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## FIELD TRIP

L. Nedelcu, P. Hârtopan, Al. Szakács, C. Moga, I. Podașcă



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Editorial Office:  
Geological Institute of Romania  
Str. Caransebeş Nr. 1  
RO - 79 678 Bucureşti - 32  
Tel. (+40) 1 224 20 91, 224 15 30  
Fax (+40) 1 224 04 04  
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## A. GENERAL GEOLOGICAL SETTING

### THE CRYSTALLINE-MESOZOIC ZONE OF THE EAST CARPATHIANS. A REVIEW

I. BALINTONI

Babeş-Bolyai University, Cluj-Napoca

#### I. STRUCTURE

The Crystalline-Mesozoic Zone of the East Carpathians, if we are referring to the mobile Alpine belt, belongs to the eastern Getides. It means that the margin of the craton of the Getic plate adjacent to the outer Dacic rift, in the area opposite to the Moldavian Platform margin of the major Eurasian plate, was sheared in order to generate several nappes. These are (from top to bottom): Bucovinian, Subbucovinian and Infrabucovinian Nappes (e.g. Săndulescu, 1984). The Bucovinian Nappe is overlain by the eastern Transylvanids, nappes devoid of a crystalline basement. In their turn, at least the Bucovinian and Subbucovinian Nappes, consist of several Variscan tectonic units, as follows: (from top to bottom): Rarău Nappe, Putna Nappe, Pietrosu Bistriței Nappe and Rodna Nappe (Balintoni, 1981; Balintoni in Săndulescu et al., 1981; Balintoni et al., 1983).

#### 1. Alpine tectonic units

##### a. Bucovinian Nappe

The Bucovinian Nappe – the uppermost nappe of the Getides – preserves the Mesozoic sedimentary cover on large areas. We shall present below schematically the constitution of the Bucovinian Nappe based on the papers of Săndulescu et al. (1975), Kräutner et al. (1975), Săndulescu, Ștefănescu (1981), Săndulescu (1984), Săndulescu et al. (1987).

- Werfenian: conglomerates and quartzitic sandstones;
- Campilian: grey plate or bedded limestones;
- Upper Campilian-Anisian: massive dolomites;
- Ladinian: beds with jaspers (Pojorata) and white limestones, limestones with *Diplopora annulata*;
- Sinemurian-Carixian: hematitic oolitic limestones;
- Dogger: marly-sandy (gritty) limestones; brown siltstones;
- Callovian-Oxfordian: radiolarites, radiolarite siltstones;
- Tithonian-Valanginian:
  - Lunca Beds in the main body of the Bucovinian Nappe;
  - Aptychus Beds (green or red marly-limestones and marls), Pojorata-Comana Beds, calcarenites with silex, in the Sadova-Gârbova digitation;
  - Stejaru flysch in the Vârghiș digitation;
  - Clifele beds in the Târnița digitation;
- Hauterivian-Lower Barremian: Muncelu conglomerates and sandstones in the Sadova digitation;
- Upper Barremian-Lower Aptian or Albian: Wildflysch formation;
- Lunca Beds point to pelagic facies with tintinids, and are mainly represented by marly and limy-marly sequences with rare unrhythmical turbidite intercalations.
  - Pojorâta, Comana, Stejaru and Clifele flysch are of binary type, with outermost polymictic arenites (Pojorâta, Comana), with a mostly siliceous matrix.

The first angular unconformity recognized in the Bucovinian succession (Săndulescu, 1976) is found in the base of the Toarcian or Aalenian, therefore in the final part of the Lower Jurassic. According to Săndulescu (1984), it might correspond to the formation of the outer Dacic rift. The second angular unconformity observed in this sequence occurs in the base of the Lunca Beds (Patrulius et al., 1968; Săndulescu, 1975). The third angular unconformity occurs in the base of the Wildflysch formation (Patrulius et al., 1966, 1968; Săndulescu, 1969, 1975). According to Săndulescu (1984) this unconformity is pre-Alpine, possibly Upper pre-Barremian, according to the age of the lowermost levels of the wildflysch. Because the contact in the base of the wildflysch can also be regarded as tectonic, this unconformity can be lowered up to the Hauterivian, in the base of the





Muncelu conglomerates which resemble a molasse facies. Therefore, the intra-Neocomian angular unconformity in the frontal part of the Bucovinian Nappe could be synchronous with the first thrusting of the Getic Nappe over the Sinaia flysch in the Prahova Valley area (Ștefănescu, 1973; Patrușiu, 1969).

According to Săndulescu (1984), the frontal digitation of the Bucovinian Nappe, which hosts the Bucovinian flysch (Sadova-Gârbova and Târnița-Vârghiș), could be synchronous with the movements that determined the mentioned unconformity. The relationships between the Sadova digitation and Muncelu conglomerates at Pojorâta could be conclusive in this respect provided that during the emplacement of the Bucovinian, intra-Albian Nappe (e.g. Săndulescu, 1984) the pre-existing intercalations were not resumed, new ones being formed (e.g. Kräuter et al., 1975).

#### **b. Subbucovinian Nappe**

The Subbucovinian sedimentary Nappe crops out in a series of tectonic windows below the Bucovinian Nappe, e.g. Tomești window in the southernmost part of the Crystalline-Mesozoic Zone, or the windows in the basin of the Putna Valley. Likewise, in front of the Bucovinian Nappe several "rabotage" outliers, belonging to the Subbucovinian Nappe, crop out. The Subbucovinian sedimentary Series is much thinner than the Bucovinian one - less than 150 m versus more than 1,000 m - with many gaps and unconformities. We shall present below its constitution according to Săndulescu (1975), Kräuter et al. (1975) and Mureșan et al. (1986), but the best description is given by Săndulescu (1975).

Permian: verrucano;

Werfenian: conglomerates and quartzitic sandstones; marly shales and fine-bedded limestones;

Upper Campilian-Lower Anisian: dolomites;

Upper Anisian-Ladinian: cherts; red and green clay shales; red radiolaritic siltstones; jaspers and grey limestones;

Liassic (Lower?): limonitic sandstones; blackish marly siltstones; limonitic sandy-limestones; limonitic microconglomerates;

Dogger (Malm?); nodular marly limestones and plate limestones; silts and blackish clays; calcareous sandstones; siderites;

Neocomian: calcareous breccias and calcarenites.

However, it is worth mentioning that if the wildflysch does not belong to the Bucovinian Nappe, then the difference between the covers of the two tectonic units is much more insignificant.

#### **c. Infrabucovinian tectonics units**

The Infrabucovinian tectonic units are found in a series of tectonic windows as fragments without continuity; in Maramureș they are floating on the Black Flysch Nappe or on the Ceahlău Nappe. In places, they are represented only by sedimentary series, devoid of a crystalline basement. The presence of several facies groups point out a large territory, highly sheared and open. From inside to outside the Infrabucovinian Units can be grouped into facies groups with more and more complete sequences from Jurassic to Permian. The strong fragmentation of the Infrabucovinian Units indicates the close connection between the two plates during subduction and overthrusting. Outside the Maramureș Mountains, the Infrabucovinian units crop out in the Rodna Mountains, in the Rusaia, Vatra Dornei-Iacobeni and Arșița Barnarului windows. It is to note the Măgurele "rabotage" outlier in the frontal part of the Bucovinian Nappe, north of Sadova. The Units in the Rodna Mountains (from top to bottom: Anies, Stiol and Valea Vinului) are devoid of sediments and Săndulescu (1984) considers them of pre-Alpine age. The Valea Vinului Unit crops out in the Rusaia window. Further on, we shall describe the Infrabucovinian Units after the sedimentary covers, according to Bercia et al. (1976) and Săndulescu (1975, 1984):

*Vaser-Belopotoc Unit* has the innermost position. The Liassic, with which begins the sedimentary sequence, is in Gresten facies and it contains basic tuffs identical to those in the Black Flysch Nappe of the same age. The Dovgorun Series crops out on and above the border. It overlies unconformably the Liassic and is clayey-calcareous representing the Malm and, probably, the Neocomian. The whole sequence is metamorphosed at the chloritoid level and in places it is strongly faulted and slid. Excellent outcrops are found on the Vaser Valley downstream the spring area of the Bardău River, nearby its confluence with the Vaser and Botizu rivers.

*Pentaia Unit* crops out nearby Poienile de sub Munte and consists of Middle Triassic calcareous deposits with intercalations of silts and basic tuffs and Liassic deposits similar to the Vaser ones. Therefore, it is a more external unit than the previous one.

*Pietricea Unit* occupies a large area in the basin of the Repedea Brook north of Poienile de sub Munte. The sedimentary sequence starts in the Permian with red conglomerates, followed by Middle Triassic, predominantly





calcareous with dolomitic levels or nodules, as well as with bituminous bedded limestones. This unit is more external than the Pentaia Unit.

*Poleanca Unit* is characterized by a well-developed Permian which contains acid eruptive rocks and a calcareous Triassic with bituminous levels. After Săndulescu (1984), this is the outermost Infrabucovinian Unit in the Maramureş Mountains.

*Stănişoara Outlier* is similar to the Roziss Unit initially described in the Rahov massif. This succession starts with a schistous-variegated Permian, followed by massive Werfian sandstones and then by a calcareous-dolomitic Middle Triassic. Several scales comparable with the described sequence crop out in the right slope of the Suligu Brook.

*Iacobenii Nappe* displays a sedimentary series constituted of a quartzitic conglomeratic-sandy Werferian, a bedded bituminous black Anisian overlain by violaceous, pink and greenish limestones, schists and dolomites, probably Upper Triassic in age, and finally Middle Jurassic sandy limestones. Although obviously it is an outer facies, it is difficult to be correlated with the units in Maramureş.

*Panaci Unit* displays a cover formed only of Permian polymictic conglomerates and it is overlain by the Iacobenii Nappe.

*Arşiţa Barnarului Unit* is covered by a tiny outlier of Permian red conglomerates and some Triassic carbonates. The drillings carried out here penetrated the sedimentary of other Infrabucovinian units.

Another Infrabucovinian unit devoid of sedimentary deposits crops out in the bend of the Bistriţa River at Zugreni, in the Arseneasa window.

Unlike the Bucovinian and Subbucovinian Nappe, the Middle Triassic of the Infrabucovinian Units is calcareous bituminous and dolomitic devoid of jaspers and radiolarites.

Referring to the opening of the outer Dacic rift, it is to note the presence of basic tuffs in the Liassic of the Vaser unit and in the Triassic at Pentaia. Therefore, this rift could began in the Middle Triassic, existed certainly in the Liassic and one of its shores was represented by the future Vaser Nappe. In our opinion, this solves one of the main matters on the genesis of the eastern Getides, namely that they were emplaced as synthetic nappes due to the close connection with the lithosphere of the Outer Dacic rift and there is no connection with the Transylvanian Tethys. This theory was endorsed by Soroiu et al. (1985) and was in contradiction with Săndulescu's opinion (e.g. 1984) who considered the roots of the eastern Getides somewhere below the Transylvania Depression and in connection with the Transylvanian Tethys. As a matter of fact, the basement of the Transylvania Basin does not display the features of a nappe pile, the crust being thin, the heat-flow low and subsidence of foredeep-type.

## 2. Variscan Tectonic Units

### a. Succession of the Variscan Units in the basement of the Alpine Units

The basements of the Bucovinian and Subbucovinian Nappes include all the four mentioned tectonic units. In the basement of the Infrabucovinian Nappes, only at Panaci near Vatra Dornei, there occur fragments of the Putna and Pietrosu Bistriţei Nappes under the Rarău Nappe in the base of the Infrabucovinian Nappe at Iacobenii (Balintoni et al., 1981) and on the Dreptu and Borca brooks, under the Rodna Nappe in the base of the Subbucovinian Nappe fragments of the basement of the Putna Nappe are exposed (Vodă, 1986). If these two mentioned situations are interpreted as indicating fragments of the Subbucovinian Nappe basement caught below itself or below the Infrabucovinian Iacobenii Nappe during the Alpine thrustings, then anywhere the basement of the Infrabucovinian Nappe consist only of the Variscan Rarău Nappe. In this context there are difficult interpretation problems in connection with the position of the Variscan suture and with the fact if the constituting crust of the Putna, Pietrosu Bistriţei and Rodna tectonic units extended below the domain from which the Infrabucovinian Nappes come.

### b. Rodna Unit

Rodna Unit has always been delimited in the base by an Alpine shear plane and therefore it is probable that it might constitute the autochthon for the Variscan thrustings. Consequently, the Rodna Unit does not represent a Variscan nappe. One can observe once again the relativity of the geologic notions because the Rodna Unit cannot be accepted as a nappe proper, being a part of their basement. When we refer to it, we have to consider this aspect because, in fact, there are only three Variscan nappes: Rarău, Putna and Pietrosu





Bistriței.

### c. Extension of the Variscan Nappes

The Putna and Pietrosu Bistriței Nappes, although discontinuous, crop out in the Bucovinian and Subbucovinian Nappes. It means that they have a double extension in comparison with these nappes. The Rarău Nappe is part of the basement of the Bucovinian and Subbucovinian Nappes and it forms the whole basement of the Infrabucovinian Nappes. This fact could indicate an ample thrusting if we consider that the outcrop width of the Crystalline-Mesozoic Zone of the East Carpathians can exceed 30 km. The minimum length of the tectonic transport for the Putna and Pietrosu Bistriței Nappes is of 60 km and that for the Rarău Nappe of more than 100 km. The size of the tectonic transport for the Rarău Nappe depends on the position of the Variscan suture: inside the Crystalline-Mesozoic Zone or outside it (east of it). If we accept it inside, it should be sought between the origin place of the Rarău Nappe and the origin place of the Putna, Pietrosu Bistriței and Rodna Nappes. If we accept it outside, then it probably coincide with the route of the outer Dacic rift and would not be visible any more. In order to find the Variscan suture one should look for the following geological elements: ophiolites, high-pressure metamorphic mineral assemblages, coupled metamorphic belts, magmatic arcs, arc and trough sediments, nappe enrootment zones; furthermore, we should take into account paleomagnetic and fauna evidence. All this can be discussed only when the Variscan metamorphic sequences will be studied. The mentioned elements are, however, valid for the recognition of sutures of any age. If we follow transversally the components of the Bucovinian and Subbucovinian Nappes basement then we observe the predominance of the Rarău and Putna Variscan Nappes in the eastern part and of the Rodna Nappe in the western part, quite clearly due to the eastern vergence of the Alpine shear planes (Vodă, Balintoni, 1994).

## II. LITHOSTRATIGRAPHY OF THE METAMORPHITES IN THE VARISCAN TECTONIC UNITS

In order to understand this problem it is necessary to make a detailed and evolutive review of the metamorphic sequences that form the Variscan tectonic units. First of all, we shall present the lithostratigraphic content of these units according to Vodă and Balintoni (1994).

### Rarău Nappe

The nappe is mostly constituted of the Bretila lithogroup. The Variscan epizonal sequences Rusaia, Repedea and Cimpoiasa occur only in the Infrabucovinian Units of the Rodna Mts, transgressive on the Bretila Group (e.g. Kräutner, 1988).

### Putna Nappe

It consists of the Tulgheș lithogroup.

### Pietrosu Bistriței Nappe

It is formed of the Negrișoara lithogroup.

### Rodna Unit

No comment on its age will be made from now on. It is to note only that it consists of the Rebra lithogroup. The Bretila, Negrișoara and Rebra lithogroups are mesozonal polymetamorphic sequences, possible Precambrian in age. The Tulgheș lithogroup is also a polymetamorphic sequence, with a variable metamorphism in the greenschists facies, probably Lower Paleozoic in age.

## 1. Description of the metamorphic sequences

Between 1980 and 1990 Kräutner made an attempt to present a formal lithostratigraphic classification for all pre-Alpine metamorphites in the Romanian Carpathians based on terms such as supergroup, group, series (subgroup), formation and member. The supergroup had to include all the metamorphites belonging to a metamorphic cycle; the group those with a specific lithology within a certain supergroup; the series the sequences of a certain group from a specific tectonic unit, and the formation had to represent the fundamental lithostratigraphic unit. This classification was not a success because, on the one hand it did not include objective data concerning the age both for the metamorphic events and for the premetamorphic protoliths in case of most of the Carpathian metamorphites and, on the other hand, because of the confusions between the terms group and series which occur in comparison with previous descriptions, these terms being used for equivalent units or for





different entities. Moreover, there was the possibility that different sequences should belong to different plates, different geotectonic or basinal settings within which they formed. It is also worth mentioning that present descriptions are in many cases insufficient for a comparison of the sequences from different tectonic units. According to the mentioned classification, the Carpiian supergroup included Upper Precambrian A sequences (1650 m.y. to 1000-850 m.y.) from the subdivisions used for the Geological Map of Romania scale 1:50,000, the Marisian supergroup included the Upper Precambrian B + Cambrian sequences, and the Variscan supergroup included sequences from the end of the Cambrian till the end of the Middle Carboniferous (Kräutner, 1980). In 1993, in a paper on the South Carpathians, published in "Geologia Carpathica", Kräutner mentioned vaguely the "Carpiian sequence", used the term group in an orientative acception for the old term for series and the terms Precambrian, Caledonian and Variscan crust. The Precambrian crust would correspond to the Carpiian supergroup. It is to note that the term "supergroup" is maintained for sequences with very many problems, and it points out clearly the degree of confidence that can be given to it.

In order to simplify the nomenclature, considering it strictly informally, the lithostratigraphic classification used by us will be:

- lithogroup, which, broadly speaking, is an equivalent to the series or the total of sequences with comparable lithologies and metamorphic evolution in all the tectonic units constituting one of the branches of the Carpathian orogen, therefore very likely including a specific geotectonic setting within a certain period of time
- lithozone, will indicate any undivided sequence within a certain tectonic unit, usually with the same name, or the fundamental informal lithostratigraphic unit comparable to the formation;
- sublithogroup, which will include all the lithozones belonging to the same lithogroup, but without representing it on the whole, hosted by a certain tectonic unit.

This classification will be used for a continuous segment of a mobile belt.

We shall clear up this terminology using the Bretila lithogroup as an example.

### **Bretila lithogroup**

**Lithostratigraphy.** Bretila lithogroup was defined in 1938 by Th. Kräutner as the autochthonous mesozone of the East Carpathians. In 1968, H. Kräutner stressed out the lithostratigraphic correspondence of the Bretila Series with that of the Rarău gneisses. Bercia et al. (1971) included the Bretila Series in the following sequences: Bretila Series in the Bistrița and Rodna Mts; Rarău Gneisses Series in the Rarău and Hăghimaș synclines; Novăț Series in the Vaser Basin; Pop Ivan mesozone; Belopotoc Series over the border.

This represents a decisive step in the knowledge of the similar features of successions belonging to this lithogroup in all the major outcropping places, excepting the Vatra Dornei-Iacobeni mezozone, which was assigned to the Rebra Series. That confusion was cleared up by Balintoni in 1984. In the paper published by Bercia et al. in 1976 (which represents a resume of the unpublished paper from 1971), the "Rarău" name does not appear, the sequence being denominated from now on the Bretila Series. The Bretila lithogroup can be considered as poorly divided in lithologic respect, the only succession for which two formations (e.g. Kräutner, 1988) were described being the Anies Infra-Bucovinian Nappe in the Rodna Mts. The two mentioned formations are:

- the amphibolitic formation with Mireaja leptinitic rocks in a lower position;
- the gneissic formation with Lespedea leptinitic rocks in an upper position.

According to the informal nomenclature proposed by us, the Bretila lithogroup is represented by:

- Bucovinian and Subbucovinian Rarău lithozones;
- Anies sublithogroup;
- Vaser, Pentaia, Pietriceaia, Rusaia, Valea Vinului, Iacobeni lithozones.

When we are not sure to which lithogroup a certain lithozone belongs, the nomenclature will be double: Iacobeni-Bretila lithozone, Vaser-Bretila lithozone, Pentaia-Bretila lithozone etc. This is an open system which makes possible the individualization of any sequence in any tectonic unit.

**Lithology and premetamorphic geotectonic setting.** Although it is poorly divided in lithostratigraphic respect (the lack of the markers being one of the causes), the Bretila lithogroup is well known and characterized from lithologic point of view. The Infrabucovinian Nappes include: paragneisses, microclinal gneisses, fine-grained white gneisses with a leptinitic aspect alternating or not with amphibolites, augen gneisses, micaschists, porphyroids. In the Bucovinian Rarău lithozone, beside micaschists, augen paragneisses and amphibolites, a special rock suite - the Hăghimaș and Mândra metagranitoids, considered as premetamorphic intrusions - occurs, as well. From petrochemical point of view, the Hăghimaș granitoids display dioritic features, whereas the Mândra ones are potassic. Within the Vaser lithozone, Ciornei (1955) mentioned metaultrabases.





The setting in which they crop out was not studied, so that their situation is uncertain. The lithology of the Bretila lithogroup can be briefly presented as follows:

- a) it is a predominantly terrigenous sequence with intercalations of acid and basic metavolcanics;
- b) the carbonatic rocks are practically absent;
- c) a part of the lithogroup is characterized by premetamorphic granitoids;
- d) the succession does not seem to have had a sialic basement to be in discordance with it

From a basinal point of view, the setting is obviously of convergent contact, but it is hard to say if it is a foredeep, prearc or backarc basin. If we take into account the granitoids, then we can presume an implication of the arc in subduction and metamorphism, a part of the accretion prism intruded by granitoids being probably preserved. The transport of the arc into subduction could indicate a final collision.

**Metamorphism.** Bercia et al. (1971, 1976), Kräutner (1988) mentioned an initial metamorphism in the almandine amphibolite facies, followed by a Variscan and Alpine retromorphism. The migmatitic structures are considered at the expense of an initial metamorphism. Balintoni (1969) stressed out that migmatization took place after the first metamorphism. Considering the present facts on the crystalline sequences in the East Carpathians and the relationships between them, the evolution scheme would be as follows:

- Initial metamorphism in subduction regime as part of an accretionary prism and an island arc collisionally involved in subduction; this regional metamorphism was a medium-grade one.

- A second regional medium-grade to low-grade metamorphism, as part of a sub-plated sialic crust; this event is related to the migmatizations that occurred in the Rarău zone and in the Infrabucovinian Nappes.

- Variscan retromorphism highly visible especially in the base of the Rarău Nappe in the basement of the Bucovinian Nappe. It was linked to the emplacement of the Rarău Nappe and generated specific aspects of what was delimited as: Chiril Formation (Nedelcu, 1982, Kräutner et al. 1981); Mandra Formation (Balintoni, 1981; Balintoni et al., 1983); Poiana-Grebin Formation (Vodă, 1982); Balaj Formation (Runceanu, Voicu, unpublished data).

All these sequences represent different lithologic associations in the base of the Rarău lithozone, deformed and retromorphosed synchronously with the location of the nappe (Vodă, Balintoni, 1994). This moment is associated with ocular structures from the "Mandrea gneisses". The Variscan entities transgressive on the Bretila lithogroup in the Infrabucovinian Nappes were gradually metamorphosed, they being in a proximal position versus the convergent contact; during that time the Bretila lithogroup belonged to the continental crust of a lower plate. The Alpine retromorphism can be taken into account only in the Subbucovinian and Infrabucovinian Nappes.

**Age.** Kräutner (1988) mentioned K-Ar data up to 748 m.y. and Rb-Sr data up to 529 m.y., but they are quite old and can be regarded only as a probability. The pre-Variscan geologic history is, however, quite complicated, including at least two collisions, which points to a Precambrian age for the initial metamorphism of the Bretila lithogroup, like other Carpathian sequences.

**Metallogeny.** The known metallogeny of the Bretila lithogroup is poor. It is probable that the preserved sequences were not those that hosted the mineralizations. On the other hand, the accretionary prisms, in general, and the turbiditic sedimentation are not favourable for metalliferous accumulations. Only if thick parts from the subducted oceanic crust would be caught in the accretionary prism we could expect mineralizations proper to the ophiolitic associations. The involving of prearc basins in subduction could have provided Kuroko-type mineralization, but up till now no such mineralizations have been found. As regards the granitoids, if their domes are not preserved, then specific mineralizations are unlikely to be found.

### Rebra lithogroup

**Lithostratigraphy.** The Rebra lithogroup is mentioned in papers of Kräutner (1968, 1980, 1988), Bercia et al. (1971, 1976), Săndulescu et al. (1981) as well as on the four sheets of the Geological Map of Romania, scale 1:50,000, that cover the Rodna Mts (Rodna Veche, Pietrosu Rodnei, Ineu and Rebra), published by Kräutner et al. (1978, 1982, 1983, 1989). This group shows good outcrops and is more varied in petrographic respect; it was denominated by Kräutner in 1968. It could be divided into several lithozones (formations) named by Kräutner et al. (1982) (from bottom to top): Izvorul Roșu, Voșlobeni and Ineu formations. It is to note that the Izvorul Roșu and Ineu lithozones were described within the Subbucovinian Rebra lithogroup, whereas the Voșlobeni lithozone was delimited within the Bucovinian Rebra lithogroup. Doubtless, in a formal classification such an initiative is not good. The presence of the Rebra lithogroup only in the Bucovinian and Subbucovinian Nappes simplified the nomenclature according to the terms used in the above-mentioned sentence.

The *Izvorul Roșu lithozone* consists of paragneisses interstratified with micaschists that can include stau-





rolite, kyanite, sillimanite, as well as subordinated intercalations of carbonatic rocks and quartzites.

The *Voşlobeni lithozone* is represented by a thick pile of carbonatic rocks with intercalations of paragneisses, white and black quartzites. The carbonatic rocks can be laterally substituted also by the other rocks mentioned above. On large areas, at the top and the bottom of the lithozone, amphibolites or thick amphibolitic gneisses can be found which, in the Rodna Mts at Bâzdăga (the lower ones), contain pyrrhotite-chalcopryrite-magnetite mineralizations and, in the Bistrița Mts (the upper ones), lenses of massive magnetite of relatively small sizes. Due to them, the Subbucovinian Rebra lithogroup can be traced in geophysical respect between Bistricioara and Zugreni, in the right side of the Bistrița River. Also in the Rodna Mts, the calcitic portions of the Voşlobeni lithozone, especially when they are related to quartzites and other terrigenous lithons, host lead-zinc accumulations of industrial significance (Udubaşa, 1981). Graphite occurs in carbonatic rocks and there are zones where the graphitous black quartzites are very well represented. Graphite is usually accompanied by metallic minerals.

The *Ineu lithozone* consists especially of quartz micaschists with intercalations of thin lithons of limestones, dolomites, biotitic quartzites, amphibolites and microlitic gneisses, white and black quartzites. Kräutner (1980, 1988) assigned the Rebra lithogroup to the Carpathian supergroup, considering that it conformably lies at the upper part of the Bretila lithogroup. We did not and do not accept this point of view which, by the basal analysis and by other arguments is entirely underground. As a matter of fact, there is no relation of continuity between the two lithogroups and a comparison between the two sequences will be made when we shall present the metamorphism.

**Lithology.** From the beginning it is to mention the lithologic contrast between the Rebra and Bretila lithogroups. Thus, in the Rebra lithogroup the well differentiated, mature rocks, distinct one from another, certainly of a sedimentary origin, are prevailing: micaschists with aluminium silicates, quartzites, some of them with organic supply, carbonatic rocks in thick piles, paragneisses, and only few rocks of a possible acid magmatogenic origin occur at the upper part of the lithogroup. In Maramureş granitoid-like rocks are found, which could represent anatectic mobilisates due to the more intense metamorphism locally undergone by this lithogroup, especially during the metamorphism (M2), possibly in (M1) as well. The presence of amphibolites raises the problem of their origin, particularly because of their relation with carbonatic rocks. From the basal point of view, all facts indicate a premetamorphic geotectonic setting of passive continental margin. If the succession was preserved as a whole, then we have to recognize a major unconformity at its lower part because it should have been transgressive on a continental or transition crust. In this context, the amphibolites could stress out the rift magmatism toward the contact with the oceanic lithosphere, and the appearance of the acid magmatism at the upper part could indicate the closure of the oceanic basin and the proximity of the volcanic arc of the upper plate to the plate margin subducted, on which the future Rebra lithogroup deposited. We shall discuss these problems further on. It is also worth mentioning the lack of granitoids and of migmatitic structures. The clearly different geotectonic settings of accumulation of the two sequences make improbable their initial normal succession. The Bretila lithogroup could form at most the pre-existing continental crust on which the Rebra lithogroup transgressed, but the metamorphic aspects of the two sequences do not permit this presumption. The problem to be solved is the time when the two lithogroups juxtaposed because their superposition was only a tectonic one and it took place very late in course of their evolution.

**Metamorphism.** Rebra lithogroup is best studied as regards the metamorphic evolution in comparison with the Bretila lithogroup. Thus, prior to the Variscan retromorphism related to thrusting of the same age, for which the Rebra lithogroup plays the role of an autochthon, two mesozonal events (M1) and (M2), with proper mineralogical and structural features have been described (Balintoni, Gheuca, 1977; Balintoni, Bindea, 1994). The (M1) event is a low-pressure one and it is characterized by the presence of index minerals - staurolite and kyanite, in micaschists and paragneisses. The (M2) event is locally of low pressure and under the microscope one can observe the involvement of staurolite and kyanite in reactions which gave rise to andalusite and cordierite. This event is also characterized by the generation of transposition axial-plane foliations (S2) in relation to which the thermal culmination, during which cordierite and andalusite grow statically, is subsequent. The fibrolitic sillimanite is hard to be relatively dated, but it seems rather related to the event (M2). The Rebra lithogroup was part of a lower plate both in the (M1) event and in the (M2) event, unlike the Bretila lithogroup which in the (M1) event, or at least before collision, evolved in an upper plate setting. During the Variscan and Alpine orogeneses the Rebra and Bretila lithogroups evolved together. Therefore, the juxtaposition of the two lithogroups is one of the major problems that have to be solved.

**Age.** Isotopic data mentioned by Kräutner (1988) indicate for the Rebra lithogroup an age similar to that of the Bretila lithogroup, the metamorphic developments being more conclusive. Therefore, two metamorphic





events correlatable with two different orogeneses, both pre-Variscan, could be accepted as evidence of the Precambrian age of the Rebra lithogroup. According to Zincenco (1993), who mentioned data of the Ukrainian geologists obtained on U-Pb and Pb-Pb isotopic systems from zircons, the idiomorphic crystals from the Pietrosu porphyroids point to ages of about 480 m.y. We shall describe these rocks when we present the Negrișoara lithogroup. If the respective zircons are of magmatic origin, then this age ends the accumulation of the Rebra lithogroup for the known sequence. If they are of metamorphic origin, then they indicate the age of the (M1) event. We shall discuss this matter further on.

**Metallogeny.** Rebra lithogroup is of economic importance for the Pb-Zn mineralizations hosted by the carbonatic rocks of the Subbucovinian Voslobeni lithozone in the Rodna Mts. A synthesis paper on these mineralizations was published by Udubașa et al. in 1983. The premetamorphic origin of these mineralizations is undebatable. The micaschist and amphibolite levels related to these mineralizations indicate notable enrichments in apatite, sphene and barite. Mineralization occurs either disseminated in the carbonatic rocks or as massive pyritous flattened lithons. The major metallic minerals in the mineralized parts of the carbonatic sequence are pyrite, sphalerite, galena and subordinately pyrrhotite, chalcopyrite and magnetite. The source and the way of enrichment in metals are unclear; however, mention should be made of graphite and baryte as well as the Ti enrichment of the mineralized sequence. According to the mentioned authors, the mostly carbonatic environment, the ore mineralogy, the regional extension of the mineralized lithons and their stratigraphic control are common for all ores of Mississippi Valley and Triassic type in the Alps. Mitchell and Garson (1981) assigned the Mississippi Valley and Alpine type mineralizations to those formed on passive continental margins. Therefore, it is to note that the origin of the Rebra lithogroup in a geotectonic setting of passive continental margin is based both on lithology and on metallogeny.

### Negrișoara lithogroup

**Lithology.** This lithogroup was delimited by Balintoni and Gheucă in 1977 and consists of a mostly terrigenous lower sequence similar to the Subbucovinian Ineu lithozone and of metadacitic upper level (Balintoni, Neacșu, 1980), quite typical mesoscopically, the Pietrosu Bistriței porphyroid gneisses. Although it crops out on large areas both in the Bucovinian Nappe and in the Subbucovinian Nappe, the Negrișoara lithogroup is generally very thin and fragmentary. The lower sequence will be named Pinu lithozone after the name of the left tributary of the Negrișoara Brook downstream the locality of Darmoxa, where it is well exposed and easily accessible both in the basement of the Bucovinian Nappe and in that of the Subbucovinian one. The Pietrosu Bistriței porphyroid gneisses, or shortly the Pietrosu porphyroids, do not require any other denomination.

**Lithology.** In petrographic respect, the Pinu lithozone is quite similar to the upper part of the Rebra lithogroup. The petrographic content is represented by biotite quartzitic paragneisses with intercalations of thin and discontinuous lithons of carbonatic rocks, amphibolites and microclitic white gneisses. The appearance of the last ones could be interpreted as the beginning of the huge eruption that emplaced the acid eruptive material which generated the Pietrosu porphyroids. It is to note that the outcropping area of the Pietrosu porphyroids is equal to that of the Bucovinian and Subbucovinian Nappes, that is several thousands of square kilometres, their initial extension being probably greater. At the same time they occur as a unique level, practically horizontal, geochemically homogeneous, which ends the Negrișoara lithogroup succession. Such formations are at present known only in the ignimbritic plateaus or as tuff levels e.g. the Dej tuff which covered the whole Transylvania Basin. Consequently, the Pietrosu porphyroids might represent products of an intracrustal magmatic reservoir (like in the western part of the U.S.A.) or of an island arc or continental margin. However, in so far as the Negrișoara lithogroup is accepted as the uppermost part of the Rebra lithogroup, obviously somewhere east of its present outcropping zone, it ends, in fact, the accumulation of supracrustal material on a passive continental margin, forecasting the closure of the oceanic basin and the imminence of the collision.

**Metamorphism.** The metamorphic development of the Negrișoara lithogroup is similar, to a certain extent, to that of the Rebra lithogroup. The difference consists in the absence of the low-pressure metamorphism area during the (M2) event. The mineralogical association of the event (M1) is restructured and partially recrystallized syn-(M2); however, the thermodynamic equilibrium does not change significantly, being somewhere at the upper part of the medium-grade metamorphism. This aspect is also valid for most of the Rebra lithogroup. Unlike it, the Variscan retromorphism is quite stressed and for this reason, in the past, the largest part of the Negrișoara lithogroup was assigned to the Tulgheș lithogroup. These characteristic features are found in the retromorphic parts of the Pietrosu porphyroids, which are retrograded up to the chlorite zone and because of the transport of the upper nappes on their surface, which constituted a clear discontinuity,





the simple shearing generated ocellar structures. Plagioclase was decalcified, giving rise to albite and epidote, and albite recrystallized as ocellus with the long axis up to 2 cm. The (M2) event is characterized by mesoscopic folds, with decimetric to metric sizes or even more, whose axial planes are parallel to the limits between lithons. The hinges of these folds are parallel to those of the similar contemporaneous folds from the Rebra lithogroup. Because of the central position of the Negrișoara lithogroup in the basements of the Bucovinian and Subbucovinian Nappes, the influence of the Alpine movements is hard to be separated from that of the Variscan movements.

**Age.** The logic used for the Negrișoara lithogroup is identical with that applied to the Rebra lithogroup. Therefore, the Negrișoara lithogroup started its metamorphic evolution in the Precambrian. According to Zincenco (1993), the age of 840 m.y. can be admitted for the moment of the Pietrosu porphyroid setting or for the event (M1).

**Metallogeny.** Up till now no mineralizations of economic interest are known in the Negrișoara lithogroup. Considering the lithology and the small thicknesses of this sequence, the prospect is null.

### Tulgheș Lithogroup

**Lithostratigraphy.** Kober (1931) and Streckeisen (1934) assigned the "epizonal formations" of the East Carpathians to the "Tulgheș Series". Bercia et al. (1976) included in the Tulgheș Series only sequences comparable to what we accepted as Tulgheș lithogroup, excepting the parts attributed by Balintoni et al. (1983) to the Negrișoara lithogroup. The "Vaser Formation" (Bercia et al., 1976) represents a pile of metamorphites well exposed in the right side of the Vaser River, downstream the confluence with the Botizu Brook, which includes all the Variscan units of the Subbucovinian Nappe basement, excepting the Rarău unit, as well as the Bucovinian Putna Nappe. Kräutner (1980, 1988) included the Tulgheș lithogroup in the Marisian supergroup and in his paper from 1988 he divided it into five formations, numbered (from bottom to top) from 1 to 5. Further on we shall use the lithostratigraphic classification of the Tulgheș lithogroup proposed by Vodă (1933), which can be recognized relatively easily in the basement of the Subbucovinian Nappe, too.

The *Caboaia lithozone*, predominantly terrigenous, non-graphitous, constitutes the first term of the Tulgheș lithogroup. It crops out on small areas, south of Zugreni, in the basement of the Bucovinian Nappe and in the upper course of the Vaser River in Maramureș in the basement of the Subbucovinian Nappe, where it is known as Gliganu quartzites.

The *Holdița lithozone*, quartzitic-graphitous, occurs along the East Carpathians, in the basement of both the Bucovinian Nappe and the Subbucovinian Nappe. Due to its black colour given by the presence of graphite, it can be easily recognized. This lithozone hosts the Fe-Mn and baryte premetamorphic mineralizations.

The *Leșu Ursului lithozone*, also well represented in the two upper Getides, consists of an acid sedimentary volcanogene sequence which contains significant accumulations of stratiform metallic sulphides.

The *Arșița Rea lithozone*, phyllitous-quartzitic, ends the succession of the Tulgheș lithogroup. As the Caboaia lithozone it is absent on several profiles.

**Lithology.** Tulgheș lithogroup displays a varied lithology, dominated by the two rock types: white or black quartzites and quartz-feldspathic rocks. The almost continuous variation of the ratio between quartz, feldspar, chlorite and sericite (in fact a phengite variety) makes difficult the mapping of the varieties of these rocks, the more so as the lithons lose relatively quickly their individuality. The carbonatic rocks are poorly represented; they crop out especially in the Holdița lithozone where a characteristic association is found: black quartzites, white quartzites, carbonatic rocks, chloritous and feldspathic green rocks which do not represent metabasites but sedimentary rocks whose origin was favoured by the iron abundance. Metabasites, like the carbonatic rocks, are scarce or absent. The Mn abundance in the quartzitic-graphitous lithozone and that of the metallic sulphides in the volcano-sedimentary lithozone beside the two prevailing rock types, the quartzites and the quartz-feldspathic rocks lead to the hypothesis that the Tulgheș lithogroup formed in a basin nearby an island arc. We shall discuss about this kind of basin when we shall present the relationships between lithogroups.

**Metamorphism.** Tulgheș lithogroup is polymetamorphic, like the other lithogroups, and its pre-Variscan evolution is less complicated. A corroboration of Balintoni and Chițimș's data (1973), who stressed out that the development of the Ti minerals from the Tulgheș lithogroup is evidence of polymetamorphism, with Nedelcu's data (1986), who proved that the initial mineral of this evolution was ilmenite not brookite, indicates the following stages of evolution:

1. ilmenite crystallization;
2. ilmenite transformation into rutile I;
3. pseudomorphosis transformation into S2 and recrystallization of rutile I into rutile II.





The key problem in this succession is that of ilmenite. As the initial metamorphism of the Tulgheş lithogroup seems to exceed only in places the biotite zone, it is hard to explain the ilmenite formation. If, however, we admit that from unknown reasons ilmenite crystallized during the first metamorphism which affected the Tulgheş lithogroup, then the transformation of ilmenite into rutile indicates the drastic modification of the thermodynamic conditions under which ilmenite crystallized (at least an intense oxidation). This could have taken place during the same metamorphic event or in a subsequent one. The pseudomorphosis transposition and the recrystallization of rutile I into rutile II can be assigned to the Variscan metamorphic event. The question is: had the Tulgheş lithogroup one pre-Variscan event or two? Zencenco (1993) tried to solve this matter and he presumed a clastic origin of the ilmenite. This hypothesis is a tempting one but it is as difficult to prove as the ilmenite crystallization in (M1). However, Zencenco's hypotheses is supported by the association of ilmenite with classical zircon and tourmaline in metapelites. If we consider this hypothesis, then the Tulgheş lithogroup records a major pre-Variscan metamorphic event - namely the one indicated by the alteration of clastical ilmenite into rutile I.

**Age.** The isotopic data mentioned by Kräutner (1988) and Zencenco (1993) seem to indicate the Lower Paleozoic age for the Tulgheş lithogroup and the Caledonian orogenesis for the (M1) event, the phase from the beginning of the Ordovician.

**Metallogeny.** The Tulgheş lithogroup is the major Mn producer in Romania and it represents a notable percentage from the output of Pb, Zn, Cu and pyrite, as well as of baryte. The metallic sulphide mineralizations are of Kuroko type, and those of Fe-Mn, stressing out their relationship with the graphitous quartzites, point to an extrabasinal source, prior to the priming of the acid extrusive magmatism. Once again the association of quartz-feldspathic rocks with Kuroko-type mineralizations is a basin evidence in the subduction setting.

### Rodna lithogroup

On sheets Rodna Veche, Pietrosu Rodnei, Ineu and Rebra of the Geological Map of Romania scale 1:50,000 (Kräutner et al., 1978, 1982, 1983, 1989), as well as in Săndulescu et al. (1981), Kräutner separated, described and divided the Infrabucovinian Nappes in the Rodna Mts into several piles of Variscan metamorphites, which lie transgressively on the Bretila lithogroup. From bottom to top, these nappes are known as: Valea Vinului, Stiol and Anieş, and the respective sequences are denominated Rusaia and Cimpoiasa Series. The Cimpoiasa Series lies transgressively over the Rusaia Series in the Valea Vinului Nappe and over the Repedea Series in the Stiol and Anieş Nappes. As regards the age, the Rusaia and Repedea Series are assigned to the Silurian, and the Cimpoiasa Series to the Devonian-Lower Carboniferous. According to the informal lithostratigraphic scheme adopted by us, because this is a sequence accumulated within a well-determined geotectonic setting, we shall group all these series within the Rodna lithogroup with the Valea Vinului, Stiol and Anieş sublithogroups. We consider that a further classification of the sublithogroups should be revised, in our opinion the term series has to be used no longer by the mentioned author.

**Lithology.** Although the legends of the mentioned maps show a quite complex petrography, the rock varieties can be easily grouped into some major groups: metapsaphites and metapelites, white and black quartzites (metapsamites), carbonatic rocks, metabasites. All the rocks of sedimentary origin can be more or less graphitous. Hematite-magnetic, magnetite-sideritic and metallic sulphides mineralizations are also known. Considering that the Rodna lithogroup lies transgressively over the Bretila lithogroup, we can assign it to a basinal geotectonic setting of passive continental margin. Metabasites are likely to represent a rift basic magmatism as it was reiterated at several levels. We are referring to the rifts of the continental margin not to the main rift within which the spreading took place.

**Metamorphism.** The metamorphism of the Rebra lithogroup is a low-grade one and is characterized by the presence of chloritoid, chlorite, actinote (e.g. Kräutner, in Săndulescu et al., 1981).

**Age.** According to Bercia et al. (1976) and Kräutner (in the above-mentioned paper), the Rodna lithogroup is Silurian-Lower Carboniferous in age. Although they are of palynologic origin, and we generally do not agree to date metamorphites relying on such evidence, the low-grade metamorphism and the obvious transgression of the Rodna lithogroup over the Bretila lithogroup make them acceptable.

**Metallogeny.** The hematite-magnetitic and magnetite-sideritic mineralizations related to the sedimentary rocks indicate a passive continental margin, too. The metallic sulphides hosted by metabasites have to be linked to them.





## 2. Other crystalline sequences considered Variscan

In the paper from 1976, Bercia et al. described as Variscan the Dămuc, Țibău, Izvorul Mureșului and Argeștru series. According to Săndulescu et al. (1981), only the Țibău and Argeștru series are Variscan in age. The Dămuc Series was admitted implicitly on the basis of the relationships with the Bucovinian Rarău lithozone, being part of it; a check route at Izvorul Mureșului effectuated by Kräutner and Balintoni before the publication of the mentioned paper (Săndulescu et al., 1981) led to the conclusion that the Izvorul Mureșului Series includes the mylonites at the contact between the Bucovinian Rebra and Negrișoara lithogroups. As regards the Țibău and Argeștru Series, their existence as independent Variscan entities was questioned by Balintoni (1984, 1985). Later on the researches confirmed Vodă and Balintoni's point of view (1994) according to which the Țibău Series consists of retromorphic sequences of the Bucovinian Rebra lithogroup and the Argeștru Series of portions of the same lithogroup or of the Subbucovinian Negrișoara lithogroup, also retromorphosed and mylonitized.

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## THE CĂLIMANI-GURGHIU-HARGHITA (CGH) VOLCANIC CHAIN

Ioan SEGHEDI, Alexandru SZAKÁCS

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

CGH is the southeasternmost and youngest, ca. 160 km long segment of the East Carpathian volcanic arc. The volcanic chain is geographically subdivided in four sectors corresponding to the Călimani, Gurghiu, Northern Harghita and Southern Harghita Mountains. The volcanic history lasted ca. 9 Ma, from Pannonian to Upper Pleistocene, with the earliest activity occurring in the northern part and the latest one at the southern end of the chain.

Most of CGH lies at the boundary between two major structural units, the Eastern Carpathians and the Transylvanian Basin, being underlined by a ca. 30 km thick crust.

The volcanic structure and morphology of the CGH chain is dominated by an axial row of closely spaced, adjoining or partially overlapping andesitic composite edifices with largely developed and merged peripheral volcanoclastic aprons that form a continuous fringe especially along the western side of the chain.

Rock types mostly range from basaltic andesites to dacites, with porphyritic two pyroxene andesites and pyroxene and amphibole andesites as the most common petrotypes. Aphyric andesites and dacites, as well as volcanics containing biotite are less voluminous. Garnet-bearing andesites are found in rare occurrences in the Călimani Mts.

Petrogenetic studies pointed out the subduction-related mantle origin of the magmas in CGH (Rădulescu, 1973, Peltz et al. 1984, Mason et al., 1995) with the exception of minor crust-derived rocks (Seghedi et al., 1995). Major petrogenetic processes responsible for the observed petrographical and petrochemical features include fractional crystallization, crustal assimilation and magma mixing (Seghedi et al., 1995, Mason et al., 1995, 1996).

### THE CĂLIMANI MTS

#### Volcanic evolution

The magmatic evolution started in the Călimani Mts. with intrusions at the southeastern extension of the "subvolcanic zone" (ca. 12 - 9.5 Ma, Pécskay et al., 1995). The Dragoiasa dacites occurring at the eastern periphery of the Călimani Mts. are the oldest volcanic rocks (ca. 9.3 Ma, Peltz et al., 1987). Then volcanic activity follows up to 6.8 Ma in the central part of the area during several evolutionary stages, including construction and destruction phases. A large-volume basaltic andesitic edifice consisting of a series of NNE trending partially overlapping stratocones (Rusca-Tihu, Tamaul, Pietrele Roșii, Lucaciul) was firstly built up, whose voluminous volcanoclastic aprons are found almost in the entire Călimani area. Instability and failure of the southern part of the edifice ca. 8 Ma ago resulted in a huge debris avalanche deposit, widespread over the western and southern peripheries of the Călimani Mts. (Szakács & Seghedi, 1996). Construction of the stratovolcanic complex resumed after the debris avalanche event until a large-volume eruption of ca. 10 km<sup>3</sup> andesitic lava through eastern upper flank vents culminated in formation of the big Călimani Caldera (Seghedi, 1987) ca. 7 Ma ago (Szakács & Seghedi, 1996). The Călimani caldera with its summit rim altitude of ca. 2000 m. a.s.l. and ca. 8 km in diameter, is the most outstanding volcanic feature of the whole CGH. Its north-northwestward-open amphitheatre or horseshoe shape is assumed to be a result of downward tilting of the intracaldera block starting from a NE-SW oriented hinge, in a trap-door caldera model (Seghedi, 1995).

Postcaldera evolution of the volcanic structure includes three major phases (Seghedi, 1987): (1) intracaldera eruptions giving rise to andesitic lava flows and a stratocone (Negoiul Romanesc), (2) resurgent intrusion of a large shallow monzodioritic body, and (3) extrusion of several small-volume dacitic lava domes on the caldera rim (Pietricelul) or on the southern flank of the volcanic edifice (Drăgușul, Puturosul).

Volcanic rocks in the central intracaldera area have undergone extensive hydrothermal alteration processes (Teodoru & Teodoru, 1966, Stanciu & Medesan, 1971, Seghedi et al., 1985).

#### Petrological summary

Medium-K andesites prevail in the Călimani Mts., as in the whole CGH, but rock types range from basalt to rhyodacite. Low-K (<1 % K<sub>2</sub>O) dacites are rarely found in the southern half of the area. The volcanic rocks





are typically porphyritic with microcrystalline or glassy groundmass and frequent glomerophyric accumulations of phenocrysts. Afanitic andesites are characteristically present in the northwestern Călimani area. Cognate xenoliths are widespread, commonly including orthopyroxene, amphibole, feldspar and opaque minerals. Upper crustal xenoliths displaying lithologies of the local prevolcanic basement, are also frequent.

The principal petrogenetic processes responsible for the formation of the Călimani volcanics are documented by major and trace element (including REE) as well as isotope geochemistry (Peltz et al., 1974, 1987, Seghedi et al., 1995, Mason et al., 1995, 1996). They can be summarised as follows:

- mantle source with obvious subduction signature of magmas for most of the Călimani volcanics, excepting for the earliest Dragoiasa dacites for which a crustal source is suggested by Seghedi et al. (1995);
- ca. 10-15 % partial melting of the asthenospheric mantle source material (Seghedi et al., 1995);
- fractional crystallisation of plagioclase, pyroxene, amphibole and Fe-Ti oxides led to magma diversification;
- crustal assimilation was a major petrogenetic process;
- assimilation and fractional crystallisation modelling suggest the consumption of 5-35 % upper crustal material belonging to the palaeo-accretionary wedge (Mason et al., 1996);
- magma mixing was pointed out by the presence of disequilibrium mineral assemblages in some small-volume extrusive domes, such as Pietricelul (Seghedi, 1987, Nițoi, 1987).
- clinopyroxene-orthopyroxene geothermometry indicates crystallisation temperatures in the range 860-1150°C for dacitic to basaltic magmas, while temperatures determined using ulvospinel-ilmenite activities are 830-950°C (Mason et al., 1995).

#### **Mineralogy and mineral chemistry of volcanic rocks**

*Plagioclase* is the most common phenocryst phase occurring in all rock types. It displays a wide range of compositions from oligoclase to bytownite (An<sub>23-90</sub>). Oscillatory zoning commonly develops in bands surrounding a more homogenous core in phenocrysts. Rim composition is typically more sodic than that of the core, and is similar to microlithic plagioclase. Inclusions of volcanic glass, in places abundant (sieve-texture) is common. Opaque minerals and pyroxene are also found as inclusions in plagioclase. Typical plagioclase compositions are given in Table 1.

*K-feldspar (orthoclase)* is merely present in the resurgent monzodioritic intrusion within the caldera interior, as submillimetric interstitial anhedral crystals, sometimes displaying microgranophyric intergrowths with quartz (Seghedi, 1982).

*Olivine* is rare but is present in some more basic rocks from the southeastern Călimani.

*Clinopyroxene and orthopyroxene* are both present in most of the rocks with the former more abundant in basaltic andesites and the latter in andesites. Augite and titanaugite prevail among clinopyroxene species. Slight zoning, both normal and reverse, can be observed. Opaque inclusions, mostly magnetite, are frequent. A few xenocrysts of sub-calcic augite were identified in a basaltic andesite sample (Mason et al., 1995). Orthopyroxene range from 50 to 90 % enstatite (Mason et al., 1995). Phenocrysts rims of slightly zoned orthopyroxene show equilibrium composition with groundmass orthopyroxene microliths.

*Amphibole* is a common phenocryst in the more silicic rocks (commonly those with SiO<sub>2</sub> > 59 %). Rim opacitisation of amphibole is frequent, as well as resorption or total replacement by plagioclase, pyroxene and opaques.

*Biotite* is present in some early dacites in the eastern Călimani (Dragoiasa dacite), as well as in the late-stage domes (e.g. Pietricelul).

*Quartz* is present as a late-stage interstitial phase in the monzodioritic intrusive body, as well as a mineral phase interpreted as phenocrysts (Seghedi, 1982) or xenocrysts (Nițoi, 1987) in the Pietricelul dome showing the obvious evidence of magma mixing.

The opaque minerals are accessory but ubiquitous as groundmass phase or microphenocrysts, often as inclusions in phenocryst phases. Titanomagnetite, or less common magnetite, coexists with ilmenite in most rock types.

*Almandine garnet* was found as phenocryst phase in a few small-volume amphibole andesite intrusive domes in the northwestern and eastern parts of the Călimani Mts. Garnet inclusions in biotite have been reported in the Dragoiasa dacite (Nițoi, 1986).

Representative microprobe analyses for plagioclase, clino- and orthopyroxene, and amphibole in Călimani volcanic rocks, according to Mason et al., 1995, are given in Table.





Table

Sample	Plagioclase		Clinopyroxene		Orthopyroxene		Amphibole	
	C1	C7	C1	C9	C4	C9	C7	C9
SiO <sub>2</sub>	53.40	52.69	51.17	52.69	52.58	54.92	44.68	45.80
TiO <sub>2</sub>			0.98	0.42	0.61	0.20	1.70	1.87
Al <sub>2</sub> O <sub>3</sub>	28.85	29.77	3.35	2.37	1.43	2.06	10.87	11.57
FeO	0.58	0.32	8.19	7.04	16.85	12.03	15.13	7.94
MnO			0.20	0.23	0.57	0.29	0.41	0.25
Cr <sub>2</sub> O <sub>3</sub>			0.28	0.26		0.37		
MgO			15.65	15.94	18.49	28.64	2.35	16.65
CaO	12.16	12.99	19.24	20.50	8.78	1.29	10.35	10.85
Na <sub>2</sub> O	4.15	4.04	0.77	0.53	0.43	0.20	1.90	2.89
K <sub>2</sub> O	0.49	0.14					0.22	0.22
Total	99.63	99.95	99.83	99.98	99.74	100.00	97.61	98.20

### Postvolcanic mineral assemblages

Post-emplacement transformations of volcanic rocks in the Călimani Mts partly occur within the caldera or its near neighbourhoods. They are related to (1) postcaldera volcanic activity, mostly in connection to the sulphur-depositing hydrothermal system and solfataric activity of the Negoiiul Romanesc stratocone, (2) intracaldera resurgent intrusion of the monzodioritic body, and (3) fracture-controlled late-stage hydrothermal circulation. These processes led to alteration and replacement of the primary magmatic minerals as well as filling of cavities and vein fractures with assemblages of new lower temperature and lower pressure, mostly hydrothermal minerals.

1. Low-temperature hydrothermal and solfataric activity accompanied sulphur deposition in the intracaldera area, closely related to the Negoiiul Romanesc postcaldera stratocone (Seghedi, 1987). Formerly, Balintoni (1970) assigned these processes to the latest extrusion of biotite-hornblende-quartz andesites (of Pietricelul type). According to this author, hydrothermal transformations, such as formation of secondary quartzites and alunitisation, that accompanied sulphur deposition, have overprinted an earlier hydrothermally altered background (propylitisation, chloritisation).

Detailed mineralogic and chemical studies by Stanciu & Medeaşan (1971a, b) established the mineral assemblages and their zonation accompanying genesis of the sulphur deposit, as well as their host volcanics (two-pyroxene andesites predating the Pietricelul rocks). The alteration zones are, from outside to inside with respect the sulphur mineralisation: weak alteration zone - chlorite zone - clay-mineral zone - siliceous zone, of which the two inner zones are most important. The mineral assemblages identified in these zones are: (1) montmorillonite (smectite), kaolinite, dickite, gypsum, alunite, quartz (cristobalite in the argillised zone), and (2) kaolinite, alunite, quartz, (cristobalite and opal in the siliceous zone). Mineralisation consists of impregnation of sulphur and iron sulphides (pyrite, marcasite, melnicovite) and their oxidised products (iron oxides-hydroxides, such as goethite, in the upper part of the deposit) in the spongy siliceous matrix, resulted from acid leaching. This sequence suggest that during formation of the sulphur deposit, of replacement type, Ph varied from acid to slightly alkaline. The neoformed mineral assemblage was later completed by Seghedi et al. (1992) who added some newly found minerals such as natroalunite, zunyite, illite, tridymite and baryte.

We may suggest that the mentioned minerals do not exhaust the whole spectrum of hydrothermal-fumarolic origin minerals that can be found in this area. There are some indications that several minerals of the iron sulphate group, new for Romania, is very probably present as well (Marincea, personal communication, 1997).

2. High- to low-temperature postmagmatic mineral assemblages characterize the contact zone of the intracaldera monzodioritic intrusion, especially its eastern part where NW-SE striking fractures are present (Seghedi et al., 1985). Five assemblages, typical for different zones of the hydrothermal transformation, have been identified here by the mentioned authors. (1) The neoformed minerals of the albite zone are albitised plagioclase and, in places, epidote. (2) In the biotite zone, the neoformed biotite replaces mafic minerals and even plagioclase, and fills veinlets together with quartz and K-feldspar. (3) In the actinolite zone, the hydrothermal amphibole fills veins, veinlets and cavities, or forms impregnations, being associated with epidote, quartz, albite, biotite, magnetite, pyrite, seldom calcite and K-feldspar; (4) Mineral associations of the argillic zone are illite-quartz, illite-montmorillonite (smectite)-kaolinite-quartz, or montmorillonite (smectite)-illite-quartz, that





often overprint the mentioned earlier-stage assemblages. (5) The quartz-sericite-tourmaline zone is localised in both hydrothermalised monzodiorites and their thermally affected and hydrometasomatised andesitic wallrocks near the contact. Illite is also part of the association. The presence of schorlite as the tourmaline variety is suggested.

In the farther hydrothermal halo of the intrusion zeolites are found up to one kilometre from the intensely hydrothermalised zone (Seghedi, 1982). The zeolite association occur as vein or cavity fillings in the host volcanics (both andesite lavas and volcanoclastics). It includes laumontite, chabasite and epistilbite in association with quartz, calcite, dolomite, prehnite, pyrite and hematite. This mineral assemblage together with fluid inclusion data indicate formation conditions in the range  $T=180-260^{\circ}\text{C}$  and  $P=1-2\text{ Kb}$  (Seghedi & Pomârleanu, 1983).

3. Fracture-related hydrothermal alteration is found in several occurrences along the southern caldera rim, the most developed of which being located in the saddles west of the Pietricelul dome and between the Retitis and Bradul Ciont peaks. It consists of low-temperature mineral assemblages with opal, cristobalite, alunite, kaolinite  $\pm$  sulphur, tridymite, pyrite, marcasite, anhydrite (Seghedi, Rădan, 1992). Opal frequently occurs as opal-CT lepispheres (Rădan et al., 1992). This alunite-bearing association is thought to be deposited when  $\text{H}_2\text{S}$ -rich hydrothermal solutions interact with oxidising surface waters in shallow fracture zones; formation temperatures of  $120-250^{\circ}\text{C}$  were inferred from the alunite-opal association (Seghedi et al., 1992).

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Fig. 1 – Tectonic sketch map of the northern part of the East Carpathians (modified and completed after H. Kräutner (1985), and Al. Vodă, I. Balintoni, Al. Szakács, I. Seghedi (1989).

**Legend:** 1, Quaternary swamp on lake deposits; 2, Tertiary synvolcanic and postvolcanic sediments; 3, Tertiary prevolcanic molasse sediments of the Transylvanian Basin; 4, Cretaceous-Tertiary sediments of the Flysch zone of East Carpathians; 5, Late Paleozoic-Cretaceous sediments of East Carpathians; 6, Neck; 7, Crater; 8, Caldera-like depression; 9, Collapse caldera (caldera fault); 10, Porphyritic intrusive rocks; 11, Fine porphyritic intrusive rocks; 12, Volcanic core complexes; 13, Extrusive domes; 14, Lava flows; 15, Pyroclastic cone; 16, Stratovolcanic cone; 17, Effusive cone; 18, Coarse pyroclastic rocks - proximal facies; 19, Mudflow, debris avalanche, debris flow and ephemeral stream epiclastic volcanic rocks; 20, Neogene volcanics; 21, Alkali basaltic monogenetic volcanic field; 22, sedimentary covers; 23, Perimoldavides: Curbicortal Flysch Nappe (Cc), Audia Nappe (Au), Tarcău Nappe (Tc), Marginal Folds Nappe (Cm), Subcarpathian Nappe (Sc); 24, Severinides: Black Flysch Nappe (Fn), Baraolt Nappe (Ba), Ceahlău Nappe (Ch), Bobu Nappe (Bo); Eastern Getides; 25, Rodna lithogroup (Rusaia, Repedea, Cimpioasa sequences) in the Infrabucovinian Nappes; 27, Negrișoara lithogroup in Pietrosu Bistriței Variscan Nappe; 28, Rebra lithogroup in Rodna unit; 29, Bretila lithogroup in Rarău Variscan Unit and in Infrabucovinian Nappes; 30, Alkaline Massif Ditrău (in Bucovinian Nappe); 31, Geological fractions boundary; 32, Fault; 33, Variscan overthrusts; 34, Alpine overthrust in general; 35, the base Getides overthrust; 36, the base Bucovinian Nappe overthrust; 37, the base Subbucovinian Nappe overthrust; 38, the base Severinides overthrust; 39, reverse overthrust; 40, excursion itinerary; 41, excursion stops. **Map indexes:** b, Bucovinian Nappe; Sb, Subbucovinian Nappe; Ib, Infrabucovinian Nappe.









# STRUCTURE, LITHOSTRATIGRAPHY, METAMORPHISM AND METALLOGENY OF THE CRYSTALLINE ZONE OF THE EAST CARPATHIANS (NORTHERN BISTRITA MOUNTAINS)

L. NEDELCU<sup>1</sup>, P. HARTOPANU<sup>1</sup>, C. MOGA<sup>2</sup>, I. PODAŞCA<sup>2</sup>

<sup>1</sup> Institutul Geologic al României

<sup>2</sup> GEOMOLD S.A., Câmpulung Moldovenesc

The metamorphites of the East Carpathians belong, with their Mesozoic sedimentary cover, to the "Crystalline Mesozoic Zone" of the central part of the chain. This tectonic unit, consisting of superposed nappes, overthrust eastwards the "Flysch Zone".

The regional researches in the Crystalline-Mesozoic Zone lead in time to some structural models and evolution hypotheses of the East Carpathians metamorphites. Despite, sometimes, of fundamental differences existing among these opinions, for a better understanding, a general view about structure, lithostratigraphy, metamorphism and metallogeny of the Crystalline-Mesozoic Zone should be drawn (Table 1). This one is based on the following structural scheme:

Alpine Nappes	Variscan nappes Transylvanian Nappes	Lithostratigraphic units
Perşani Nappe Hăghimaş Nappe		
	Central-East Carpathians Nappes	
Bucovinian Nappe		Mesozoic sedimentary series
	Rarău Nappe	Bretila lithogroup
	Chiril Nappe (?)	Chiril formation (?)
	Putna Nappe	Tulgheş lithogroup
	Pietrosu Bistriţei Nappe	Negrişoara lithogroup
	Rodna Nappe	Rebra lithogroup
	Chiril Nappe (?)	Chiril formation (?)
Subbucovinian Nappe		Mesozoic sedimentary series
	Rarău Nappe	Bretila lithogroup
	Putna Nappe (?)	Tulgheş lithogroup
	Pietrosu Bistriţei Nappe	Negrişoara lithogroup
	Rodna Nappe	Rebra lithogroup
Infrabucovinian Nappe		Permo-Mesozoic sedimentary series
	Rarău Nappe	Bretila lithogroup
	Putna Nappe	Tulgheş lithogroup
	Pietrosu Bistriţei Nappe	Negrişoara lithogroup
	Rodna Nappe	Rebra lithogroup





Table 1  
STRUCTURE, LITHOSTRATIGRAPHY, METAMORPHISM AND METALLOGENY OF THE  
CRYSTALLINE ZONE OF THE EAST CARPATHIANS (NORTHERN BISTRIȚA MOUNTAINS)

Tectonic units		Lithostratigraphic units and their lithologic content	Metamorphism	Age Orogenesis	Metallogeny
Alpine	Variscan				
1	2	3	4	5	6
TRANSYLVANIAN NAPPE					
1. Persani Nappe		- Werfen beds, Campil schists, limestones and dolomites (sometimes bituminous) - ophiolites, jaspers - sedimentary deposits		Triassic	
2. Hăghimaș Nappe		- sedimentary deposits containing sometimes basic rocks at the bottom		Triassic Lower-Middle Jurassic Upper Jurassic and Lower Cretaceous	
CENTRAL-EAST CARPATHIAN NAPPE (MEDIAN DACITES, SÂNDULESCU, 1980)					
1. Bucovinian Nappe		<i>Sedimentary series:</i> - conglomerates, sand- stones, limestones, dolomites, jaspers - limestones, dolomites, radiolarites - marls, calcarenites, conglomerates, sandstones, wildflysch formation		Lower-Middle Triassic Jurassic Upper Jurassic - Lower Cretaceous	
	a. Rarău Nappe	<i>Bretia lithogroup:</i> micaschists, paragneisses, amphibolites, augengneisses and metagranitoides (Mândra, Hăghimaș)	Polymetamorphism: (Balintoni, 1997) (M1)-medium-grade (M2)-medium → lower grade; migmatization (M3)-Variscan retromorphism	Upper Precambrian 748 m.y. K-Ar, 529 m.y. Rb-Sr (Kräutner, 1988)	insignificant



1	2	3	4	5	6
1. Bucovinian Nappe	b. Chiril Nappe	<p><i>Chiril formation:</i> (Nedelcu, 1982; Kräutner et al., 1981) Lithology (Nedelcu, 1982): gneisses, metabasites, amphibolites, porphyroids, limstones, quartzites, paragneisses, biotite schists</p> <p><i>Mândra formation</i> (Balintoni, 1981; Balintoni et al., 1983) <i>Poiana-Grebin formation</i> (Vodă, 1982) <i>Bălaj formation</i> (Runceanu, Voicu, unpubl.)</p> <p>All these formations are considered as different lithological associations from the lower part of Rarău lithozone, synchronous deformed and retromorphosed by Rarău Nappe overthrust (Vodă, Balintoni, 1994)</p>	Polymetamorphic, medium-grade	Upper Precambrian ? Pb-Pb 636± 15 m.y. (Popescu, 1975, unpubl.)	
	c. Putna Nappe	<p><i>Tulgheș lithogroup:</i> - 5 formations: Tg1-5 (Kräutner, 1988) - 4 lithozones (Vodă, 1993): - Căboia lithozone (Tg1): mainly terrigenous - Holdița lithozone (Tg2): mainly quartzitic-graphitic - Leșu Ursului lithozone (Tg3): acid volcanogen-sedimentary sequence containing stratabound sulphide deposits - Arșița Rea lithozone (Tg4): phyllitic-quartzitic</p>	Polymetamorphic, low-grade: Three stages (Nedelcu, 1986): 1. Ilmenite crystallization (M1?) 2. Ilmenite-rutile transformation 3. Transposition of the pseudomorphose in S2 planes and the recrystallisation of rutile I as rutile II	Lower Paleozoic (Kräutner, 1988, Zencenco, 1993) Caledonian orogenesis for (M1) event	- Stratabound Pb-Zn-Cu-Fe sulphide deposits (Kuroko type) at Leșu Ursului and Fundu Moldovei



1	2	3	4	5	6
1. Bucovinian Nappe	d. Pietrosu Bistriței Nappe	<i>Negrișoara lithogroup</i> (Balintoni, Gheuca, 1977): - Pinu lithozone, at lower part: biotite quartzitic paragneisses and interlayered carbonatic rocks, amphibolites, white microcline gneisses - Pietrosu Bistriței porphyroid gneisses at upper part	Polymetamorphism -medium-grade (M1, M2) - Variscan retromorphism (M3) in chlorite zone	Precambrian 840 m.y. U-Pb, Pb-Pb, determined on the zircon crystals of Pietrosu porphyroids (fide Zincenco, 1993)	
	e. Rodna Nappe	<i>Rebra lithogroup</i> (Kräutner, 1968): - Izvorul Roșu lithozone (formation): paragneisses interbedded with micaschists ± staurolite, kyanite, sillimanite and subordinately with carbonatic rocks and quartzites - Voșlobeni lithozone (formation): thick carbonatic rocks-pile with interbedded paragneisses, micaschists, white or black quartzites; sometimes at the lower and the upper part thick amphibolites and amphibolitic gneisses can appear  - Ineu lithozone (formation): quartz micaschists with interbedded limestones, dolomites biotite quartzites, amphibolites, microcline gneisses, white and black quartzites	Polymetamorphism: medium-grade (two mesozonal events: Balintoni, Gheuca, 1977; Balintoni, Bindea, 1994): (M1)-medium pressure: mineral index staurolite, kyanite (M2)-low pressure: cordierite, andalusite (static growth related to a thermic dome) -low-grade Variscan retromorphism	Upper Precambrian 800 m.y. K-Ar (Bercia et al., 1976) 840 m.y. U-Pb, Pb-Pb (fide Zincenco, 1993)	-Stratabound Pb-Zn-pyrite ore deposits is Rodna Mts, similar to the Mississippi Valley type as well as to the Triassic ores in the Alps (Udubașa et al., 1983)  Ore mineralogy: pyrite, sphalerite, galena with subordinate pyrrhotite, chalcopyrite, magnetite (Udubașa et al., 1983)



1	2	3	4	5	6
2. Subbucovinian Nappe		<p><i>Sedimentary series:</i></p> <ul style="list-style-type: none"> <li>- Verrucano conglomerates</li> <li>- conglomerates, sandstones, marly schists, limestones</li> <li>- dolomites</li> <li>- silicolites, argillaceous schists, radiolarite silts, jaspers, limestones</li> <li>- limonitic sandstones, marl silt, limonitic gritty limestones and microconglomerates</li> <li>- nodular marly limestone, silts, clay, calcareous sandstones, siderites</li> <li>- calcareous breccias and calcarenites</li> </ul>	<p>Permian Werfenian</p> <p>Upper Campilian-Lower Anisian</p> <p>Upper Anisian-Ladinian</p> <p>Lias (Lower ?)</p> <p>Dogger (Malm?)</p> <p>Neocomian</p>		
	Rarău Nappe	<i>Brețila lithogroup</i> <sup>1</sup>			
	b. Putna Nappe	<p><i>Tulgheș lithogroup:</i></p> <ul style="list-style-type: none"> <li>- Holdița lithozone (Tg2)</li> </ul>			<ul style="list-style-type: none"> <li>- Mn syngenetic ore deposit at Tolovanu, Iacobeni, Dealul Rusului</li> <li>- Ba syngenetic deposits at Holdița (Broșteni) and Steghioara (Borca)</li> <li>- stratabound sulphide deposits (Kuroko type) at Fărăoane, Puin-Su-härzel</li> </ul>
	c. Pietrosu Bistriței Nappe	<i>Negrișoara lithogroup</i> <sup>1</sup>			
	d. Rodna Nappe	<p><i>Rebra lithogroup:</i></p> <ul style="list-style-type: none"> <li>- Izvorul Roșu lithozone</li> <li>- Voșlobeni lithozone</li> <li>- Ineu lithozone</li> </ul>			<ul style="list-style-type: none"> <li>- massive magnetite lenses in upper amphibolites of Voșlobeni lithozone</li> </ul>
3. Infrabucovinian Nappe		<p><i>Sedimentary series</i> (Bercia et al., 1976, Săndulescu, 1975, 1984):</p>			



1	2	3	4	5	6
		a. Iacobeni Nappe: - quartzitic conglomerates and sandstones - bituminous limestones - gritty limestones, schists, dolomites - gritty limestones b. Panaci Unit: - polymictic conglomerates c. Arșița Barnarului Unit: - red conglomerates Bretila lithogroup <sup>1</sup>		- Werfenian - Anisian - Upper Triassic - Middle Jurassic - Permian Permian	
	Rarău Nappe				

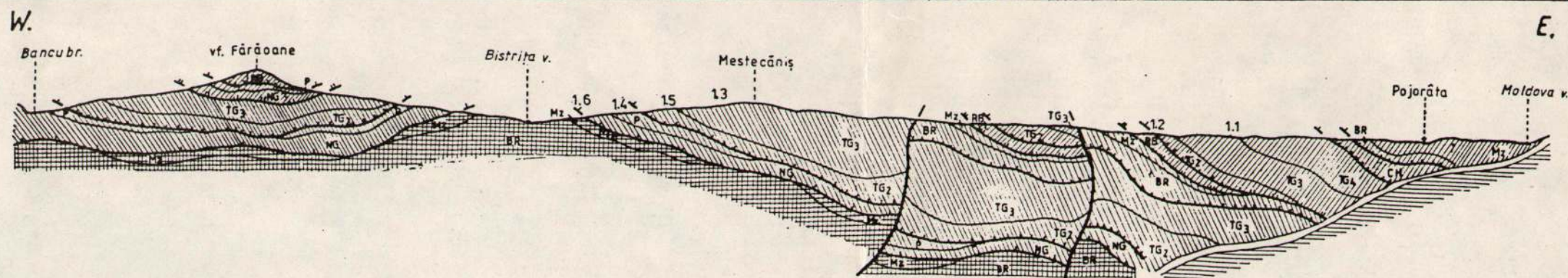
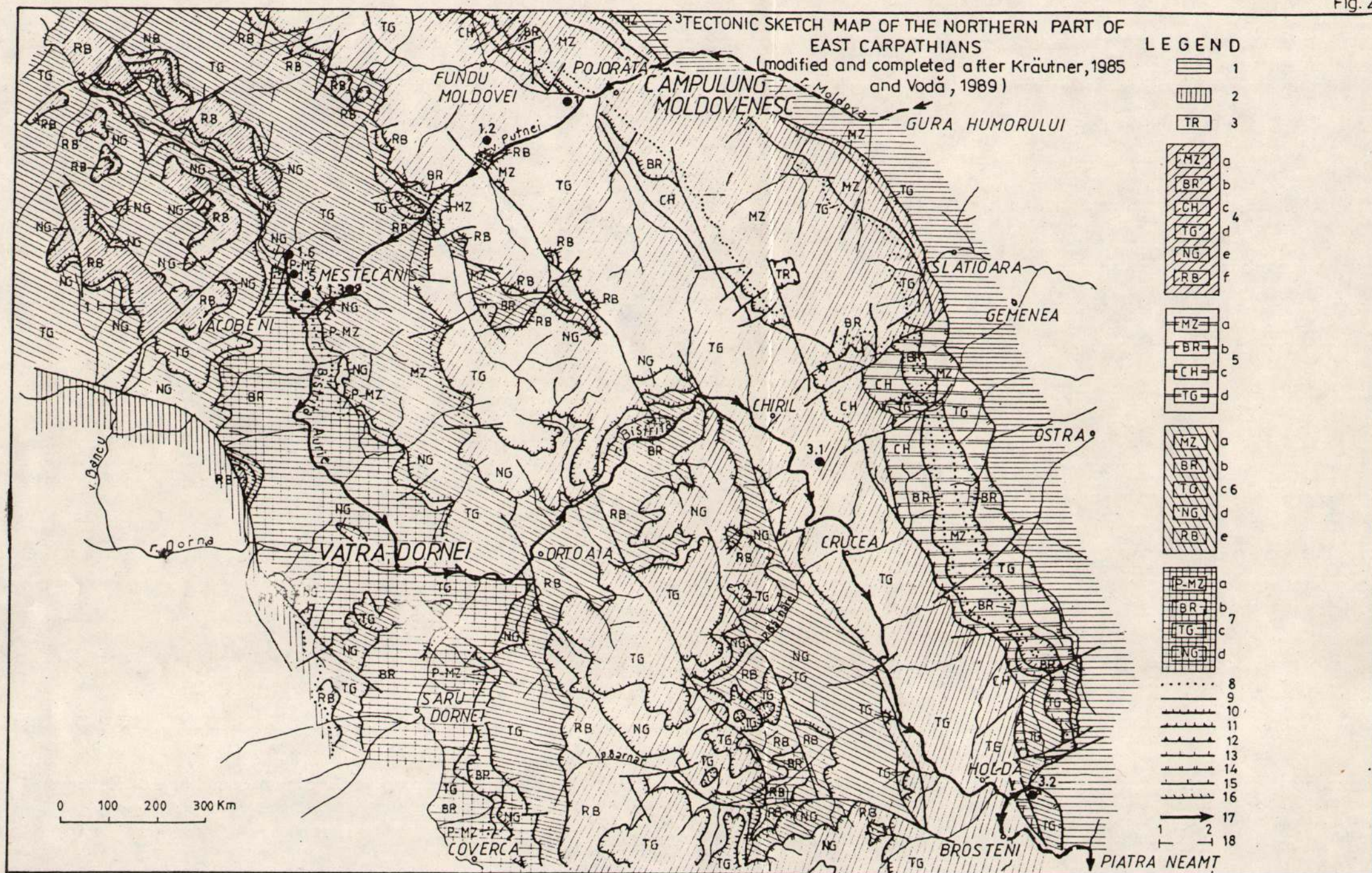
<sup>1</sup> the lithostratigraphy, lithology, metamorphism and age are similar to those of corresponding lithogroups of Bucovinian Nappe

Fig. 2 – Tectonic sketch map of the northern part of the East Carpathians (modified and completed after Kräutner, 1985 and Vodă, 1989)

Legend: 1, INNER FLYSCH ZONE (Cretaceous flysch); 2, Post-tectonical sedimentary cover; 3, TRANSYLVANIAN NAPPE. CENTRAL-EAST CARPATHIAN NAPPE: 4, Bucovinian Nappe: a, Mesozoic sedimentary formations; b, Bretila lithogroup (group); c, Chiril lithogroup (group); d, Tulgheș lithogroup (group); e. Negrișoara lithogroup (group); f. Rebra lithogroup (group); 5, Tarnița scale: a, Mesozoic sedimentary formations; b, Bretila lithogroup; c, Chiril lithogroup; d. Tulgheș lithogroup; 6, Subbucovinian Nappe: a, Mesozoic sedimentary formations; b, Bretila lithogroup; c, Tulgheș lithogroup (Tg2, Tg3, Tg4 lithozones=formations); d, Negrișoara lithogroup; e, Rebra lithogroup; 7, Infrabucovinian Nappes: a, Permo-Mesozoic sedimentary formations; b, Bretila lithogroup; c, Tulgheș lithogroup; d, Negrișoara lithogroup; 8, discordance limit; 9, fault; 10, reverse fault; 11, pre-Alpine overthrust plane; 12, Transylvanian Nappe overthrust plane; 13, Subbucovinian Nappe overthrust plane; 14, Bucovinian Nappe overthrust plane; 15, Infrabucovinian overthrust plane; 16, Tarnița scale; 17, itinerary; 18, cross-section.



Fig. 2





## B. FIELD TRIP

### FIRST DAY

#### CRYSTALLINE ZONE OF THE EAST CARPATHIANS (NORTHERN BISTRITA MOUNTAINS): STRUCTURE, LITHOSTRATIGRAPHY, METAMORPHISM AND METALLOGENY. VALEA PUTNEI - VALEA BISTRITEI

##### Itinerary:

Iassy - Humor and Voroneț monasteries - Câmpulung Moldovenesc-Pojorâta-Iacobeni-Vatra Dornei

Leaders: L. Nedelcu, C. Moga, I. Podașcă (Stops 1.1.-1.4. and 1.6), Paulina Hârtoapanu (Stop 5)

##### Stop 1.1: Pojorâta-Valea Putnei

– Outcrop of the sulphide level (s.l. belonging to the Fundu Moldovei member (FMM) of the Tulgheș lithogroup (Leșu Ursului lithozone Tg3). Ore mineral assemblage: pyrite and chalcopyrite lenses and disseminations in quartz, chlorite schists. Ore was worked in Valea Putnei mine.

##### Stop 1.2: Valea Putnei

Cross-section through the Valea Putnei tectonic window

– Outcrop of black quartzites with graphite  $\pm$  manganese (Tulgheș lithogroup: Holdița lithozone Tg2).  
– Putna Variscan nappe plane between Tg2 black quartzites and Rebra lithogroup dolomites.  
– Alpine Bucovinian Nappe plane: bedded grey-white dolomites of the Rebra lithogroup overthrust on the Triassic massive dolomites.

##### Stop 1.3: Mestecăniș mine

Mestecăniș vein (between Mestecăniș railway and Mestecăniș peak): copper-pyrite lenses, nests and disseminations hosted in massive grey-white vein quartz.

Length: about 1 km, breadth: meters to tens of meters; depth: about 250 m

Ore mineral assemblage: pyrite, chalcopyrite and galena, bornite. Sometimes, at the upper part of vein low contents of gold up to 1 g/t were determined. In the depth the vein is interrupted by Subbucovinian Nappe plane.

##### Stop 1.4: Puciosu brook

– Outcrop of Negrișoara lithogroup:

a) Pietrosu porphyroids (P=upper level) represented by porphyroid gneisses of dacitic composition affected by Variscan retromorphism (laminations, general chloritization of mafic minerals). They present a porphyroclastic structure given by grains of bluish quartz flattened on the S-planes. Augen feldspar is developed, too.

Mineral assemblage (Balintoni, Gheucă, 1977): a) quartz, plagioclase (up to An 45), albite, microcline, biotite, muscovite, chlorite, epidote, sphene (ilmenite), hematite, zircon, orthite, radioactive minerals, calcite, pyrite, sericite;

b) biotite-bearing quartzitic paragneisses (Pinu lithozone=lower level) also affected by Variscan retromorphism.

Mineral assemblage (Balintoni, Gheucă, 1977): quartz, plagioclase (An 25–45), biotite, muscovite, chlorite, almandine/hematite, opaque minerals, tourmaline, apatite, zircon, radioactive minerals, orthite, epidote, calcite.





– Sedimentary cover of the Infrabucovinian Nappe: Triassic bedded dolomites

*Stop 1.5: Tolovanu manganese mine*

The Mn ore deposits of the Bistrița Mountains are spread from N to S, covering 80 km. Starting from the north the most important are: Dadu, Oița-Colacu, Tolovanu, Iacobenii, Argeștru and Dealul Rusului. The Mn ore deposits are situated in the middle Tulgheș Series (Tg2) in the Putna nappe. The Tg2 formation is of Upper Proterozoic-Lower Cambrian age and is made up of black quartzites. The formation is intensely cataclased and microfolded. The ore deposits from Tolovanu are lens-shaped, of small and medium sizes. The primary ore of the Tolovanu deposit consists mainly of Mn-carbonate (cca 70 %), silicates (cca 20 %) and oxides + sulphides + other minerals (cca 5 %). The distribution of the mineral component in the ore is very unhomogeneous. The ore deposits are rich in rhodochrosite, which has permitted the development of large oxidation zones.

The mineralogical composition (Table 2) is very complex. About 150 minerals are described so far in the Mn-deposits of Tolovanu. The mineral paragenesis in the Mn deposits are the result of the ore complex evolution through mineral retrograde metamorphism which determined the existence of successive reactions. Not all the zones in this ore did pass through all the reactions of such a succession. There are several generations to the same mineral. Within each of the paragenesis the crystallisation was synchronous. The fugacities of O, S, CO<sub>2</sub>, Cl, F, OH etc. had an important role in the forming of the new minerals. Metasomatism with Li, Na, K, Fe<sup>+3</sup> was important and it also contributed to the appearance of many interesting minerals.

The primary ore of the deposits from the Bistrița Mountains had the paragenesis succession, from the old to the new, as follows:

A<sub>0</sub> Mn-Fayalite (?) + Spessartine-Calderite-Rhodochrosite ferroan + Apatite;

A<sub>1</sub> Tephroite ferroan + Rhodochrosite ferroan + Spessartine + Apatite;

A<sub>2</sub> Tephroite + Jacobsite + Galaxite + Rhodochrosite;

A<sub>3</sub> Mn-Humite + Alabandine + Pyrophanite + Co-Ni-As sulphosalts;

B. Pyroxmangite + Rhodochrosite + Rhodonite + Apatite;

C. Mangangrunerite + Spessartine + Celsian + Apatite + Magnetite;

D. Substitution paragenesis:

Rhodonite + Aegirine + Albite + Quartz;

Rhodonite + Nambulite + Na-Nambulite + Aegirine + Albite;

Rhodonite + Na-Nambulite + Kozulite;

Mangangrunerite + Rhodochrosite + Quartz + Hematite;

Rhodonite + Ferro-glaucophane + Clorapatite + Quartz;

Riebeckite + Aegirine + Microcline + Hematite + Albite + Quartz;

Kozulite + Braunite + Bixbyite;

E. Almandine manganoan + Grunerite + Quartz

New paragenesis	and	Vein monomineral
Friedelite + Rhodochrosite + Quartz		Friedelite
Rhodochrosite + Frie		
Rhodochrosite + Manganpyrosmalite		Manganpyrosmalite
Friedelite + Mn-Chlorite + Baryte + Rhodochrosite		Mn-Chlorite
Rhodochrosite + Friedelite + Mn-Chlorite + Parssetensite		
Friedelite + Caryopilite		Caryopilite
Bannisterite + Quartz		Bannisterite
Friedelite + Caryopilite + Mn-Chlorite + Rhodochrosite		
Caryopilite + Calcite + Parssetensite		
Baryte + Nelenite + Chlorite + Bemmentite		Baryte
Mn-Chlorite + Quartz		
Schallerite + Rhodochrosite + Baryte		Schallerite
Parssetensite + Quartz + Pyrite + Magnetite		Parssetensite

The parageneses A<sub>0</sub>, A<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, B, C belong to the almandine amphibolite facies and the last parageneses are the result of a retrograde metamorphism under conditions of greenschist facies.





Table 2 Mineral species and varieties so far identified at Tolovanu

<b>A. PRIMARY ORE:</b>		
<i>I. CARBONATES</i>		
1. Rhodochrosite, ferriferous $\text{MnCO}_3$		The most abundant mineral from Tolovanu
2. Rhodochrosite, $\text{MnCO}_3$		Very abundant mineral
3. Rhodochrosite, magnesian $(\text{MnMg})\text{CO}_3$		Associated with cummingtonite, mangangrunerite, quartz,
4. Kutnohorite $\text{CaMn}(\text{CO}_3)_2$		Veins, associated with rhodonite and quartz
5. Calcite, manganoan $(\text{CaMn})\text{CO}_3$		Veins, associated with quartz, pyrite, ripidolite
6. Calcite $\text{CaCO}_3$		Veins associated with pyrite, chlorite, quartz
7. Aragonite $\text{CaCO}_3$		Veins in weathered carbonate ores
8. Ankerite $(\text{CaFeMg})(\text{CO}_3)_2$		Associated with cummingtonite, mangangrunerite, spessartine, quartz
9. Siderite $\text{FeCO}_3$		Associated with grunerite, mangangrunerite, magnetite
<i>II. SILICATES</i>		
1. Spessartine $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$		The constituent of gonditic ore
2. Calderite, calcian $(\text{MnCa})_3(\text{Al}_2(\text{SiO}_4)_3)$		Associated with rhodonite, kutnohorite, pyrophanite
3. Spessartine, andraditic $(\text{MnFe})_3(\text{Fe,Al})_2(\text{SiO}_4)_3$		In oxidized assemblages
4. Almandine, manganoan $(\text{FeMn})_3\text{Al}_2(\text{SiO}_4)_3$		In black quartzites
5. Tephroites, ferriferous $(\text{MnFe})_2\text{SiO}_4$		In reduced assemblages associated with ferriferous rhodochrosite
6. Tephroite $\text{MnSiO}_4$		In reduced assemblages associated with rhodochrosite
7. Pyroxmangite $\text{MnSiO}_3$		Abundant, many generations
8. Alleghanyite $\text{Mn}_5(\text{SiO}_4)_2(\text{OH, F})$		Simple twins
9. Ribbeite $(\text{MgMn})_5(\text{SiO}_4)_2(\text{OH, F})_2$		Associated with pyrophanite
10. Sonolite $\text{Mn}_9(\text{SiO}_4)_4(\text{OH, F})$		Polysynthetically twinned
11. Rhodonite $\text{MnSiO}_3$		In saturated and subsaturated ores
12. Nambulite $\text{LiNaMn}_8\text{Si}_{10}\text{O}_{28}(\text{OH})_2$		Formed by Li-metasomatism on rhodonite
13. Natronambulite $\text{NaMn}_4\text{Si}_5\text{O}_{14}(\text{OH})$		Associated with rhodonite and nambulite





14. Aegirine $\text{NaFeSi}_2\text{O}_6$	Zoned composition on colourless pyroxene
15. Aegirine-augite $(\text{Na,Ca})\text{FeSi}_2\text{O}_6$	Associated with aegirine, nambulite, kozulite, albite
16. Mangangrunerite (dannemorite) $\text{Mn}_2\text{Fe}_3\text{Si}_8\text{O}_{22}(\text{OH})_2$	Associated with spessartin, magnetite, quartz
17. Grunerite $\text{Fe}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Associated with manganoan almandine, quartz
18. Cummingtonite $\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	Associated with magnesiorhodochrosite
19. Riebeckite $\text{Na}_2\text{Fe}_3\text{Fe}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$	Compositional zoning on mangangrunerite in oxidized assemblages
20. Magnesioriebeckite $(\text{Na,Ca})_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	Associated with hematite, spessartine-calderite, riebeckite
21. Kozulite $(\text{Na,K})(\text{Mn,Mg,Fe,Al})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	In oxidized assemblages with nambulite, natronambulite
22. Winchite $(\text{Ca,Na})(\text{MgMn})_4(\text{AlFe})\text{Si}_8\text{O}_{22}(\text{OH})_2$	In oxidized assemblages
23. Ferroglaucophane $\text{Na}_2(\text{FeAlMg})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$	Zoned composition on mangangrunerite
24. Phlogopite, manganoan $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}\text{F}_2(\text{OH})_2$	Associated with hematite, rhodochrosite
25. Norrishite $\text{K}(\text{Mn,Li})\text{Si}_4\text{O}_{12}$	Formed by Li-metasomatism
26. Bannisterite $\text{KCaMn}_{21}(\text{SiAl})_{32}\text{O}_{76}(\text{OH})_{16} \cdot 12\text{H}_2\text{O}$	Vein mineral
27. Stilpnomelane, manganoan $(\text{KNaCa})(\text{FeMnMg})_{12}(\text{FeAlTi})_{16}(\text{O,OH})_{54} \cdot \text{H}_2\text{O}$	Vein mineral
28. Ferrostilpnomelane $\text{Mg}(\text{FeMn})_6\text{Al}_2(\text{OH})_{16}\text{Si}_{12}\text{O}_{20} \cdot n\text{H}_2\text{O}$	Vein mineral associated with magnetite
29. Ferristilpnomelane $\text{Mg}_2(\text{FeMn})_6\text{Al}_2(\text{O,OH})_{16}\text{Si}_{12}\text{O}_{20} \cdot n\text{H}_2\text{O}$	Vein mineral associated with hematite
30. Biotite, manganoan $\text{K}_2(\text{FeMnMg})(\text{FeAlTi})_6(\text{SiAl})_8\text{O}_{20}(\text{OH,F})$	In black quartzites
31. Manganpyroxmalite $(\text{MnFe})_8(\text{Si}_8\text{O}_{18})(\text{OH,Cl})$	Formed on tephroite by Cl-metasomatism
32. Friedelite $\text{MnSi}_6\text{O}_{15}(\text{OH,Cl})$	Formed by Cl-metasomatism
33. Caryopillite $(\text{MnMg})_3\text{Si}_2\text{O}_5(\text{OH})_4$	Radially disposed, associated with chlorites
34. McGillite $(\text{MnFe})\text{Si}_6\text{O}_{15}(\text{OH})_6(\text{Cl})_{12}$	Vein mineral, formed on chlorapatite
35. Schallerite $(\text{MnFe})_8(\text{SiAs})(\text{OH,Cl})_{10}$	Associated with Co,Ni,As-sulphosalts, formed on them
36. Neleite $(\text{MnFe})_{16}\text{Si}_{12}\text{As}_3\text{O}_{36}(\text{OH})_{17}$	Retromorph mineral, associated with nimite
37. Inesite $\text{Ca}_2\text{Mn}_7\text{Si}_{10}\text{O}_{28}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	Formed on rhodonite
38. Minnesotaite $\text{Fe}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	Associated with magnetite and grunerite



39. Carpholite $\text{MnAl}_2(\text{OH})_4\text{Si}_2\text{O}_6$	Fibrous mineral, associated with spessartine
40. Clinochrosite $\text{Mg}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Associated with Mn-chlorite and rhodochrosite
41. Pennantite $(\text{MnAl})(\text{SiAl})_4\text{O}_{10}(\text{OH})_8$	Formed on galaxite in tephroitic ore
42. Clinochlore ferroan $(\text{MgFe})_6(\text{SiAl})_4\text{O}_{10}(\text{OH})_8$	Associated with nelenite, rhodochrosite, tephroite
43. Ripidolite $(\text{MgFeMnAl})_{12}(\text{SiAl})_8\text{O}_{20}(\text{OH})_{16}$	Wormshaped grains
44. Greenalite $\text{Fe}_3\text{Si}_2\text{O}_5(\text{OH})_4$	Submicroscopic grains, isotropic
45. Nimite $(\text{NiMgFe})_5\text{Al}(\text{Si}_3\text{Al})_{10}(\text{OH})_8$	Retromorph, associated with nelenite
46. Takovite $\text{Ni}_6\text{Al}_2(\text{OH})_{16}(\text{CO}_3, \text{OH}) \cdot 4\text{H}_2\text{O}$	Associated with calcite, rancieite, brushite
47. Kelyite $(\text{MnMg})(\text{FeAl})(\text{SiAl})\text{O}_{10}(\text{OH})_8$	Instable in excess quartz presence. Associated with galaxite, jacobsite
48. Jusite $(\text{CaNaK})_5(\text{SiAl})_6\text{O}_{15} \cdot 5\text{H}_2\text{O}$	In rhodochrosite ore, with friedelite, nelenite, greenalite
49. Lennilenaite $\text{K}_7\text{Mg}_{48}(\text{SiAl})_{72}(\text{O}, \text{OH})_{216} \cdot 16\text{H}_2\text{O}$	In gonditic ore, associated with magnetite, hematite
50. Bementite $\text{Mn}_5\text{Si}_4\text{O}_{10}(\text{OH})_6$	Lamellar grains, in manganese humite ore
51. Neotocite $\text{MnSiO}_3 \cdot n\text{H}_2\text{O}$	Veins in rhodochrositic ore and in Mn-humitic ore
52. Fraipontite $(\text{ZnAl})_3(\text{SiAl})_2\text{O}_5(\text{OH})_4$	Associated with nambulite, rhodonite, aegirine
53. Genthelvite $\text{Zn}_3\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$	Associated with glaucodot, arsenopyrite, groutite
54. Bafertisite $\text{BaFe}_2\text{TiSi}_2\text{O}_9$	Accessory mineral, associated with nambulite
55. Homilite $\text{Ca}_2\text{FeB}_2\text{Si}_2\text{O}_{10}$	Associated with rhodonite, Na-nambulite, quartz
56. Allanite $(\text{CaCeLa})_2(\text{AlFe})_3(\text{FeMg})_3(\text{OH})\text{Si}_4\text{O}_{12}$	More frequently than accessory in all type ore
57. Piemontite $\text{Ca}_2(\text{AlFeMn})_3(\text{OH})\text{Si}_3\text{O}_{12}$	In hausmannitic ore, associated with braunite
58. Albite $\text{NaAlSi}_3\text{O}_8$	Associated with aegirine, nambulite, kozulite
59. Microcline $\text{KAlSi}_3\text{O}_8$	Associated with aegirine, riebeckite, albite
60. Thorite, uranoan $(\text{ThUCe})\text{SiO}_4$	Accessory mineral
<b>III. OXIDES</b>	
1. Jacobsite $\text{MnFe}_2\text{O}_4$	Frequent in tephroitic and Mn-humitic ore
2. Magnetite $\text{FeFe}_2\text{O}_4$	In gonditic ore





3. Bixbyite $Mn_2O_3$	In oxidized assemblages
4. Braunite $MnMn_6SiO_{12}$	In oxidized assemblages
5. Hausmannite $MnMn_2O_4$	In oxidized assemblages
6. Pyrophanite $MnTiO_3$	Veins with ribbeite and alabandite
7. Hematite $Fe_2O_3$	In oxidized assemblages
8. Iwakiite $MnFe_2O_4$	Associated with jacobsonite, bixbyite, in tephroitic ore
9. Galaxite $MnAl_2O_4$	In tephroitic ore
10. Gahnite $ZnAlO_4$	Associated with spessartine and rhodochrosite
11. Hercynite $FeAl_2O_4$	Associated with spessartine and quartz
12. Ferrocolumbite $(FeMn)(NbTa)_2O_6$	Opaque, in rhodochrositic ore
13. Ashanite $(NbTaUFeMn)_4O_8$	Microscopic grains, enclosed in pyroxmangite
14. Ixiolite $(MnTaNb)O_2$	Microscopic grains associated with spessartine, kutnohorite, quartz
15. Cobalt manganese spinel $Co_2MnO_4$	In tephroitic ore, with As, Co, Ni -sulphosalts
16. Samarskite $YNb_2O_6$	In old pyroxmangitic ore
17. Franklinite $(ZnMnFe)(FeMn)_2O_4$	In manganese humite ore, with ribbeite, alabandite

#### IV.SULPHIDES

1. Pyrite $FeS_2$	Veins, with quartz, stilpnomelane, chlorite, magnetite
2. Chalcopyrite $CuFeS_2$	Sporadically as milimeter sized grains
3. Galena $PbS$	Associated with chalcopyrite
4. Galena, bismuthian $Bi_{0.22}Pb_{0.89}S_{1.22}$	Associated with pyroxmangite, quartz, pyrrohoite
5. Sphalerite cadmian $(ZnCd)S$	Associated with pyroxmangite, stannite, quartz
6. Pyrrhotite $FeS$	Associated with chalcopyrite in Mn-carbonate ore
7. Alabandite $MnS$	In reduced assemblages, with ribbeite, pyrophanite, cattierite
8. Hauerite $MnS_2$	In reduced assemblages, with high sulphur fugacity
9. Stannite $Cu_2FeSnS_4$	In pyroxmangitic ore, associated with wurtzite
10. Wurtzite $ZnS$	Associated with pyrochroite, quartz, pyroxmangite





11. Cattierite $\text{CoS}_2$	In reduced assemblages with ribbeite, alabandite, pyrophanite
12. Gersdorffite $(\text{NiCo})\text{AsS}$	Frequent in microscopic grains
13. Carrollite $\text{CuCoS}_4$	Accessory in gonditic ore
14. Chalcostibite $\text{CuSbS}_2$	Associated with magnetite, rhodochrosite, asbolane
15. Chatkalite $\text{Cu}_6\text{FeSn}_2\text{S}_8$	Accessory in gonditic ore, with calderite(calcian), quartz
16. Lollingite $\text{FeAs}_2$	Microscopic grains in silicates ore
17. Lollingite, cobaltian $(\text{CoFe})\text{As}$	Associated with other sulphosalts, jacobsite, tephroite
18. Glaucodot $(\text{CoFe})\text{AsS}$	Associated with genthelvite, arsenopyrite, groutite
19. Arsenopyrite $\text{FeAsS}$	Associated with glaucodot, genthelvite
20. Breithauptite $\text{NiSb}$	Associated with other Ni,As,Co-sulphosalts
21. Penroseite , sulphurian $(\text{NiCoCu})(\text{SSe})$	Associated with spessartine, gahnite, rhodochrosite
22. Rammelsbergite, cobaltian $(\text{NiCo})\text{As}_2$	Microscopic grains in tephroitic ore with $\text{Mn}_3\text{AsO}_4(\text{OH})_4$
23. Talnakhite $\text{Cu}_9(\text{FeNi})_8\text{S}_{16}$	Veins, with nambulite, rhodonite, fraipontite
24. Safflorite $\text{CoAsS}_4$	In rhodochrositic ore, with other Co,Ni,As-sulphosalts

#### V. OTHER MINERALS

1.Barite $\text{BaSO}_4$	Associated with schallerite
2.Quartz $\text{SiO}_2$	Very frequent mineral
3. Moganite $\text{SiO}_2$	in oxidised zone
4.Fluorapatite $\text{Ca}(\text{PO}_4)_3\text{F}$	Frequent in all type of ore
5.Chlorapatite $\text{Ca}(\text{PO}_4)_3\text{Cl}$	Frequent in all type of ore
6.Switzerite $\text{Mn}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$	In oxidized and reduced assemblages
7.Monazite $\text{CePO}_4$	More frequent than accessory mineral
8.Huebnerite $\text{MnWO}_4$	In rhodochrositic ore, with pyrite and quartz
9.Barium vanadate $\text{Ba}_3\text{V}_4\text{O}_{13}$	Associated with spessartine, carrollite, quartz
10.Graphite C.	Very rare in ore
11.Unnamed mineral $\text{Mn}_3\text{AsO}_4(\text{OH})_4$	Associated with Co-rammelsbergite and other Co-sulphides





<b>B.OXIDISED ZONE</b>	
1. Nsutite $\text{Mn}(\text{O},\text{OH})$	The most common mineral from oxidised zone
2. Nsutite, manganooan $\text{Mn}_{1.6}\text{Mn}_{0.32}\text{O}_{3.1}(\text{OH})_{0.9}$	Frequent mineral
3. Pyrolusite $\beta\text{-MnO}_2$	Widespread
4. Ramsdellite $\gamma\text{-MnO}_2$	Formed on rhodochrosite
5. Groutite $\alpha\text{-MnO}_2$	Formed on pyroxmangite and rhodochrosite
6. Akhtenskite $\epsilon\text{-MnO}_2$	In oxidized zone of oxidized assemblages
7. Birnessite $(\text{NaCaK})(\text{MgMn})\text{Mn}_6\text{O}_{14} \cdot 5\text{H}_2\text{O}$	Frequently formed on rhodochrosite
8. Todorokite $(\text{NaCaKBaSr})_{1-x}(\text{MnMgAl})_6\text{O}_{12} \cdot 3\text{-}4\text{H}_2\text{O}$	Associated with rancieite, birnessite, löellingite.
9. Rancieite $(\text{CaMn})\text{Mn}_4\text{O}_9 \cdot 3\text{H}_2\text{O}$	Associated with calcite, brushite, takovite
10. Manganite $\gamma\text{-MnO}(\text{OH})$	Well crystallized grains
11. Coronadite $\text{MnPbMn}_6\text{O}_{14}$	Rare mineral
12. Crednerite $\text{CuMnO}_2$	Formed probably on chalcopyrite
13. Cryptomelane $\text{KMn}_8\text{O}_{16}$	Widespread mineral
14. Hollandite $(\text{BaK}_2)\text{MnMn}_7\text{O}_{16} \cdot \text{H}_2\text{O}$	Formed on Ba-feldspars
15. Vernadite $\delta\text{-Mn}(\text{OH})_4$	Associated with manjiroite, hollandite
16. Allophane $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$	Associated with safflorite, löellingite, diaspore
17. Diaspore $\text{AlO}(\text{OH})$	Associated with groutite, nsutite, rhodochrosite
18. Halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	Associated with rancieite, birnessite, akhtenskite
19. Khademite $\text{Al}(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$	Associated with jarosite
20. Argutite $\text{GeO}_2$	Associated with quartz, nsutite, manganite, moganite
21. Pyrochroite $\text{Mn}(\text{OH})_2$	In tephroitic ore, associated with galaxite
22. Goethite $\alpha\text{-FeO}(\text{OH})$	Formed on hematite and on magnetite
23. Brushite $\text{CaPO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$	Associated with calcite, rancieite, takovite
24. Opal $\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Frequent mineral





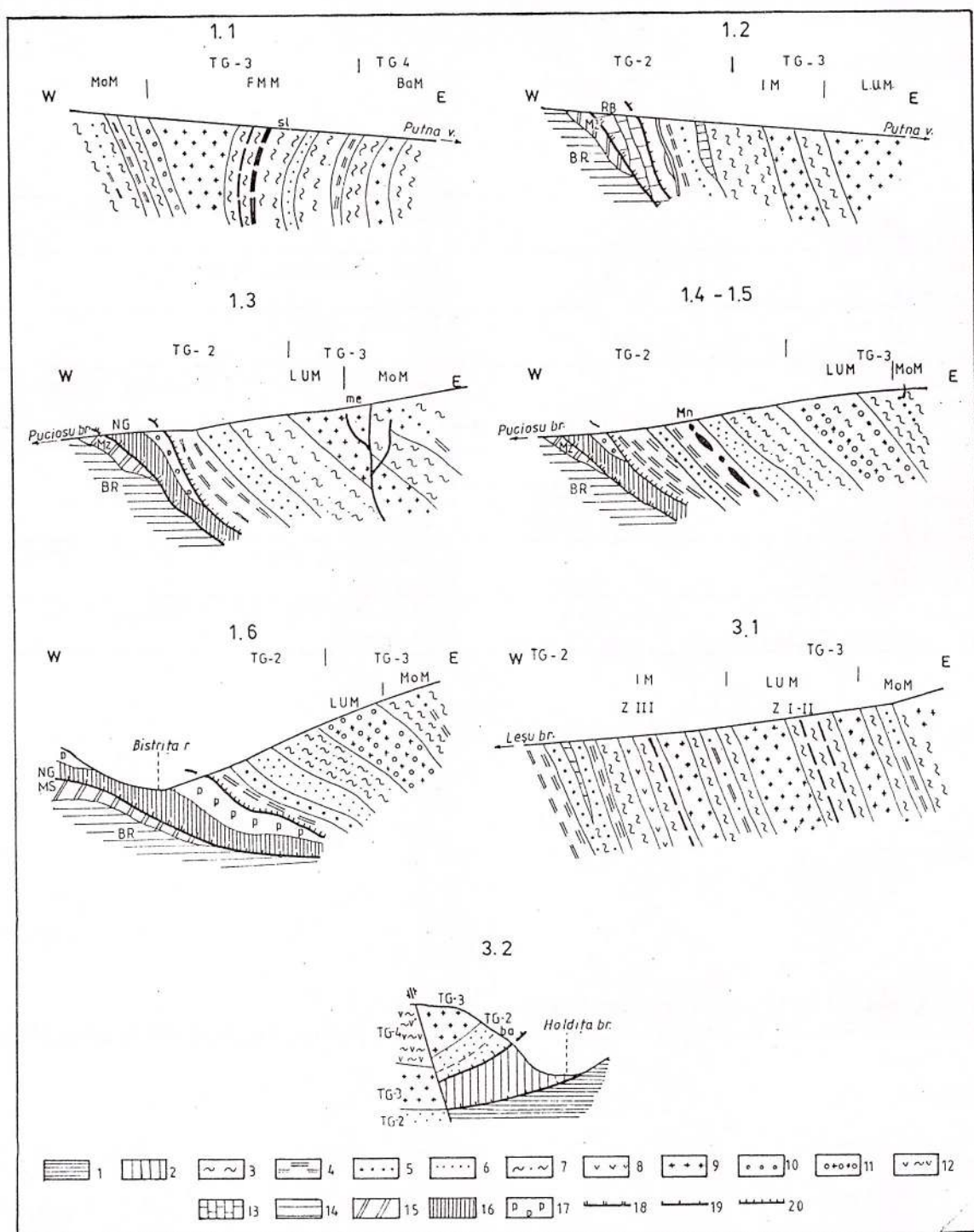
25. Asbolane $\text{NiMn}_2\text{O}_3(\text{OH})_4 \cdot \text{H}_2\text{O}$	Associated with quartz, rhodochrosite
26. Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Rare , well crystallized grains
27. Jarosite $(\text{FeMg})\text{SO}_4 \cdot 7\text{H}_2\text{O}$	Formed on pyrite
28. Lepidocrocite $\gamma\text{-FeOOH}$	Frequently formed on hematite, magnetite, goethite
29. Lithiophorite $(\text{AlLi})(\text{OH})_2\text{MnO}_2$	Formed on nambulite and natronambulite
30. Manjiroite $(\text{NaK})\text{MnO}_8\text{O}_{10} \cdot \text{H}_2\text{O}$	Associated with vernadite, hollandite, coronadite
31. Manganbelyankinite $\text{Mn}(\text{TiZrNb})_5\text{O}_{10} \cdot 9\text{H}_2\text{O}$	Amorphous, associated with aegirine and monazite
32. Coalingite $\text{Mg}_{10}\text{Fe}_2(\text{OH})_{24}(\text{CO}_3) \cdot 2\text{H}_2\text{O}$	Associated with ajoite, hematite, maghemite, fluorapatite

*Stop 1.6: Brezuța brook - Bistrița valley confluence*

– Outcrop of Pietrosu porphyroids showing a massive ocular texture (Negrișoara lithogroup, Subbucovinian Nappe)









## SECOND DAY

## Itineraray:

Vatra Dornei - Gura Haitei - Neagra Valley - Big sulphur quarry - Călimani caldera rim - Vatra Dornei

Leader: Al. Szakács

## Stop 2.1. Gura Haitei village

Andesite lava flow belonging to the earlier stages of precaldra edifice building is exposed at the roadside in the left side of the Neagra valley. The outcrop displays the interior of a thick lava flow with massive irregular jointing in the middle and platy jointing in the upper part. The rock is a typical calc-alkaline medium-porphyrific rare amphibole-bearing pyroxene andesite that includes sedimentary xenoliths. The K-Ar age of this rock is  $7.94 \pm 0.37$  Ma (Pécskay et al., 1995). Its major element composition is given below.

SiO <sub>2</sub>	57.4	K <sub>2</sub> O	1.5
Al <sub>2</sub> O <sub>3</sub>	21.62	Na <sub>2</sub> O	3.15
Fe <sub>2</sub> O <sub>3</sub>	1.98	TiO <sub>2</sub>	0.47
FeO	3.3	P <sub>2</sub> O <sub>5</sub>	0.2
MnO	0.12	CO <sub>2</sub>	0.29
MgO	2.09	S	0.09
CaO	7.08	H <sub>2</sub> O+	0.87
		Total	100.51

## Stop 2.2. Hagiul Mic brook, western tributary of the Neagra valley

A long roadside outcrop near the confluence displays fine to medium sized pale green, slightly propylitised volcanoclastic breccia, probably of debris flow origin, in which small (centimetric to decimetric) nests, pockets or irregular veinlets of friable white zeolite aggregates occur sporadically. Laumontite and epistilbite were determined, along with amethyst quartz crystals (Seghedi, Pomârleanu, 1983).

## Stop 2.3. Abandoned quarry near the confluence between Haita and Rachitis brooks in the caldera interior

The quarry exposes the marginal part and contact of the monzodioritic intrusion with obvious thermal and metasomatic effects.

The large (ca. 7x5 km) late-stage resurgent intrusion is located in the central and western parts of the caldera, cropping out in an altitude range of more than 500 m, whereas borehole data indicate more than further 1,100 m development in depth.

The intrusion consists of equigranular or porphyric holocrystalline rock displaying the following magmatic mineral assemblage: plagioclase (45-62 %), augite (9-20 %), hypersthene (10-19 %), K-feldspar (4-22 %), opaque and other accessory minerals (2-4 %), with additional biotite (up to 4 %) and amphibole (up to 4 %) in places. Their major element composition (see below) place them in the fields of monzodiorites and diorites (Seghedi, 1982).

SiO <sub>2</sub>	59.23	K <sub>2</sub> O	2.68
Al <sub>2</sub> O <sub>3</sub>	18.33	Na <sub>2</sub> O	2.76
Fe <sub>2</sub> O <sub>3</sub>	1.25	TiO <sub>2</sub>	0.6
FeO	3.93	P <sub>2</sub> O <sub>5</sub>	0.38
MnO	0.05	CO <sub>2</sub>	0
MgO	3.91	H <sub>2</sub> O+	1.0
CaO	4.91	Total	99.23

Repeated attempts to date the intrusion event by the K-Ar method failed, likely because excess argon is present due to the pervasive hydrothermal circulation throughout the entire accessible part of the body.





Marginal facies of the intrusion is exposed in the old quarry including its diffuse contact with wallrock pyroxene andesite obscured by post-emplacement thermic and metasomatic contact processes. Hornfels-like rocks are common in the contact zone.

Both relatively unaltered monzodiorites and contact-metamorphosed wallrock andesite can be examined. Contact phenomena induced metasomatic effects in both surrounding volcanics and the intrusive body itself. High-temperature metasomatic associations include veinlets and impregnations of clinopyroxene (diopside), biotite and amphibole. Later mineral association (quartz, pyrite, epidote, calcite, andradite) is controlled by fissures and voids and overprints the contact zone and earlier paragenesis. Lower-temperature hydrometamorphism (albitisation, actinolitisation and argillisation) is the final contact-related process observable in the quarry.

#### *Stop 2.4. Interfluvial crest between the two spring-branches of the Haitii valley*

Ca. 300 m downcrest, in a heavily vegetated zone, from a small saddle of the crest where the road climbs through serpentine. Quite difficult access by foot.

Remnants of a surface exploration pit, and further down of an exploration trench, expose abundant hydrothermally altered andesite fragments, related to the hydrometamorphic halo of the monzodioritic intrusion.

The white-coloured altered pyroxene andesite fragments of the pit dump still preserve the relics of their original porphyritic texture, with plagioclase phenocrysts largely replaced by sericite.

The alteration process is much more advanced at the trench where the white-grey hydrothermally transformed rocks do not preserve any relic textures. The most striking feature of these rocks is the abundant presence of fine black prisms of hydrothermal tourmaline which impregnate patchily a whitish aggregate of quartz and clay minerals.

In the roadside outcrop hydrothermal biotite can be seen by fortune as small aggregates in the white, mostly argillised altered volcanic rock.

#### *Stop 2.5. Negoiiul Romanesc sulphur quarry*

A small-sized postcaldera stratocone with its highest point in the Negoiiul Românesc peak (1840m) developed in the interior of the Călimani caldera. A very large open-pit quarry dug for sulphur exploration and exploitation opens the interior of the cone. In the numerous terrace walls of the quarry the stratovolcanic structure consisting of alternating pyroxene andesite lavas and pyroclastics pierced by breccia bodies (pipes?) is exposed but it is largely obscured by the pervasive hydrothermal alteration overprint. Slightly altered or even fresh lava rocks were found at the peripheral parts of the volcanic structure, today mostly removed by the mining works. One fresh pyroxene andesite lava sample yielded a K-Ar age of  $6.75 \pm 0.45$  Ma (Pécskay et al., 1995).

Postvolcanic processes led to intense, in places pervasive alteration of the volcanics. Control factors of the alteration processes are structural (volcanic conduits), tectonic (fractures) and lithologic (levels of pyroclastics). Strong acid leaching in the vicinity of circulation paths, leaving behind a spongy siliceous rock (secondary quartzites) predates the precipitation of medium to low temperature hydrothermal minerals. Two mineral assemblages with contrasting redox conditions have been identified: (1) one alunite-bearing association indicating an oxidic environment (quartz, alunite-natroalunite, kaolinite  $\pm$  zunyite, illite, baryte, pyrite, or cristobalite, tridymite, alunite, quartz, kaolinite), and (2) another native sulphur-bearing one, of anoxic environment (quartz, kaolinite, montmorillonite, sulphur  $\pm$  pyrite, marcasite, melnikovite) (Stanciu & Medesan, 1971a, Seghedi et al., 1992). Red-coloured secondary quartzites impregnated by iron oxides-hydroxides are visible in the upper part of the quarry, whereas its lower parts are white and yellow-coloured due to the ubiquitous presence of clay minerals and sulphur.

Field-trip participants are encouraged to collect samples and to look for new minerals.

#### *Stop 2.6. Uppermost part of the sulphur quarry, in the saddle between the Negoiiul Romanesc peak and the Pietricelul dome*

In this part of the Negoiiul Romanesc cone, the upper part of the hydrothermally altered zone is accessible. Here red-coloured secondary quartzites, impregnated with iron oxide and hydroxide minerals, prevail. They resulted from strong acid leaching and removal of most components of the host volcanic rocks, excepting for the residual silica that was deposited "in situ" as a spongy mass. Breccious texture of the secondary quartzite is frequent suggesting the dynamics of the pressurised shallow hydrothermal system near the top of the stratocone,





by hydrofracturing and/or hydrothermal explosions. A summary description of the secondary quartzites in the Negoil Romanesc area is given in Russo (1964).

Detailed iron oxide-hydroxide mineralogy has not yet been undertaken. Rare iron minerals such as sulphates or borates, can eventually be found here.

It is worthwhile to mention that the term "volcanokarst" originates from this place where three caves were found within the secondary quartzite zone. One of them, the "Chocolate Palace" was richly ornated with iron hydroxide stalactites, stalagmites and draperies (Naum et al., 1962). They disappeared afterwards, during the sulphur exploration works.

#### *Stop 2.7. Pietricelul dome on the southern caldera rim*

It is the result of the latest volcanic activity in the Călimani Mts. The extrusive dome (summit elevation: 1993 m), ca. 1 km across and ca. 250 m high, overtops the southern caldera rim, preserving well its original morphology. Its K-Ar age is  $6.75 \pm 0.29$  Ma (Pécskay et al., 1995).

The dome rock is compositionally quite heterogenous. According to their major element geochemistry, samples plot at the boundary between andesites and dacites ( $\text{SiO}_2$  ranges between 59.63 and 65.41 %), (Seghedi, 1982, Nițoi, 1987). The magmatic mineral assemblage is a typical disequilibrium one, including most mineral species from quartz to olivine. Modal analysis (Nițoi, 1987) shows plagioclase (38-40 %), biotite 93-3.7 %), amphibole 92-2.6 %), augite (1.5-2 %), hypersthene (1-1.5 %), Fe-Ti oxides and other accessories (1-1.5 %), olivine (0.1-0.15 %), and groundmass (46.5-50.7 %). Quartz crystals are rounded or embayed, always displaying a zoned reaction rim consisting of fine-grained pyroxene (diopside), hornblende, plagioclase, K-feldspar, opaque minerals and volcanic glass, suggesting their xenocrystic origin (Nițoi, 1987). All these features are consistent with genesis of this peculiar rock type, unique in the Călimani Mts., by magma mixing of two contrasting melts (an acidic melt and an intermediary one) (Seghedi, 1987, Nițoi, 1987).

A representative major element composition of the Pietricelul dome rock is given below from Seghedi (1987).

$\text{SiO}_2$	63.16	$\text{K}_2\text{O}$	2.2
$\text{Al}_2\text{O}_3$	16.58	$\text{Na}_2\text{O}$	3.7
$\text{Fe}_2\text{O}_3$	2.05	$\text{TiO}_2$	0.5
FeO	2.36	$\text{P}_2\text{O}_5$	0.17
MnO	0.1	$\text{CO}_2$	0.27
MgO	3.26	$\text{H}_2\text{O}^+$	0.13
CaO	4.76	Total	99.98

#### *Stop 2.8. Saddle between the Retitis and Bradul Ciont peaks on the caldera rim*

A beautiful panoramic view is available from this point northward over the whole Călimani caldera, as well as southwards, over the southern Călimani Mts and the Gurghiu Mts. with many volcanic features expressed in the local morphology visible. Topographic features of the caldera and the whole volcanic edifice can be viewed: the steep inner wall of the caldera, truncated step-like lava flow units in the upper caldera wall, the Negoil Românesc intracaldera stratocone deeply dissected by the sulphur exploration works, Pleistocene glacier morphology in the inner caldera wall, gentle external slopes of the caldera-generating lava flows, external flank postcaldera domes (e.g. Drăgușul, similar to Pietricelul), etc.

Fracture-related hydrothermal alteration can be also seen in the saddle with mineral associations including alunite, opal, cristobalite, kaolinite + sulphur, tridymite, pyrite, marcasite, anhydrite (Seghedi et al., 1992).





GEOLOGICAL MAP OF THE CĂLIMANI CALDERA AREA  
(Modified and simplified after Seghedi, 1987)

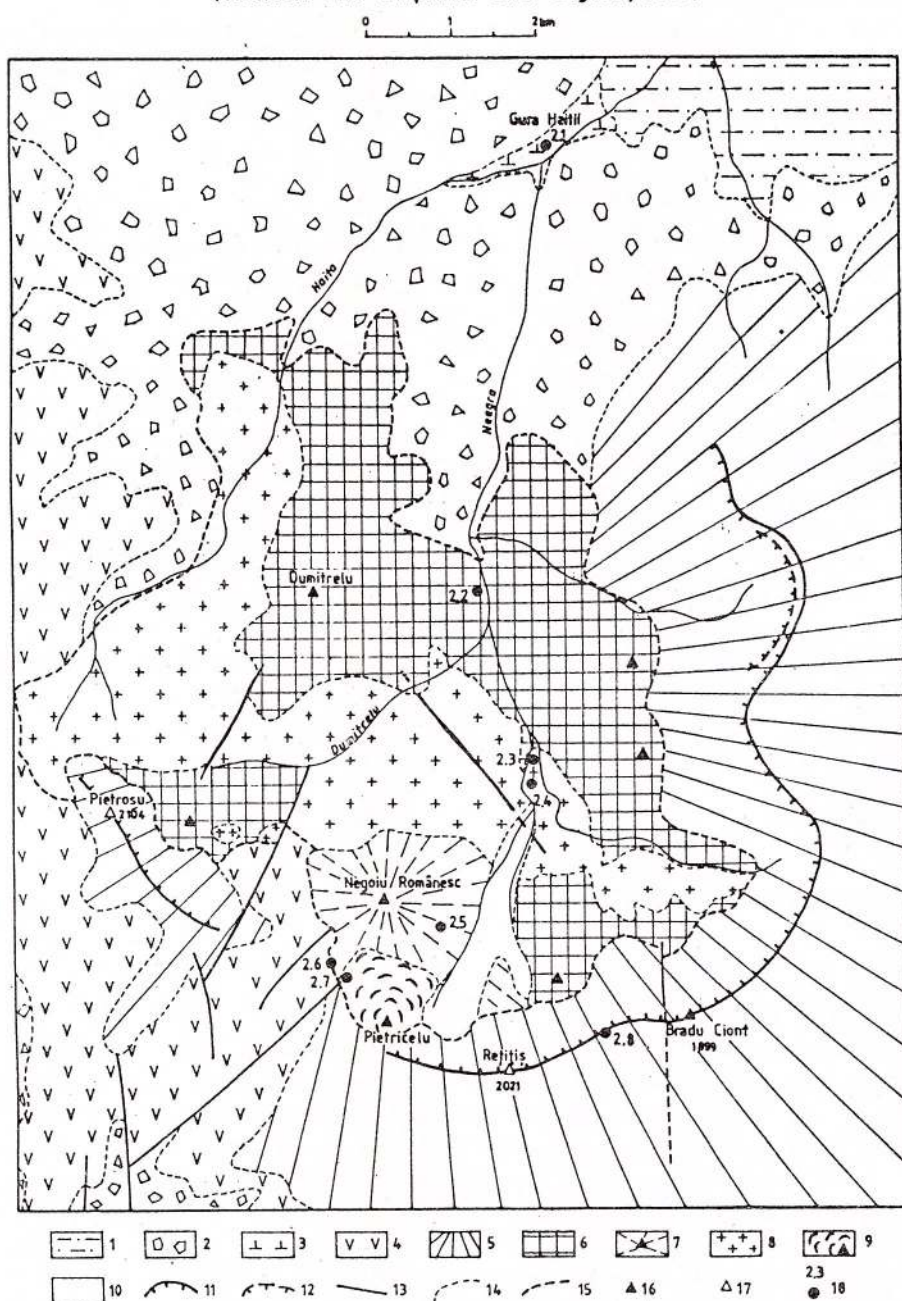


Fig. 4 – Simplified geological map of the Călimani Caldera area (modified after Seghedi, 1987).

1, Peripheral volcaniclastic apron; 2, Precaldera stratovolcanic facies with prevailing andesitic volcaniclastics; 3, Andesite lava flow intercalation in precaldera volcaniclastics; 4, Precaldera stratovolcanic facies with prevailing andesitic lava flows; 5, Călimani-type andesite lava-flows related to the caldera formation; 6, Postcaldera andesitic volcanics, mostly lava flows in the caldera interior; 7, Negoiul Românesc postcaldera stratocone; 8, Postcaldera resurgent intrusion, of mostly monzodioritic composition; 9, Pietricelul postcaldera lava dome; 10, Quaternary deposits; 11, Topographic caldera rim; 12, Remnant crater rim; 13, Fracture; 14, Geological boundary; 15, geological boundary between pre- and postcaldera rocks; 16, Inferred eruptive centre; 17, Peak; 18, Field-trip stop.



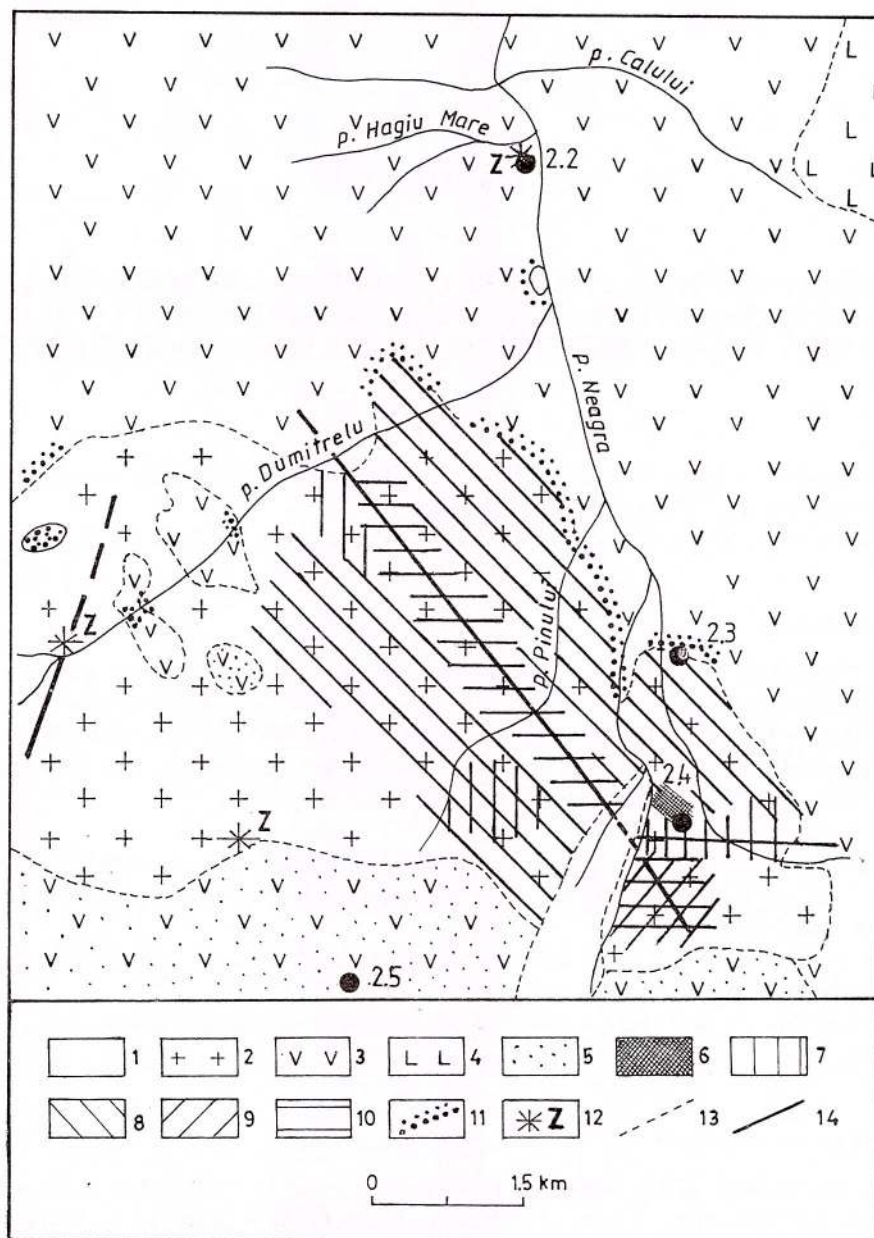


Fig. 5 – Sketch of part of the Călimani caldera interior with occurrence areas of different types of contact phenomena and hydrometasomatic processes (after Seghedi, 1986).

1, Quaternary deposits; 2, Resurgent postcaldera intrusion; 3, Postcaldera volcanics; 4, Precaldera volcanics; 5, Pervasive low-temperature hydrothermal alteration related to the Negoiu Românesc sulphur deposit; 6-11, Contact and hydrometasomatic transformations related to the resurgent intrusion; 6, Quartz-sericite-turmaline zone; 7, Argillic zone; 8, Actinolite zone; 9, Biotite zone; 10, Albite zone; 11, Contact metamorphism (hornfels); 12, Zeolite occurrences; 13, Geological boundary; 14, Fracture.



## THIRD DAY

### CRYSTALLINE ZONE OF THE EAST CARPATHIANS (NORTHERN BISTRITA MOUNTAINS): STRUCTURE, LITHOSTRATIGRAPHY, METAMORPHISM AND METALLOGENY. VALEA BISTRITEI BETWEEN VATRA DORNEI AND BROȘTENI

#### Itinerary:

Vatra Dornei - Zugreni - Leșu Ursului - Holdița (Broșteni) - Bicaz accumulation lake - Bistrița Monastery - Piatra Neamț - Iassy

Leaders: L. Nedelcu, C. Moga, I. Podașcă, Paulina Hârtoapanu, Al. Szakács

#### Stop 3.1 : Leșu Brook

Cross-section through the Leșu Ursului syngenetic Pb-Zn-Cu-Fe sulphide deposits (Kuroko-type; interbedded in Leșu Ursului lithozone rocks, Tulgheș lithogroup in Bucovinian Putna Nappe).

– Outcrop of III zone (lower): a Pb-Zn compact ore lens with lateral disseminations that can pass southward towards a Cu disseminated lens. These ore lenses are hosted in sericite and sericite-chlorite schists, interbedded between Isipoaia metabasite, in the lower part (Isipoaia member: IM).

– Outcrop of II+I zones (upper):

a) II zone includes more pyrite-copper compact ore bodies tectonically separated;

b) I zone, with the same polymetallic composition as the III zone, consists of superposed little lenses with compact to disseminated aspects.

Hosted rocks: sericite and sericite-chlorite schists interlayered between two rhyolitic metavolcanite levels (Leșu Ursului member: LUM).

Ore mineral assemblages (I+II+III zones): pyrite, sphalerite, galena, chalcopyrite, arsenopyrite, tetrahedrite, pyrrhotite.

#### Stop 3.2 : Holdița barite quarry

– Barite beds interlayered at the upper part of black quartzite formation of Holdița lithozone (Tulgheș lithogroup of Putna Subbucovinian Nappe). The Holdița-Broșteni ore deposit (Vodă, Vodă, 1982) is constituted of 2-3 barite beds (0,2-4 m thick) separated by black quartzite layers (5-10 m thick).

The sequence of barite mineralization presents the following succession, from bottom to top:

– graphitous black quartzites with pyrite, quartz, carbonates;

– barite + quartz layers sometimes rhythmically interbedded with pyrite bands ("banded texture").

Ore mineral composition: barite, quartz (prevalent), pyrite, carbonates (calcite, witherite, rhodocrosite, siderite) (subordinate).

The syngenetic origin of barite deposits is supported by the following arguments:

– lithostratigraphical concordance and control of barite beds;

– synchronous and concordant folding of barite beds with the metamorphites of the black quartzite formation they included.





## LIST OF FIELD GUIDEBOOKS AVAILABLE FOR SELLING (price 10 USD per copy if not otherwise stated)

- EXCURSION GUIDE: MINERAL OCCURRENCES IN THE METALIFERI MTS. ROMANIA. **First National Symposium on Mineralogy**. *Romanian Journal of Mineralogy*, Vol. 75, Suppl. No. 2, 1992.
- EXCURSION GUIDE: MINERAL OCCURRENCES IN SOUTHWESTERN BANAT, ROMANIA. **Second Symposium on Mineralogy**. *Romanian Journal of Mineralogy*, Vol. 76, Suppl. No. 2, 1993.
- FIELD GUIDEBOOK: SOUTH CARPATHIANS AND APUSENI MOUNTAINS, ROMANIA. **ALCAPA II. "Geological Evolution of the Alpine-Carpathians-Pannonian system"**. *Romanian Journal of Tectonics and Regional Geology*, Vol. 75 Suppl. No. 2, 1994.
- GUIDE TO EXCURSION B2: UPPER NEOGENE FROM THE DACIC BASIN. **X<sup>th</sup> Congress RCMNS, Bucureşti 1995**. *Romanian Journal of Stratigraphy*, Vol. 76, Suppl. No. 1, 1995.
- GUIDE TO EXCURSION A2: SARMATIAN OF THE MOLDAVIAN PLATFORM. **X<sup>th</sup> Congress RCMNS, Bucureşti, 1995**. *Romanian Journal of Stratigraphy*, Vol. 76, Suppl. No. 2, 1995.
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*Adriana Năstase, Mariana Borcoș*

Editorial Staff:  
*Anca Andăr, Cristian Toth*

Illustration:  
*Paraschiv Toader*

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