, formed after the regional metamorphism. Macroscopically it is intense pink in colour, thus differing from pyroxmangite, which is pink-russet. It forms bandings with rhodochrosite, dannemorite, spessartine, hematite. Chemically it resembles

Table 1
Chemical composition of the pyroxmangite at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	P ₂ O ₅	Total
D 56 A	44.71	0.06	0.14	2.00	8.72	37.98	3.59	2.32	0.23	99.75
D 98 A	46.27	0.02	0.62	1.19	5.72	39.50	2.83	3.53	0.25	99.93
D 48 A	43.51	0.05	0.29	1.02	5.90	41.64	4.25	3.03	0.39	100.00
D 1	47.26	0.20	0.10	2.22	4.03	38.57	3.35	3.70	0.09	99.52
D 13 A	47.36	0.06	0.11	1.64	0.46	41.32	3.80	4.60	0.17	99.52
Răzoare	45.16	0.01	0.00	3.19	18.57	28.73	1.83	1.69	0.15	99.33
Oița	46.17	0.09	0.03	1.11	6.96	39.78	0.91	1.97	0.03	99.62

Table 2
Trace elements within rhodonite and pyroxmangite (ppm)

Sample	Ti	Zr	Y	Cr	V	Sc	Ni	Co	Cu	Zn	Sr	Ba
1 ST Rhodonite	30	10	15	2.5	42	3	70	44	14	210	95	1000
D 37 "	46	11	5	2.0	9	3.5	70	110	2.5	270	170	1000
D 47 "	435	16	5	4.0	19	3	125	250	6.5	300	300	1000
D 53 "	750	57	33	13.0	38	5.5	58	215	90	100	65	1000
D 68 "	170	40	9.5	17.0	13	3.5	66	125	4.5	100	70	1000
D 48 Pyroxmangite	210	30	16	9.0	20	3.5	57	56	33	100	250	1000
D 54 "	320	30	17	18.0	32	5.5	95	90	25	400	48	300
D 56A "	250	23	13	11.0	33	4.5	100	95	3	420	5	300
D 59 "	420	25	19	14.0	42	6	105	100	4	300	52	300
D 98 "	42	10	5	2.0	5	3	57	215	15	340	280	1000

Ga, Ge and Be is between 1-9 ppm.

pyroxmangite. The difference lies in the fact that rhodonite has a much higher content in MnO and CaO, while pyroxmangite has higher FeO and MgO contents (Tab. 3). The trace elements of rhodonite show qualitative and quantitative similarities to those of pyroxmangites (Tab. 2). The Ba content within rhodonites exceeds 1000 ppm, which can be explained by its close association with barite and barium feldspar, in the case of the vein-like variety, and by the baritization process, in the case of the metamorphic variety. The sensibly higher Ti content of rhodonite, comparable with that of pyroxmangites, is explained by the close association of pyrophanite, most often with rhodonite (especially with the vein-like one) than with pyroxmangite (Tab. 3).

nemorite on pyroxmangite was not noticed as is the case with the manganese deposits in the Bistrița Mountains. This fact can be explained by the different local conditions that consisted especially in the different fugacity of oxygen, water, hydrogen, etc.

The chemical composition of the dannemorite is noted in Table 4.

Magnetite

The metamorphic magnetite forms bandings with rhodochrosite, pyroxmangite, rhodonite, dannemorite, being a frequent mineral in the quelusitic type ore. It shows xenomorphic, slightly oriented grains differing from the idiomorphic magnetite porphyroblasts, statically grown in the subsequent stages of the ore evolution.

Table 3
Chemical composition of the rhodonite at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	P ₂ O ₅	Total
D 37 A	45.35	0.01	0.74	0.92	2.66	43.32	2.49	3.91	0.22	99.62
D 47	46.00	0.06	0.52	1.76	1.23	43.22	1.74	4.66	0.63	99.82
D 68 A	45.61	0.35	1.78	0.62	1.47	44.63	1.45	3.32	0.34	99.57
D 92 A	45.23	0.01	0.60	0.83	3.41	44.05	1.76	3.68	0.37	99.94
D 65 A II	42.89	0.15	0.22	1.42	3.64	44.92	2.25	3.43	0.24	99.16

Table 4
Chemical composition of the dannemorite at Delinești

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	H ₂ O ^H	Total
D 62 F	53.88	0.72	3.47	11.42	14.77	12.80	0.73	2.01	99.80

Dannemorite

It is an old metamorphic mineral; it forms bandings with rhodochrosite, spessartine, rhodonite, pyroxmangite, magnetite, hematite. Dannemorite appears as large (up to 1 cm) crystals, oriented and sometimes bent or folded. It is frequently cummingtonite type twinned. The fibrous, white-grey variety, optically resembling the prismatic dannemorite, is more rarely found. The great development of a younger metamorphic generation of dan-

Hematite

The old metamorphic hematite forms banding with spessartine, quartz, more rarely pyroxmangite or dannemorite. The metamorphic hematite is the result a regional metamorphism of some deposits that contained hydrated iron oxides, siderite, etc., intercalated in the premetamorphic manganese deposits. Table 5 presents the chemical composition of some metamorphic hematites (D₂, D₄) and of some vein-like ones (D₅, D₁₁). The chemical

composition of the two hematite types of varied origin do not differ.

Hematite

The vein-like hematite forms clusters and veinlets in the primary metamorphic ore,

Table 5
Chemical composition of the hematite at Delinești

Sample	SiO ₂	TiO ₂	Fe ₂ O ₃	FeO	MnO	P ₂ O ₅	Total
D 2	1.51	2.53	94.89	0.12	0.36	0.31	99.72
D 4	1.32	2.22	94.13	0.38	1.94	0.91	99.90
D 5	1.63	2.12	95.18	-	0.68	0.20	99.81
D 11	1.71	3.41	91.71	-	2.04	0.57	99.44

Apatite

It occurs in the metamorphic ore of gondite type as well as in that of quelusitic type. In the Delinești deposit apatite is a constituent and not an accessory mineral of the ore. In thin sections apatite layers (a few mm to 1 cm thick), banded with rhodochrosite, pyroxmangite, spessartite, magnetite, were noticed.

B. Metasomatic minerals

Spessartine-calderite

The occurrence, optical properties, paragenesis, chemism and genesis of this mineral were described in another paper (Hârtopan et al., in press). This mineral formed through Fe⁺³ metasomatism at the expense of the old metamorphic spessartine.

Acmite type alkali pyroxene

It formed through Na and Fe⁺³ metasomatism upon an old hedenbergite type pyroxene. A complete description of this mineral will be made in another paper.

being one of the main constituents of the hybrid ore. It is associated with spessartine-calderite, alkali pyroxene, vein-like rhodonite, pyrophanite, monazite (Pl. II, Fig. 2).

Rhodonite

The vein-like rhodonite is much more widespread than the metamorphic rhodonite and is associated with hematite, Mn-calcite (Pl. II, Fig. 4), spessartine-calderite.

Magnetite

The porphyroblastic magnetite is idiomorphic and statically grown. It is formed after the regional metamorphism, cross-cutting the banding (Pl. II, Fig. 11), as a result of a thermal metamorphism of low pressure and relatively high temperature. This magnetite is associated with Mn-tremolite, Mn-anthophyllite, apatite. The chemical composition of magnetite (Tab. 6) indicates that it is a slightly manganiferous one. The Al₂O₃ content may be due to spessartine inclusions or replacements of Fe⁺³ by Al⁺³ in the spessartite framework,

Table 6
Chemical composition of the magnetite at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	Total
D 52	0.89	2.88	1.06	75.07	17.66	2.32	99.88
D	1.55	1.88	1.21	73.19	17.60	4.37	99.80

while the TiO_2 contents may be due to the substitution of Fe^{+3} by Ti.

Sitaparite

It is a bixbyite in which part of the Fe^{+3} is replaced by Ca. In polished sections it is vaguely yellow, a tint which distinguishes it from braunite, jacobsonite or magnetite. It is isotropic. The zonal structure and the leucite type twins are very characteristic.

Braunite

In polished sections it is untwinned, weakly anisotropic and equigranular. It is associated with hematite, jacobsonite, magnetite, sitaparite, hausmannite, rhodonite, spessartine.

Mn-phlogopite

It is an important mineral in the hybrid type ore. It is brown-yellowish to red-brown in colour. In thin section it is colourless, pale yellow or brownish red with obvious pleochroism in these shades. The chemical composition of the Mn-phlogopite is noted in Table 7. Statically grown (Pl. II, Fig. 3) it is often associated with aegirite type alkali pyroxenes, yellow alkali amphiboles, microcline, hematite, pyrophanite, piemontite.

It occurs in the metasomatic veins associated with hematite, monazite, alkali pyroxenes, braunite, sitaparite, but also in the metamorphic ore.

extinction ($c\wedge\beta$) of 30° , low birefringence colours, a small optic axial angle ($2V_\alpha=25-30^\circ$) and are untwinned.

Mn-tremolite

In thin section it is colourless, vaguely green (when grading to actinolite). It is not pleochroic. It differs from dannemorite by smaller refractive indices, lower birefringence and a less frequent twinning. Within the manganeseiferous tremolite variety only one of the five places of the Y position from the network (occupied by Mg and Fe) can be occupied by Mn so that Mn content in most tremolites or actinolites is not higher than 0.3% because the crystalline network does not allow it.

Mn-anthophyllite

It occurs as grey, white-grey or white fibrous aggregates, colourless in thin sections. The habitus does not allow the exact determination of the optical properties. It was determined by Rx and IR analyses. It is associated with magnetite, Mn-tremolite.

Mn-apatite

The vein-like, Mn-apatite appears as clusters and veins of slightly green idiomorphic grains. It is associated with phlogopite, alkali pyroxenes, hematite, yellow alkali amphiboles. It is probably a fluorine apatite.

Table 7
Chemical composition of the Mn-phlogopite at Delinești

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	K_2O	H_2O^+	F	Total
D 9	38.52	1.39	11.90	5.76	7.40	5.95	16.75	8.21	1.96	2.02	99.86
D 22	45.20	1.93	9.92	0.64	7.00	3.66	17.48	10.15	1.80	2.00	99.78

Yellow alkali amphiboles

These are amphiboles specific for the hybrid ore, being closely associated with alkali pyroxenes, vein-like rhodonite, hematite, microcline, spessartite-calderite, phlogopite (Pl. II, Fig. 2). In thin section they are yellow, show

Hausmannite

It is the most frequent Mn oxide next to hematite and magnetite. In polished section it is bireflex, anisotropic and twinned. It occurs associated with magnetite, hematite, braunite in the hybrid type ore.

Monazite

It is an accessory mineral within the veinlets that occurred after the regional metamorphism, associated with pyrophanite, alkali pyroxenes, spessarine-calderite, hematite, phlogopite.

Dravite

It is an accessory mineral of hybrid type ore. In thin sections it is pleochroic, with brown shades, shows approximately regular separations along two directions and short prismatic habitus. It is positive biaxial with $2V\gamma=60-70^\circ$. It has twins of two individuals after (100) (Pl. II, Fig. 6).

Hisingerite

Amorphous variety. In thin section it is orange to gold-brown in colour, isotropic.

Mn-humite

It was determined in a sample at Tâlva Bobului after the specific twinning. It is associated with the old metamorphic rhodochrosite. It likely originates from tephroite through a metasomatism with F and OH.

C. Hydrothermal type minerals

The mineral assemblages of this type form veins and clusters in the hybrid ore of gonditic or quelusitic type (Pl. I, Figs. 3, 4). The veinlets range between a few millimetres to a few centimetres in thickness. In the approximate order of frequency these minerals are: albite, microcline, barite, rhodonite, manganocalcite, calcite, brown manganiferous chlorite, neotokite, bementite, hyalophane, manganpyroxmalite, friedelite, alabandite, dannemorite.

Albite

It occurs associated with rhodonite, microcline, quartz but also in the metasomatic associations with acmite type alkali pyroxenes, yellow alkali amphiboles, hematite, piemontite. It shows fine polysynthetic twins. The high values of the optical axial angle, the small refractive indices, the extinction angle ($\alpha:001=20^\circ$) and the low birefringence indicate

a low temperature albite, confirmed by the Rx and IR data. Sometimes, albite is transformed into a tiny red, leafy mineral; it likely belongs to a category of minerals of kaolinite or palygorskite type. The red colour and the high birefringence are probably due to the presence in its chemical formula of the Fe^{3+} and Na cations, the more so as the mineral was observed newly formed and on alkali pyroxenes.

Microcline

It is a low temperature microcline variety. The parameters of the elementary cell determined from the Rx analysis data are: $a=8.581\text{Å}$, $b=12.972\text{Å}$, $c=7.206\text{Å}$, and the volume of the elementary cell $=718.606\text{Å}^3$.

Barite

It occurs as large tabular crystals (20 x 5 mm in cross section) in veinlets that cross the quelusitic or gonditic ore, being associated with carbonates and quartz. Barite occurs also as irregular grains when associated with Ba feldspars (Pl. III, Fig. 3) or when it shows laced aspect or corrodes pyroxmangite (Pl. I, Figs. 5, 6). The following associations are very frequent and specific for the Delinești ore: barite + brown manganese chlorite (Pl. III, Fig. 4) and barite + neotokite. In the later assemblage, barite seems to replace neotokite. In thin section barite is colourless, has a cleavage after three directions and a $2V\gamma=30^\circ$. It rarely shows polysynthetic twins with irregular boundaries among individuals.

Rhodonite

It occurs in the hydrothermal type veins in addition to albite, quartz, Mn-calcite, hematite, pyrophanite. As compared to the metamorphic rhodonite or the vein-like one, the hydrothermal rhodonite shows a very tiny granulation.

Mn-calcite

Macroscopically, it is white, vaguely pinkish in colour and shows large idiomorphic crystals. It is associated with rhodonite, hematite (Pl. II, Fig. 4) or with quartz and green mangan-

iferous chlorite. It was determined by Rx and IR analyses. The chemical composition of the Mn-calcite is present in Table 8. yellow colours. It is often associated with rhodonite and spessartine.

Table 8
Chemical composition of the Mn-calcite at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	CO ₂	Total
D 10	0.97	0.0	0.05	0.12.	0.0	12.18	2.3	40.1	43.9	99.65

Calcite

It is white, the colour indicating the lack of the rhodochrosite term. Two calcite assemblages are known: calcite + neotokite and calcite + quartz + pyrite + chlorite.

Brownish manganiferous chlorite

In thin section it is yellow, slightly brownish, fibrous. It is closely associated with neotokite and barite (Pl. III, Fig. 4).

Neotokite

It is the hydrated and amorphous variety of the brown manganiferous chlorite; neotokite usually forms amorphous, isotropic nuclei, surrounded by anisotropic, fibroradial bands of manganiferous brown chlorite.

Bementite

It is a brown-reddish lamellar, sometimes fibrous manganiferous chlorite. It has a high birefringence and a $2V_{\alpha}=0$. It often occurs associated with the alkali pyroxenes, with the yellow alkali amphiboles but also with albite, barite.

Hyalophane

It occurs associated with rhodonite and barite (Pl. III, Fig. 3) as discordant veinlets in the primary ore or in irregular clusters when it is associated with acmite alkali pyroxenes. It shows discontinuous and irregular twins.

Manganopyrosmalite

It occurs in the hybrid type ore when this becomes yellow. It much resembles muscovite from which it differs by the pleochroism with

Friedelite

It was optically and X-ray determined. The ore shows small, short-prismatic grains with perfect basal cleavage, very similar to micas. It is colourless in thin sections, slightly yellowish, with weak pleochroism. It differs from micas by the smaller refractive indices. It is negative uniaxial.

Alabandite

In thin sections it is opaque, which indicates a ferriferrous alabandite variety. In reflected light it is grey, has green inner reflexes and is isotropic. It contains fine chalcopyrite inclusions with which it is also associated in veins.

Dannemorite

A very recent dannemorite generation seems to have been formed on the brown manganiferous chlorite. It is acicular and shows cumingtonite type twins (Pl. III, Fig. 6).

The minerals within the surrounding rock

Some minerals from the rock surrounding the Delinești deposit were also determined and described.

Grossular

It occurs within skarn type rocks from the immediate vicinity of the deposit which, in addition to grossular, also contain: epidote, calcite, Ca-feldspar. Grossular was optically, Rx, IR, and chemically determined. It shows zonations

and polysynthetic twins (Pl. III, Fig. 5). The chemical composition of grossular is given in Table 9.

and is red-ruby in colour. It is closely associated with ferrimuscovite on whose cleavage planes it develops, and with hematite.

Table 9
Chemical composition of the grossular at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	MnO	FeO+Fe ₂ O ₃	CaO	Total
D 36	40.20	1.32	5.43	0.27	11.32	41.64	99.85
D 36A	40.30	1.22	5.61	0.43	12.18	40.21	99.95

Ferrimuscovite

The ferrimuscovite is a frequent mineral in the micaschists, which have been largely transformed due to their vicinity with the manganese ore. The most important transformations are due to the strong oxidation stage, which, as already mentioned, determined remarkable mineralogical modifications in the deposit, mainly characterized by the occurrence of the minerals with Fe³⁺ in their composition.

Table 10 presents the chemical composition of ferrimuscovite. The lack of FeO and the presence of Fe only as Fe³⁺ are noticed.

A few genetic considerations

The mineralogy of the Mn-Fe Delinești deposit is the result of the metamorphism of the premetamorphic Mn-carbonate or siliceous material mixed with Mn and Fe hydrated oxides. The first type of material gave rise to the quelusitic ore, and the second type is responsible for the formation of the gonditic ore. The metamorphism of the prevailingly carbonatic deposits, produced in the almandine amphibole facies, determined the appearance of tephroite (?), rhodonite, pyroxmangite and braunite, according to the following reactions:

Table 10
Chemical composition of the ferrimuscovite at Delinești

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	K ₂ O	H ₂ O	F	Total
D 42	46.86	1.19	24.13	8.08	0.0	2.16	2.24	11.15	2.0	1.85	99.67

Spessartine-calderite

The garnet within the above-mentioned micaschists is of spessartine-calderite type, originating from the former almandine garnet of the rock. It exhibits a tiny granulations, is yellow, idiomorphic and isotropic.

Piemontite

It was microscopically noticed in the micaschists with ferrimuscovite. It displays a tiny granulation, a prismatic or irregular habitus

- rhodochrosite + SiO₂ → rhodonite, when Mn/Si=1;
- rhodochrosite + SiO₂ → tephroite, when Mn/Si>1;
- rhodochrosite + SiO₂ → braunite, at higher O₂ fugacity.

The present lack of tephroite from the deposit can be explained as a consequence of a high O₂ fugacity since the paroxysmal phase of the metamorphism of the manganese sedimentary deposits, even if the Mn concentration was higher than that of silicon. The high oxy-

gen fugacity in this metamorphic stage is documented by the existence of some primary minerals with iron and manganese in high oxidation states (hematite, braunite, bixbyite, etc.). If one admits that there existed, however, zones from the deposit (at present devoid of hematite, bixbyite, etc.) within which the oxygen fugacity was not high, therefore favourable conditions for the tephroite genesis, this could not survive owing to the high oxygen fugacity from the stages subsequent to the metamorphism. The Mn-Fe Delinești deposit underwent, at least in the last important phase of its evolutions, a subsequent oxidation process materialized by minerals specific for the main metamorphic phase (spessartite-calderite, acmite type pyroxenes, hematite, etc.). In this oxidation stage, tephroite (supposing that it existed) changed into rhodonite or hausmannite, according to the reaction:



These transformations were noticed to a less extent also in the case of rhodonite and pyroxmangite. Thus rhodonite changes into hausmannite according to the reaction: $6 \text{MnSiO}_3 + \text{O}_2 = 2\text{Mn}_3\text{O}_4 + 6\text{SiO}_2$, or in braunite: $7\text{MnSiO}_3 + 3/2 \text{O}_2 = 3 \text{Mn}_2\text{O}_3 + \text{MnSiO}_3 + 6\text{SiO}_2$. Pyroxmangite also underwent sometimes an oxidation process changing into jacobsite and rhodonite: $7(\text{Mn, Fe})\text{SiO}_3 + 3/2 \text{O}_2 = \text{MnFe}_2\text{O}_4 + \text{MnSiO}_3 + \text{SiO}_2$.

The gonditic ore resulted from the metamorphism of a material which consisted of a mixture of Mn and Fe oxides and hydroxides with silica and clay. Thus, the following minerals were formed: spessartite, quartz, dannemorite, magnetite, hematite, braunite, bixbyite, pyrophanite.

It is largely worldwide accepted the division of all the manganese deposits in two large categories, volcanic and nonvolcanic, according to the Mn source, which can be represented by the volcanism in the former case, and by the alteration crust in the latter case. Therefore, the old gonditic-quelusitic metamorphic ore from the Delinești deposit originates from

an initially nonvolcanic sedimentary material which, metamorphosed in the almandine amphibolite facies, led on the whole to the present mineralogical composition. Beside the nature of the initially premetamorphic material, the mineralogical evolution of the Mn-Fe Delinești deposit was determined by temperature and oxygen fugacity. The temperature, unaccompanied by an oriented pressure, increased due to the existence of a granitic body in the vicinity of the deposit. In the case of the thermal metamorphism, metasomatism greatly contributes to the appearance of new mineral phases, especially in the case of the manganese deposits. This led to the formation of the statically grown minerals such as magnetite, spessartine-calderite, Mn-antophyllite, metasomatic pyrophanite, etc. The oxygen fugacity was high since the main metamorphic stage, especially in the spessartine-oxidic ore, a situation suggested by the appearance of some minerals in a high oxidation state (Fe^{+3} , Mn^{+3}) (hematite, bixbyite, braunite). Within the quelusitic ore the above-mentioned minerals appear during a phase, subsequent to the metamorphism, which we named oxidation phase. Thus the silicate minerals, specific to this ore such as tephroite, rhodonite, pyroxmangite were transformed (some of them totally, e.g. tephroite) into hausmannite, braunite, jacobsite. The low stability of tephroite as compared to that of rhodonite and pyroxmangite, suggests the existence of a tephroite with a low iron content, an instable component in this oxidation phase. On the other hand, the pyroxmangite at Delinești has a relatively iron poor composition (close to that of rhodonite), which also explains its great stability with respect to tephroite. On the whole, this oxidation phase comprises the formation of the minerals of metasomatic type, whose origin is uncertain owing to the exo- and endo- (in situ) contribution of Na, Fe^{+3} , K, F, B, Cl, OH, etc. Another, weakly represented stage in the ore evolution is the occurrence of the minerals of hydrothermal type, whose ori-

gin would be linked to the residual granitic magma rather than to the metamorphic remobilizations. The subsequent weathering, likely began during the Cretaceous time, has been almost ineffective in the case of the Delinești deposit, which is prevailingly Mn-silicatic and has no alteration zone but only a very thin crust of maximum a few centimetres.

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Plate I

- Fig. 1** — Spessartine (black) banding with dannemorite + quartz (white). Sample D 4, waste dump of gallery 1, N +, x 20.
- Fig. 2** — Dannemorite (grey), rhodochrosite (white), magnetite (black) banding. Sample D 41, waste dump of gallery 2, N +, x 20.
- Fig. 3** — Spessartine (black) crossed by a lot of veinlets with hydrothermal minerals. Sample D 11, waste dump of gallery 1, N +, x 20.
- Fig. 4** — Small, discordant veins within spessartite (black) with baryte (white) and barium feldspars (grey). Sample D 11, waste dump of gallery 1, N +, x 20.
- Fig. 5** — Pyroxmangite (dark grey with two cleavage directions), corroded by baryte (light grey). Sample D 94, waste dump of gallery 2, N II, x 20.
- Fig. 6** — Pyroxmangite rests (vaguely grey white with cleavage) included in baryte (dark grey without cleavage), hematite (black). Sample D 11 P, waste dump of gallery 1, N II, x 20.



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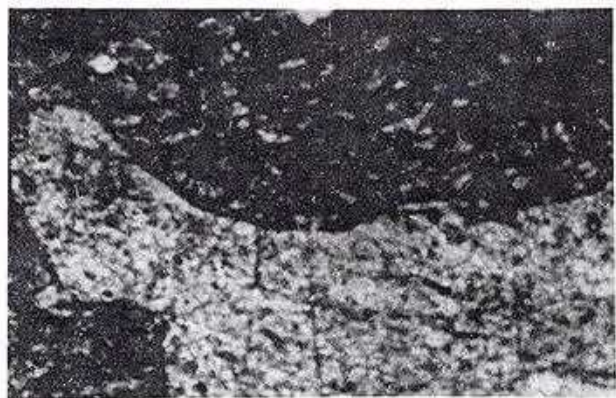
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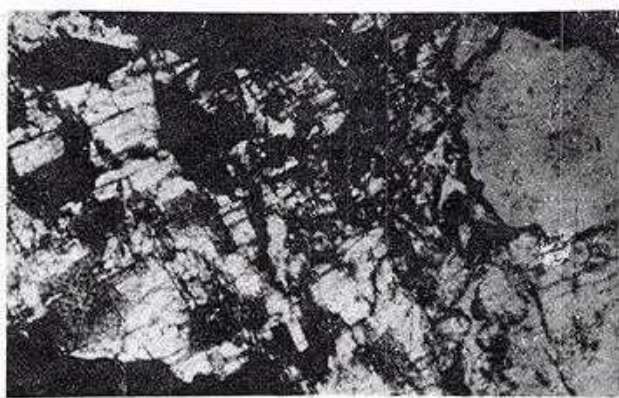
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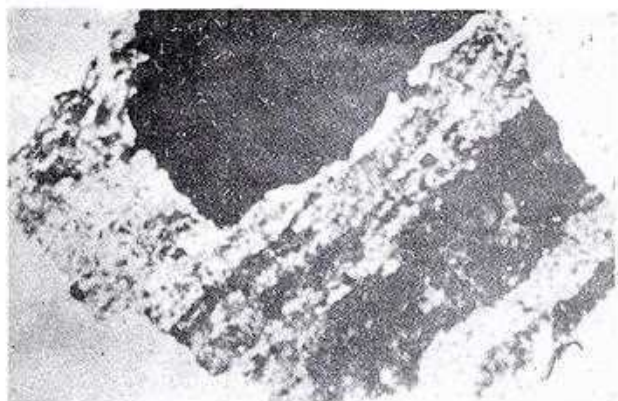


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Plate II

- Fig. 1** — Magnetite porphyroblast (Black) statically grown in the banded carbonate ore. Sample D 53, waste dump of gallery 2, N II, x 20.
- Fig. 2** — Yellow alkali-amphibole (large, short prismatic crystal), quartz (white), albite (grey, twinned), hematite (black). Sample D 22a, waste dump of gallery 1, N +, x 20.
- Fig. 3** — Mn-phlogopite (short prismatic, grey), statically grown, albite (white), statically grown, albite (white), hematite (black). Sample D 22b, waste dump of gallery 1, N II, x 20.
- Fig. 4** — Hematite (black), rhodonite (white, vaguely grey, with cleavage), Mn-calcite (white), vein. Sample D 14c, waste dump of gallery 1, N II, x 20.
- Fig. 5** — Mn-humite (twins) in carbonate ore. Sample D 0, Tálva Bobului, N +, x 40.
- Fig. 6** — Huebnerite vein (large, twinned crystal), quartz (white), crossing the spessartitic ore (black). Sample D 91, waste dump of gallery 2, N +, x 40.



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Plate III

Figs. 1, 2 — Baryte vein (white-grey, with cleavage in N II), barium feldspars (twins in N+) crossing a spessartitic ore (black in N +). Sample D 11, waste dump of gallery 1, x 20.

Fig. 3 — Barium feldspars (twinned) + baryte (white, tiny). Sample D 11, waste dump of gallery 1, N +, x 20.

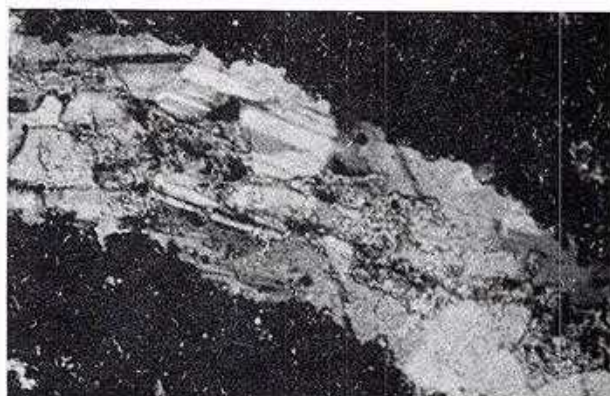
Fig. 4 — Baryte (light grey, slightly punctiform), brown-white manganiferous chlorite (bands round baryte or isolated rosettes), fibrous, rhodonite (with cleavage), hematite (black). Sample D 73, waste dump of gallery 2, N II, x 20.

Fig. 5 — Grossular (twins) + calcite (white). Sample D 36, waste dump of gallery 1, N +, x 40.

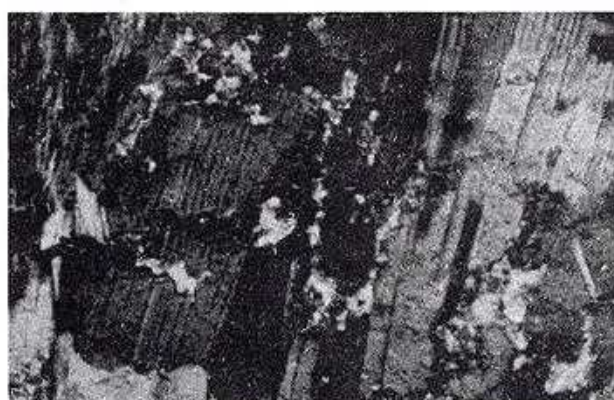
Fig. 6 — Dannemorite (acicular, twinned) grown on brown manganiferous chlorite (white, fibrous), baryte (grey, slightly punctiform), hematite (black). Sample D 11, waste dump of gallery 1, N +, x 40.



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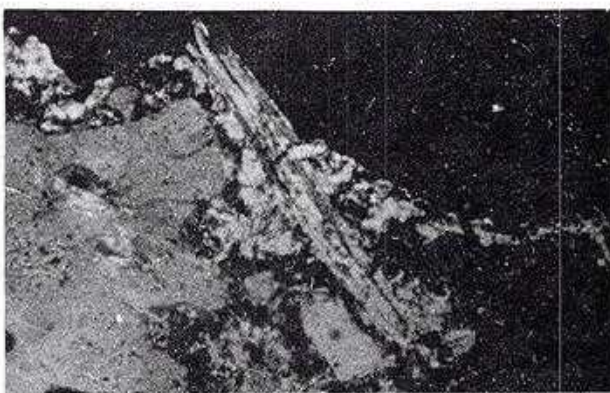
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CONSIDERATIONS REGARDING THE EPIGENETIC MINERALIZATIONS IN THE CÂRLIBABA-ȚIBĂU ZONE (BISTRÎȚEI MOUNTAINS))

Viorel MACALEȚ

Mircea-Ionuț PETRESCU

Polytechnical University, Splaiul Independenței 313, 77206 București.



Key words: Metamorphics. Sulphide. Sulphosalts. Paragenesis. Microprobe analysis. X-ray data. Chemical composition. Epigenetic mineralizations. East Carpathians-Bistriței Mountains. Romania.

Abstract: The main metallic minerals are pyrite, arsenopyrite, sphalerite $\pm$ cubanite, chalcopyrite, galena, tetrahedrite, bournonite, pyrargirite and gangue ones are quartz, albite, siderite, calcite, chlorite. If both the metallic minerals and the gangue minerals are taken into account, four paragenesis can be outlined. In comparison with host metamorphic rocks, this mineralizations is epigenetic in character.

Geological setting

Geostructurally, the Cârlibaba-Țibău zone belongs to the Northern compartment of the Crystalline-Mezozoic Unit of the East Carpathians Chain.

Up to the present, most of the researchers (Balintoni et al., 1983, Săndulescu, 1984, Vodă, Vodă, 1985, Kräutner, 1988), agree with the idea that the Crystalline-Mezozoic Unit consist of a system of Alpine Mesocretaceous Nappes (Infra-bucovinian, Sub-bucovinian and Bucovinian), each of them comprising a sequence of pre-Alpine (Hercynian) Nappes.

The sequence of the pre-Alpine Nappes is the following:

- Rodna Nappe, acting as a bottom and consisting of the Rebra Group formations;

- Pietrosul Bistriței Nappe, comprising the Negrișoara and Pietrosul Bistriței formations;

- Putna Nappe, comprising the Tulgheș Group;

- Chiril Nappe, comprising the Chiril Formation;

- Rarău Nappe, consisting of the formations of the Bretila Group.

The present study is based on the examination of a large number of samples, taken from the waste dumps of several old ore exploitations opened in the eighteenth century by the Austrian Company Manz (in Walter, 1876) and reopened at different time interval up to nowadays (in Nedelcu, 1977). These works are located on the right slope of the Cârlibaba brook in the vicinity of the confluence with Bistrița river - Fluturica sector - and also on the Canal brook, this last one being a right tributary of the Țibău brook.

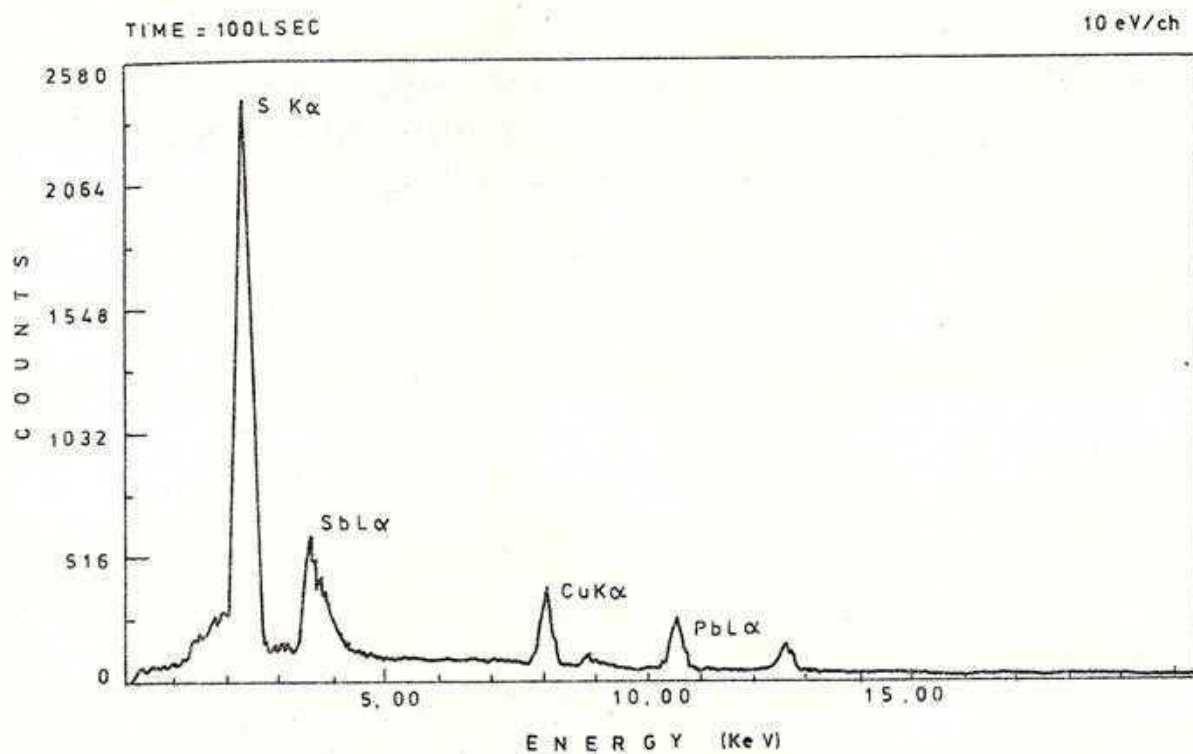


Fig. 1 - Characteristic energy spectrum for bournonite.

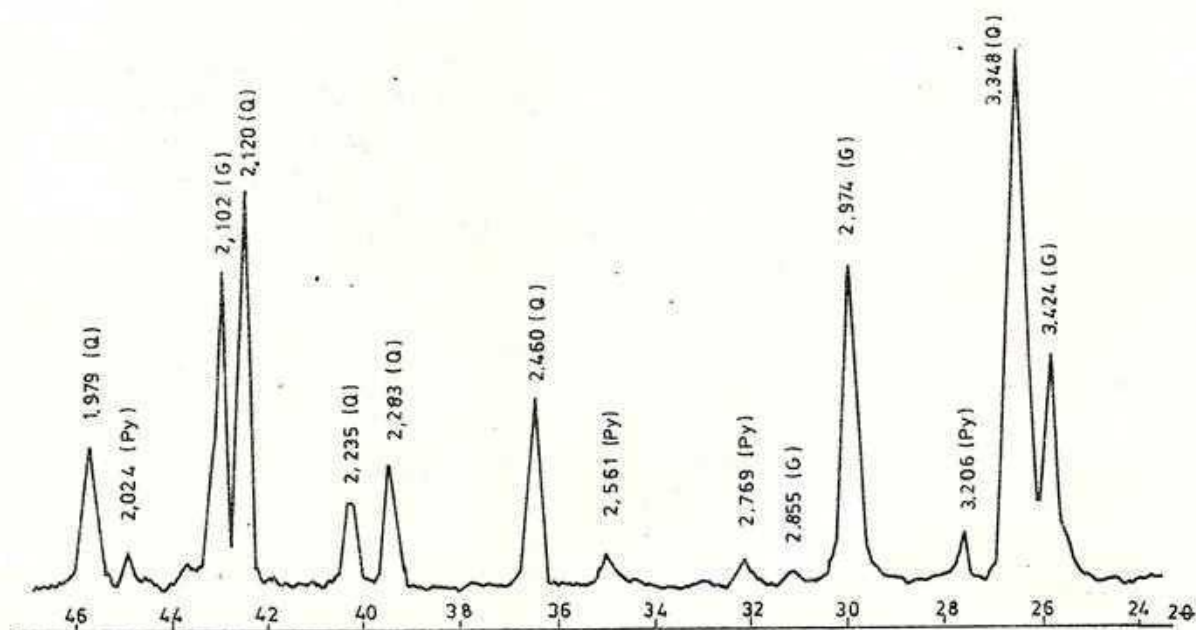


Fig. 2. - X - ray diffraction pattern of a quartz (Q) + galena (G) + pyrargirite (Py) sample.

Nedelcu (1977) pointed out that these mineralizations would be situated in the formations of the Tulgheș Group (Tg₁ especially), near the contact with Țibău (Rebra) limestones.

In both sectors the mineralizations are located in micaschists and in muscovite-biotite (chlorite) gneisses in different stages of milonitizations and retromorphism, most of this rocks are characterized by the presence of tourmaline and titanium minerals, such as ilmenite, shene, rutile, associated with the micaceous sequences. The abundance and the nature of these minerals seems to be in close correlation with the degree of retromorphism (according to Nedelcu, 1986), increasing as the degree of retromorphism gets higher. While the presence of the biotite is out of any doubt, the presence of garnet in these rocks is questionable even if often the garnet is suggested by chlorite agglomerations. The polymetamorphism and the mineralogical constitution offer arguments for the affiliation of these rocks to the Rebra Group in the Bucovinian Nappe, probably.

Mineralization

The mineralization consists of pyrite (frequently associated with the arsenopyrite), sphalerite (sometimes presenting cubanite separations), chalcopyrite and galena in paragenetic association with tetrahedrite, bournonite and pyrargirite.

In the past, the greenockite, in association with sphalerite and proustite (Cădere, 1925) as well as bornite, bismuthite and another Bi-minerals (Nedelcu, 1977), have been described among metallic minerals.

The mineralizations are mainly controlled by the tectonic factor, the minerals being deposited in the high cataclastic zones. They occur as impregnations, small veins or massive pockets having a fine or medium grain size texture (0.5–2.0 mm) in the case of pyrite, arsenopyrite, arsenopyrite, chalcopyrite and

galena or a fine grain size texture (0.05–0.50 mm) in the case of sphalerite.

Pyrite is found in different stages of catagenesis with a low degree of idiomorphism.

Arsenopyrite appears in association with pyrite, with a stronger trend to idiomorphism.

Sphalerite includes and corrodes the grains of pyrite and arsenopyrite; it may also contain numerous tabular micronic (<0.1 mm) cubanite crystals.

Chalcopyrite seems to be contemporary with sphalerite, belonging to a late mineralization stage as compared to pyrite and arsenopyrite; from quantitative point of view, the chalcopyrite and sphalerite are in a negative correlation.

Galena appears either in the mass of the gangue minerals or in the mass of pyrite, sphalerite and chalcopyrite.

Tetrahedrite and bournonite are associated, in various amounts, to galena. The bournonite has been detected by the energy dispersive microprobe analysis. The characteristic energy spectrum for chemical elements in the bournonite is shown in Figure 1. Also, the X-ray analysis of a galena-rich sample point out the presence of pyrargirite (Fig. 2) (analyst dr. Gh. Neacșu).

Quantitatively, the main gangue minerals are quartz and siderite.

Quartz may be present either alone as well developed crystals, which consolidate the fragments of the host rock, or as gangue mineral associated to the metallic minerals of all stages. The quartz of the earlier generations may be accompanied by albite, while the quartz that occupies the space between the metallic minerals within the massive pockets may be accompanied by calcite and chlorite.

Siderite first appears after the deposition of the pyrite and the arsenopyrite mineralization, before or simultaneously with the mineralizations of the sphalerite and/or chalcopyrite. The predominant mineral deposit form is that of small veins or pockets, usually having a medium grain size texture.

Table
Chemical and spectral analysis

Element	Fe	Cu	Pb	Zn	Cd	Au	Ag	Sb	As	Ge	Co
Sample	%	%	%	%	%	g/t	g/t	g/t	g/t	g/t	g/t
211	29.24	0.09	21.10	0.38	—	1.10	>100	2.00	>3.000	—	—
212	28.65	0.02	1.48	0.42	—	1.72	5	100	500	—	—
213	5.08	0.08	0.87	37.45	0.17	0.30	80	250	3.000	70	30
214	7.20	0.06	4.23	46.40	0.31	0.20	20	180	—	30	25
215	8.90	0.12	1.46	44.90	0.27	0.14	35	150	—	150	150
223	32.72	9.80	1.93	0.34	—	0.22	30	1.50	—	—	—
224	53.64	0.05	3.58	17.80	0.12	0.12	20	100	—	—	—
234	2.53	0.10	16.50	23.70	0.15	0.19	60	400	—	—	—
236	0.69	0.09	14.60	0.62	—	0.18	>100	300	—	—	—

211, 212, 213, 214, 215, 223, 224 samples - Fluturica sector

234, 236 samples - Canal sector

If both the metallic minerals and the gangue minerals are taken into account, the following paragenesis can be outlined:

- 1) quartz $\pm$ albite $\pm$ pyrite;
- 2) pyrite $\pm$ arsenopyrite $\pm$ quartz $\pm$ calcite $\pm$ chlorite;
- 3) sphalerite (with cubanite separations) and/or chalcopyrite + siderite $\pm$ quartz $\pm$ calcite $\pm$ chlorite;
- 4) galena $\pm$ tetrahedrite $\pm$ bournonite $\pm$ pyrargirite $\pm$ quartz $\pm$ calcite $\pm$ chlorite.

As a result of the alteration of the primary minerals, new minerals have appeared, such as the limonite, cerussite, chalcocite, covellite, malachite and azurite.

If the chemical compositions are examined (Table elements), strong positive correlations become obvious between the elements within each of the following groups:

- cadmium, germanium, cobalt and zinc;
- silver, antimony and lead.

Conclusion

If all the mentioned considerations are taken into account, namely the predominant tectonic control, the mineralogical constitution and the paragenesis sequences, we can con-

clude that the mineralizations we have studied may be correlated genetically and temporally with the epigenetic alpine mineralizations of the Ostra-Gemenea-Slătioara and the Delnița-Botoșel zones [Balintoni, Țimpău, 1971; Vodă et al., 1985, 1987; Macaleț et al. (in press)].

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PREHNITE IN CALCIC ENDOSKARNS FROM SURDUC: A LOOK ON A NEGLECTED MINERAL SPECIES IN ROMANIA

Stefan MARINCEA, Doina RUSSO-SÂNDULESCU

Geological Institute of Romania, 1 Caransebeș Str., RO-79678 Bucharest 32.



Key words: Prehnite. Calcic skarns. Banatites. Parageneses. Morphology. SEM study. Physical properties. Chemistry. XRD data. Infrared data. DTA - DTG - TGA data. Genesis. Surduc - Banat Mountains.

Abstract: Prehnite, an ubiquitous alteration product in calcic systems, was found in an unreported endoskarn occurrence, at Surduc (Banat Mountains). This endoskarn is developed at the contact between monzodiorites belonging to a second phase of the Surduc 1 intrusive stage (Coniacian-Maastrichtian in age) and gabbros belonging to an earlier intrusive phase of the same stage. The primary skarn paragenesis consists of andradite (andr. 91.04 to andr. 98.36), calcic plagioclase (Ab. 44.79 Or. 4.02 An. 51.19) and diopside. Prehnite is clearly pseudomorph on plagioclase, occurring as a late hydrometasomatic product. The average of three microprobe analyses gave: $\text{SiO}_2 = 40.87\%$, $\text{Al}_2\text{O}_3 = 27.03\%$, $\text{FeO} = 0.39\%$, $\text{Fe}_2\text{O}_3 = 1.20\%$ (assumed after wet-chemical tests), $\text{CaO} = 25.50\%$, $\text{MgO} = 0.32\%$, $\text{MnO} = 0.14\%$, $\text{H}_2\text{O} = 4.31\%$ (thermogravimetric). The mineral is white to greenish in colour and has as main physical constants: $n_{\text{mean}} = 1.615$, $D_{\text{meas.}} = 2.950$, $D_{\text{calc.}} = 2.944$. SEM, XRD and IR studies indicate the orthorhombic symmetry and a high-ordered structure. Lattice constants, refined on the basis of the X-ray powder data (23 reflections obtained) are: $a = 4.623(4) \text{ \AA}$, $b = 5.477(4) \text{ \AA}$ and $c = 18.460(1) \text{ \AA}$. The thermal pattern shows that dehydration took place during two stages, marked by endothermic effects on the DTA curves at 785°C ($-0.65\% \text{ H}_2\text{O}$) and 868°C ($-2.66\% \text{ H}_2\text{O}$). The infrared absorption spectrum recorded in the frequency range between 4000 and 250 cm^{-1} has as a main feature the dominance of the pattern of hydroxyl groups (bands at 3484, 940 and 870 cm^{-1}), Si-O bonds (bands at 1090, 1072 and 1000 cm^{-1}) and Al-O bonds (bands at 812 and $756 - 740 \text{ cm}^{-1}$). Si-O, Al-O librations and some other cation (essentially Ca)-oxygen vibrations were recorded below 700 cm^{-1} (bands at 668, 640, 532, 472, 426, 380, 346, 298 and 262 cm^{-1}) and are difficult to be assigned.

Introduction

Prehnite, an ubiquitous alteration product in calcic systems, was either unreported or ig-

nored in the about 40 skarn occurrences in Romania. Only few mentions certify its presence at Băița Bihor (Ciofică, Vlad, 1968, 1977), Vălișoara (Berbelec, 1975) or Țibleș

(Udubaș et al., 1982). Taking into account that its stability range closely overlaps a major stage of retrogressive evolution of the calcic systems and even accepting its susceptibility to local chemical conditions, it is to be presumed that the spread of prehnite in the Romanian skarns is however larger.

The new find of prehnite at Surduc, in a so far unreported skarn area, enlarges at four the number of its occurrences in hydrometamorphic context. This discovery prompted a minute examination of this neglected mineral species. The chemical, SEM, XRD, thermal and IR studies used in this paper aim therefore to give a desirable and more fully characterization of prehnite in skarns, peculiarised for a new occurrence.

Geological setting

The unusual setting of the calcic skarns from Surduc, which lie far away from any carbonaceous formation, put off their discovery until comparatively recent times. It is of note that the closest metamorphites, which belong to the Tâlva Drenii formation (of Precambrian age), consist in an alternance of ocular gneisses and biotite-garnet micaschists.

The first mention of the skarns at Surduc belongs to Russo-Săndulescu (1979 - unpublished data), who carried out extensive studies on the magmatites in the area (Russo-Săndulescu et al., 1984, Russo-Săndulescu, 1986, Russo-Săndulescu et al., 1986 e. a.). They clearly show that the magmatites belonging to the major banatitic massifs in western Banat (the so-called "plutonic banatitic zone"), namely those at Surduc and Bocșa, can be ascribed to two main magmatic stages, with different petrogenetical characters and of different ages. The polyphasic pluton at Surduc contains consequently rocks belonging to the both stages: Surduc 1, of 75-68 m.y., and Surduc 2, of 62-55 m.y. (Russo-Săndulescu, 1986). The Surduc 1 intrusive stage is represented by a gabbro-monzodiorite to monzonite in-

trusive complex which includes layered nodules of gabbro-norites and anorthosites (Russo-Săndulescu, 1986). The older ones, namely the gabbro-norites and anorthosites, were inherited as xenolites by the younger monzodiorites. They were consequently exposed to an intense erratic metasomatism and were enough calcic to generate skarns as their plagioclase was a "bytowntite" with 82 to 84 mole percent anorthite in solid solution (Russo-Săndulescu, 1986).

Skarns at Surduc are consequently developed on gabbros and monzodiorites. They are generally banded and parallel to the contact between the nodules of cumulate gabbros and monzodiorite. The outer zone of the gabbro, near the contact, was entirely replaced, forming skarns with andradite, plagioclase + diopside. No essential changes can be observed in the inner zone, where only the initial clinopyroxene (augite) was recrystallised to diopside and the plagioclase seems to be poorer in calcium. Together with epidote, prehnite extensively replaces the initial skarn assemblages, practically defining pseudoskarn zones *sensu* Korzhinskii (1965), in which the essential primary minerals (i.e. andradite, plagioclase) have been preserved as relicts.

Associated minerals

Because its tendency to develop bundles of radiating crystals with an enough large extension, prehnite closely associates only with primary minerals of the initial skarn paragenesis and with epidote. Euhedral to anhedral grains of plagioclase and garnet are embedded and partly altered by the later prehnite.

As expected, chemically contrasting plagioclases were found in the Surduc 1 intrusive rocks. Representative electron microprobe of these plagioclases are presented in Table 1. They were performed on an energy-dispersive JEOL-JSM 850 electron microprobe housed by IMGB SA Bucharest. Operating conditions were 15 kV and 20 nA probe current on brass.

Table 1
Electron-probe analyses of andradite and plagioclases from Surduc*

wt. % oxides	PLAGIOCLASES			ANDRADITE	
	sample 546	sample 542	sample 526	sample 481	sample 1031
SiO ₂	54.50	62.37	61.10	34.39	35.71
TiO ₂	-	-	-	0.21	0.00
Al ₂ O ₃	28.82	23.57	23.60	1.88	0.00
Fe ₂ O ₃	-	-	-	28.96 ⁽¹⁾	29.76 ⁽¹⁾
CaO	10.63	4.73	5.63	32.92	32.72
MnO	-	-	-	0.00	0.50
MgO	-	-	-	0.17	0.11
K ₂ O	0.70	1.00	1.77	-	-
Na ₂ O	5.14	8.06	7.47	-	-
Total	99.79	99.73	99.57	98.53	98.80

Number of cations on the basis of N⁽²⁾ oxygen anions

Si ⁴⁺	9.866	11.092	10.964	5.869	6.093
Ti ⁴⁺	-	-	-	0.027	0.000
Al ³⁺	6.149	4.940	4.991	0.378	0.000
Fe ³⁺	-	-	-	3.719	3.821
Ca ²⁺	2.062	0.901	1.082	6.019	5.982
Mn ²⁺	-	-	-	0.000	0.072
Mg ³⁺	-	-	-	0.043	0.028
K ⁺	0.162	0.277	0.405	-	-
Na ⁺	1.804	2.779	2.599	-	-

Composition in end-members⁽³⁾

Ab	44.79	71.13	63.61	And ⁽⁴⁾	93.81	98.36
An	51.19	23.06	26.48	Gro	6.15	-
Or	4.02	5.81	9.91	Pyr	0.04	-
				Cal	-	1.18
				Kho	-	0.46

* analyst I. Dina, IMGB S.A. Bucharest.

(1) - the oxidation state of iron was assumed to be trivalent based on the wet-chemical data.

(2) - N = 32 for plagioclases and 24 for andradites.

(3) - Ab = albite; An = anorthite; Or = orthoclase; And = andradite; Gro = grossular; Pyr = pyrope; Cal = calderite; Kho = khoharite.

(4) - schorlomite included.

The minor amounts of iron, calculated as FeO, were neglected. Each analysis represents the mean of three punctual determinations. As seen in Table 1, the analysed plagioclase in unmetasomatised gabbros (sample 546) is a "labradorite" with up to 45 mole percent albite and about 4 mole percent orthoclase in solid solution. It was found to be poorer in Ca than previously reported (Russo-Săndulescu, 1986), but is considerably more calcic than plagioclase in monzonites (sample 542) and in some potassic syenites (sample 526). There are no available analyses of plagioclase from skarns. It is to be noted however that the optical estimation of its composition by means of the universal stage yielded anorthite contents of 50 to 55 mole percent, close of that previously reported for plagioclase in gabbros. It is to be presumed therefore that both plagioclases have the same basic composition.

Calcic garnet is the other main constituent of skarn assemblages. It generally shows concentric-lamellar optical anomalies in which isotropic zones (generally the nuclei) alternate with birefringent ones which display "dodecahedral twinning". A wet-chemical analysis, which reflects the bulk composition, gave: $\text{SiO}_2 = 35.80\%$; $\text{TiO}_2 = 0.22\%$; $\text{Al}_2\text{O}_3 = 1.96\%$; $\text{Fe}_2\text{O}_3 = 29.36\%$; $\text{CaO} = 32.32\%$; $\text{MnO} = 0.35\%$ and $\text{MgO} = 0.14\%$. Structural formula refined on the basis of 24 oxygens is: $(\text{Ca}_{5.785} \text{Mn}^{2+}_{0.050} \text{Mg}_{0.035}) (\text{Al}_{0.366} \text{Fe}^{3+}_{3.691} \text{Ti}^{4+}_{0.028} [\text{Si}_{5.980} \text{Al}_{0.020} \text{O}_{24}])$, indicative of an andradite (91.04 %) with minor grossular (7.51 %), pyrope (0.60 %) and spessartine (0.85 %).

The X-ray powder diffraction study of the same sample does not show any doubling of the main reflections of andradite as expected for a mechanical mixture of two chemically different calcic garnets. The obtained data, which are listed in Table 2, lead to a cell parameter of $12.057(3)\text{\AA}$, which was calculated using the least-squares refinement program AP-PLM (Appleman, Evans, 1973). Its value is higher than that one given by Skinner (1956) for the stoichiometric andradite ($a = 12.048$

$\text{\AA}$). Taking into account that Huckenholz and Yoder (1971) have reported for the synthetic andradite end-member a closer "a" value ($a = 12.056\text{\AA}$) and the presence of Ti^{4+} in octahedral sites increases the cell parameter because their larger ionic radius (Novak, Gibbs, 1971), our value is not unexpected and clearly characterises an andradite nearby the end-member.

Considering however the optical zoning, reflected at macroscopic scale by colour changes (from black-brown in nuclei to yellowish-brown at rims), it is to be expected that garnets in skarns from Surduc also exhibit a compositional zoning with respect to Al and $\text{Fe}^{3+} + \text{Ti}^{4+}$. Consequently, microprobe analyses were carried out on both a "yellow" rim (sample 481) and a "black" core (sample 1031). Both analyses are given in Table 1. As expected, the rims are titanium- and iron-poor as compared to the cores and implicitly more aluminous. This behaviour would be consistent with optical observations which indicate that titanian andradites (schorlomite and melanite) are black (Loeffler, Burns, 1976).

Analyses in Table 1 also show that garnet in skarns from Surduc is andradite-rich (andradite end-member ranges from 93.81 to 98.36 %). They also point out that other four components are represented: grossular and pyrope in sample 481 and calderite and khoharite in sample 1031. The calculation of calderite and khoharite end-members are not unexpected taking into account that the analysed sample is aluminium-deficient, situation which is not surprising for andradites nearby the end-member. Similar situations were however described by Vlad (1974: wet-chemical analyses) or by Meinert (1984: microprobe analyses).

In addition to plagioclase and garnet, epidote is one of the characteristic minerals of the skarn assemblages. Both garnet and plagioclase show alteration to epidote. Optical properties (biaxial negative, yellowish-green to pale yellow pleochroism, high birefringence, extinction c:n:p of 8-11) indicate in all cases an iron-

Table 2
X-ray powder diffraction data for andradite from Surduc*

Crt. no.	d Å(obs)	d Å(calc) ⁽¹⁾	I/I ₀	(hkl)
1	4.255	4.2626	15	(220)
2	3.017	3.0141	90	(400)
3	2.695	2.6959	100	(420)
4	2.563	2.5705	20	(332)
5	2.465	2.4610	65	(422)
6	2.365	2.3645	25	(431)
7	2.200	2.2012	20	(521)
8	1.955	1.9558	35	(611)
9	1.907	1.9063	14	(620)
10	1.742	1.7402	11	(444)
11	1.670	1.6719	40	(640)
12	1.611	1.6111	90	(642)
13	1.501	1.5071	11	(800)

* Cu K α , λ = 1.54056 Å, analyst C. Cristea.

⁽¹⁾ - calculated for a cubic cell with a = 12.0566 Å, using the APPEM program (Appleman, Evans, 1973).

rich term (an epidote s.s. according to Deer et al., 1962).

Morphology

At Surduc, prehnite occurs as fan-shaped aggregates of parallel or subparallel intergrown crystals which conserve their continuous aspect. Bundles of crystals seem to be nucleated in succession, forming composite radiating aggregates with a flamboyant texture, similar to that one described by Metcalf-Johansen (1983) at Ilimaussaq (Greenland). As mentioned before, relicts of plagioclase and garnet are embedded in the prehnite mass. A centripetal replacement of both primary phases, and peculiarly of plagioclase, by the later prehnite, is obvious. This preferential pseudomorphic replacement has resulted in a high degree of preservation of original grain-boundary relationships between plagioclase and andradite, even that the later did not maintain its normal euhedral outline.

A minute morphological study of prehnite crystals was carried out by standard secondary electron imaging techniques, using a Phillips 515 SEM apparatus housed by METAV SA Bucharest. This was operated at 30 kV and 15 nA, after covering two times the analysed surfaces with graphite, under vacuum. Typical images showing prehnite aggregates are given in the photos on Plate 1. Individual crystals, up to 0.2 mm large, 5 mm long and 0.05 mm thick, are elongated parallel to the X axis and are generally tabular owing to predominant development of the {001} form. Three other forms, i.e. $a=\{100\}$, $b=\{010\}$ and $m=\{110\}$, can be distinguished, the former having a smaller extension. The rectangular growth-pattern mentioned by Akizuki (1987) on the (110) faces, as well as the vertical striations of the (010) faces caused by the interchange of the narrow (110) faces (Zunic et al., 1990) can be observed.

The SEM study shows unambiguously the orthorhombic tract of the mineral, indicating a P2cm or Pncm polymorph. As the P2cm

structure is more stable because its greater homogeneity (Akizuki, 1987) and consequently more widespread (Aumento, 1968; Zunic et al., 1990) we suspect that the prehnite from Surduc has a P2cm symmetry.

Physical properties

Taking into account its association with andradite, it is to be expected that prehnite from Surduc has physical properties characteristic of an iron-rich member. The macroscopic colour (white to greenish yellow) indicates however a moderate iron content since the massive presence of strong chromophores such as Fe^{2+} or Fe^{3+} induces green tints (Chaudhry, Howie, 1969; Matsueda, 1975).

In thin sections prehnite appears colourless. No optical anomalies (i.e. anomalous interference colours, "hourglass" textures) which characterise iron-rich members (Matsueda, 1975) can be observed. The wavy extinction which occurs locally is rather due to the flamboyant texture reported before. The birefringence is moderate (the mineral polarises in colours belonging to the first half of the second order), which also accounts for a medium iron content. The mineral is biaxial positive with $2V\gamma=64-68$. Taking into account the inverse relationship between $2V\gamma$ and the iron content (Chaudhry, Howie, 1969) these values also characterise a term with a moderate participation of "ferriprehnite" in solid solution.

Last but not least, another optical property accounts for an enough low ferricity of the analysed prehnite: its refringence. The mean refractive index measured in immersion using a standard determinative technique (i.e. the Schröder method) was found to be 1.615. That value, which probably corresponds to n_p or n_m , is much lower than those reported by Matsueda (1975) or Metcalf-Johansen (1983) for ferrian prehnites ($n_p = 1.618-1.627$; $n_m = 1.628-1.647$).

As regards other physical properties it is to be noted that the measurement of specific

gravity yielded an unusual high value, of 2.95. It was measured by means of a pycnometer, using toluene as displacement fluid, and is considerably higher than those previously reported for the mineral (e.g. 2.920 as measured by Kitahara, 1966; 2.902 measured by Conti et al., 1974; 2.919 measured by Metcalf-Johansen 1983 etc.). As the specific gravity also appears to be controlled by the iron content (Chaudhry, Howie, 1969) this value seems to characterise a ferrian prehnite. This dependency should not be taken however as a rule since an increased participation of aluminium in the tetrahedral sites has basically the same effect of increasing specific gravity. As the prehnite from Surduc is aluminium-rich (see below) a high specific gravity can be expected even for a medium iron content.

As a last remark it is to be noted that the measured specific gravity compares favourably with the calculated one ($D_{calc} = 2.944$).

Chemical data

Because the small quantity of the material available, the microprobe investigation was preferred over the wet-chemical one. Consequently, prehnite from Surduc was chemically analysed using the energy dispersive Phillips 515 SEM electron microprobe at METAV SA Bucharest. Operating conditions were 15 kV as accelerating voltage and 20 nA as sample current, standardised on brass. A slightly defocused beam for a counting time of 100 s was used in order to minimise the sample volatilisation. It is to be noted that the investigated samples are remarkably homogeneous from the chemical point of view within the limits of each analysed grain. Consequently, the analyses summarised in Table 3 represent punctual determinations on three separate grains.

Water (4.31 % H_2O^+ and 0.24 % H_2O^-) was determined thermogravimetrically and then allocated to each analysis as well as to the average composition (analysis 4 in Table 3). The oxidation state of the iron was determined by wet-chemical analysis of a small quantity of

Table 3

Representative microprobe analyses of prehnite in skarns from Surduc (wt. % oxides)*

Oxides	sample 1031 a	sample 1031 b	sample 1031 c	Average
SiO ₂	40.08	42.90	39.62	40.87
Al ₂ O ₃	26.62	28.01	26.45	27.03
Fe ₂ O ₃ ⁽¹⁾	1.05	0.93	1.61	1.20
FeO ⁽¹⁾	0.35	0.31	0.53	0.39
MgO	0.32	0.33	0.31	0.32
MnO	0.43	0.00	0.00	0.14
CaO	26.09	23.16	27.24	25.50
H ₂ O ⁺ ⁽²⁾	4.31	4.31	4.31	4.31
Total	99.25	99.95	100.07	99.76

Number of ions based on 12 (O, OH)

Si ⁴⁺	2.798	2.920	2.760	2.827
Al ³⁺	2.191	2.247	2.171	2.203
Fe ³⁺	0.055	0.048	0.084	0.062
Fe ²⁺	0.020	0.018	0.031	0.023
Mg ²⁺	0.033	0.033	0.032	0.033
Mn ²⁺	0.025	-	-	0.008
Ca ²⁺	1.952	1.689	2.033	1.890
(OH) ⁻	2.007	1.957	2.002	1.988
Al ^{IV} (%)	30.05	27.00	31.00	29.33
Fe ³⁺ /(Fe ³⁺ +Al)	5.27	3.95	8.28	5.68

* analyst C. Bunescu, METAV S.A. Bucharest.

(1) - assumed on the basis of wet-chemical analysis.

(2) - determined by thermogravimetric means.

sample. The FeO content was determined titrimetrically following a modified Pratt method as indicated by Maxwell (1968), whereby Fe²⁺ is titrated in a boric-phosphoric hydrofluoric acid medium against K₂Cr₂O₇, using barium diphenylamine sulphonate as an indicator. The total iron content was determined by the volumetric method of Hume and Kolthoff (1957) from which the Fe₂O₃ content was obtained in a straightforward manner. The obtained results are: FeO=0.45%; Fe₂O₃=1.35%; total iron (as Fe₂O₃)=1.85%. They are in good agreement with the FeO content in the average microprobe analysis (1.77% Fe₂O₃ in equivalent FeO). They agree at the

same time with the previous analytical data (e.g. Kitahara, 1966; Chaudhry, Howie, 1969; Saravanan et al., 1971) which show that in prehnite Fe³⁺ prevails over Fe²⁺. All the electron-probe analyses in Table 3 were consequently corrected for the oxidation state of iron by applying the same ferrous/ferric ratio as was found by wet-chemical analysis.

The study of the number of cations calculated on the basis of 12 oxygen atoms in view to obtain the structural formulae (Table 3) shows as main features that:

1 - The occupancy factor for Al in tetrahedral co-ordination is considerably high: between 24 and 31 % of the tetrahedral sites,

then more than reported by Kitahara (1966), Saravanan et al. (1971), Conti et al. (1974), Matsueda (1975) or Verma (1979) are occupied by Al^{3+} ;

2 - The recognisable substitutions for octahedral Ca include Mn^{2+} , Mg, Fe^{2+} and Fe^{3+} or even Al taking into account the undercompensation in divalent elements of the second sample in Table 3;

3 - The ferric iron is the sole substitute for the octahedral Al. The $\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$ ratio ranges between 3.95 and 8.28 %, being as expected higher than those reported for metamorphic prehnites in the prehnite-pumpellyite zone (up to 5 % Fe^{3+} as substitute for Al according to Hashimoto, 1966) but lower than those reported by Matsueda (1975) in some iron-rich prehnites from Japanese skarns (more than 15 % "ferriprehnite" in solid solution).

As a last remark it is to be noted that the average structural formula calculated for the prehnite from Surduc on the basis of the data in Table 3 is: $(\text{Ca}_{1.890} \text{Mg}_{0.033} \text{Mn}^{2+}_{0.008} \text{Fe}^{2+}_{0.023}) (\text{Al}_{1.030} \text{Fe}^{3+}_{0.062}) (\text{OH})_{1.988} \text{O}_{0.012} (\text{Si}_{2.827} \text{Al}_{1.173} \text{O}_{10})$.

It leads to a molecular mass of 414.574, which was used for the specific gravity calculation.

Infrared absorption data

Despite the widespreading of the mineral and the variety of its occurrences, there are few published data on the infrared behaviour of prehnite. The few works which brought new IR data (i.e. Matsueda, 1975; Metcalf-Johansen 1983) take as reference the spectrum given for mineral by Moenke (1962). No band assumption or structural correlations were attempted. Consequently, the infrared study of prehnite from Surduc was used as an expected occasion to more fully characterise the mineral.

An infrared absorption spectrum of a prehnite sample was recorded in the frequency range between 250 and 4000 cm^{-1} using a

SPECORD M-80 spectrometer. It was obtained using a standard pressed disk technique, after embedding a small amount of mechanically ground prehnite (2.5 weight %) in dry potassium bromide and compacting under 250 kgf/cm^2 pressure. The spectrum, which is given in Figure 1, shows all the features expected for a hydroxyl-silicate with four-fold coordinated aluminium.

A main and striking feature of this spectrum is the presence in the high-frequency region between 3000 and 4000 cm^{-1} of the fundamental OH stretching vibration, materialised by an intense and sharp band centred at 3484 cm^{-1} . The sharpening of this band may be related to an ordered cation arrangement around OH and agrees well with the slight differences between $(\text{Al}, \text{Fe}^{3+}) - \text{O}$ and $(\text{Al}, \text{Fe}^{3+}) - \text{OH}$ distances found by Zunic et al. (1990) in a P2cm prehnite. On the other hand, the position of this band reflects a medium to strong hydrogen bonding, corresponding to an enough short OH...O distance, since the OH stretching frequency is an almost linear function of this distance (Nakamoto et al., 1955). However it is to be noted that in the spectrum presented by Moenke (1962) the fundamental stretching band is splitted into two sub-bands (recorded at 3485 and 3475 cm^{-1}) which normally reflect two intensities of hydrogen bonding and consequently a more disordered structure.

The corresponding OH bending vibration is expected to lie in a restricted frequency range between 950 and 850 cm^{-1} as in all the other layer silicates which contain octahedral Al referred by Farmer (1974). Taking into account that the $\text{Al}_2\text{-OH}$ librations were recorded in the frequency range between 915 and 950 cm^{-1} in all these species (Farmer, 1974) the band recorded in our spectrum at 940 cm^{-1} must represent such kind of vibrations. As the OH librational frequencies are functions of the coordinating cations, it seems reasonable to consider that the other band in the region, that one at 870 cm^{-1} , is due to Ca-OH-Al vibrations. Both frequencies discussed above seem

to correspond to in-plane librations. The positions of the out-of-plane bendings are less certain and appear to lie at still lower frequencies, probably between 600 and 700 cm^{-1} .

AlO_4 tetrahedra also occur (see before) and their vibrational modes must be found on the IR spectra. Bands which can be associated with tetrahedral Al-O vibrations are expected

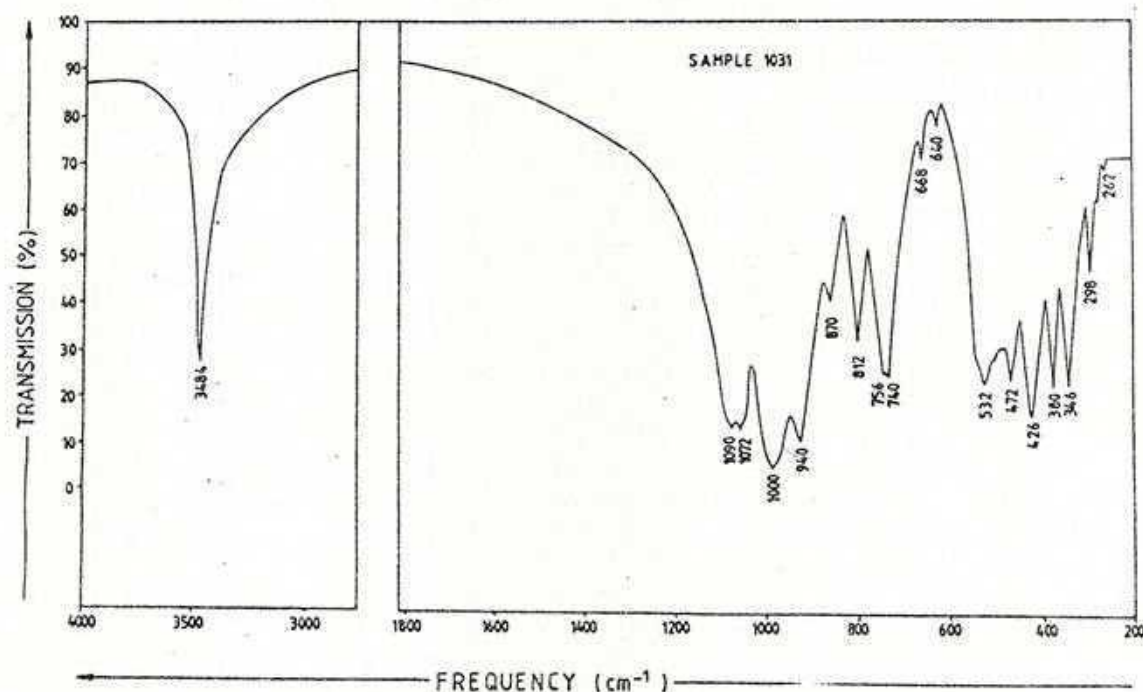


Fig. 1 - Infrared spectrum of a prehnite sample from Surduc.

As can be seen in Figure 1, another feature of the infrared spectrum of prehnite is the presence of a broader and enough intense group of bands in the 950–1100 cm^{-1} region. Their assignment follows immediately from the fact that this region hosts the classical stretching vibrations of the (SiO_4) groups in all silicates. It results therefore that the bands at 1090, 1072 and 1000 cm^{-1} express (antisymmetric) stretching motions of these groups. As concerns the corresponding bending motions, they are expected to lie at lower frequencies. Their assumption by parallelism (i.e. 532 cm^{-1} = in-plane bending of SiO_4 groups and 426 cm^{-1} = out-of-plane bending of SiO_4 groups) is risky because the coupling with other vibrations in the structure such as lattice vibrations or OH (out-of-plane) librations (Farmer, 1974).

Silicon is not however the sole four-fold coordinated cation in the prehnite structure.

to lie near 820 and 760 cm^{-1} , as in the pure micas and trioctahedral chlorites (Farmer, 1974). Peculiarising for our spectrum, these bands are those at 812 and 756–740 cm^{-1} . Their considerable intensity suggests increased Al-for-Si substitutions, in good agreement with chemical data reported before. The splitting into two components of the band at 756–740 cm^{-1} , recorded at 745 cm^{-1} by Moenke (1962), is another peculiarity of the spectrum in Figure 1. Taking into account that this band is essentially assignable to Al-O-Si in-plane vibrations, its splitting can signify an increased ordering of Al in tetrahedral sites, as in the "ordered" low-cordierite (Langer, Schreyer, 1969). In full agreement with this assumption are the other data which prove the "ordered" $P2_1$ symmetry of the investigated sample. On the other hand it is to be noted that since octahedral Al is also present in the

Table 4
Comparative X-ray powder diffraction data for prehnite*

Crt. no.	SURDUC			PROSPECT		ZLOTEGO STOK ⁽³⁾		(hkl)
	d (Å) meas. ⁽¹⁾	d (Å) calc. ⁽²⁾	I/I ₀	d (Å)	I/I ₀	d (Å)	I/I ₀	
1	-	-	-	9.280	14	-	-	(002)
2	5.253	5.251	8	5.267	26	5.307	30	(011)
3	4.603	4.614	13	4.641	28	4.655	20	(100)
4	4.140	4.134	6	4.149	7	-	-	(102)
5	3.523	3.519	25	3.544	43	3.501	80	(110)
6	3.480	3.470	50	3.481	91	-	-	(111)
7	3.288	3.299	35	3.311	60	3.313	60	(112)
8	3.261	3.266	30	3.276	42	-	-	(104)
9	3.080	3.077	100	3.079	100	3.071	100	(006)
10	2.805	2.805	20	2.811	34	2.815	40	(114)
11	2.630	2.625	8	2.630	15	-	-	(022)
12	2.555	2.561	65	2.564	70	2.557	100	(106)
13	-	-	-	2.380	10	-	-	(017)
14	2.355	2.355	25	2.360	37	2.362	40	(024)
15	-	-	-	2.341	18	-	-	(121)
16	2.310	2.308	50	2.316	34	-	-	(008)
17	-	-	-	2.204	5	2.199	10	(025)
18	2.117	2.113	5	2.118	4	2.112	10	(117)
19	2.070	2.067	12	2.072	12	2.063	30	(204)
20	-	-	-	2.050	4	-	-	(026)
21	1.932	1.932	14	1.938	15	1.939	50	(118)
22	1.845	1.845	13	1.850	12	1.842	30	(215)
23	1.768	1.767	30	1.772	32	1.773	90	(220)
24	1.695	1.698	5	1.700	9	-	-	(034)
25	1.652	1.657	6	1.660	11	1.657	40	(217)

* analyst C. Cristea, Geological Institute of Romania.

(1) - reflections at 1.552 Å (25), 1.463 Å (6), 1.450 Å (4) and 1.410 Å (6) were also recorded until 80° 2Θ.

(2) - refined for an orthorhombic cell with a = 4.623 Å, b = 5.477 Å and, c = 18.460 Å, using the computer program of Appleman and Evans (1973).

(3) - 12 reflections corresponding to higher 2Θ values also given.

structure, the splitting of the 745 cm⁻¹ band and Al-OH librations and translations referred can also be due to an overlap of an octahedral Al-O vibration. before. It is noteworthy however that:

This kind of vibrations, caused by octahedral linkages, must occur below 750 cm⁻¹. Their assignment to specific mechanical motions is difficult because the occurrence in the same spectral range of Si-O, Al^{IV}-O, Si-OH 1 - Bands associated with Fe³⁺-O and Fe³⁺-O-Si vibrations obviously lie at frequencies lower than those involving Al and probably in the 650-750 cm⁻¹, as in biotites (Farmer, 1974); it is then presumable that the band at 668 cm⁻¹ and eventually that one at 640 cm⁻¹

materialise such kind of vibrations, the later being rather a combination between a Fe^{3+} -O mode and a hydroxyl libration;

2 - As already observed by Matsueda (1975), Fe^{3+} -for-Al substitutions don't cause a substantial shift of the bands in the 550-750 cm^{-1} region;

3 - The broader and spread-out group of bands in the 250-550 cm^{-1} region essentially contains bands assignable to Me^{2+} -O vibrations, coupled with tetrahedral and OH vibrations referred before. The most important ones are normally the Ca-(O,OH) vibrations, which are expected to lie below 400 cm^{-1} .

X-ray powder diffraction data

The X-ray powder diffraction analyses of two prehnite samples from Surduc were performed with a DRON-3 diffractometer, using graphite-monochromatised Cu K α radiation ($\lambda=1.5418$ Å) and a goniometer scan speed of 1° 2 θ /min. Synthetic silicon, with $a = 5.4309$ Å (J.C.P.D.S. card 27-1402) was used as internal standard. Because the lack of major differences between the two patterns, only one of them was quantified. The corresponding data are given in Table 4, together with similar ones given by Phillips and Rickwood (1975) for a prehnite from Prospect (New South Wales, Australia): J.C.P.D.S. card 29-290, and by Kowalsky (1966) for a prehnite from magnesian skarns at Zlotego Stok (Poland).

As a first remark is to be noted that the splitting of the reflection at about 16° 2 θ , observed by Phillips and Rickwood (1975), is obvious in our patterns, where two lines centred at $d = 3.261$ Å and $d = 3.288$ Å were recorded. Taking into account the polymorphism reported for the mineral (e.g. Aumento, 1968; Akizuki, 1987; Zunic et al., 1990), this splitting could be diagnostic for one of the (orthorhombic) polymorphs, especially because it was unreported by many of the authors quoted by Phillips and Rickwood

(1975). The fact that the supplementary reflection at about 3.30 Å was ignored by Nuffield (1943) vide Phillips and Rickwood (1975) in a P2cm prehnite, which has the same symmetry as supposed for the Surduc one, can be eventually due to the presence in his sample of other admixed polymorphs. The assumption that the prehnite from Surduc has an orthorhombic symmetry is supported by the minimal differences between calculated and measured d-spacings in Table 4. None of the indexed reflections was moreover rejected as orthorhombic by the program used for refinements (AP-LEM by Appleman and Evans, 1973).

Another striking feature of the diffraction pattern described here consists in the marked difference between the values of its d-spacings and those recorded for the two other samples presented in Table 4. The X-ray reflections of the Surduc prehnite were systematically recorded at higher values of 2 θ angles (smaller d) than those of the other samples in the table. This fact suggests a continuous series of lattice substitutions. The Fe^{3+} -for- Al^{VI} substitution was already discussed (e.g. Phillips and Rickwood, 1975) and it seems to play an important role in the positioning of d-spacings. Another substitution, this time in the tetrahedral sites, may be however as important as the reported one: The substitution of Si^{4+} by Al^{3+} . Both replacements influence the cell dimensions and clearly conduce to an increase (Fe^{3+} -for- Al^{VI}) or a decrease (Al^{IV} -for-Si) of the recorded d-spacings. As in the analysed sample the percentage of tetracoordinated Al are unusually large (see before), the effect of Al^{IV} -for-Si substitution must prevail if consider the enough low Fe^{3+} contents which were reported.

Replacement of Si^{4+} ions by the smaller Al^{3+} must give rise to a decrease in lattice dimensions. Accordingly, the unit cell parameters of prehnite from Surduc were determined by three cycles of least-squares refinement of the data in Table 4, using the computer program of Appleman and Evans (1973). The ob-

Table 5
Comparative crystallographic data for prehnites from various occurrences

Crt. no.	Reference	Sample location	Cell parameter (Å)		
			a	b	c
1	Nuffield (1943)	Ashcroft (Canada)	4.642	5.487	18.490
2	Kitahara (1966)	Hirose (Japan)	4.595	5.495	18.423
3	Saravanan et al. (1971)	Sankaridrug (India)	4.596	5.520	18.700
4	Conti et al. (1974)	Cala Francese (Italy)	4.610	5.470	18.450
5	Matsueda (1975) ⁽¹⁾	Sampo (Japan)	4.641	5.500	18.516
6	Matsueda (1975) ⁽²⁾	Sampo (Japan)	4.630	5.495	18.522
7	Phillips, Rickwood (1975) ⁽³⁾	Prospect (Australia)	4.642	5.487	18.490
8	Metcalf-Johansen (1983)	Ilimaussaq (Greenland)	4.628	5.485	18.478
9	Zunic et al. (1990)	Komiza (Yugoslavia)	4.646	5.491	18.520
10	present work	Surduc (Romania)	4.623	5.477	18.460

(1) - iron-rich prehnite.

(2) - iron-poor prehnite.

(3) - as given by J.C.P.D.S. card 29-290.

tained values are listed in Table 5, together with similar ones given by various authors for prehnites in other occurrences. As expected, our values are considerably lower than those quoted by different other sources and offer a good explanation for the unusual small cell volume which was deduced ($V = 467.467 \text{ Å}^3$). This value, correlate with the molecular mass reported before, gives, for $Z = 2$, a calculated specific gravity of 2.944, in perfect agreement with the measured one.

Thermal behaviour

The DTA, DTG and TGA curves of prehnite from Surduc were performed using a MOM 1500 D derivatograph with Pt-Pt Rh thermocouple, at a mean heating rate of 10°C/min , in air.

As expected taking into account the mineral chemistry, the effects recorded on the three curves given in Figure 2 are essentially due to the depletion of water. The other possible effects, caused by the oxidation of Fe^{2+} and Mn^{2+} to Fe^{3+} and Mn^{3+} must be minor since

the Fe^{2+} and Mn^{2+} contents are not significant. A minute study of the TGA curve in Figure 2 reveals that the sample lost 4.31 wt. % in two well-defined single-steps weight loss between 725 and 900°C . The two major weight losses are recognisable from DTG (and DTA) curves as endothermic effects centred at 765 (785) and 848 (868) $^\circ \text{C}$ respectively. The weight losses recorded in this thermic interval can be undoubtedly assumed to the dehydration of prehnite since they closely approximate the stoichiometric content of water in prehnite: 4.37 wt. % for a formula of $\text{Ca}_2\text{Al}(\text{OH})_2(\text{AlSi}_3)\text{O}_{10}$. The fact that the hydroxyl is expelled as H_2O in different steps during prehnite heating was moreover already mentioned by Mackenzie (1957) or Conti et al. (1974).

It is also of note that more than one third of the total weight loss of 6.51 wt. % recorded on the TGA curve took place up to 725°C . This unusually high weight loss may be however attributed to the adsorbed water whose content is major because the preparatory technique which was used. This technique involves

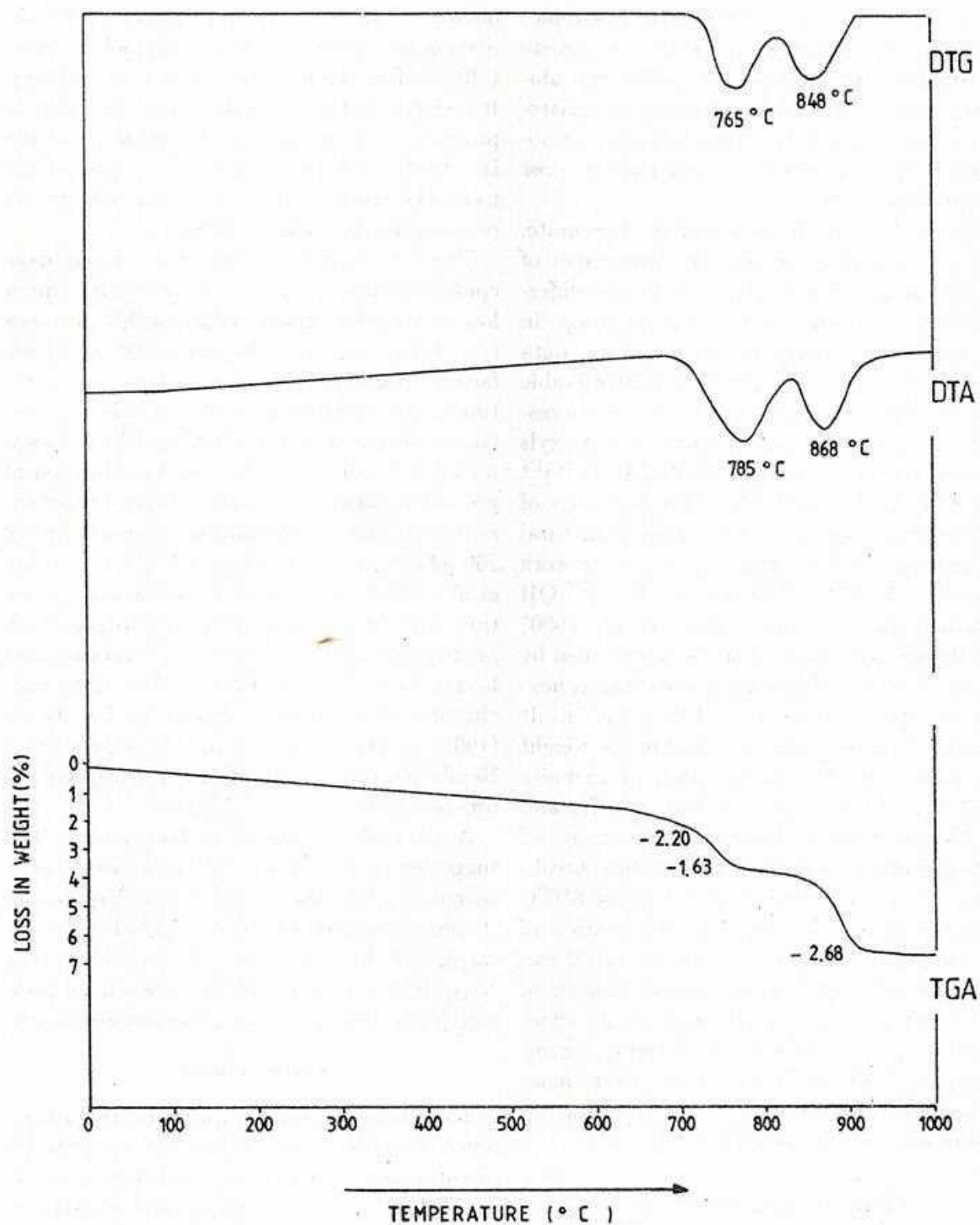


Fig. 2 – Thermal curves of prehnite from Surduc showing its progressive (two steps) dehydration.

the mixing of prehnite (0.25g for 1g of sample) with preheated alumina in order to complete the small quantity of sample. Although alumina is generally used as reference inert material, its hygroscopicity after calcination is noticeable and explains the supplementary loss of adsorbed water.

Coming back to the dehydration of prehnite, it seems logical to assume the two stages of weight loss previously reported to two different thermal motions of the hydroxyl groups in the structure. Based on the structural data given by Zunic et al. (1990), it is predictable that the first step of weight loss in succession corresponds to the expulsion of hydroxyls which simultaneously co-ordinate $(\text{Al}, \text{Fe}^{3+})^{\text{VI}}$ and $(\text{Ca}, \text{Fe}^{2+}, \text{Mn}^{2+})^{\text{VI}}$. This first step of dehydration does not cause major structural changes and the breakdown of the network since the $(\text{Al}, \text{Fe}^{3+})^{\text{VI}}\text{-O}$ and $(\text{Al}, \text{Fe}^{3+})^{\text{VI}}\text{-OH}$ distances are very close (Zunic et al., 1990) and the charge balance may be maintained by the simultaneous oxidation of the divalent hexacoordinated cations (e.g. $\text{Fe}^{2+}, \text{Mn}^{2+}$). It amounts to more than one third of the weight loss caused by the dehydration of prehnite (1.63 wt. % for a total of 4.31 wt. %) and practically expresses the maximal capacity of hydroxyl extraction without structure breakdown. The second endotherm at about 850°C certainly marks the complete dehydration of the sample since there is no weight loss thereafter. It evidently causes the breakdown of the structure. The small exothermic effect recorded on the DTA curve at 900°C (mentioned at 850°C by Conti et al., 1974) must consequently indicate a normal structural reorganisation of the resulted compounds.

Genetic considerations

As shown by many authors (e.g. Einaudi et al., 1981; Pan et al., 1991 etc.), hydration is a characteristic retrograde alteration in skarn areas and equally affects Fe-rich skarns. Peculiarising for the occurrence at Surduc, it is

obvious that prehnite and epidote, both replacing andradite and calcic plagioclase, crystallised after the primary mineral assemblage. It seems therefore normal to consider them as products of a retrograde alteration or of the late hydrometasomatism which is more likely to be the latest stage of a protracted episode of skarn development in the area.

The low-variance mineral assemblage epidote-prehnite is very similar to that one in low-to very low grade metamorphic terranes (prehnite-pumpellyite to greenschist transition facies). Consequently it seems logical to estimate for prehnite in both behaviours similar conditions of crystallisation. As the estimated P-T conditions for the equilibration of prehnite-epidote (Ps_{30}) assemblage in metabasites indicate crystallisation temperatures of 260–320°C for pressures of 1.5–2 kbars (Liou et al., 1985), we consider that the crystallisation of prehnite in skarns from Surduc, which are in equilibrium with epidote, was controlled by the same P-T conditions. The same conclusions were moreover drawn by Pan et al. (1991) in their analysis on the skarns from Hemlo (Ontario), judged in a more restricted pressure context ($P = 1.7$ kbars).

A low mole fraction of carbon dioxide, also suggested by Pan et al. (1991), is entirely consistent with the normal conditions required by the crystallisation of the Ca-Al(Fe) hydrosilicates, including prehnite. The estimation that X_{CO_2} did not exceed 0.05 at the assumed pressure (of 1.5–2 kbars) seems reasonable enough.

Conclusions

The present study emphasises the occurrence of prehnite, an ubiquitous low-pressure phase in calcic systems, in skarns from Surduc. These skarns may be considered endoskarns *sensu* Korzhinskii (1965) since the primary skarn assemblages include plagioclase (An 51 Ab 45 Or 4) and diopside pseudomorph on amphibole.

Morphological aspects, peculiarities of the infrared spectrum and of the X-ray diffrac-

tion pattern suggest that prehnite from Surduc has an orthorhombic symmetry and an increased degree of ordering which accounts for the P2cm polymorph.

Prehnite from Surduc has a low- to medium-iron content but is more aluminous than the great majority of the samples from other localities. Al occupies more than 25 % of the tetrahedral sites and, consequently, an unusual small cell volume and a higher specific gravity were recorded. Thermal data suggest that hydroxyl groups are located in two different structural sites, being therefore expelled in two distinct steps.

Microscopic analysis reveals that at Surduc epidote is always found in paragenesis with prehnite. It seems obvious that as temperature decreases during the retrograde evolution of the skarn system, prehnite may crystallise together with epidote as complex pseudomorphs on plagioclase.

Lastly, it seems reasonable to consider that similarity in chemistry and P-T-X conditions favours the prehnite crystallisation and therefore prehnite is more widespread than previously reported in Romanian calcic skarns.

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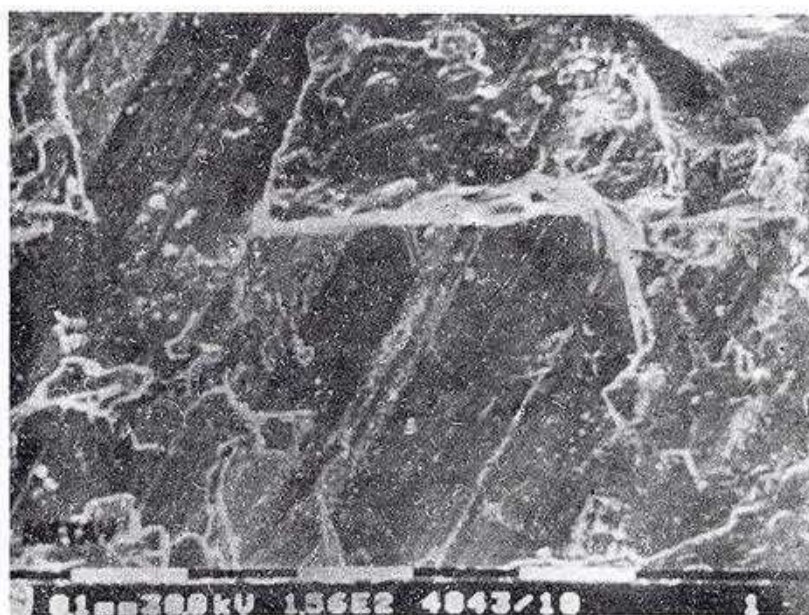
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Fig. 1 - Scanning-electron microphotograph of prehnite. The rectangular growth-pattern on the (110) face can be observed. Bar scale represents 0.1 mm.

Fig. 2 - Scanning-electron microphotograph of a prehnite aggregate, taken in approximate parallelism with (001) faces. (110) and reduced (100) faces can be inferred. Bar scale represents 0.1 mm.



1



2



PROPUNERI DE ÎMBUNĂTĂȚIRE A SISTEMULUI ACTUAL DE CLASIFICARE ȘI ANALIZĂ A POTENȚIALULUI DE SUBSTANȚE MINERALE UTILE SOLIDE

M. BORCOȘ, B. GĂBUDÉANU, Șt. SIMESCU

Institutul Geologic al României. Str. Caransebeș nr.1, R 78344 București 32.

Key words: Mineral potential. Reserves - Resources. Classification and Promotion System.

Abstract: The proposed classification system and analysis methodology make possible the reintegration of the existing reserves and resources according to the tridimensional scheme of representation of the geological, technological and economic features, recently adopted by the Economic Commission for Europe (United Nations). The aspects determined for the representative types of metalliferous ores permit a clear differentiation of the economic reserves from the noneconomic ones and take into discussion the position of the perspective reserves whose integration and economic significance are to be better specified. The results obtained for the base-metal, cupriferous, gold-silver and ferrous ores confirm, for the main ore deposits, ore deposit groups and genetic - mining units (districts, mining fields), the high geo-economic confidence degree of the system and, at the same time, they can contribute to the establishing of the policies and strategies of development in the fields of fundamental and applicative surveys (geologic and technologic) and of the capitalization of the mineral resources.

Considerații preliminare

Sistemele de clasificare a potențialului mineral au evoluat concomitent cu intensificarea proceselor de valorificare, criteriile de sistematizare fiind influențate de caracteristicile politicilor economice. Pe plan internațional, deși există mai multe sisteme de clasificare, acestea pot fi raportate la două modele: adjectival - utilizat de țările cu economie de piață și alfa-numeric specific fostelor țări cu economie planificată - dirijată. În principiu, ambele modele se sprijină pe scheme tridimensionale de determinare a gradului de cunoaștere geologică, tehnologică și economică. Neconcordanța fundamentală dintre cele două sisteme de clasificare constă în modul diferit în care este structurat - sistematizat potențialul geologic de substanțe minerale utile în grupe și categorii de rezerve și resurse pe criterii geologice - tehnologice (cantitate, calitate, condiții de extracție, preparare), în acord cu posibilitățile de valorificabilitate economică.

Utilizarea terminologiei diferite a celor două sisteme nu constituie un impediment esențial în realizarea unor posibile corespondențe între grupele și categoriile de rezerve și resurse. Dificultatea, și chiar imposibilitatea unor asemenea corespondențe, apare însă atunci când

se încearcă caracterizarea și analiza economică a rezervelor și resurselor, chiar și în situațiile în care acestea ocupă poziții ierarhice comparabile (în parte) în structura celor două modele de clasificare. La aceasta se pot adăuga și implicațiile negative generate de modul de evaluare a parametrilor geologici (cantitate, calitate) și tehnologici în sistemul alfa - numeric, evaluare care nu constituie însă un viciu al modelului, ci erori determinate de condițiile sistemului cu economie planificată.

Deciziile adoptate în activitățile de valorificare a bazei de materii prime în condițiile utilizării sistemului de clasificare specific fostelor țări comuniste explică, în bună măsură, colapsul economic al industriei miniere și lipsa de relevanță a datelor utilizate, de regulă, în stabilirea activităților productive și a strategiilor de dezvoltare. Această situație, cu efecte negative, ce se mențin parțial și în prezent, a determinat reanalizarea potențialului în scopul identificării unor posibile corespondențe între diversele categorii de rezerve și resurse din cele două sisteme în vederea eficientizării activității în industria minieră, printre primele țări din Europa Centrală și de Est care au acționat în acest sens numărându-se Polonia, Cehia și Slovacia (Jakubiak, Smalowski 1994).

În România, preocupări ce au vizat metodologia de evaluare a potențialului și structura acestuia, cu privire specială asupra relațiilor existente între rezerve și resurse, a promovării acestora în baza de materii prime exprimată în rezerve B + C₁ de bilanț, precum și în metal echivalent pentru minereuri metalifere au început în cadrul I.G.R. încă din anul 1970. În intervalul 1970-1990 s-au realizat și studii de reevaluare a potențialului pentru celelalte substanțe minerale utile solide (nemetallifere, cărbuni, roci de construcție și ornamentale) (Borcoș et. al. 1974, 1983, 1988; Boștinescu et. al. 1983; Vlad et. al. 1977, 1987, 1989). Din 1990, odată cu trecerea la sistemul economic de piață, activitatea de cercetare în domeniu a continuat prin resintetizarea datelor existente, făcând apel și la rezultatele studii de metalogenie cantitativă (Borcoș et. al. 1991, 1994-1996; Vlad et. al. 1990-1992; Găbudeanu 1994; Andrieș et. al. 1997; Harosa et. al. 1997; Simescu et. al. 1997). Într-o primă fază, au fost scoase în evidență principalele curențe ale activității de cercetare - valorificare în domeniul resurselor minerale, semnalandu-se încadrarea incorectă a rezervelor și resurselor, menținerea în activitate a numeroase obiective lipsite de importanță economică, raportarea incorectă a volumelor de rezerve și resurse, precum și incoerența unora din programele de cercetare geologică (Borcoș et. al. 1991). În activitatea care a urmat au fost făcute propuneri de adaptare a încadrării rezervelor și resurselor pe considerente economice conform sistemului de clasificare adjectival utilizat în țările cu economie de piață (Borcoș et. al. 1994). Aceste studii au ținut cont și de solicitările Direcției Generale Strategia Industrii Miniere și Geologiei din Ministerul Industriilor interesată de elaborarea unui sistem de clasificare a rezervelor compatibil cu cele existente pe plan internațional și au decurs în paralel cu activitatea desfășurată pe plan internațional sub egida Comisiei Economice pentru Europa de pe lângă O.N.U. Concluziile reuniunilor de lucru ale acestei comisii (1994-1997) au accentuat și motivat, în special sub aspect economic, utilitatea identificării cadrului, criteriilor și elementelor fundamentale, inclusiv a terminologiei adecvate, în vederea elaborării unui sistem de referință tridimensional de clasificare a rezervelor și resurselor față de care pot fi raportate, adaptate și/sau modificate sistemele de clasificare naționale existente (Energy/WP.1/R.54 ECE-UN document 1996). Neconcordanțele identificate, în special cele care vizează aspectele de valorificare economică a potențialului, au determinat numeroase demersuri pentru revizuirea sistemului actual de clasificare, ca și pentru elaborarea și omologarea unui nou sistem compatibil cu noua situație economică în vederea asigurării unei mai bune cunoașteri a diverselor categorii de rezerve și resurse, a determinării semnificației economice

reale a acestora și a creerii posibilităților de dialog internațional în domeniu (Borcoș et. al. 1994, Găf - Deac, Bogatu 1995).

Structura potențialului natural mineral

Structura redefinită și metodologia de analiză a potențialului mineral ce respectă criteriile specifice economiei de piață și utilizează o terminologie adecvată - adjectivală, au fost elaborate în scopul obținerii de elemente în măsură să fundamenteze politicile și strategiile în activitățile de cercetare și valorificare a substanțelor minerale utile solide. Noua structură a potențialului oferă o imagine coerentă a relațiilor existente între diversele categorii și grupe de rezerve și resurse, între acestea și activitățile specifice de cercetare geologică, tehnologică și analiză economică și, în final, stabilește modul de promovare a potențialului mineral, prin transformări succesive în funcție de rezultatele evaluărilor geologice, tehnologice și economice, în produse miniere finite, vandabile.

Au putut fi astfel obținute date preliminare privind semnificația economică a diverselor obiective, date care urmează să fie verificate prin studiile de fezabilitate sau prefezabilitate. O asemenea metodologie se dovedește a fi, în această etapă de adoptare a unui sistem unitar de clasificare, cu atât mai necesară cu cât, în România, gradul de cunoaștere a potențialului și imposibilitatea corelării riguroase a categoriilor și grupelor de rezerve/resurse din cele două sisteme nu permit o estimare și încadrare corectă a acestora. Metodologia va trebui menținută până la reconsiderarea tuturor rezervelor și resurselor determinate în sistemul alfa-numeric existent, în funcție de conceptul de clasificare promovat pe plan internațional. Aplicarea schemei și metodologiei de clasificare presupune o bună cunoaștere metalogenetică și geologică a obiectivelor analizate (în principal localizare, morfologie, ordin de mărime, compoziție mineralogică și chimică, tendințe de variație și distribuție, productivitatea tipurilor genetice ș.a.), a condițiilor de zăcămint, precum și a celor de exploatare, preparare și valorificare.

Schema de clasificare propusă de către I.G.R. (fig. 1), răspunde dezideratelor menționate, ținând seama totodată și de situația existentă în România. Se asigură astfel delimitarea tipurilor de rezerve și resurse în funcție de gradul de cunoaștere geologic, bazat pe complexitatea tipurilor de investigație (explorare detaliată și foarte detaliată, explorare generală, explorare informativă, prospecțiune, studii și recunoașteri), pe analiza tehnologică și economică, echivalentă parțial studiilor de fezabilitate/prefezabilitate, de oportunitate, rapoartelor și altor documentații cu caracter geoeconomic. În funcție de criteriile menționate, rezervele și resursele (rezerve și resurse măsurate, indicate și

probabile și resurse posibile) se pot separa în trei grupe (rezerve de interes imediat - R.I.¹, rezerve de perspectivă - R.p.² și resurse - r.³), cu valori economice distincte (economice, marginal economice și neeconomice) și cu implicații conjuncturale în dinamica activității de cercetare geologică - tehnologică.

Principala problemă în aplicarea acestei scheme o constituie încadrarea rezervelor și resurselor existente, clasificate conform modelului alfa-numeric (A, B, C₁, C₂, P₁, P_{1c}, P₂, de bilanț, afară de bilanț și neclasificate), în sistemul adjectival. Din fig. 2 rezultă inadvertențele identificate în încercarea de raportare a datelor, determinate în special de caracteristicile economice. Astfel, din studiile de reevaluare a potențialului pentru substanțe minerale utile metalifere (minereuri polimetale, cuprifere, auro-argentifere și feroase), se constată că o mare parte

din rezervele superioare (A, B, C₁) de bilanț (considerate economice) care stau la baza activităților productive nu îndeplinesc condiții de valorificabilitate economică, parametrii de calcul (tehnologici - economici) plasându-le în sfera rezervelor marginal economice sau chiar a resurselor neeconomice. Celelalte categorii de rezerve (B, C₁) în afară de bilanț sau neclasificate, C₂, precum și rezervele de prognoză (P₁, P_{1c}, P₂) prezintă aceeași fluctuație funcție de criteriile tehnico - economice, în general existând tendințe de trecere spre grupe și categorii inferioare.

Mișcarea rezervelor și resurselor determinate, de la categorii și grupe inferioare spre cele superioare, presupune activități specifice de cercetare geologică, tehnologică și analiză economică, care uneori pot fi influențate și de condiții conjuncturale de politică economică (fig. 3).

Metodologia de analiză și promovare a potențialului mineral

Metodologia de analiză și promovare a potențialului mineral ia în considerare elementele primare cu accepțiune riguroasă definită, respectiv potențialul geologic natural (cuantificat și necuantificat), repartizat pe grupe (R.I., R.p. și r.) și diferențiat pe categorii în funcție de gradul de cunoaștere (fig. 4).

În prima treaptă de promovare - evaluarea geologică, potențialul geologic natural - P.G.N. cuantificat (R.I. + R.p. + r) este transformat, prin aplicarea coeficienților de promovare cantitativă (r_1 , r_2) și calitativă (r_{1i} și r_{2i}), în potențial geologic echivalat în rezerve măsurate de interes imediat (P.G.E.R.m.I.). Acest potențial care reprezintă baza de materii prime reală, respectiv volumele de minereu definite cantitativ și calitativ, exprimate unitar, fundamentează deciziile privind investițiile necesare activităților de producție, precum și politicile de dezvoltare.

A doua treaptă de promovare - evaluarea industrială decurge în trei faze în care se estimează succesiv volumele de minereu obținute în procesul de extracție minieră (prin aplicarea coeficienților de transformare cantitativă și calitativă (k_{qi} și k_{ci})) (faza 1), cantitățile de elemente utile recuperabile în concentrate - produse miniere (prin utilizarea indicatorilor de extracție - v , a_i , m_i , c_i) (faza 2) și produsele finite, respectiv cantitățile de elemente utile rezultate în urma prelucrării chimico - metalurgice și fizico - chimice a produselor miniere, toate acestea prin utilizarea randamentelor de prelucrare metalurgică și chimică (η_i) (faza 3). Se obține astfel potențialul geologic echivalat în rezerve industrializabile (P.G.E.R.I.) care permite evidențierea dinamicii gradului de recuperare a elementelor utile în fazele de extracție, preparare și prelucrare, până la obținerea produselor finite, reflectând

¹ Rezerve de interes imediat (R.I.):

- rezerve măsurate (R.m.) - grad înalt de certitudine geologică obținut prin explorare detaliată și foarte detaliată (E.D.); valorificabilitate actuală confirmată de studii de fezabilitate cu rezoluție economică pozitivă (eroare $\pm 10\%$);
- rezerve în exploatare;
- rezerve indicate (R.i.) - certitudine geologică satisfăcătoare obținută prin explorare generală (E.G.); indicații tehnologice și economice favorabile, comparabile cu R.m., motivate de studii de fezabilitate, ocazional și de studii de fezabilitate;
- rezerve probabile (R.p.) - grad scăzut (local satisfăcător) de cunoaștere geologică obținut prin lucrări de explorare informativă (prospecțiune E.I.-Pr.); informații tehnologice punctuale cu posibile semnificații economice sugerate de studii de oportunitate și/sau de documentații geologice.

² Rezerve de perspectivă (R.p.):

- rezerve măsurate (R.p.m.) - grad înalt de certitudine geologică obținut prin E.D.; valorificabilitate actuală grevată, în principal, de dificultăți tehnologice, economice $\pm$ caracteristici naturale nefavorabile determinate prin studii de fezabilitate și fezabilitate;
- rezerve indicate (R.p.i.) - certitudine geologică satisfăcătoare obținută prin E.G.; indicații tehnologice parțial satisfăcătoare, cu posibile semnificații economice actuale, semnalate de studii de fezabilitate, ocazional și de studii de fezabilitate;
- rezerve probabile (R.p.p.) - grad scăzut (local satisfăcător) de cunoaștere geologică obținut prin E.I.-Pr.; informații tehnologice orientative, în general fără relevanță economică actuală, sugerate de studii de oportunitate și/sau de documentații geologice.

³ Resurse (r.):

- resurse măsurate (r.m.) - grad înalt de certitudine geologică obținut prin E.D.; fără posibilități de valorificare actuală și în perspectiva imediată, cu rezoluție economică lipsită de interes, determinate prin studii de fezabilitate și fezabilitate;
- resurse indicate (r.i.) - certitudine geologică satisfăcătoare obținută prin E.G. și indicații tehnologice parțial satisfăcătoare; fără posibilități de valorificare în perspectiva imediată, determinate prin studii de fezabilitate, ocazional și de studii de fezabilitate;
- resurse probabile (r.p.) - grad relativ scăzut (local satisfăcător) de cunoaștere geologică obținut prin E.I.-Pr. și studii (S.); informații tehnologice punctuale neconcludente, semnalate de studii de oportunitate și/sau de documentații geologice;
- resurse posibile (r.ps.) (ipotetice-speculative) - argumentare geologică speculativă obținută prin S, recunoașteri (R) (Pr.; informații obținute, în special prin cercetare geologică fundamentală).

în acest fel nivelul procesului tehnologic aplicat.

A treia etapă de promovare - evaluarea economică, permite estimarea gradului de valorificabilitate a potențialului pe criterii economice. Utilizând parametrii economici (prețuri ale produselor finite, prețuri de cost specifice activităților derulate) se obține potențialul geologic echivalat în produse valorificabile (P.G.E.P.V.) care, funcție de raportul între valoarea tonei de minereu și costurile de producție, permite încadrarea economică a produselor finite (economice, marginal economice, neeconomice). Această ultimă etapă de transformare a potențialului constituie, în prezent, o problemă încă nerezolvată datorită lipsei informațiilor care concură la stabilirea costurilor reale ale activităților specifice valorificării bazei de materii prime minerale. Parcurgerea integrală a procesului de promovare, implicit cu crearea posibilității efectuării unei analize economice concludente, va asigura o determinare corectă a valabilității încadrării tipurilor de rezerve și resurse în schema de clasificare tridimensională adoptată.

Coeficienții utilizați pentru promovarea P.G.N. la P.G.E.P.V., cu limitele de variație prezentate în fig. 5 se stabilesc pentru fiecare obiectiv în funcție de dinamica rezervelor pe perioade lungi de timp și de studiile de condiții industriale - r_1, r_2, r_{11}, r_{21} , de studiile de condițiile industriale și de eficiența metodelor de extracție minieră - k_q, k_c , de eficiența metodelor de preparare - v, a_i, m_i, c_i , și, în final, de eficiența metodelor de prelucrare metalurgică - η_i .

În metodologia utilizată, pornind de la valoarea elementelor utile, s-a obținut un element de analiză, respectiv metalul echivalent, utilizat atât pentru produsul finit cât și pentru tipurile de potențiale geologice din care acesta derivă prin promovare. Metalul echivalent permite astfel stabilirea, în diferite etape de promovare a potențialului, a gradului de recuperare în metal, respectiv a eficienței metodelor tehnologice aplicate (extracție și preparare) și oferă implicit posibilități de analiză comparativă între obiective cu compoziții diferite.

Pentru eficientizarea aplicării metodologiei, ținând seama de numărul extrem de mare de date primare, de complexitatea procesului de promovare (numeroase informații de natură geologică, tehnologică și economică) și de necesitatea interpretării integrate a acestora a fost elaborat un produs informatic - GEODA (fig. 6) (Călțan 1993; Călțan, Muntean 1996). Acesta se bazează pe criterii de sistematizare, stocare și prelucrare a datelor în coordonate constante (geologice) și variabile (tehnologice - economice) ce pot asigura abordarea unor scenarii în funcție de diverse situații conjuncturale. Programul a fost aplicat pentru obținerea unei situații globale, preliminară, pentru minereurile metalifere menționate (Pb, Zn, Cu, Au, Ag, Fe, Mn).

Concluzii

Studiile efectuate demonstrează necesitatea reanalizării potențialului mineral pe coordonate, riguros determinate, de natură geologică, tehnologică și economică, în măsură să asigure o gestionare rațională a acestuia și o dezvoltare coerentă a activităților de cercetare și producție, în concordanță și cu exigențele actuale existente pe plan internațional. Sistemul de clasificare și metodologia de analiză a potențialului propuse asigură o reîncadrare a rezervelor și resurselor existente, cu evidențierea semnificației economice reale a acestora, înlesnind totodată posibilități de comparare cu situațiile existente pe plan mondial.

Rezultatele obținute pentru tipurile reprezentative de minereuri metalifere analizate (polimetalice, cuprifere, auro-argentifere, feroase) permit, în această fază, o departajare clară a rezervelor economice de cele neeconomice, constatându-se o tendință de diminuare severă a volumelor aferente categoriilor și grupelor cu valoare economică ridicată. Într-o poziție neconcludentă se situează rezervele de perspectivă, care în unele accepțiuni sunt considerate ca reprezentând resurse, a căror încadrare și semnificație economică nu a putut fi încă determinată, și care, în prezent, sunt considerate ca rezerve marginal economice; informațiile suplimentare ce pot fi obținute prin studiile de fezabilitate și prefezabilitate ce se impun a fi efectuate prioritar, urmând să permită stabilirea tendințelor de migrare a acestora, fie în sfera rezervelor economice, fie în cea a resurselor neeconomice.

Determinarea semnificației potențialului în contextul noii metodologii propuse oferă elementele ce pot contribui la stabilirea politicilor și strategiilor de dezvoltare în domeniul activităților de cercetare fundamentală și aplicativă (geologică - tehnologică) și de valorificare a substanțelor minerale utile. Astfel pot fi luate decizii privind menținerea, sistarea sau abandonarea obiectivelor de cercetare sau exploatare, pot fi orientate politicile de subvenționare, concesionare, reorganizare etc.

Schema de clasificare și metodologia de analiză a potențialului mineral, elaborată pe baza cercetărilor efectuate pentru minereuri, confirmă gradul ridicat de confidență geo-economică determinat la nivelul principalelor zăcămintă, grupe de zăcămintă și unități genetice - miniere (districte, câmpuri miniere). Ele pot sta în atenția instituțiilor interesate în vederea omologării și aplicării pentru toate substanțele minerale utile, ținând seama de specificul acestora, de la nivelul entităților componente ale unui obiectiv până la ansamblul teritoriului.

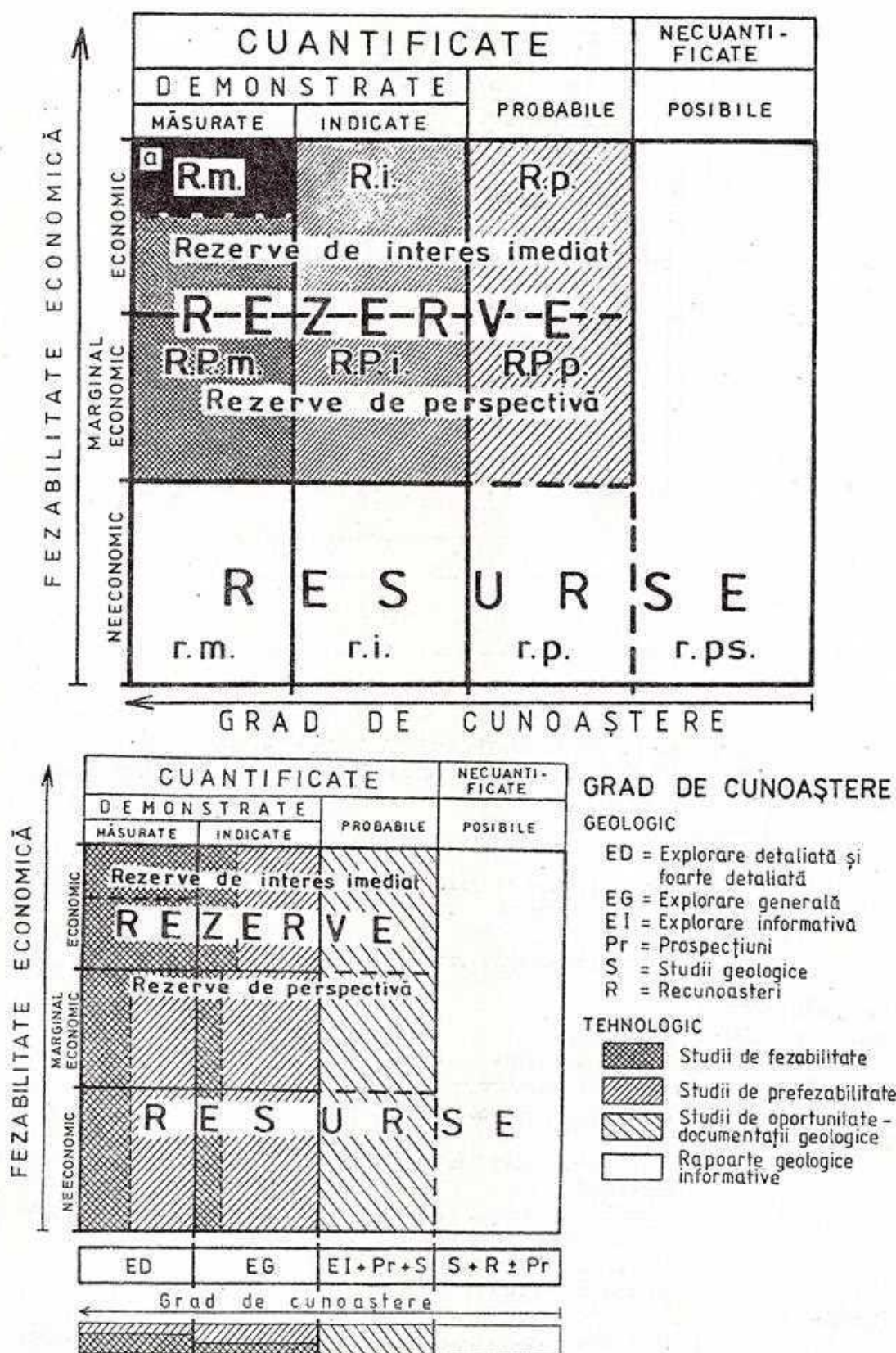


Fig. 1. SISTEM PROPUȘ PENTRU CLASIFICAREA REZERVELOR ȘI RESURSELOR

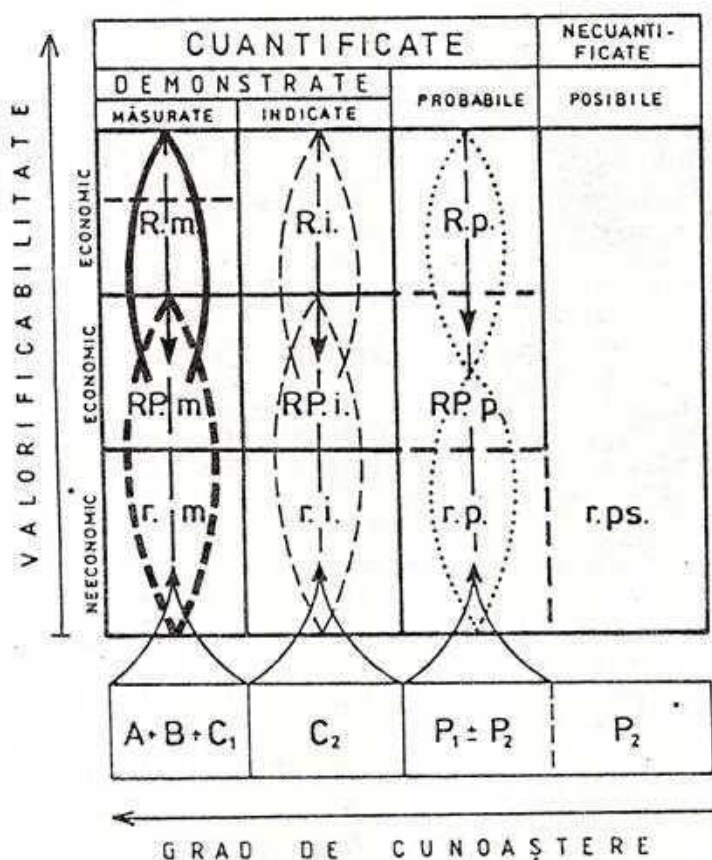


Fig. 2. TRANSPUNEREA STRUCTURII POTENȚIALULUI MINERAL DIN SISTEMUL DE CLASIFICARE ALFA-NUMERIC ÎN CEL ADJECTIVAL



Rezerve de bilanț

Rezerve în afară de bilanț și/sau neclasificate și rezerve de bilanț necorespunzător încadrate, parțial cumulate

Rezerve de prognoză, parțial cumulate

CORESPONDENȚE:

Rezerve de interes imediat - R.I.i.

R.m. = $A+B+C_1$ rezerve grupa de bilanț;

R.i. = C_2 rezerve în extinderea rezervelor de bilanț;

R.p. = $P_1 \pm P_2$ rezerve de prognoză.

Rezerve de perspectivă - R.P.

R.P.m. = $B+C_1$ rezerve grupa afară de bilanț și, parțial, $A+B+C_1$ rezerve grupa de bilanț; C_1 rezerve neclasificate;

R.P.i. = C_2 rezerve în extinderea rezervelor în afară de bilanț și, parțial, $B+C_1$ rezerve de bilanț $\pm C_2$ rezerve în extinderea rezervelor de bilanț; C_2 rezerve în extinderea rezervelor neclasificate C_1 ;

R.P.p. = $P_1 \pm P_2$ rezerve de prognoză.

Resurse - r.

r.m. = $B+C_1$ rezerve grupa afară de bilanț și, parțial, $A+B+C_1$ rezerve grupa de bilanț; C_1 rezerve neclasificate;

r.i. = C_2 rezerve în extinderea rezervelor în afară de bilanț și, parțial, $B+C_1$ rezerve de bilanț $\pm C_2$ rezerve în extinderea rezervelor de bilanț; C_2 rezerve în extinderea rezervelor neclasificate C_1 ;

r.p. + r.ps. = $P_1 \pm P_2$ rezerve de prognoză.

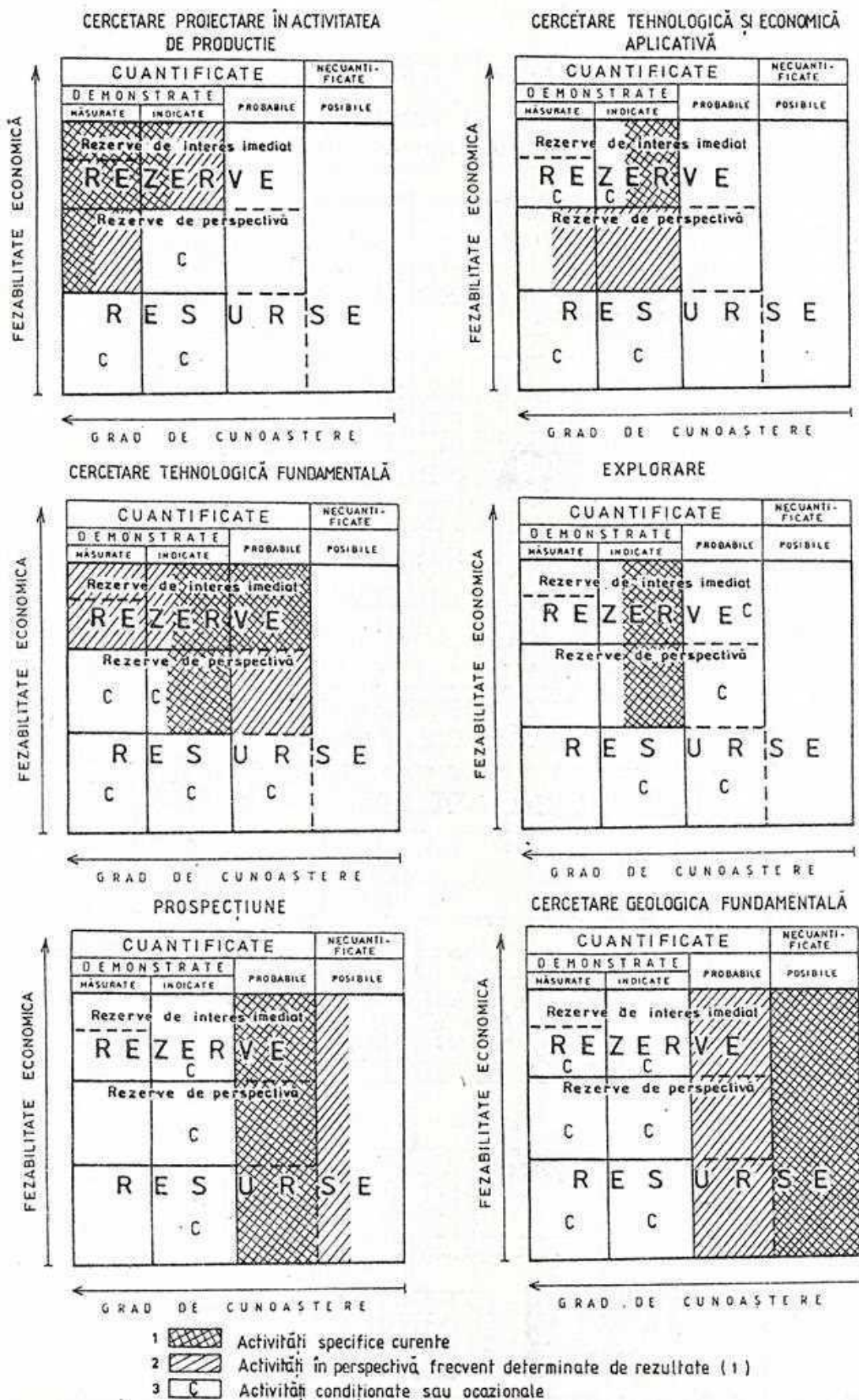


Fig. 3. RELAȚIA POTENȚIAL MINERAL/DOMENII SPECIFICE ACTIVITĂȚILOR DE CERCETARE/PROIECTARE

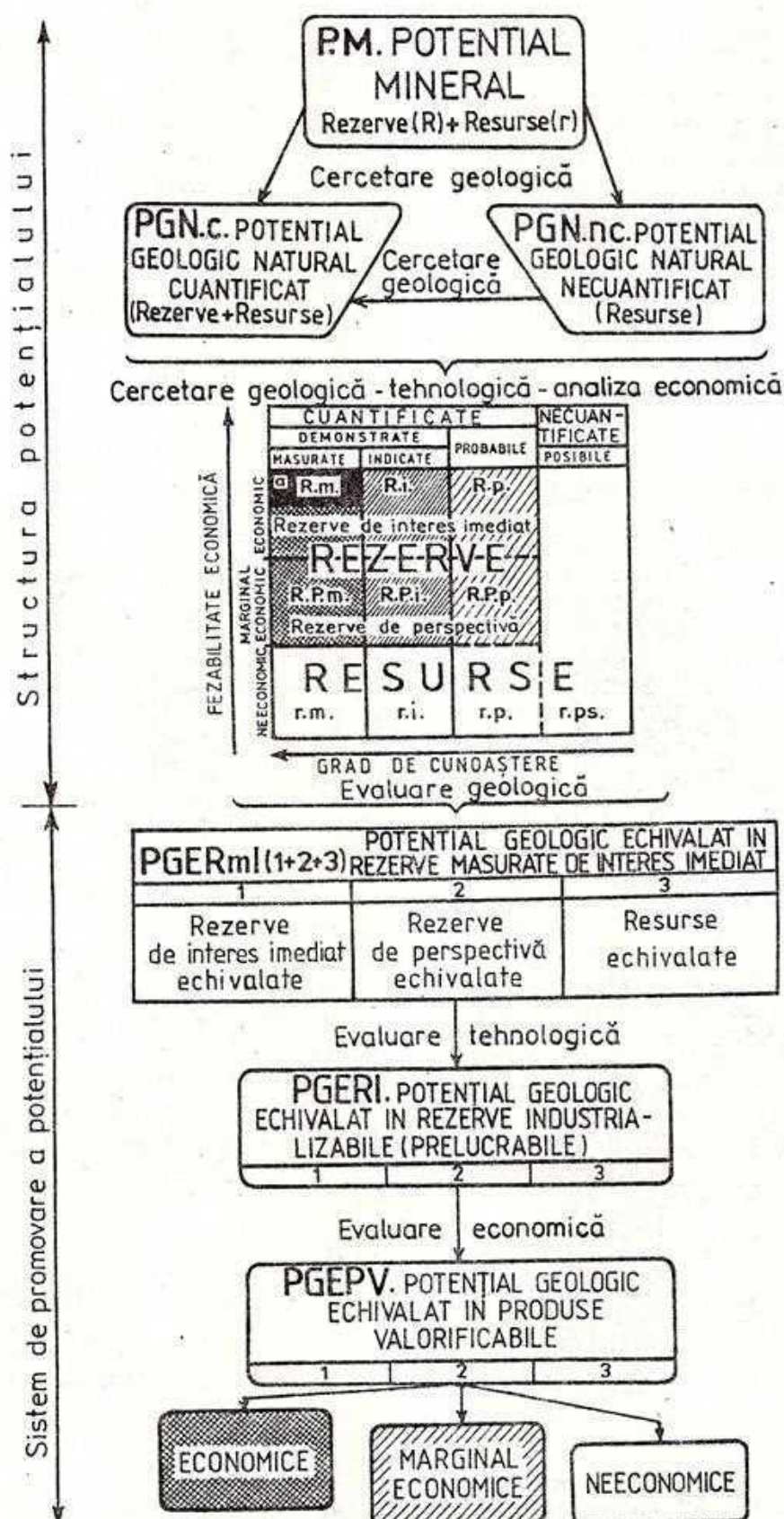
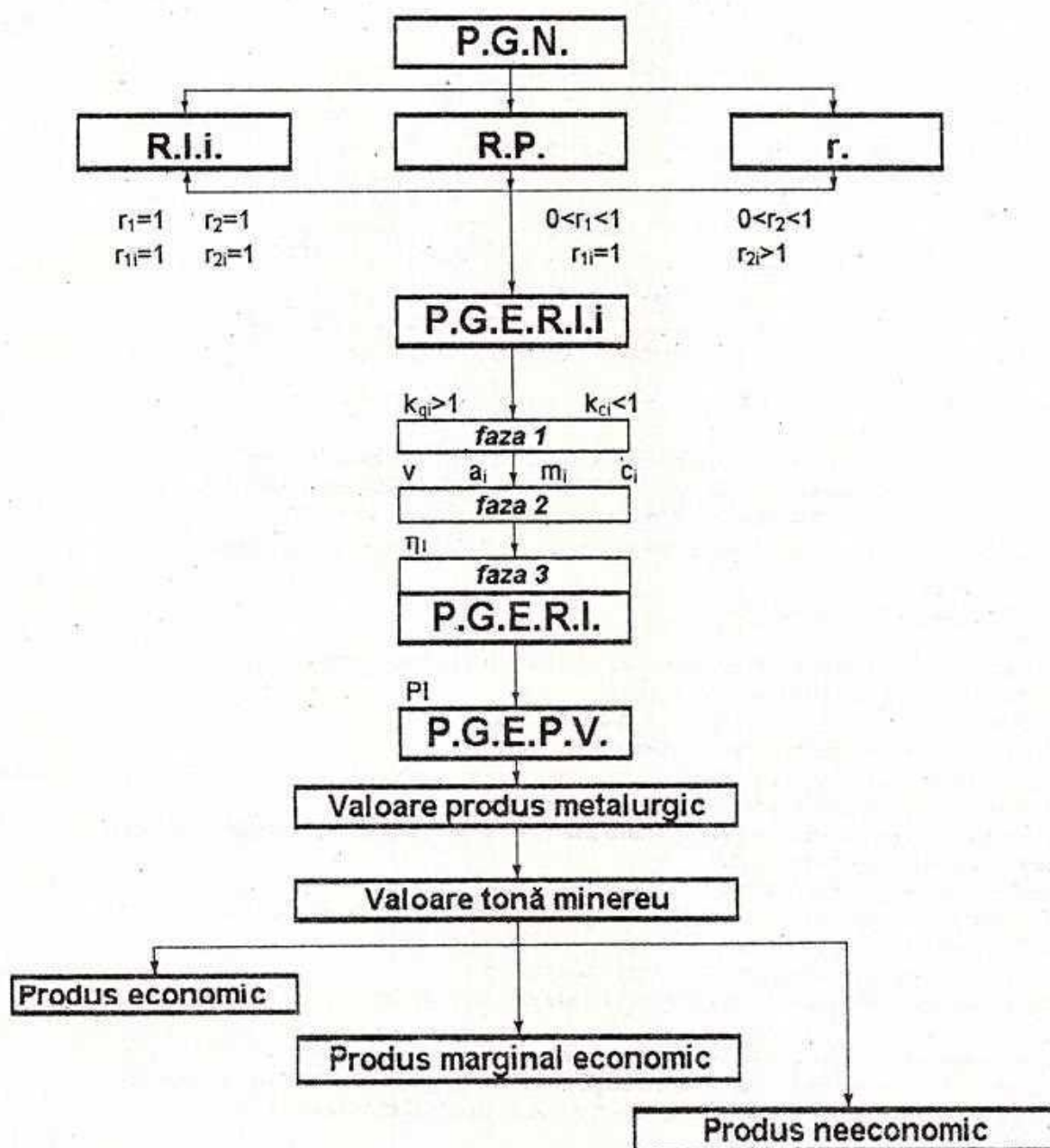


Fig 4. STRUCTURA ȘI SISTEMUL DE PROMOVARE A POTENȚIALULUI MINERAL
(detalii în fig. 1 și 5)



r_1, r_2 - coeficienți de transformare cantitativă;

r_{1i}, r_{2i} - coeficient de transformare calitativă;

k_{qi} - coeficient de transformare cantitativă; k_{ci} - coeficient de transformare calitativă

v - extracție în greutate (%); a_i - conținutul minereului de alimentare în elemente utile (g/t, %);

m_i - extracția în metal din minereul de alimentare (%); c_i - conținutul concentratelor (g/t, %);

η_i - randament de extracție metalurgică (%)

PI - preț de livrare

Fig. 5. SCHEMA DE ANALIZĂ ȘI DE PROMOVARE A POTENȚIALULUI GEOLOGIC

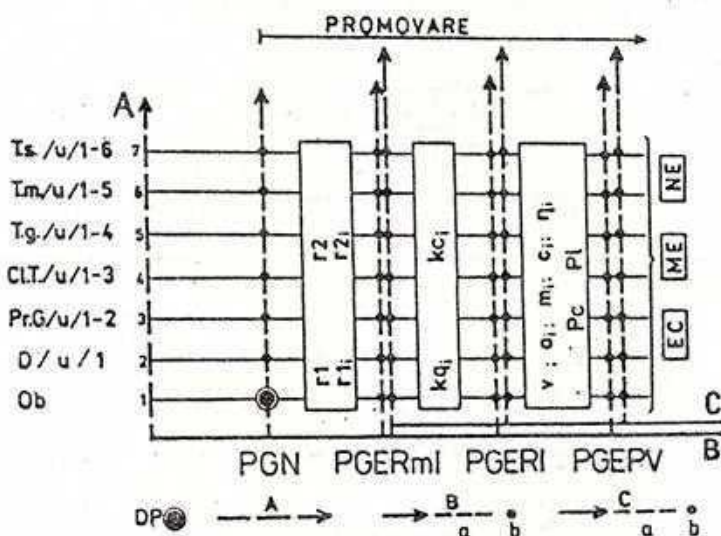


Fig. 6. SCHEMĂ DE STOCARE - ANALIZĂ ȘI PROMOVARE
A POTENȚIALULUI GEOLOGIC NATURAL - PROGRAM GEODA
(model logic - matematic elaborat de I. Călțan 1993, 1996)

A. Coordonată cu elemente fundamentale geologice - metalogenetice, sistematizate temporal/spațial:

1. obiectiv (zăcămint - acumulare);
2. district;
3. proces geologic generator (ex. vulcanism acid caledonian, magmatism neogen etc.);
4. ciclu geotectonic (ex. alpin, hercinic etc.);
5. tip genetic de minereu (ex. hidrotermal, lichid magmatic etc.);
6. tip compozițional de minereu (ex. cuprifer, aurifer etc.);
7. tip substanță (ex. Au; Ag; Pb, Zn etc.);
- U - unități geografice/geologice majore (Carpații Orientali, Dobrogea etc.).

B. Coordonată cu elemente ale potențialului geologic natural (cantitate, calitate, coeficienți de promovare, indicatori tehnologici):

- P.G.N. = Potențial geologic natural;
P.G.E.R.m.I. = Potențial geologic echivalat în rezerve măsurate de interes imediat;
P.G.E.R.I. = Potențial geologic echivalat în rezerve industrializabile;
P.G.E.P.V. = potențial geologic echivalat în produse vandabile.

C. Coordonată cu elemente economice: costuri globale de producție, preț livrare etc.

A coordonată cu elemente constante; B și C coordonate cu elemente variabile.

a. Direcție de cumulare secvențială și cumulativă; b. masive de date cu rezoluție geoeconomică specifică, în relație și cu elemente geologice - metalogenetice fundamentale (A 1 - 7).

DP = Date primare.

Coeficienți de promovare, indicatori tehnologici și economici:

- r_1 - coeficient de transformare cantitativă P.G.N. $\rightarrow$ R.m.+r.m.;
 r_2 - coeficient de transformare cantitativă R.m.+r.m. $\rightarrow$ P.G.E.R.m.I.
 r_{11} - coeficient de transformare calitativă P.G.N. $\rightarrow$ R.m.+r.m.;
 r_{21} - coeficient de transformare calitativă R.m.+r.m. $\rightarrow$ P.G.E.R.m.I.
 k_{q1} - coeficient de transformare cantitativă P.G.E.R.m.I. $\rightarrow$ P.G.E.R.I. (faza 1);
 k_{u1} - coeficient de transformare calitativă P.G.E.R.m.I. $\rightarrow$ P.G.E.R.I. (faza 1).

v - extracție în greutate (%)*;

a_1 - conținutul minereului de alimentare în elemente utile (g/t, %)*;

m_1 - extracția în metal din minereul de alimentare (%)*;

c_1 - conținutul concentratelor (g/t, %)*;

* v, a_1 , m_1 , c_1 : P.G.E.R.I. (faza 1) $\rightarrow$ P.G.E.R.I. (faza 2).

η_1 - randament de extracție metalurgică (%) P.G.E.R.I. (faza 2) $\rightarrow$ P.G.E.R.I. (faza 3).

P_c - Cost global de producție;

P_1 - Preț de livrare a produselor finite

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Footnotes should be numbered consecutively.

Citations in the text should include the name of the author and the publication year. Example: Ionescu (1970) or (Ionescu, 1970). For two authors: Ionescu, Popescu (1969) or (Ionescu, Popescu, 1969). For more than two authors: Ionescu et al. (1980) or (Ionescu et al., 1980). For papers which are in course of print the publication year will be replaced by "in press". Unpublished papers or reports will be cited in the text like the published ones.

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Key words (max. 10 items), in English or French, following the language used in the text, given in succession from general to specific, should be typed on the abstract page.

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Examples:

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Giuşcă, D. (1952) Contributions à l'étude cristallographique des niobates. *An. Com. Geol.*, XXIII, p. 259-268, Bucureşti.

—, Pavelescu, L. (1954) Contribuţii la studiul mineralogic al zăcămintului de la Muşca. *Comm. Acad. Rom.*, IV, 11-12, p. 658-991, Bucureşti.

b) special issues:

Strand, T. (1972) The Norwegian Caledonides. p. 1-20. In: Kulling, O., Strand, T. (eds.) *Scandinavian Caledonides*, 560 p., Interscience Publishers.

c) books:

Bălan, M. (1976) Zăcămintele manganifere de la Iacobeni. *Ed. Acad. Rom.*, 132 p., Bucureşti.

d) maps:

Ionescu, L., Popescu, P., Georgescu, G. (1990) Geological Map of Romania, scale 1:50,000, sheet Cîmpulung. *Inst. Geol. Geofiz.*, Bucureşti.

e) unpublished papers or reports:

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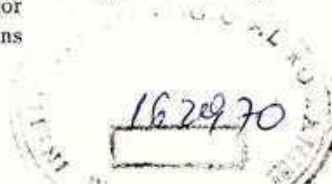
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Translation and language review by:
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