MUD-VOLCANOES OF ROMANIA. PRELIMINARY DATA ON THE MINERALOGY OF PÂCLELE MARI AND PÂCLELE MICI MUD-VOLCANOES

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Abstract. The paper presents results of a preliminary mineralogical study of the mud-volcanic products from Pâclele Mari and Pâclele Mici mud-volcanic fields, East Carpathian Mountains, Romania. The presence of Boron and of some less described minerals is evidenced. A comparison with the mud-volcanoes from the Kerch – Taman region is given.

Key words: Mud-volcanoes; mud-volcanic breccia; mineralogy of the breccia; exogenic efflorescence.

INTRODUCTION

The mud-volcanic processes occur in many regions in Romania. Among them the Pâclele Mari and Pâclele Mici mud-volcanoes fields are the most important. They are located on the same anticline structure called Berca-Arbănaşi. The studies related to this geological phenomenon started in 19-th century. The first scientists that described the mud-volcanism in Romania were Cognand (1867), Cobălcescu (1883) and Stefănescu (1890). Although since then a large number of papers were dedicated to the mud-volcanoes from Romania, the information about the mineralogy of the mud-volcanic formations is limited. Instead, the mineralogy of the geological formations the mud-volcano necks are crossing through (Dacian, Pontian, Meotian, Oligocene and even Precambrian) was studied in detail. Recently, Dicu (2005) published a quite complete description of the Pâclele Mari and Pâclele Mici mud-volcanoes fields.

This paper presents preliminary data of our study on the Pâclele Mari and Pâclele Mici mud-volcanic fields, located in the vicinity of the Berca town within the East Carpathians (Fig.1). A special attention was paid to the specific mud volcanic formations and to the changes of rock fragments under the influence of the mud-volcanic processes. Mineralogical analyses of some detrital fragments from the mud-volcanic breccia were carried out, as they could give some information about the age and the relative stratigraphic position of the formations the fragments originated from, and consequently indications about the depth of mud-volcanic roots and about the timing of volcanic activity. The seasonal minerals such as sulphides, chlorites, borates, carbonates, etc., formed within the mud-volcanic processes, are also described.

THE MUD-VOLCANIC BRECCIA

The main interest of this study was the volcanic breccia and its clayey matrix from both volcanic fields.

As shown by preliminary chemical analyses, the lithologic constitution of the breccia from the two fields is very similar. The breccia contains 50 – 60 % of fine-grained (less than 0.001 mm) fraction. The mud volcanoes are formed of clayey breccia with millimetric clayey fragments or aggregates in the same clayey matrix and some terrigenous elements.

The clays have been studied by lithologic, chemical and X-ray difractometry methods. The chemical composition was studied in the Laboratory of Geochemistry of the Institute of Geology of Mineral Resources of the Ukrainian Academy of Sciences. The X-ray analyses have been carried out in two lab-

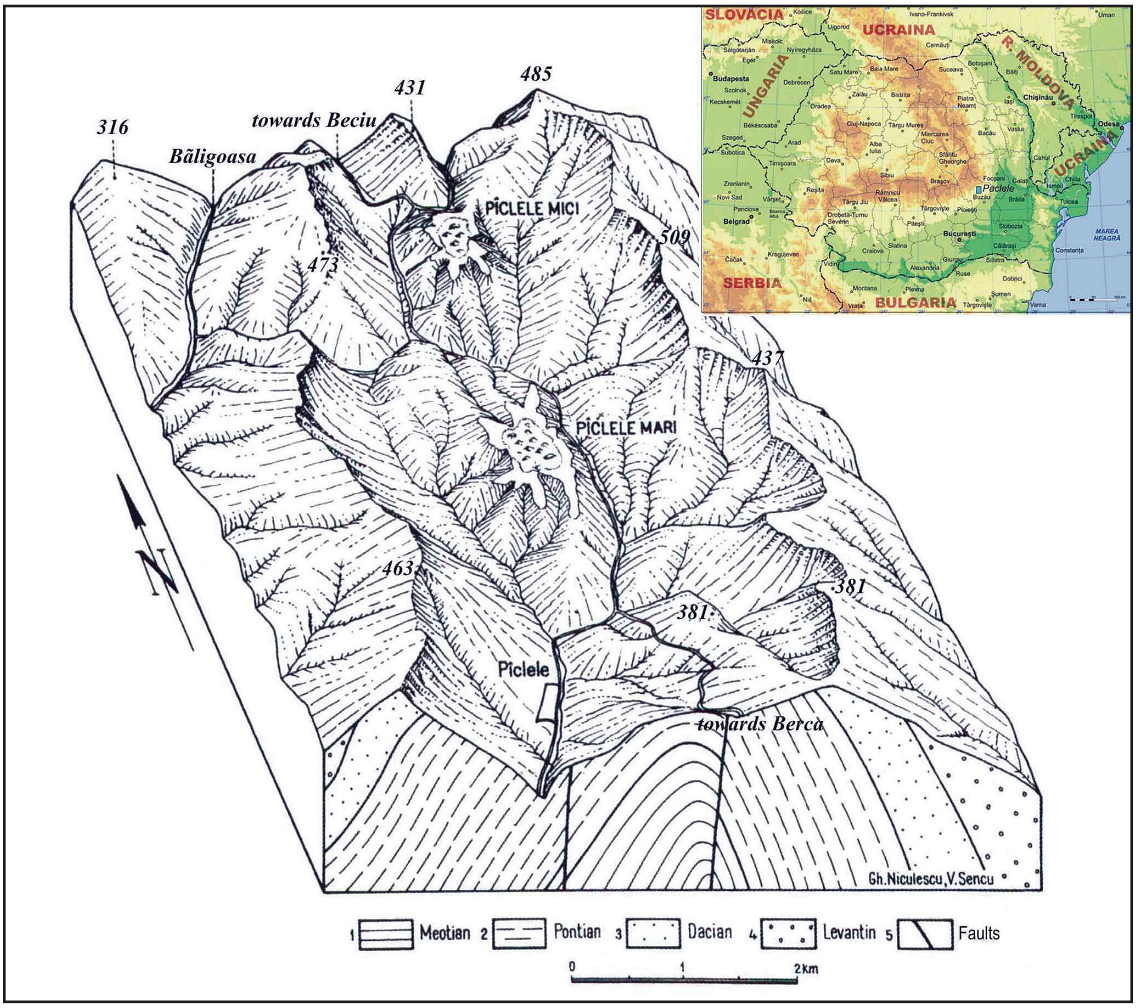

Fig. 1 Location of the Pâclele Mari and Pâclele Mici mud-volcanoes fields (after Dicu, 2005)

oratories: the Laboratory of structural X-ray analysis, with the difractometer DRON-3 and the Laboratory of crystalochemistry and structural analyses of the Institute of Geology of Mineral Resources, the Academy of Sciences of Ukraine, with the difractometer DRON-2. Spectral analyses were performed in the Laboratory of spectral analyses of the Institute of Geology of Mineral Resources, Academy of Sciences of Ukraine. Electronic microscope analyses of sulphides were carried out on an electronic sound JXA-5 at the Institute of Geology of Mineral Resources, Academy of Sciences of Ukraine. Calcite studies were performed on the micro-analyser JSM-606-LA. Inclusions in calcite were studied in the Laboratory of thermo-barochemistry within the Department of regional and genetic mineralogy of the Institute of Mineral Resources Geology, Academy of Sciences of Ukraine.

Preliminary results of the chemical composition of the neck facies of breccia are presented in the Table 1. The chemical composition of the breccias from the two volcanic fields is very similar. This can be explained by the fact that the two fields are placed at only 3 km distance one from the other on the same anticline structure, formed of Sarmatian formation, which generates the main material for the breccias.

The mineralogical constitution of the fine-grained fraction (less than 0.001 mm) from the mud volcanic breccia is presented in the Table 2.

Table 1 Chemical composition of the neck facies of breccia (%)

Location	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O	Pp	S_{total}	Σ
Pâclele Mari	51.72	0.82	12.78	2.18	3.43	0.20	2.64	5.14	3.89	2.36	0.18	1.89	12.26	0.34	99.83
Pâclele Mici	51.58	0.78	12.81	2.19	3.58	0.23	2.43	5.31	3.38	2.38	0.20	2.01	12.10	0.32	99.75

Analyst: Dr. O.P. Krasyuk

Table 2 Mineralogy of the mud-volcanic crater breccia facies

Mud-volcanic initial breccia			
DRON-3		DRON-2	
Pâclele Mari	Pâclele Mici	Pâclele Mari	Pâclele Mici
Quartz, feldspar, calcite, micas, kaolinite, chlorite	Quartz, feldspar, micas, calcite, kaolinite, chlorite	Calcite, quartz, plagioclaz, micas, Fe-chlorite	Quartz, plagioclaz, calcite, micas, Fe-chlorite
Clayey fraction less than 0.001mm			
not analysed	Micas, quartz, chlorite, kaolinite, calcite, feldspar	not analysed	Calcite, hydromica, kaolinite, quartz

Analyst: Dr. G.I. Sirotenko   Analyst: Dr. E.E. Gretchanovskaya

Spectral analyses in the mud-volcano breccia showed minor and disperse elements in concentrations of following orders of magnitude: Mn, Ni, V, Cr, Zr, Cu, Pb, Ce, La, Li, Ba – hundreds ppm; Co, Mo, Zn, Ga, Sc, Y – tens ppm and Nb, Ag, Bi, Sn, Be, Yb – few ppm. The content of boron varies from 0.06 to 0.08%.

The detrital material of the mud-volcano breccia is predominantly formed by limestones of different ages (Sarmatian, Meotian, Pontian, Dacian, Levantine, Quaternary) composed mainly of calcite. One of the fragments found in the Pâclele Mari field of mud-volcanoes visually resembled a slag. If true, this would allow the supposition of explosive events during the volcano evolution. A detailed study of this fragment showed that this is not a slag but a shally limestone of Sarmatian age transformed and sulphurised, locally having oolithic structure. One can suppose that the process of sulphurisation was of mud-volcano origin, as iron-sulphides often occur within the mud-volcanoes. Examination of thin sections revealed the occurrence of sulphides within the hydro-goethitic oolithic structures and in the inter-oolithic space as non-regular deposition (Fig. 2). The electronic microscope analyses showed that these sulphides are represented by pyrite of common composition with some content of As, Co, Ni (Table 3).

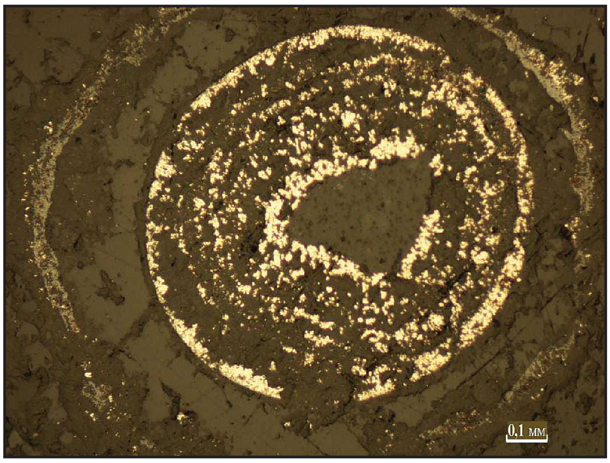

Fig. 2 Pyrite in the fragments of the Pâclele Mari mud-volcano breccia

The pyrite from the mud-volcano breccia of the Kerch – Taman region is also characterised by the presence of As from 0.04 to 2.63 % (data on 30 analyses).

The electronic microscope analyses reveal small (submilimetric) grains of ferrous ilmenite (Table 4).

Table 3 Chemical composition of pyrites from the Pâclele Mari mud-volcano (in %)

Sample	Fe	Co	Ni	S	As	Σ
a	46.522	0.002	0.014	53.220	0.117	99.875
b	46.255	0.030	0.022	52.879	0.061	99.247

Note: sample a – pyrite $Fe_{1.002}\,As_{0.002}\,S_{1.996}$; sample b - $Fe_{1.002}\,As_{0.001}\,S_{1.996}$.

Table 4 Chemical composition of the ferrous ilmenite from the Pâclele Mari mud-volcano (in %)

Sample	Fe	Mn	Cr	V	Ti	Σ
a	29.818	0.477	0.065	0.695	68.414	99.469
b	48.443	0.490	0.045	0.577	48.725	99.280

Note: sample a –$(Fe_{1.05}\,V_{0.02}\,Mn_{0.01})_{1.08}\,Ti_{0.95}O_3$; sample b - $(Fe_{0.58}\,V_{0.02}\,Mn_{0.01})_{0.61}\,Ti_{1.2}O_3$.

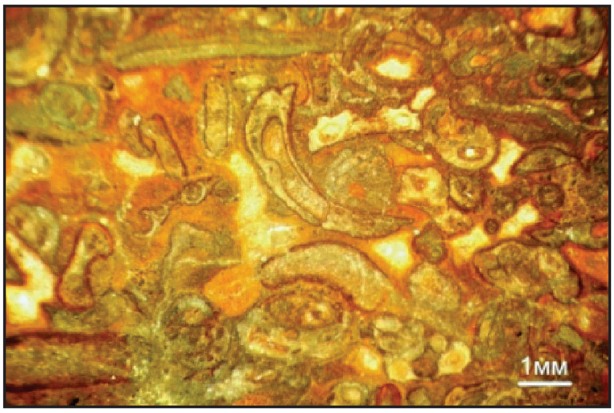

Fig. 3 Limestone with Sarmatian fauna

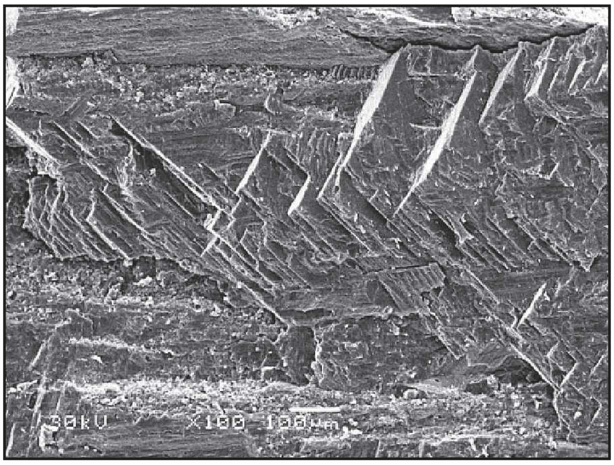

Fig. 4 Massive calcite from the mud-volcanic breccia of Pâclele Mici volcanoes

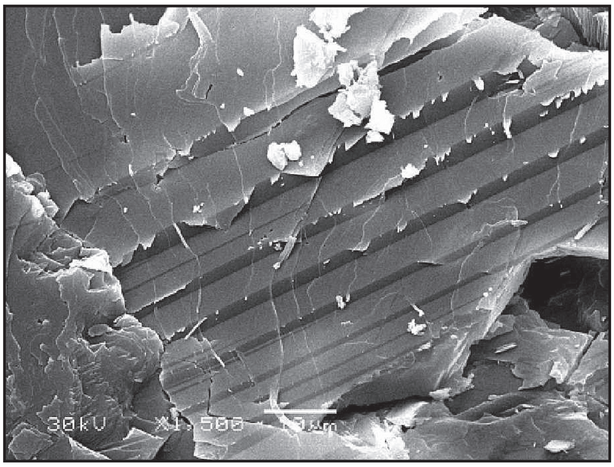

Fig. 5 Transverse-fibrous calcite from the mud-volcanic breccia of Pâclele Mici volcanoes

We can suppose that the ilmenite is supplied from the clayey Sarmatian formations crossed by the volcano neck.

The macro and micro-fauna from the limestones are represented by fragments of *Gastropoda*, *Ostracoda* and *Foraminifera* (predominantly of *Miliolidae* family). The micropaleontological determinations, carried out by Dr. L.V. Stupina, showed that Sarmatian foraminifera are predominant: *Articulina* sp., *Spiroloculina* cf. *kolesnikovi* Bogd., *Spiroloculina* sp., *Elphidium* cf, *fichtellianum* (Orb.), *Elphidium crispum* (L.), *Elphidium* sp.

A special attention was paid to the numerous fragments of massive calcite and of transverse-fibrous calcite (analyses carried out by Dr. D.P. Demenko) (Fig. 4, 5). A similar type of calcite is known from the mud-volcanoes of Kerch-Taman and Azerbaydzhan regions, and most probably it is formed as the result of mud-volcanic activity.

The spectral analyses show that the trace elements concentrations have similar orders of magnitude in both massive and fibrous types of calcite: Ba and Ce - hundreds ppm; Ni, Co, Cr, Mo, Zr, Nb, Zn, Li – tens ppm and Cu, Pb, Ag, Bi, Sc, Y, Yb – few ppm.

The content of Boron varies from 0.06 to 0.2 %. The only difference between the two types of calcite is the content of Mn – in the massive calcite the content of Mn is up to 0.4 %, while in the transverse-fibrous calcite it is only 0.2 %.

The inclusions within the calcite were studied by Dr. A.A. Kultchitskaya in thin sections (fraction 0.5-1.0 mm). The fragments were drawn in ethylic alcohol or in an immersion liquid with n=1.5.

The crystals of massive calcite have an irregular aspect, their transparency is low and they do not fracture along the cleavage. In thin sections the calcite crystals are yellowish because of light diffusion. With crossed polars, the mineral does not extinct completely, remaining intensively doubled. The inclusions are rare, their dimensions vary around 1 µ and they are grouped in parallel lines not coinciding with the direction of the cleavage or crystal twinning. Some inclusions are solid, anisotropic, with $n \approx 1.5$, while others are fluid, showing similar dimensions and with $n << 1.5$. It was not possible to analyse the fluid inclusions due to their very small dimensions. In the UV light the calcite is slightly luminescent in pink-brown, showing areas with whitish lighting of almost circular aspect and tens of microns in diameter, invisible in a normal light.

The apparently transverse-fibrous calcite is actually not fibrous. By crashing it forms transparent lamellas. The calcite shows lines or clouds of inclusions, which are white in reflected light and almost black in transverse one (due to total internal reflection). The lines or clouds consist of microscopic inclusions or canal-like ones with length up to 100 microns. These inclusions have irregular walls covered by mineral phases. That is why it is sometime impossible to say if this is a single large inclusion or an aggregate of microscopic inclusions oriented along a line. The canal-like large inclusions are parallel, marking the crystal growing zones. They are definitely initial inclusions, probably filled-in with aqueous solution. The inclusions are mono-phasic, none of them has bubbles of gas and this shows that the calcite was formed in a low temperature environment (probably less than 40ºC). Only taking into consideration the difficulty of a gas bubble trapping in a small inclusion, the upper limit of the temperature could be shifted to maximum 70ºC.

Around the canal-like inclusions and not connected with them, there are rare isometric inclusions smaller than 2 microns. At room temperature, these inclusions show a very small, moving gas bubble, formed probably by gaseous CO_2 in halogenation with liquid CO_2 (fig. 6). These inclusions are interpreted as CO_2 inclusions, the density of which are lower than a critical one (0.4), and not higher than 0.7 g/cm^3; this means that the pressure of the fluid within the calcite forming environment was higher than the critical pressure for CO_2 (7.3 MPa) reaching 10 MPa (100 atmospheres) and even higher if the temperature was higher than 40°C.

In the UV light, some of calcite sections are slightly luminiscent in blue-whitish tones; on this background, bands of inclusions luminiscent in a sandy colour are visible. Other sections of the same calcite sample have a yellow-brown luminiscence.

The data obtained show that the calcite was formed in a low temperature hydrothermal environment. The luminiscence of samples in UV is due to the presence of Mn.

The calcite is the most suitable mineral for thermo-barometric research, as it occurs very frequently in the mud-volcano deposits. Calcite studies, including thermal and geochemical investigation, allow to establish certain physical and chemical parameters of the mineral genesis related to the mud-volcanism (Shniukov *et al*., 1989).

The mud-volcanoes in the Kerch-Taman region are located on Maikopian deposits containing horizons of siderite concretions. Within the mud-volcanic breccia of this region there are numerous concretions or fragments of siderites.

The volcanoes of Pâclele Mari and Pâclele Mici are formed on the Sarmatian clayey deposits. In the breccia of these areas the fragments of carbonate concretions are not very frequent. Sometimes the dimensions of these fragments reach 20cm. Theyshow iron oxydes crusts on the surface, and a dark-gray aphanitic texture. Although the field observation suggested that the fragments are siderites, a detailed laboratory study showed that some of the fragments are manganeous ankerite (also confirmed by roentgen determination with the difractometer DRON-3 and chemical analyses).

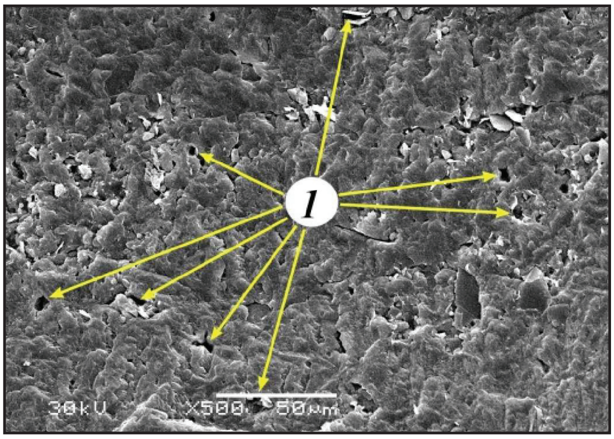

Fig. 6 Pores of open gas-liquid inclusions (1) in the calcite of Pâclele Mici volcano

The spectral analyses of ankerite shows the following concentrations of the analysed elements: Mn >1%, Ti, B – tenth parts of a percent; Ba – hundreds ppm; V, Ni, Co, Cr, Zr, Mo, Nb, Cu, Pb, Ag, Bi, Zn, Sn, Ga, Be, Sc, Y, Yb, Li – tens ppm.

Adolomite fragment analysed contains Al, Mg, Ca, Fe – from 3 to 5%; Mn – about 1%; and minor and trace elements as follows: P – tenth parts of a percent; Ti, Ba – hundreds ppm; V, Cr, Ge, Zr, Cu. Pb, Zn, Y, Li – tens ppm; Nb, Bi, Sn, Ga, Be, Yb – ppm. The results of the analyses are presented in the tables 5 and 6.

Table 5 Chemical composition of the manganeous ankerite from the mud-volcano breccia in the Pâclele Mici area (in %)

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O^-	Pp	S_{tot}	Σ
Ankerite	4.22	0.06	1.01	17.82	0.29	1.09	7.02	30.06	0.65	0.30	0.24	1.06	36.21	-	100.03
Dolomite	9.84	0.17	3.11	1.29	5.72	0.69	13.93	24.58	0.50	0.43	0.18	0.62	38.18	-	99.72

Table 6 The intensity of lines and the inter-planes distance for the ankerite and the dolomite from the Pâclele Mari mud-volcano breccia

Ankerite														
I	2.89	2.68	-	2.41	2.19	-	2.01							
α/η	100	10	-	20	35	-	10							
Standard ASTM														
I	2.899	2.685	2.552	2.411	2.199	2.067	2.02							
α/η	100	3	1	3	6	<1	3							
Dolomite														
I	3.69	3.32	2.88	2.67	2.54	2.40	2.19	2.07	2.015	1.849	1.807	1.781	1.565	1.546	1.465
α/η	5	10	100	5	5	10	30	5	20	5	20	25	5	5	5
Standard ASTM														
I	3.69	-	2.896	2.67	2.54	2.405	2.192	2.066	2.015	1.848	1.804	1.781	1.567	1.545	1.465
α/η	5	-	100	10	3	10	30	5	15	5	20	30	9	10	5

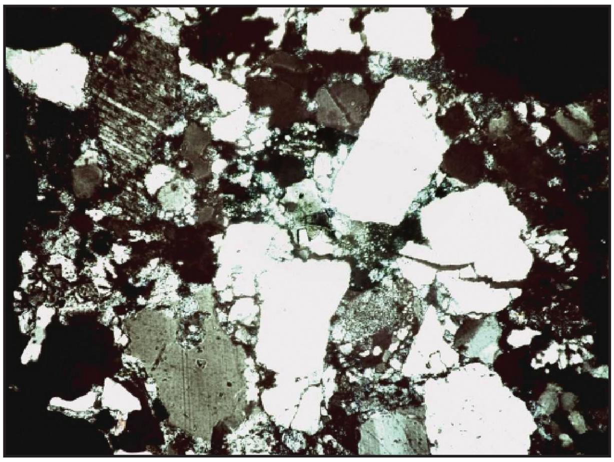

Fig. 7 Sandstone from the Pâclele Mici colcanic breccia (crossed nicols)

Fig. 8 Whitish efflorescences on the surface of Pâclele Mari mud-volcano breccia

Fig. 9 Efflorescences of seasonal minerals on the surface of Pâclele Mari mud-volcanoe

Among the breccia fragments there are conglomerates and sandstones. Probably the rounded fragments of the Precambrian green schists that can seldom be found are derived from the conglomerates.

A sample from the southwestern part of the Pâclele Mici mud-volcano field is a polymictic sandstone (Fig.7). The grain size varies from 0.1 to 1.0 mm, grains of about 0.4 mm being dominant. The mineralogical constitution is: quartz – 70-80%, plagioclase (not too basic, maybe oligoclase, possibly also some K feldspars) – 10-20%, fragments of rounded quartzite or quartzitic schists – up to 10%. The cement is neoformation carbonate (the determination by E.E.Shniukova.

THE EFFLORESCENCES ON MUD-VOLCANOES

In both areas, the large effusions of mud-volcanic breccia are covered by whitish efflorescences of neoformated minerals (Fig. 8, 9). These are seasonal minerals that precipitate from the mud-volcanic waters, or form as the result of different atmospheric factors.

Engulescu (1911) was the first to mention salty efflorescences within the Romanian mud-volcanoes. The author mentioned the "strong weathering of salts, silty-like or crystallised as nails, among them the sulphates are predominant and the chlorites are quite rare or occur only in certain areas". A very specific flora related to Romanian mud-volcanoes is witnessing the presence of sulphates.

Dicu (2005) remarks the occurrence of sulphates, sometimes chlorites within the mud-volcano efflorescence. This author points out that crystals of halite occur in the mud-volcano at Tulburea, not far from the town of Buzău. The presence of a water with H_2S spring suggests the existence of crystallised sulphur. Samples collected during the field work confirm this information. The XR analyses show lines characteristic for barite, anhydrite and calcite.

The contamination of samples with clayey material has not permitted their separation into phases. For example, for the Kerch region, biogenic and chemogenic sulphur, as well as seasonal minerals as astrakhanite (bloedite), gypsum, epsomite, hexahydrite, hallotrichite, etc. have been revealed within the gaseous mud-volcanoes. The mud-volcano breccia from the Kerch region is characterised by a high content of Boron and Boron containing minerals. In mud-volcanoes from Romania, the existence of boron is confirmed by the samples collected in the field. Boron content varies between 0.04 and 0.2 %. In the mud-volcano neck the content of boron is 0.06 – 0.08%. Within the detrital material of mud-volcano breccia the boron content is about hundredth parts of a percent and only in the fibrous calcite its content rises up to 0.2%.

Probably a large part of the white seasonal mineral efflorescences is represented by borates, mainly by easily soluble borax. Sometimes the accumulations of boron, particularly of borax, can constitute exploitable reserves (as the boro-natrocalcite – ulexite deposits of Bulganak, which were exploited in the fourth decade of the XX-th century).

CONCLUSIONS

The mud-volcanoes of the Buzău county and of the Kerch-Taman region show similarities, as well as certain different, very specific characters, connected to the specificity of the geological environment of their occurence.

The mineralogy of the mud-volcano breccia corresponds to the geological formations crossed by the volcanic neck. Specifically, the fragments of limestones, sandstones, conglomerates are similar to the constitution of initial formations.

The processes of pyritisation and carbonatisation, in particular the occurrence of calcite veins fragments which are very frequent in the breccia, can be considered as results of mud-volcano neoformation processes.

The fragments of carbonate concretions from the breccia are formed mainly by ankerite and dolomite.

The presence of boron represents an important characteristic of mud-volcanic processes in Romania and in the Kerch-Taman region as well.

The exogenic efflorescences on the surface of the mud-volcanic breccia consist mainly of borax and other seasonal minerals.

The mineralogical study of the Romanian mud-volcanoes should be continued and deepened, as it can give essential information about mud-volcanic processes in general and can contribute to a better understanding of mud-volcanic processes.

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