CONTENTS

Institutul Geologic al României

CONTENTS

THE FIRST REPORTED OCCURRENCE OF METATYUYAMUNITE -
Ca(UO$_2$)$_2$(VO$_4$)$_2$•3-5H$_2$O IN ROMANIA

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Abstract: Metatyuyamunite, Ca(UO$_2$)$_2$(VO$_4$)$_2$ 3-5H$_2$O, a new mineral for Romania, occurs as canary yellow sub-millimeter-size plate-like crystals in the Valea Rea Cave (Bihor Mts.). This unusual mineral has precipitated on and in between delicate needle-like aragonite crystals. X-ray diffraction, optical and scanning electron microscope (including EDS), and luminescence have been used to identify metatyuyamunite. The X-ray diffraction pattern can be indexed with the orthorombic cell a=10.77; b=8.53; c=17.62 of metatyuyamunite. From a genetic point of view it seems that tyuyamunite has first precipitated from hydrothermal solutions and in a later stage it dehydrates to metatyuyamunite.

1. Introduction

During the mineralogical sampling undertaken in the Valea Rea Cave. an unidentified yellow mineral growing over a white crust has been collected from a side passage. X-ray powder patterns indicate the presence of metatyuyamunite, a hydrated uranyl vanadate.

This is the first reported occurrence of metatyuyamunite in Romania. Furthermore, it is the third occurrence in a cave environment worldwide. The two other known cave occurrences are Spider Cave, New Mexico, USA (Polyak, Mosch, 1996) and Caverns of Sonora, Texas, USA (Onac et al., 2000). In the outside environment, metatyuyamunite is rather a common mineral, associated with uranium and vanadium deposits (Langmuir, 1997).

The presence of metatyuyamunite in the Valea Rea Cave adds one more species to cave mineral association described by Onac et al. (1995), Ghergari et al. (1997), Ghergari, Tamas (in press), and Damm (in press).

2. Geographic and geological setting

Valea Rea Cave is located in the upper part of the Valea Rea Valley, just below the top of Carligaţi (Bihor Mts., Romania) (Fig. 1) (Damm et al., 1996). Since its discovery in 1986, over 18 km of passages have been mapped to a total depth of 360 m. The main axis of the cave, the Colectorului (Collector) Gallery, is an active stream passage (20-25 l/s) approximately 3.5 km in length. Two other fossil galleries are located above the active one at 20 m and 50 to 70 m respectively. Typically, large chambers or labyrinth passages are to be found where all the three galleries interconnect.

Due to a large variety of rocks that occur in the Valea Rea - Cornu Munţilor region, it can be considered a petrographic mosaic. All geological deposits occur as narrow stripes oriented NE-SW. Three compartments are evident starting from the north and going to the south (Fig. 2) (Bleahu et al., 1985):

• The North Compartment consists of andesites (bearing pyroxenes and hornblende) formed during the Ist cycle of banatitic eruptive activity (Maastrichtian Paleogene) (Stefan et al., 1988).

• The Central Compartment includes a Permian to Triassic sedimentary formation belonging to the Upper Sebişel Member of the Finiş-Ferice Nappe (Bordea, Bordea, 1972; Balintoni, 1997).
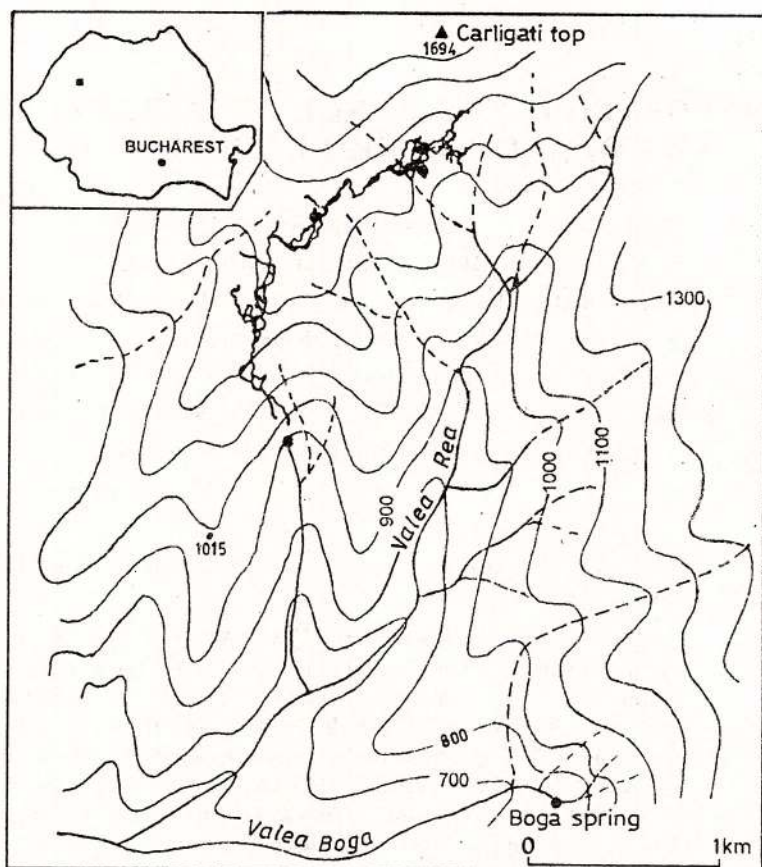
Fig. 1 — Location of the Valea Rea Cave.
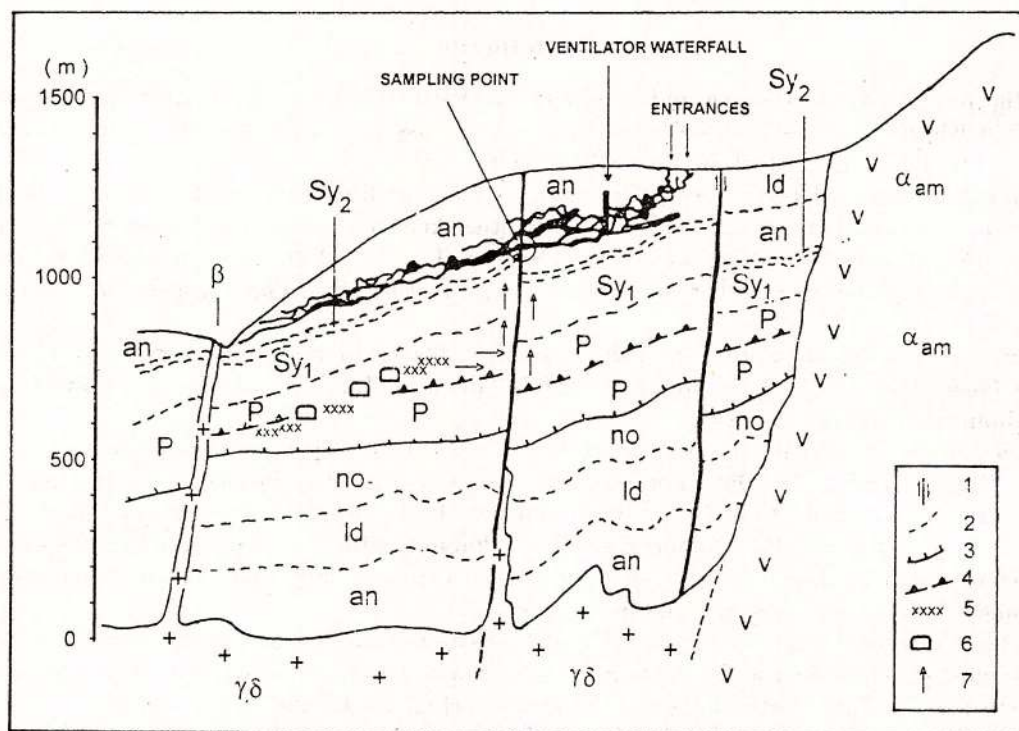
Fig. 2. Geological cross-section along Valea Rea Valley showing the lithology, tectonic features and the cave network. 1, Faults; 2, Geologic boundaries; 3, Nappe overthrusts; 4, Reverse faults; 5, Mineralization zones; 6, Mining galleries; 7, Ascending geothermal solutions; α_{am}, andesite; $\gamma\delta$, granodiorite; β, basalt; P, Permian; Sy_1, Lower Scythian; Sy_2, Upper Scythian; an, Anisian; ld, Ladinian; no, Norian.

The geological succession begins with purplish-red colored quartzite sandstone, conglomerates, and shales on Verrucano facies. Locally, within some of these horizons, important concentrations of uranium have been found during mining prospecting.

The unit above consists of white conglomerates and quartzite sandstone of Lower Triassic age, covered by a series of 600-m thick black dolomites (chert), shales and limestone breccia. Valea Rea Cave is mainly developed within the dolomite horizon of Anisian (Middle Triassic) age.

• The South Compartment consists mainly of granodiorite formed during the IInd cycle of the banatitic activity. Dykes of granites and microgranites with a SE-NW trending cut through the sedimentary rocks.

The metallogenesis in the Bihor Mountains is associated with the IInd cycle, characterized by bodies of intrusive, hypabyssal and plutonic rocks. Mineralizations are of pyrometasomatic and hydrothermal origin. The main paragenesis assemblages are V-Ni-Co; Zr-Ti-Cr; Cu-Mn, and Pb-Zn. Uranium was originally concentrated syngenetically in a fluvial environment. Later on, it was mobilized by hydrothermal solutions and redeposited along fault lines in organic rich gray sandstones of Permian age (Matyasi, 1998). Hydrothermal ore minerals build up mainly in veins and hydrometasomatic bodies; locally there are impregnation bodies or simple nests (Stefan et al., 1988).

Geochemical studies of banatitic magmatites in the northern Apuseni Mountains show values of 3.4 to 6.6 ppm for uranium, while the vanadium content range between 6 and 170 ppm (exceptionally) (Ştefan et al., 1992). These values are equal or lower than those obtained by Matyasi (1998), who sampled Permian rocks occurring immediately below the cave.

2.1. Occurrence of metatyuyamunite

Metatyuyamunite forms yellow patches that cover white delicate crystals on both walls of a narrow-side passage (20 m in length), 300 m downstream Ventilator Waterfall (in the upper third of the cave system) (Fig. 2). Each of these yellow patches are a few square centimeters, but altogether are spread over several square meters.

The cave temperature in the close vicinity of sample location is about 9 C whereas the relative humidity is 99-100
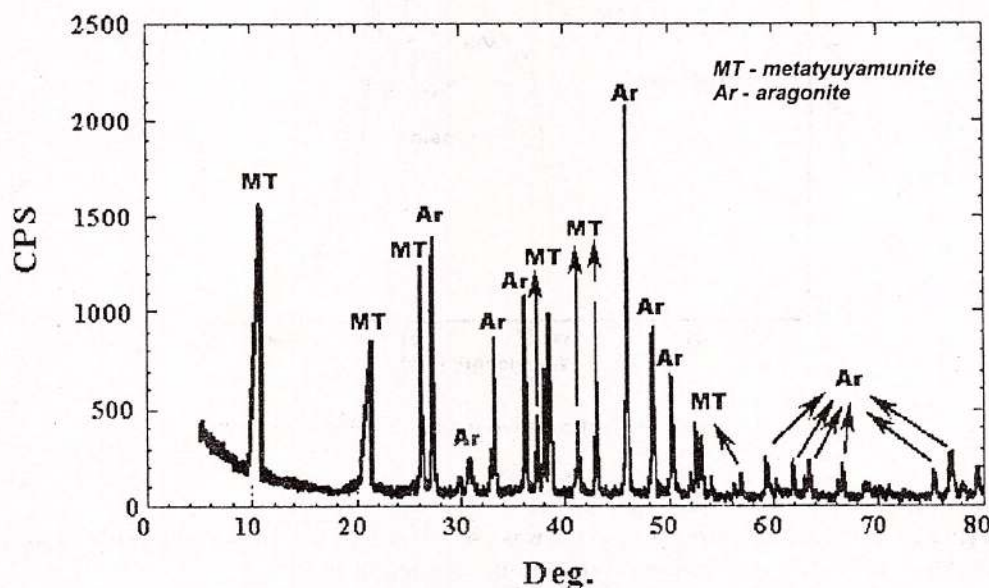
Fig. 3 - X-ray diffraction pattern of metatyuyamunite.

3. Analytical methods

3.1. X-ray diffraction data

The X-ray diffraction powder pattern for metatyuyamunite was obtained on a Scintag V Pad diffractometer, (Cu-Kα), using quartz as an internal standard. The scanning was continuous at a speed of $1^0 2\theta/min$ and a time constant of 2.5 seconds. The diffractometer was operated at 45 kV and 40 mA within the 2⁵

range of 5 to 80^0, and refined between 8 and 33^0. The X-ray pattern shows a number of lines, all well-marked and sharp. The strongest five lines 8.32 (90), 4.16 (40), 3.25 (55), 2.36 (26), 2.10 (40) are presented in Fig. 3. Since the X-ray diffraction pattern comprises only 8 lines, the indexing of these reflections may look uncertain, but nevertheless gave a clear orthorhombic cell having a=10.77, b=8.53, c=17.62. These values are close to those from ICDD file 8-287 and to those obtained by Polyak, Mosch (1996) and Onac et al. (2000).

The X-ray diffraction pattern for the white crust on which metatyuyamunite was precipitated is almost identical to that of synthetic aragonite (ICDD file 5-453).

3.2. Optical and scanning electron microscope analyses

Observations made on a Stemi 2000-C (Zeiss) binocular (50x magnification) revealed that bladed crystals of metatyuyamunite (0.1-0.3 mm in size) are sprinkled over millimeter-size, transparent to translucent, colorless to white acicular crystals and radial aggregates of aragonite. Metatyuyamunite crystals have a canary yellow color and adamantine luster.

In thin section, metatyuyamunite is colorless to pale yellow, the extinction is parallel and shows perfect rectangular cleavage.

The scanning electron microscope (SEM) investigation was conducted on a Hitachi S-3500N device. The SEM images revealed euhedral to subhedral decimicron platy-like crystals of metatyuyamunite (Plate I, Fig. 1) as well as acicular crystals of aragonite (Plate I, Fig. 2). Some of the aragonite crystals are twinned.

Several crystals of metatyuyamunite were examined by means of electron probe microanalysis using an energy dispersive spectroscopy (EDS) detector attached to the SEM. The semi-quantitative elemental analysis provided by EDS confirmed the presence in all samples of uranium ($\approx$ 67 %), vanadium ($\approx$ 21 %), calcium ($\approx$ 6.5 %), and oxygen.
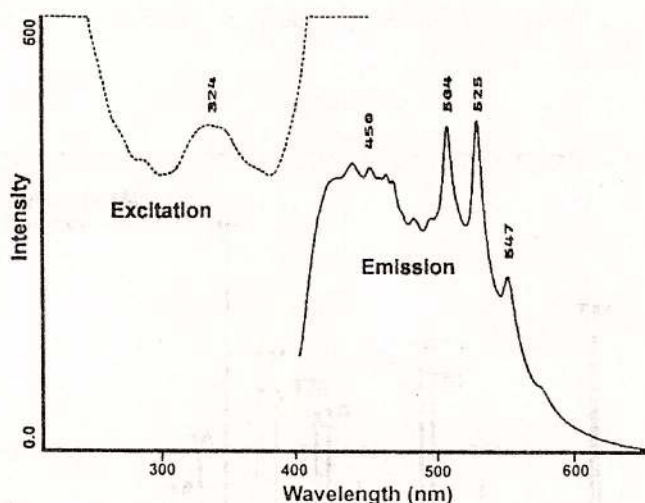
Fig. 4 – Excitation and emission spectra of metatyuyamunite.

3.3. Luminescence

A Hitachi (model 4010) spectroflurophotometer was used to investigate the luminescence of the metatyuyamunite. Under short wave UV, the yellow crystals luminisce bright green.

Measurements of the excitation and emission spectra show the characteristic emission of the uranyl ion (Fig. 4). The sharp lines at 504, 525, and 547 nm are characteristic of the uranyl ion and in good agreement with the results obtained on the Sonora specimen by Onac et al. (2000). The broad band centered at 450 nm is not part of the uranyl spectrum and likely arises from fulvic acid and related organic compounds incorporated into the co-existing aragonite.

4. Results and discussion

Hydrothermal solutions are responsible for the origin and development of the Valea Rea Cave. Diagnostic features supporting this origin include exotic mineral deposits (celestine, barite, dickite, nacrite, quartz etc.),

tree-form effluent chimneys, multi-story mazes, and highly corroded wall crusts (Onac et al., 1995; Ghergari et al., 1997; Damm, in press).

Eh, the concentration of vanadium, and the amount of carbon dioxide mostly control the geochemical behavior of uranium (Langmuir, 1978; Maynard, 1983). Carnotite and all other uranyl minerals are soluble at low CO_2 pressures similar to those found in a cave environment. The following features are sufficient for a general understanding of the behavior of uranium in natural waters: it is soluble under oxidizing conditions unless vanadium is present, and is insoluble under reducing conditions (Drever, 1997).

We believe uranium and vanadium were mobilized by hydrothermal solutions moving upward through the Permian sandstones occurring below the cave. After development of cave and under subsequent vadose evolution of the cavity, uranium was transported as highly soluble uranyl carbonate complexes in neutral to alkaline, oxidizing waters. The presence of even small amounts of vanadium in solution led to immobilization of uranium as carnotite, tyuyamunite or other uranyl minerals. Uranium could also have precipitated under reducing conditions, created by a reducing zone in the dolomite due to rich organic matter and/or sulfide minerals such as pyrite (Langmuir, 1997).

The problem in interpreting the presence of metatyuyamunite in the Valea Rea Cave is whether it is primary or of secondary origin (i.e. formed by dehydration of tyuyamunite). According to Stern et al. (1956) determined the number of moles of water was a function of the partial pressure of water vapor. Plateaus on the dehydration curve were found at values of 5 and 8.5 moles of water per moles of Ca $(UO_2)_2(VO_4)_2$. Considering the wide range of water vapor partial pressure (relative humidity) recorded in cave environments the two minerals can theoretically co-exist. Our analytical investigation revealed only the presence of metatyuyamunite, which was successfully rehydrated to tyuyamunite by placing it in a moist atmosphere (the rehydrated mineral was confirmed by X-ray diffraction). Therefore, the problem mentioned above is still an open question.

Regarding the precipitation of the mineral association, the following succession is suggested. Either metatyuyamunite or tyuyamunite (dehydrated in one step to metatyuyamunite in a later stage) or both could have precipitated where CO2-rich groundwater equilibrated with cave atmospheric CO2 levels. This succession would only occur after aragonite was first deposited as wall crust from a uranyl-rich carbonate complex. The presence of metatyuyamunite crystals, randomly disposed between or over aragonite crystals, may be evidence to support our theory.

The presence of uranium-vanadium compounds in the Valea Rea Cave add new insight into the hydrothermal interpretation of its speleogenesis, regardless of which the two minerals were precipitated first.

Note added in proof: The second occurrence of the mineral was nearly simultneously reported by Onac, B. P., Veni, G., White, W.B. (2001). Depositional environment for the metatyuyamunite and related minerals from Caverns of Sonora, TX (U.S.A.) Eur. J. Mineral., 13, 135-143.

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Fig. 1 — SEM image of metatyuyamunite.

Fig. 2 — SEM image of aragonite crystals.

ZEOLITE FORMATION IN THE LOWER MIOCENE TUFFS, NORTH-WESTERN TRANSYLVANIA, ROMANIA

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Key words: Rhyolites. Clinoptilolite. Opal-CT. Mordenite. Diagenesis. Transylvanian Basin.

Abstract: Zeolites are common alteration products of silicic, mostly vitric, Badenian (Lower Miocene) tufts in the northwestern part of the Transylvanian Basin. This study of 50 samples from sections at Tărpiu, Vale, Bobâlna, Aluniş and Şoimeni showed that reworked fallout tuffs and ash-flow tuffs had been extensively altered to a mineral assemblage dominated by zeolites. The relative abundance of zeolites and associated minerals were determined by X-ray powder diffraction. Selected samples were also studied by SEM and optical methods to ascertain the genesis and paragenetic relationships of the minerals. Zeolitic tuffs consist mostly of clinoptilolite (40-90 %) and opal-CT. Trace amounts of fibrous mordenite and phillipsite were detected by SEM. The common paragenetic sequence is volcanic glass-clinoptilolite-mordenite. Opal-CT crystallized at the same time as clinoptilolite or later. The origin of the zeolites and associated minerals in these deposits is shown to be diagenetic. Hydrolysis of the silicic glass brought about by saline alkaline pore water, trapped during marine sedimentation of the pyroclastic material and subsequent burial accompanied by increase of temperature (up to $80^\circ C$), was followed by formation of zeolites at the expence of glass and zeolite and opal-CT precipitation in pore spaces.

Introduction

This investigation deals with the diagenetic history of an important bedded tuft sequence deposited mainly in the Badenian (Lower Miocene) time over a large area, mostly in the Transylvanian Basin. The stratigraphic position of the tuff sequence within the Miocene sedimentary rocks provides an excellent marker horizon. Drilling has shown that this tuff complex occurs throughout the whole Transylvanian Basin with outcrops along the southeastern, western and northern margins. It is also widespread in other parts of the region, as intramountain basins of the Apuseni Mountains, or external border of the Carpathian bend (Fig. 1). The present investigation is restricted to its classical occurrence area, where the tuff sequence crops out between the towns of Cluj-Napoca and Dej. In this area it is known in the literature as the "Dej Tuff" (Posepny, 1867). Evidence of zeolites, mainly clinoptilolite, in the Dej Tufts was reported by Popescu et al., (1975) and later confirmed by Popescu and Asvadurov (1978). Mordenite was recorded by Istrate (1980) and later by Bedelean and Avram (1991). Other investigations recording the presence of zeolites in the study area include those by Bedelean (1982), Ghergari et al., (1991), Răcătăianu et al., (1991) and Bărbat et al., (1991).

General geology

In the Transylvanian Basin the Lower Miocene sedimentary strata, which followed the epicontinental-continental Eocene-Oligocene sedimentation, form a discontinuous post-tectonic cover sequence over the Upper Cretaceous-Paleogene deposits (Săndulescu, 1984). The Dej Tuff Complex, some 20-100 m thick, occurs near to the top of the Lower Miocene succession (Popescu et al., 1995). During the Early Miocene the Transylvanian Basin underwent progressive tectonic subsidence. The whole complex comprises 4 to 5 major volcaniclastic cycles, each including reworked ash-flow and fallout tuffs at the base, fallout tuffs and reworked tuffs in the middle part, and tuffites interbedded with psamitic to siltic sediments in the upper
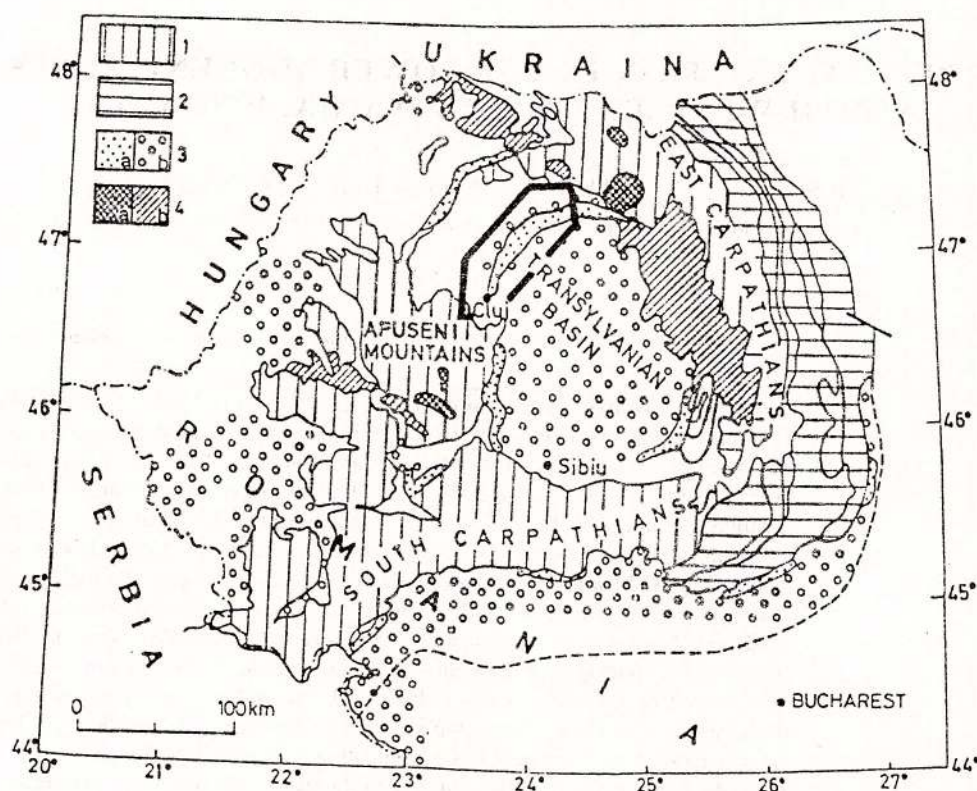
Fig. 1 - Location and distribution of Neogene igneous rocks in Romania 1: Inner Carpathian Units; 2: Outer Carpathian Units; 3: Acid calc-alkaline volcanism: a) cropping out, b) buried; 4: Intermediate cab-alkaline magmatism: a) intrusive, b) stratovolcanic. The frame shows the study area.

part. As a whole, the complex has a rhyolitic character (Seghedi and Szakacs, 1991). Stratigraphically, the Dej Tuff Complex is constrained to Langhian (Lower Badenian) (Popescu, 1970), but a K-Ar age determination, obtained on biotite from the basal level of the complex, gave 18.0±0.5 Ma (Berggren and Popescu, unpublished data). The volcanic source area is still unknown.

Sampling and methods of study

Samples were collected along the western outcrops of the Transylvanian Basin, between Ciceu-Giurgeşti and Cluj-Napoca (Fig. 2). Generalized lithological columns of the Bobalna Hill and Aluniş are shown in Figure 3 with the sampled intervals. Material was collected wherever an obvious change in lithology was observed. Stratigraphic sections were measured at all the locations (Ciceu-Giurgeşti, Tirulul Hill-Dej, Rapa Dracului, Aluniş, Paglişa, Şoimeni and Coruş) with a complex sampling for petrographical observations. 50 samples were examined from all the studied profiles. Their mineral composition (Table 1) was determined by X-ray powder diffraction technique (XRD) after heat treatment at 550°C, using a Dron-3 instrument and Ni-filtered CuKα radiation. S···   electron microscopy (SEM) was carried out with a REMMA 202 instrument.

Petrography and mineralogy

Macroscopic and microscopic features

Two main volcaniclastic rock types have been found: reworked pyroclastics and tuffites. The first ones are grouped in secondary ash-flow tuffs and second fall-out tuffs. The color of these rocks is white, light green or green. The last color characterizes zeolite-rich vitroclastic tuffs. The rocks are indurate, having conchoidal fractures. The tuffs generally are fine-grained, well-graded, showing parallel bedding stratification. The reworked ash-flow tuffs are massive and richer in crystals.
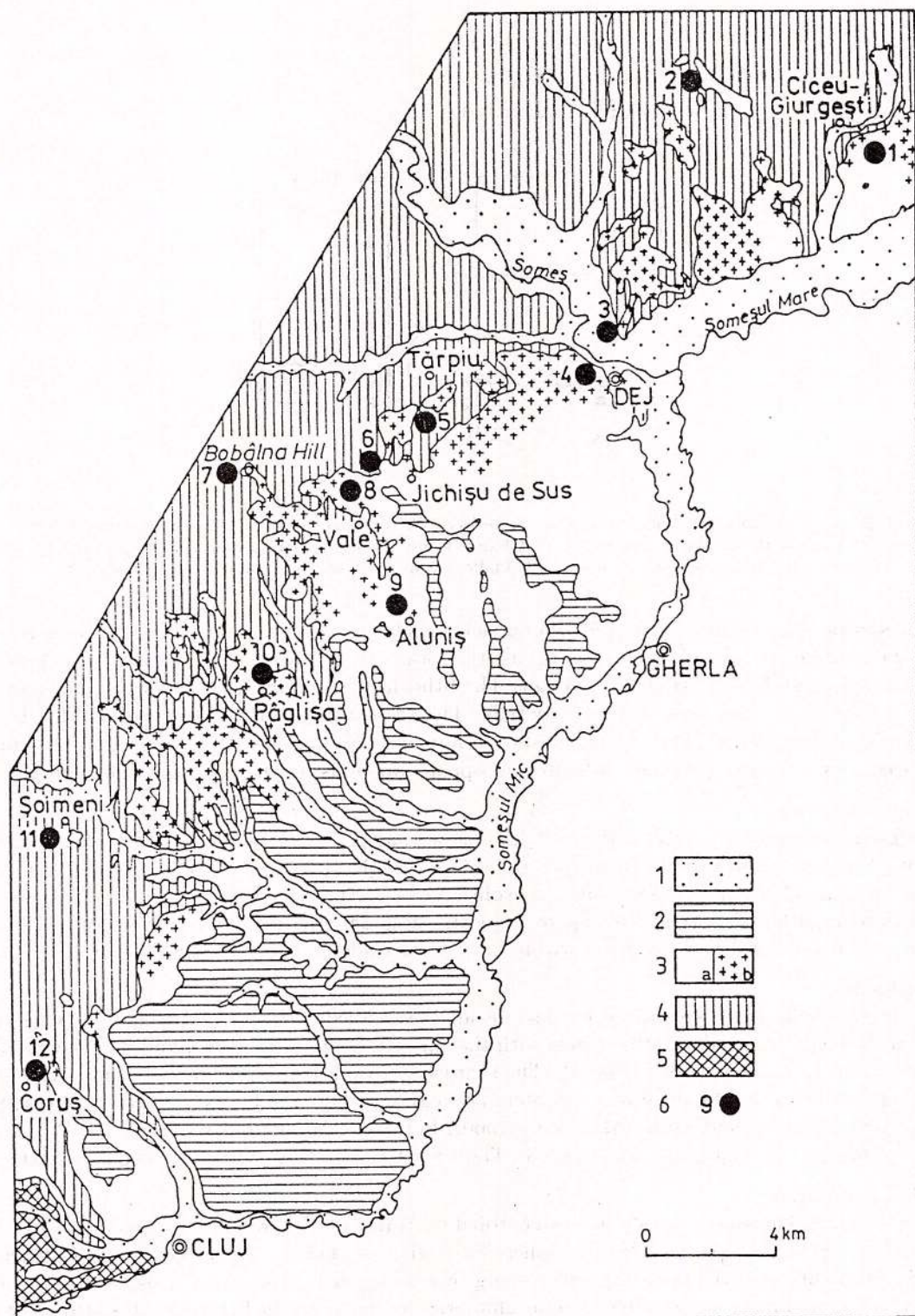
Fig. 2 - General geological sketch of the northwestern border of the Transylvanian Basin showing the area of investigation.
1: Quaternary deposits: 2: Sarmatian strata; 3: Badenian: a) Dej strata, b) Mireş strata; 4: Lower Miocene strata; 5: Paleogene strata; 6: Location of the sections.
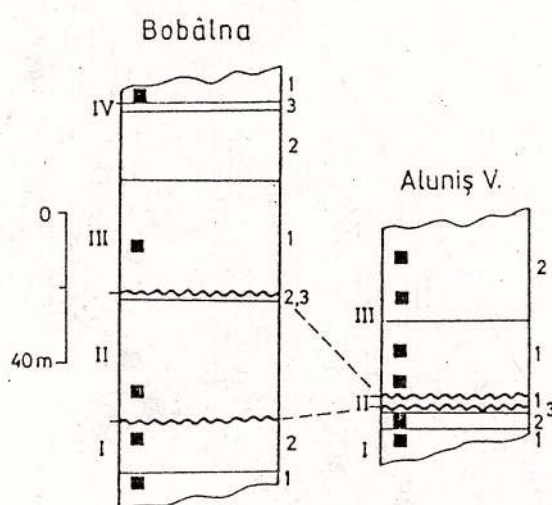
Fig. 3 - Generalised lithologic columns of the Dej Tuff sequences from Bobâlna Hill and Aluniş;
sections show the sampling intervals. I, II, III and IV indicate the major volcaniclastic sequences: 1:
ash-flow tuffs; 2: fallout tuffs; 3: interbedded fallout tuffs, epiclastic rocks and sedimentary strata.

In thin section, the main petrographic components include vitroclasts, crystaloclasts and lithoclasts.
Based on the relative amount of these components, the rocks can be defined as vitroclastic and/or crystalo-
clastic tuffs, and crystal-vitric/vitric-crystal tuffs The lithoclastic component is less abundant, particularly
found at the base of the main reworked ash-flow tuffs. The vitric component consists of glass, shards, pumice
and massive glass fragments. The crystaloclasts are mostly quartz, plagioclase, biotite, green amphibole,
alkali-feldspar and accessory pyroxene, allanite and opaque minerals (titano-magnetite, ilmenite).

Secondary minerals

Thin-section petrography, XRD and SEM data show that the vitric matrix of the tuffs was partially
or entirely altered to zeolites and cristobalite (opal-CT) (Table 1). Other minerals, such as quartz and
plagioclase, represent primary constituents. Rhyolitic glass in the samples from the locality of Coruş is
mostly unaltered, although interstitial calcite is locally abundant In the altered samples the growth of
euhedral secondary minerals was observed within interstitial voids between the shards.

Clinoptilolite

This mineral is the main secondary product in all the studied sections occurring in a wide range of
euhedral forms, including blades, laths, plates with the characteristic coffin shape, and blocky crystals. The
crystals are about 1-30 microns long (Fig. 4). The shards are pseudomorphosed and the larger crystals have
grown perpendicular to the shards, filling the interstitial cavities (Fig. 4). The XRD pattern of clinoptilolite
is very similar to that of heulandite (Mumpton, 1960), but after thermal treatment at 550 ^{0}C heulandite
breaks down, whereas clinoptilolite is unaffected. The 8.95 Å and 3.95 Å peaks are unequivocal (Fig. 5).

Opal-CT lepispheres

Diagenetic silica, known previously as low-cristobalite, is frequently present besides clinoptilolite in the
studied sections. Silica lepispheres are microspheroidal bodies of bladed crystals, consisting of more or less
disordered cristobalite and trydimite, randomly intergrown, being defined as opal-CT by Oehler (1975) (Figs.
6, 7). Opal-CT crystallized at the same time as clinoptilolite, or later. In Figure 5 the sharp peak at 4.05
Å is due to opal-C and not opal-CT (Jones and Segnit, 1971). As a result of the heat treatment the very
broad reflection of Opal-CT around 4.3, 4.1 and 3.9 Å has been converted to the low-cristobalite-like peak
in this difractogram.

Mordenite

This mineral, found only in vitric fallout tuffs at Tărpiu, Aluniş and Vale, was detected by SEM. It
occurs as randomly distributed fibers on clinoptilolite and opal-CT, but never as a direct alteration product
of the volcanic glass (Fig. 6).

Table

Mineral associations and relative frequency of mineral species of selected Dej Tuff samples determined by XRD analyses.

Sample number	Location	Original rock type	Mineralogy	Frequency
TD-143-1	Tărpiu (5)	Tuff	clinoptilolite quartz	++++ +
TD-144-2a	Bobâlna (7)	Ignimbrite	clinoptilolite quartz	+++ +
TD-144-2a	Bobâlna (7)	Ignimbrite	clinoptilolite quartz cristobalite	++++ ++ +
TD-144-6	Bobâlna (7)	Ignimbrite	clinoptilolite quartz opal-CT	+++ + +
TD-145-1A	Bobâlna (7)	Ignimbrite	clinoptilolite quartz	+++ +++
TD-154-4A	Bobâlna (7)	Ignimbrite	clinoptilolite quartz plagioclase	+++ +++ +++
TD-141-6B	Vale (8)	Coarse tuff	clinoptilolite	++++
TD-139	Aluniş (9)	Medium tuff	clinoptilolite plagioclase opal-CT	+++ +++ +
TD-139-1A	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ ++
TD-139-1B	Aluniş (9)	Fine tuff	clinoptilolite quartz opal-CT	+++ + +++
TD-139-4	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ +
TD-139-5C	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ +
TD-139-3A	Aluniş (9)	Fine tuff	clinoptilolite quartz	++++ ++
TD-140-3	Aluniş (9)	Fine tuff	clinoptilolite	++++
TD-140-6	Aluniş (9)	Fine tuff	clinoptilolite	++++
TD-134-4-2	Pâglişa (10)	Fine tuff	clinoptilolite	++++
TD-145-4-2	Şoimeni(11)	Fine tuff	clinoptilolite quartz	++++ +
TD-137-1	Coruş (12)	Tuffite	amorfous material quartz calcite plagioclase kaolinite	+++ + + + +
TD-137-0	Coruş (12)	Tuffite	calcite amorfous material quartz plagioclase	++++ ++ + +

Frequency symbols:++++ - very abundant
+++ - abundant
++ - small amount
+ - sporadic
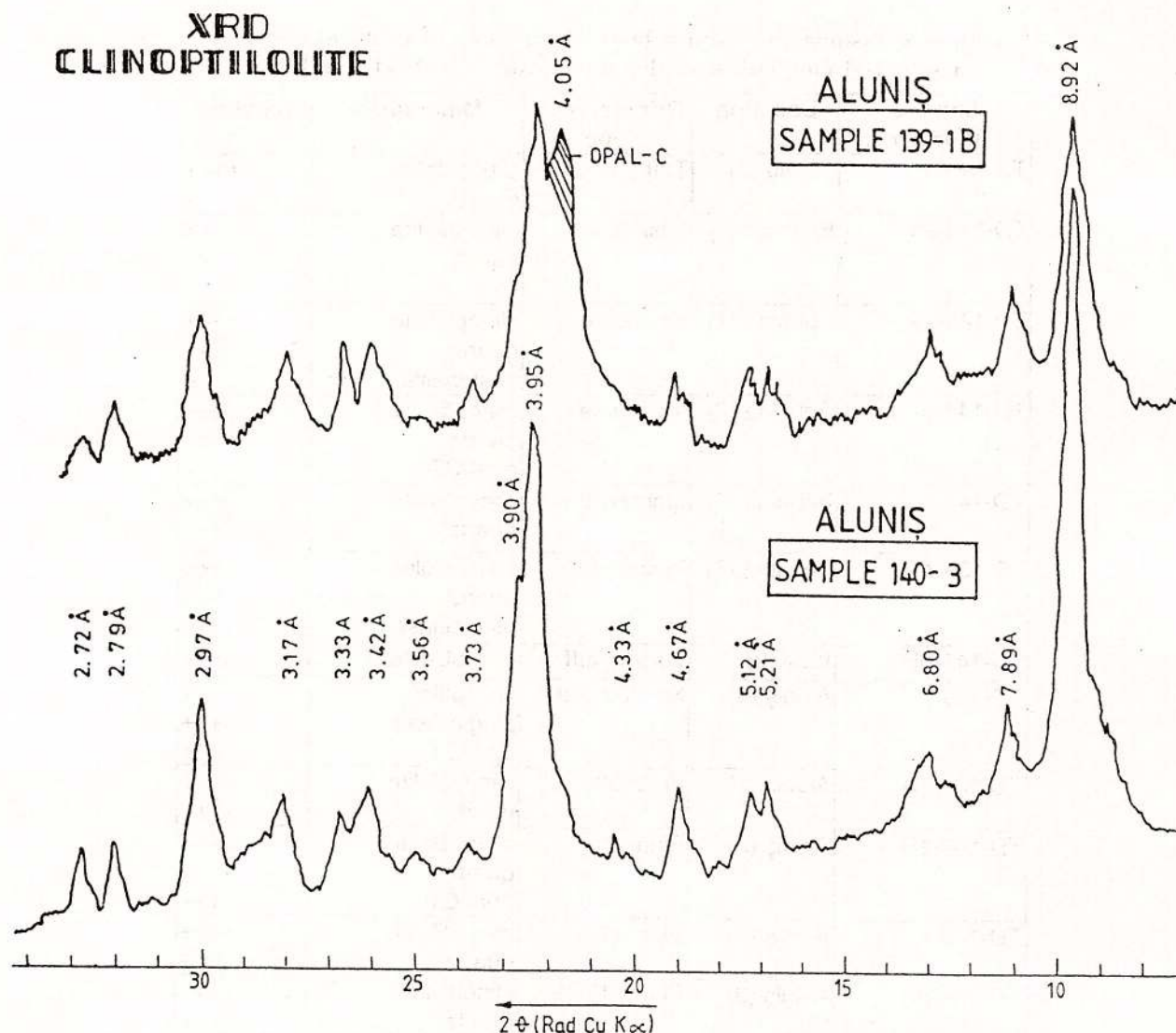
Fig. 4 – X-ray powder diffraction diagrams for clinoptilolite (sample 140-3) and clinoptilolite associated with opal-C (sample 139-18) from Aluniş, after heat treatment at 550°C.

Phillipsite

Phillipsite occurs only at Tărpiu as a secondary alteration product of clinoptilolite associated with opal-CT. It was detected by SEM and appears as laths of prismatic crystals (Fig. 7).

Carbonate minerals

Calcite is the most abundant secondary mineral in the tuffs at Coruş. Its formation seems to have inhibited the development of zeolites so the glass shards are practically unaltered.

Paragenesis of secondary minerals

The paragenetic relations are closely connected with the amount of volcanic glass in the deposit. No evidence was found that zeolites replaced other minerals. The main observed parageneses are: (1) ctinoptilolite; (2) clinoptilolite - opal-CT; (3) clinoptilolite - opal-CT - mordenite.
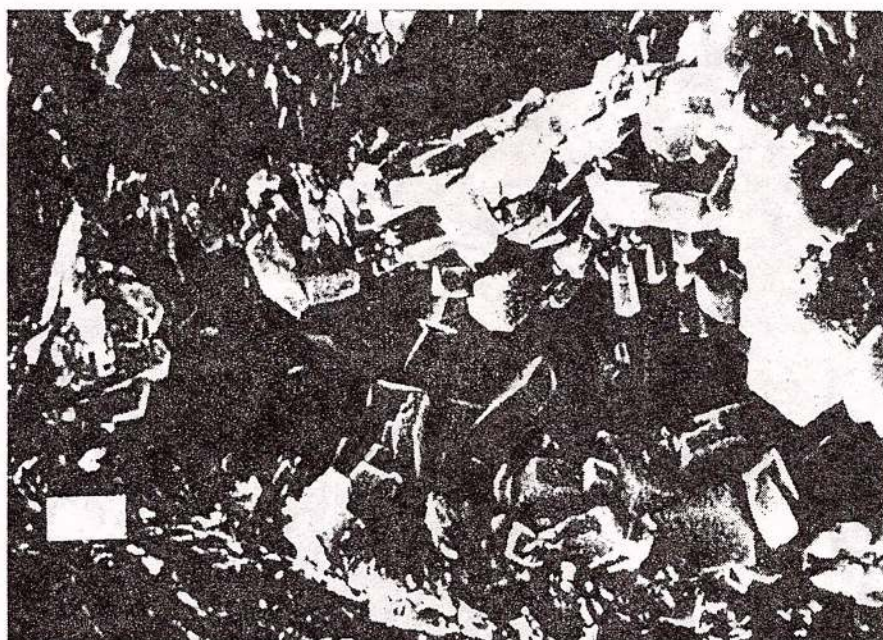
Fig. 5 – Scanning electron micrograph showing relationships between blade- and lath-shaped clinoptilolite filling voids between diagenized glass shards; Pâglişa occurrence; scale bar is 7 μm long.

Fig. 6 – Scanning electron micrograph of opal-CT lepisphereş, fibmus mordenite and clinoptilolite blades from Aĺuniş: scale bar is 0.5 μm long.
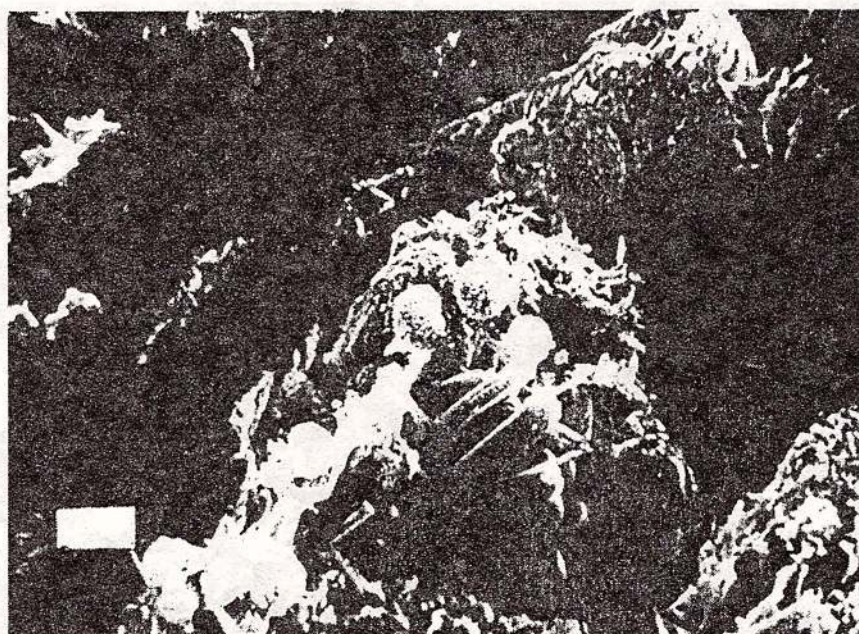
Fig. 7 – Scanning electron micrograph of lath-shaped phillipsite crystals associated with opal-CT lepispheres from Ta rpiu; scale bar is 3 μm long.

Genesis of zeolites and associated minerals

All the evidence provided by these investigations support the view that the described alteration products are authigenic in origin. Hay (1993) has summarized the major factors controlling the formation and distribution of zeolites and other authigenic minerals. These include mineralogical composition, permeability and age of the host rock, temperature variation, pressure and chemistry of the pore waters.

The examined rocks are mainly rhyolitic reworked fallout and ash-flow tuffs, rich in volcanic glass. The primary volcaniclastic deposits were redeposited in a marine environment. In all observed sections the deposits have a similar mineralogical composition and structure, and are more or less equally affected by zeolitization. The roughly constant mineralogical composition of the rocks, in the whole deposit, suggests that no significant mass transfer was involved in the formation of diagenetic minerals. The distribution of any authigenic minerals in the deposits should reflect the chemistry of the pore fluids present during diagenesis. Experimental and theoretical approaches (e.g. Hess, 1966) suggest that the main characteristics of the pore water controlling the dissolution and precipitation of either argillic phases or zeolites are closely related to the relative activity of alkalis and hydrogen. High alkali ions/hydrogen ions ratio and a relative high activity of silica favor the prevailing generation of zeolites as opposed to clay minerals. This situation would characterize generation of the zeolites described here. Such situations are typical of alkaline saline lake or marine environment (Hay, 1978, Iijima, 1978). The presence of alkaline saline water favorizes zeolitization, but additional factors must also be involved. The Dej Tuff Complex was buried during the Miocene under a significant cover of later sediments up to 3.5±0.5 km Sanders, 1998). It seems likely that the deposits suffered enough burial to give rise to significant changes in temperature and pressure, which favored the diagenetic processes. The burial temperature of $80\ ^0\pm10\ ^0$C (Sanders, 1998) is in the estimated range for clinoptilolite formation and stability (49-83 ^{0}C) in the present-day diagenesis in various areas worldwide (Iijima, 1986, Ogihara, 1996).

Paleoenvironmental conditions during the Early Miocene times suggest that the secondary minerals in the Dej tuffs were generated through hydrolysis and dissolution of silicic glass by interstitial saline waters in a marine environment. The subsequent burial favored the diagenetic processes during the rise of temperature and pressure. The almost complete zeolitization of the volcanic glass-rich deposits suggests that the pore water, which caused the diagenesis, was of cognate type, trapped in the sediments during or shortly

after the underwater deposition of the volcaniclastics. Some mineralogical variation in the different studied profiles could be related to different compositions of the interstitial pore fluids, but also to differences in the composition of the protoliths. The crystallization sequence during tuff diagenesis was probably controlled by growth kinetics allowing the metastable precipitation of clinoptilolite and opal-CT as a result of kinetic barriers (Murata and Larson, 1975), followed in some cases by mordenite or phillipsite generation. The lack of transformation of volcanic glass in the case of the occurrence suggests that there were not favorable conditions for zeolitization. The abundant presence of authigenic calcite in the Coruş tuffs suggests a slightly acidic environment, inherited by pore waters, that precluded the formation of zeolites at the expense of volcanic glass.

We can assume that the amount of zeolites in the diagenetically transformed tuffs closely reflects the amount of primary volcanic glass initially present in the volcaniclastic deposits.

Acknowledgements

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CLASIFICAREA ŞI NOMENCLATURA SUBSTANŢELOR MINERALE ŞI ORGANICE, NATURALE ŞI SINTETICE, UTILIZATE ÎN GEMOLOGIE

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Abstract: *The classification and nomenclature of the mineral and organic, natural and synthetic substances used in gemmology.* An up-to-date classification and nomenclature of the mineral and organic, natural and synthetic substances used in gemmology are presented in the paper, according to both IMA (International Mineralogical Association) and CIBJO (Confederation Internationale de le Bijouterie, Joaillerie, Orfevrerie, Paris) recomendations.

Gemologia este ramura mineralogiei care se ocupă cu determinarea naturii gemelor, cu identificarea, autentificarea, expertiza şi clasificarea gemelor, respectiv a produselor naturale care prin calităţile lor estetice şi fizice (culoare, duritate, luciu, rezistenţă, strălucire etc.) pot fi utilizate la confecţionarea obiectelor de podoabă, artă şi ornament. La acestea se adaugă caracteristici speciale, gemologice, cum sunt: frumuseţea, raritatea, durabilitatea, cererea pieţii, tradiţia utilizării, portabilitatea.

I. Clasificarea gemologică clasică

Cea mai veche clasificare, uneori încă utilizată (Allaby & Allaby, 1990), cuprinde categoriile:

1. Pietre preţioase
2. Pietre semipreţioase
3. Pietre decorative (ornamentale)

Termenul de pietre nobile era conferit tuturor pietrelor preţioase, semipreţioase sau decorative.

Pietre preţioase erau considerate mineralele cristalizate, în general foarte pure, transparente, cu aspect atrăgător (culoare, luciu), cu duritate mai mare sau cel puţin egală cu 8 şi care se găsesc mai rar în natură. În această categorie sunt cuprinse **diamantul**[1], *safirul, rubinul, smaraldul,* **topazul.** Termeni sinonimi pentru piatră preţioasă sunt: "piatră rară", "piatră scumpă", "nestemată".

Pietrele semipreţioase cuprind, în această clasificare, produse naturale minerale şi organice transparente, translucide sau opace, cu duritatea mai mică decât a *pietrelor preţioase.* Exemple din această categorie sunt: unele varietăţi de **cuarţ** *(ametist, agat, calcedonie),* **granat, opal,** *turmalina,* **elbait, dravit,** *alexandrit,* **andaluzit, cordierit,** *spinel,* **hematit, turcoază, zircon, crisoberil, jadeit, topaz,** *lapis lazuli, aventurin, kunzit* precum şi unele exemplare excepţionale de perle, corali, *chihlimbar* (ambra).

Pietrele decorative (ornamentale) sunt minerale sau asociaţii de minerale cu duritate mai mică de 7, care prezintă calităţi estetice şi fizice mai puţin potrivite pentru bijuterie, utilizându-se la confecţionarea unor obiecte decorative: statuete, amulete, vase, casete, etc. În funcţie de duritate, se clasifică în pietre dure şi pietre moi.

Pietrele (decorative) dure au duritatea cuprinsă între 5 şi 7. Reprezintă varietăţi sau exemplare mai puţin valoroase de minerale în general considerate ca "pietre semipreţioase": varietăţi de **cuarţ**-*calcedonie,* **opal,** *apatit,* **diopsid, jadeit,** *amazonit, lapis lazuli,* **spodumen, rodonit, vezuvian** etc.

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[1] Denumirile de specii minerale validate sunt redate în lucrare cu caractere îngroşate (Bold); denumirile corecte ale varietăţilor gemologice sunt redate cu caractere italice iar cele incorecte (dar încă frecvent utilizate), cu caractere normale.

Pietre (decorative) moi au duritate în general mai mică de 5. În această categorie sunt cuprinse substanţe minerale ca: **azurit, malachit, crisocol, aragonit, fluorină, rodocrozit,** *alabastru, agalmatolit,* dar şi perlele, ambra *(chihlimbarul)*, fildeşul, coralii.

Această clasificare este însă considerată ca fiind depăşită.

II. Clasificarea mineralogică a substanţelor minerale naturale utilizate în gemologie

Întrucât substanţele utilizate în gemologie nu cuprind întregul spectru mineralogic, clasificarea lor pe baze mineralogice se rezumă doar la unele clase şi subclase de minerale:

A. MINERALE

1. Clasa elementelor native
1.1. Semimetale şi nemetale (metaloizi); ex. **diamant**
2. Clasa sulfurilor; ex. **pirită, marcasită. sfalerit, stibină**
3. Clasa oxizi şi hidroxizi
3.1. Oxizi simpli; ex. **periclaz, corindon, hematit, rutil, anatas, casiterit**
3.2. Oxizi multipli; ex. *spineli*, **crisoberil**
4. Clasa carbonaţi
4.1. Carbonaţi anhidri; ex. **calcit, rodocrozit, aragonit**
4.2. Carbonaţi cu hidroxil; ex. **azurit. malachit**
5. Clasa boraţi
5.1. Boraţi hidrataţi; ex. **howlit**
6. Clasa sulfaţi
6.1. Sulfaţi hidrataţi; ex. **gips** *(selenit. alabastru)*
7. Clasa fosfaţi, arseniaţi şi vanadaţi
7.1. Fosfaţi, arseniaţi şi vanadaţi anhidri; ex. **berillonit**
7.2. Fosfaţi, arseniaţi şi vanadaţi anhidri, cu hidroxil; ex. **ambligonit, brazilianit,** *apatit,* **lazulit**
7.3. Fosfaţi, arseniaţi şi vanadaţi hidrataţi, cu hidroxil; ex. **turcoază**
8. Clasa silicaţi
8.1. Subclasa nezosilicaţi; ex. *olivină* **(forsterit)**, **zircon,** *granaţi,* **topaz, sillimanit, andaluzit, disten, staurolit, titanit**
8.2. Subclasa silicaţilor cu grupe mixte nezo-sorosilicaţi; ex. **epidot, clinozoizit, vezuvian**
8.3. Subclasa ciclosilicaţi; ex. **benitoit, rodonit, beril, cordierit,** minerale din grupa *turmalinei* **(elbait. dravit, uvit), dioptaz, crisocol**
8.4. Subclasa inosilicaţi; ex. piroxeni **(jadeit, spodumen. diopsid),** *amfiboli:* **actinolit** *(nefrit),* **antofilit** *(nefrit),* **riebeckit** *(crocidolit)*
8.5. Subclasa filosilicaţi; ex. minerale *serpentinice* **(lizardit),** sepiolit. talc *(steatit),* **pirofilit** *(agalmatolit)*
8.6 Tectosilicaţi; ex. *feldspaţi (amazonit,* **ortoclaz.** *adular, labradorit),* **lazurit, sodalit,** minerale de SiO_2 **(cuarţ, opal)**

B. MINERALOIZI; ex. gagat (jet), ambră *(chihlimbar,* succinit)

Utilizând însă o clasificare mineralogică, cu caracter restrictiv (se referă numai la substanţe minerale naturale) o serie de alte substanţe naturale comune în gemologie, cum sunt lemnul silicifiat-opalizat, lemnul încarbonizat, perlele, fildeşul, coralii, *jaspul, obsidianul. lapis lazuli lazulitul, tectitele, cacholongul* şi altele rămân în afara clasificării.

III. Clasificarea gemologică internaţională modernă

Confederaţia Internaţională de Bijuterie. Giuvaergie, Orfevrerie - CIBJO (Confederation Internationale de le Bijouterie, Joaillerie, Orfevrerie). înfiinţată la Paris într-o primă formă, în anii '20 şi reorganizată în forma actuală în anul 1961 (cu 25 de ţări membre în 1996) şi care se ocupă în principal cu comerţul cu geme, cuprinde şi trei comisii speciale care au ca scop stabilirea unor reglementări unitare care să fie aplicate la principalele materiale utilizate în gemologie, inclusiv diamante şi perle. Această clasificare gemologică

se foloseşte in toate publicaţiile oficiale, inclusiv in documentele adresate publicului (publicitate, etichete, certificate, buletine de expertiză etc.).

Astfel, in domeniul gemologiei sunt recunoscute două categorii de substanţe: a) Substanţe naturale şi b) Substanţe (produse) artificiale.

A. SUBSTANŢE NATURALE

Materialele (produsele) naturale cuprind substanţe minerale (pietrele preţioase, pietrele fine şi pietrele decorative) şi substanţele organice produse numai pe cale naturală, fără intervenţia omului (tabelul 1).

Tabelul 1
Clasificarea gemologică a substanţelor naturale

GEME	Pietre preţioase		D = 8	**diamant**, safir, rubin, smarald, **topaz**
	Pietre fine		D = 7-8	unele varietăţi de **cuarţ**, *granaţi*, *calcedonie*, **opal**, *turmalină*, **elbait**, **dravit**, *alexandrit*, **andaluzit**, **cordierit**, *spineli*, **hematit**, **turcoază**, **zircon**, **chrisoberil**, **jadeit**, **topaz**, *lapis lazuli*, *aventurin*
PIETRE DECORATIVE (DE ORNAMENT)	Pietre dure	D = 5-7		unele varietăţi şi exemplare de *calcedonie*, **opal**, *apatit*, **diopsid**, **jadeit**, *amazonit*, *lapis lazuli*, **spodumen**, **rodonit**, **vezuvian**
	Pietre moi	D < 5		**azurit**, **malachit**, **crisocol**, **aragonit**, **fluorină**, **rodocrozit**, *alabastru*, *selenit*, *agalmatolit*

A.1. Substanţe minerale naturale reprezintă minerale sau roci formate in ocurenţe şi zăcăminte naturale, fără intervenţia omului. Din punct de vedere gemologic cuprind pietrele preţioase, pietrele fine şi pietrele decorative. Dintre acestea, numai pietrele preţioase şi cele fine pot fi denumite şi geme sau pietre-geme.

Pietrele preţioase cuprind aceleaşi categorii gemologice de minerale ca şi in clasificarea clasică.

In categoria pietrelor fine sunt cuprinse mineralele care erau incluse anterior in categoria pietrelor semipreţioase.

Pietrele de ornament (pietrele decorative) se clasifică in pietre dure şi pietre moi şi cuprind aceleaşi minerale ca şi clasificările clasice.

A.2. Substanţe organice naturale

Reprezintă produse naturale de origine vegetală sau animală utilizate in gemologie: fildeş, coral, perle, ambră, copal, jet (gagat), sidef, baga, lemn silicifiat, ammolit, grandel, os.

Perlele se clasifică in perle fine şi perle de cultură (tabelul 2).

Tabel 2.
Clasificarea perlelor după formă şi structură (cf. Cibjo, 1997)

Categoria	Tipul
PERLE FINE	Perle
	Blistere
	Perle-blister
PERLE DE CULTURĂ	Perle de cultură
	Perle cultivate 3/4 sau 1/2
PERLE DE CULTURĂ COMPUSE	Perle de cultură compuse Mabe
	Perle de cultură compuse Hankei

Perlele fine cuprind concrețiuni naturale secretate de unele moluște, accidental și fără nici o intervenție umană. Se recunosc trei categorii de perle fine: perle, blistere și perle-blister.

- *perlele* sunt concrețiuni naturale în interiorul corpului moluștelor; sunt compuse din substanță organică - o scleroproteină numită conchiolină și carbonat de calciu - în general aragonit.

- *blisterele* reprezintă protuberanțe ale zonei interne a cochiliei cauzate fie de pătrunderea unui corp străin între cochilie și manta fie de obturarea unei spărturi a cochilie prin secreție de sidef.

- *perlele-blister* sunt perle de formă sferică sau neregulată, rezultate ale unui proces de perforare a mantalei de către o perlă. Perla atinge partea internă a valvei de care se va fixa prin noi strate de sidef care le continuă pe cele ale valvei.

Perle de cultură cuprind perlele de cultură propriu-zise și perlele de cultură 3/4 sau 1/2.

- *perlele de cultură* se obțin pe cale artificială prin implant organic sau introducerea unui nucleu solid în scoicile vii.

- *perlele cultivate 3/4 sau 1/2* sunt obținute prin introducerea de nuclee solide cvasi-sferice (3/4 dintr-o sferă sau jumătăți de sfere) în interiorul unei moluște.

B. PRODUSE ARTIFICIALE

Termenul *"artificial"* se utilizează pentru produsele fabricate parțial sau total de către om. Produsele artificiale se clasifică în patru categorii: a) Pietre (produse) sintetice, b) Pietre (produse) compozite sau asamblate, c) Pietre (produse) de imitație și d) Pietre reconstituite.

Pietrele sintetice reprezintă produse cristalizate sau recristalizate a căror fabricare, totală sau parțială, a fost realizată prin diverse procedee de laborator. Proprietățile lor fizice și chimice și/sau structura cristalină corespund în esență pietrelor naturale. În această categori sunt cuprinse safirele sintetice, rubinele sintetice, smaraldele sintetice etc.

Pietre compozite (asamblate). Sunt substanțe cristalizate sau amorfe compuse din două sau mai multe părți ansamblate prin procedee artificiale (ex. lipirea). Componentele pietrelor compozite sunt adesea pietre prețioase sau fine, pietre ornamentale, pietre sintetice sau diverse produse chimice. În această categorie intră dubletele și tripletele.

Perle de cultură compuse rezultă prin ansamblarea artificială a părții superioare a unei perle de cultură cu una sau mai multe părți inferioare de aceeași natură sau cu materiale diverse.

Imitații (pietre de imitație): copiază culoarea, aspectul și efectele speciale ale pietrelor naturale sau sintetice sau ale produsele artificiale, fără a poseda proprietățile lor chimice și/sau fizice și/sau structura lor cristalină (tabelul 7).

Imitații de substanțe organice. Sunt produse sintetice care nu corespund nici fizic și nici chimic substanțelor organice pe care le imită, ci doar redau culoarea și aspectul acestora (tabelul 7).

IV. Nomenclatura substanțelor minerale și organice, naturale și sintetice utilizate în gemologie

Problema ortografiei mineralelor în limba română reprezintă de mult timp subiect de discuție în cadrul comunității geologice din România (Marza, 1997; Udubașa, 1997). Dacă pentru domeniul mineralogic, în parte, dificultățile sunt lămurite, nu același lucru se poate afirma despre domeniul gemologic, care se află la începuturile sale. Diversitatea substanțelor, naturale sau sintetice, anorganice sau organice utilizate în gemologie ridică problema acceptării unei nomenclaturi unitare, în concordanță atat cu reglementările în vigoare din domeniul mineralogiei, gemologiei, biologiei, sintezei monocristalelor cat și cu specificul comercializării gemelor. În domeniul comercial se utilizează încă termeni, denumiri comerciale, care adesea nu au nimic de a face cu produsul respectiv.

Reglementările actuale (CIBJO, 1996; Read, 1997) privesc următoarele aspecte ale nomenclaturii gemologice:

A. **Substanțe minerale naturale** (tabelul 3 și 4)

Tabel 3. Nomenclatura gemologică a substanțelor minerale naturale
(acc. to: Fleischer, 1987; Anderson & Jobbins, 1990; Nickel & Nichols, 1991, Fleischer & Mandarino, 1995; Ionescu, 1995; Nickel et al., 1995; CIBJO, 1996; Read, 1997; Marza & Udubașa, 1997)

Specie minerală	Varietăți gemologice		
Actinolit	Verde intens: *Actinolit* Smaragdit *Nefrit* *Jad-nefrit* *Jad* Nefritoid Piatră verde (Green stone) Piatră de rinichi (Kidney stone) **Piatra Maori**	**Andradit**	galben deschis: *Andradit* Andradit galben Granat *Topazolit* de culoare neagră, cu continut de Ti: *Andradit titanifer* Melanit *Andradit negru* Granat
Albit	Alb, roz, verzui: *Albit* Feldspat Verde deschis: *Albit* Feldspat Albit-jadeit	**Antigorit** / **Antigorit**	verde, verde-gălbui, verde-cenușiu, translucid sau opac; aspect lamelar: *Antigorit* Serpentină Serpentină nobilă verde-de-măr, verde-gălbui, translucid, provenit din S.U.A.: *Bowenit* *Antigorit* Serpentină Serpentină nobilă
Almandin	(**Almandin** - toate culorile) rosu, rosu-violaceu: *Almandin* Granat *Almandin* Granat Almandin-spinel Granat de Tirol Rubin de Ceylon Rubin (de) Alabanda rosu intens: *Almandin* Granat Granat nobil Granat oriental Granat sirian	**Antofilit**	toate culorile: *Antofilit* Gedrit Nuumit
		Apatit	Apatit (toate culorile)
		Aragonit	toate culorile: *Aragonit* Floare de fier Calcit de Aragon Onix mexican Marmură-onix Onix de Pakistan Onix italian pseudomorfoză după fosile de amoniti: *Ammolit* *Ammonit* Korit Calcentină
Ambligonit	alb-verzui, alb-albăstrui; translucid, opac: *Ambligonit*		
Andaluzit	toate culorile: *Andaluzit* incolor, roz, roz-rosietic, foarte transparent: *Andaluzit* Andaluzit brazilian	**Azurit**	albastru: *Azurit* Cessylit
	cu incluziuni cărbunoase dispuse în formă de cruce: *Andaluzit* Chiastolit Piatra Crucii	**Benitoit**	albastru-violet, incolor *Benitoit* Piatră celestă
	verde: *Andaluzit* *Viridin*	**Beril**	toate culorile, cu exceptia smaraldului *Beril* verde intens: *Beril* Smarald albastru deschis-verzui: *Beril* Acvamarin verde-măsliniu: *Beril verde-măsliniu* *Beril* Acvamarin-crisolit albastru intens: *Beril albastru* *Maxixe* *Beril* Maxaxit
Andradit	toate culorile: *Andradit* Granat verde: *Andradit* Granat *Andradit verde* Demantoid Crisolit siberian Smarald de Ural		

	incolor: *Beril incolor* *Goshenit* *Beril*	**Corindon**	verde: *Cordierit* *Prazeolit* toate culorile, cu exceptia culorilor rosu si albastru *Safir* sau *corindon* cu indicarea culorii Corindon (Brad) roşu: *Rubin*
	galben: *Beril galben* *Heliodor* *Beril auriu* *Beril*		roşu intens: *Rubin* Rubin sânge-de-porumbel rosu, cu efect de asterism: *Rubin stelat* rosu, cu efect ochi-de-pisică: *Rubin ochi-de-pisică* Rubin-girasol albastru: *Safir*
	verde *Beril* *Beril verde* rosu: *Beril* *Beril rosu* roz: *Beril* *Morganit* *Beril roz*		albastru, cu efect de astersim: *Safir stelat* *Safir* galben, cu efect de asterism: *Safir galben stelat* *Safir* Topaz oriental stelat albastru, cu efect ochi-de-pisică: *Safir* *Safir ochi-de-pisică* incolor:
	roz din Ural: *Beril* *Beril roz* Vorobievit, beril cu cesiu rosu-verzui: *Beril* *Bixbit*		Safir *Safir alb* Leucosafir portocaliu: *Safir* *Safir portocaliu* *Padparadscha* roz: *Safir* *Safir roz*
Berillonit	galben, galben-verzui: *Berillonit*		Hiacint oriental verde:
Brazilianit	galben, galben-verzui: *Brazilianit*		*Safir* *Safir verde* Topaz oriental
Buergerit	**Buergerit**; brun închis: *Buergerit* *Turmalină brună* Fe-turmalină		Smarald oriental albastru cu efect alexandrit: *Safir* *Safir sanjant* *Safir cu efect alexandrit*
Calcit	toate culorile: *Calcit* alb, cu aspect satinat: *Calcit* Perle Atlas verde: *Calcit* *Calcit verde* Jad mexican		Alexandrit albastru albastru-verzui: *Safir* *Safir albastru-verzui* Acvamarin oriental galben: *Safir galben* *Safir* Safir oriental Topaz-safir
	stalagmitic; alb, gălbui, brun; structură în benzi de diferite culori: *Calcit* *Calcit stalagmitic* Onix mexican		Topaz oriental Topaz indian galben-roscat: *Safir* *Safir galben-roscat* Topaz regal
Casiterit	incolor, galben-brun, rosu, rosu-brun: *Casiterit*		
Cianit= **Disten**	albastru intens: *Cianit* *Cianit albastru* *Disten albastru* *Disten*		
Cordierit	incolor, albastru: *Cordierit* Safir-linx violet: *Cordierit* *Iolit*		
	albastru, transparent: *Cordierit* Safir de apă Fals safir Safir înselător		

	negru: *Safir* *Safir negru* Diamond spar	**Cuart**	violet: *Cuart* *Ametist* *Cuart violet* Ametist occidental Piatră episcopală
	violet: *Safir* *Safir violet* Ametist oriental		**(Cuart** bicolor: violet si galben) *Cuart* *Cuart bicolor* *Ametrin* Ametist-Citrin
Crisoberil **Crisoberil**	toate culorile: *Crisoberil* verde: *Crisoberil* *Crisoberil verde* Crisolit de Brazilia cu efect ochi-de-pisică: *Crisoberil* *Crisoberil ochi-de-pisică* Ochi-de-pisică de Orient Ochi-de-pisică cu efect alexandrit: *Alexandrit* *Crisoberil cu efect alexandrit* *Crisoberil* cu efect alexandrit si efect ochi-de-pisică: *Alexandrit ochi-de-pisică* *Crisoberil ochi-de-pisică cu efect alexandrit* *Crisoberil* *Alexandrit* galben, cu incluziuni gazoase: *Crisoberil* *Cimofan* *Crisoberil-cimofan* Floarea pământului	**Cuart**	galben: *Citrin* *Cuart galben* *Cuarþ* Topaz de Bahia Cuart- topaz Topaz de Rio Grande Topaz scotian Topaz-cuart Cuart auriu de Boemia incolor, transparent: *Cuart* *Cristal de stâncă* *Cristal de munte* *Cuart hialin* Diamant de Arkansas Cristal hialin Diamant de Alaska Diamant cehesc Diamant mexican Diamant nemtesc Diamant săsesc Diamant Harkimer Diamant de Maramures incolor, transparent, cu fisuri: *Cuart* *Cristal de stâncă fisurat* *Craquelees* fumuriu închis, la negru: *Cuart fumuriu* *Morion* *Cuart* brun: *Cuart brun* *Cuart* *Cairngorn* incolor, translucid: *Cuart* *Cuart lăptos* fumuriu deschis, transparent: *Cuart fumuriu* *Cuart* Topaz fumuriu* roz: *Cuart* *Cuart roz* Rubin de Boemia* galben-brun, semitranslucid, cu incluziuni de **goethit:** *Cuart brun* *Cuart* *Binghamit*
	galben, cu incluziuni gazoase si incluziuni minerale ce determină efect ochi-de-pisică: *Crisoberil ochi-de-pisică* *Cimofan ochi-de-pisică* *Crisoberil* *Cimofan* Ochi de pisică de Ceylon		
Crisocol	toate culorile: *Crisocol* Kieselmalachit		
	din Ural: *Crisocol* Demidovit		
Crisotil	**(Clinocrisotil, paracrisotil** sau **ortocrisotil**; aspect fibros; culoare verde, verde-gălbui, verde-brună): *Crisotil* *Serpentină* *Serpentină nobilă* *Verde antic* Metaxit Jad coreean Marmolit Rhetinalit		
	verde: *Cromdravit* *Turmalină verde* *Verdelit* *Crom-turmalină* Smarald de Brazilia Smarald siberian Crisolit de Brazilia Peridot de Brazilia		

	verde, cu incluziuni de **actinolit**: *Prazem* *Cuart verde* *Cuart* Smarald-cuart Edinit fin granular, dispus în benzi concentrice: *Agat (toate culorile)* *Calcedonie*
	fin granular, dispus în benzi concentrice de diferite nuanțe de roșu-portocaliu *Agat* *Calcedonie* *Agat de foc* fin granular, dispus în benzi concentrice; prezintă irizatii multicolore *Agat cu irizatii* *Calcedonie cu irizatii* *Calcedonie* *Agat curcubeu* fin granular, dispus în benzi concentrice albe si negre) *Onix* *Calcedonie neagră* Piatră de Moka Piatra samanilor (Piatra vrăjitorilor) fin-granular, opac, de culoare neagră: *Agat negru* *Calcedonie neagră* *Onix* fin granular, translucid, dispus în benzi concentrice, maronii-brunii si albe: *Sardonix* *Onix-sarder* fin granular, opac, brun-maroniu, cu aspect ocular, cu zone circulare, în benzi fine, albe si maronii-brune concentrice: *Agat* *Nicolo* fin granular, alb, translucid, cu incluziuni dendritice de oxizi de mangan: *Calcedonie cu dendrite* *Dendrit* *Agat muschiform* fin granular, translucid, în nuante de brun: *Sarder* *Calcedonie* *Calcedonie brună* fin granular, galben-de-ceară, translucid: *Calcedonie galbenă* *Calcedonie* *Ceragat* fin granular, translucid, alb cu nuanțe albăstrui: *Calcedonie* Piatra Lunii albastră fin granular, cu incluziuni predominant lichide: *Calcedonie* *Calcedonie cu incluziuni lichide* *Enhydrus* fin granular, translucid, albastru deschis: *Calcedonie albastră* *Calcedonie* *Azurin* *Calcedonie safirinică*

·	Cuart fin granular, verde, opac sau semitranslucid, cu incluziuni de minerale din grupa cloritului: *Calcedonie verde* *Plasma*
	fin granular, translucid, rosu, galben-roscat: *Carneol* *Calcedonie rosie* *Calcedonie* *Cornalină* Carnelian Agat sânge-de-porumbel
	fin granular, translucid, galben-brun-roscat: *Carneol galben* *Semicarneol* *Calcedonie* Piatră-canar (Canary stone) fin granular opac sau semitranslucid, verde, **cu zone cu hematit**, pigmentate în rosu intens: *Heliotrop* *Calcedonie* *Piatră de sânge* Jasp de sânge Piatra martirilor fin granular, translucid sau semitranslucid, galben-verzui: *Calcedonie galben-verzuie* *Calcedonie* *Amberin* fin granular, translucid, verde deschis, cu continut de Ni: *Crizopraz* *Calcedonie* *Calcedonie verde* *Calcedonie naturală verde* *Prazer* Matostat transparent, verde, galben sau rosu-brun, cu incluziuni de **muscovit, muscovit** cromifer (fuchsit) sau hematit: *Aventurin* *Cuart aventurin* Jad indian albastru, albastru deschis, translucid: *Cuart albastru* incolor, transparent sau translucid, cu efect ochi-de-pisică: *Cuart ochi-de-pisică* transparent, incolor, cu incluziuni de **riebeckit** azbestiform (crocidolit) de culoare verde, verde-albăstruie: *Cuart ochi-de-soim* *Ochi-de-soim* transparent, incolor, cu incluziuni de **riebeckit** azbestiform (crocidolit) alterat, de culoare galbenă, galben-brună, brun-roscată: *Cuart ochi-de-tigru* *Ochi-de-tigru*
Danburit	incolor, galben deschis, galben: *Danburit*
Diamant	toate culorile: *Diamant*

	galben *Diamant galben* Diamant-canar (Canary diamond)	**Gips**	alb, roziu, gălbui, albăstrui: *Gips* *Alabastru* Spat satinat Californit fibros, galben, galben roscat, albastru deschis, verde deschis: *Gips* *Selenit*
Diopsid	incolor, verzui deschis, galben-verzui: *Diopsid* *Piroxen* cromifer verde intens: *Crom-diopsid* *Diopsid verde* *Piroxen* cu efect de asterism: *Diopsid stelat*		
Dioptaz	verde-smarald: *Dioptaz* Chrisocol-smarald Smarald de cupru Asirit	**Grossular**	toate culorile: *Grossular* *Granat* rosu-brun, brun: *Grossular* *Granat* Rubin californian Rubin (de) Montana incolor: *Grossular* *Granat* Leucogranat portocaliu, portocaliu-brun, galben, rosu, incolor, verde deschis: *Grossular* *Granat* *Hessonit* Essonit Piatră de scortisoară (Cinnamon Stone) Hiacint Jacinth verde-de-smarald, provenit din Kenia si Tanzania: *Tsavorit* *Tsavolit* *Grossular* *Grossular verde* *Granat* incolor, verde deschis, provenit din Siberia: *Grossular* *Granat* *Viliuit* Wiliuit brun: *Grossular* *Granat* Romanzovit
Disten	albastru intens: *Cianit* *Cianit albastru* *Disten albastru* *Disten*		
Dravit	galben-brun, verde-brun, brun: *Dravit* *Turmalină galben-brună*		
Dumortierit	albastru, violet:: *Dumortierit*		
Elbait	roz: *Elbait* *Turmalină roz* *Turmalină* incolor, transparent: *Acroit* *Turmalină incoloră* *Turmalină*		
Enstatit	verde, brun, galben: *Enstatit* *Piroxen*		
Epidot	verde, verde-gălbui, verde-cenusiu, galben: *Epidot* albastru sau rosu: *Piemontit* *Epidot*		
Euclaz	incolor, verde descis, albastru deschis: *Euclaz*		
Fluorină	toate culorile: *Fluorină* verde: *Fluorină verde* Smarald african Fals smarald violetă: *Fluorină violetă* Fals ametist rosie: *Fluorină rosie* Fals rubin albastră: *Fluorină albastră* Fals safir	**Hibschit**	verde deschis, galben-verzui, galben-brun: *Hibschit* *Hidrogranat* *Hidrogrossular* *Grossular verde* Jad de Transvaal Jad-granat Jad african
		Hematit	cenusiu de oțel: *Hematit*
Gahnit	verde-albăstrui, transparent: *Gahnit* *Gahno-spinel* *Spinel verde albăstrui* *Spinel* Zn-spinel	**Jadeit**	toate culorile; translucid: *Jad* *Jadeit* *Maw-sit-sit* *Piroxen* Yu Piatră sfântă Jad imperial Jad fin Jad fin de China

	verde închis, cu zone negricioase: *Cloromelanit* *Jadeit* Jad
Kornerupin	alb, galben-brun: *Kornerupin* verde: *Kornerupin verde* *Prismatin*
Labradorit	reflexe multicolore; incluziuni de **hematit, ilmenit**: *Labradorit* *Feldspat* reflexe albastre; incluziuni de **ilmenit**: *Labradorit* *Feldspat* *Labradorit ochi-de-bou* Ochi de bou efect de Piatra Lunii: *Feldspat* *Labradorit-Piatra Lunii* *Labradorit* reflexe verzui: *Labradorit* *Feldspat* *Labradorit- Ochi de linx* Ochi de linx reflexe multicolore; incluziuni de **hematit, ilmenit**: *Labradorit* *Feldspat* *Spectrolit*
Lazulit	albastru: *Lazulit* Spat albastru albastru, albastru-indigo: *Lazurit* *Lapis-lazuli* *Lapis* Ultramarin
Leucit	alb, alb-gălbui: *Leucit*
Lizardit	verde închis, verde-gălbui; semitranslucid: *Lizardit* *Serpentină* *Serpentină nobilă* *Verde antic* Marmură de Connemara Oficalcit Ofit verde de măr, foarte translucid: *Williamsit* *Serpentină nobilă* *Serpentină*
Malachit	verde: *Malachit*
Marcasit	galben-verzui, galben deschis; metalic: *Marcasit*
Microclin	toate culorile: *Microclin* *Feldspat*

	verde închis, verde albăstrui, verde gălbui, turcoaz, galben: *Amazonit* *Microclin* *Feldspat* Jad de Amazon* Piatra Amazonului
Montebrasit	alb, alb-verzui, alb-albăstrui; opac sau translucid: *Montebrasit*
Nefelin	incolor, transparent: *Nefelin* *Eleolit*
Olivină	verde, verde-gălbui: *Olivină* *Peridot* *Forsterit* Hawaiit Crisolit
Opal	în culori diverse; cu irizații: *Opal* *Opal comun* galben, translucid: *Opal de miere* *Opal* galben-brun, opac: *Opal de ceară* *Opal* negru, cu irizații: *Opal negru* *Opal nobil* *Opal pretios* *Opal* portocaliu, rosu-portocaliu, translucid: *Opal de foc* *Opal nobil* *Opal pretios* *Opal* Opal de aur cu irizatii monocolore: *Opal-fulger* (Flash opal) *Opal* brun-gălbui: *Opal* *Fiorit* cu irizatii intense: *Opal arlechin* *Arlechin* *Opal nobil* *Opal pretios* transparent, sticlos, cu irizatii: *Opal de apă* *Opal* *Girasol* verde: *Opal verde* *Opal* *Forcherit* comun, sticlos, albăstrui: *Opal* Schnide incolor, transparent, fără irizatii) *Hialit* *Opal* *Opal vitros*

	cu irizatii în nuante de albastru-violet, albastru-verde si rosu, din Slovacia: *Opal nobil* *Opal preţios* *Opal unguresc* alb, opac, **fără irizatii**: *Hidrofan* rosu comun: *Opal rosu* *Opal* *Rubolit* din trunchiuri de arbori silicifiati: *Opal* *Opal de lemn* *Opal lemnos* alb, semitranslucid, cu dendrite de oxizi de mangan: *Opal* *Opal dendritic* verde cu continut de Ni: *Prasopal* *Opal*		rosu intens: *Pirop* *Granat* Granat de Boemia Crisolit cehesc Rubin cehesc Rubin de Colorado Rubin american Rubin de Adelaide Rubin de Arizona Spinel de Arizona Rubin de Cap Caprubin
		Pirop + Almandin	roz, roz-roscat, transparent; amestec izomorf de **pirop** si **almandin**: *Rodolit* *Granat*
		Pirop + Spessartin	portocaliu, roz, rosu; amestec izomorf de **pirop** si **spessartin**; provenit din Tanzania: *Malaya* *Granat*
Ortoclaz	roz, rosu-brun, incolor; translucid, transparent: *Ortoclaz* *Feldspat* Ortoză roz, rosu-brun, translucid sau transparent, cu incluziuni de hematit, goethit sau muscovit: *Feldspat-aventurin* *Feldspat* *Piatra Soarelui* Piatra Lunii de Madagascar Heliocit Aventurin incolor, alb, alb-albăstrui, transparent sau translucid: *Adular* *Ortoclaz* *Feldspat* incolor, alb, alb-albăstrui, transparent sau translucid, ce prezintă efect de Piatra Lunii: *Adular-Piatra Lunii* *Piatra Lunii* *Adular* Filinit Opal de Ceylon alb, translucid, cu irizatii: *Adular* *Valencianit*	**Prehnit**	verde deschis: *Prehnit* Smarald de Cap Crisolit de Cap
		Rodocrozit	roz, roz-violace, roscat: *Rodocrozit* Dialogit Spat de mangan
		Rodonit	roz, roz-cenusiu, rosu, roz-violet: *Rodonit*
		Schorl	negru, opac: *Schorl* *Turmalină neagră* Piatră Jet
		Sfalerit	rosu-brun, translucid sau transparent: *Sfalerit* *Blendă* Rubin-blendă Black Jack brun-gălbui, galben, galben-roscat, translucid: *Sfalerit* *Blendă* *Cleiofan*
		Smithsonit	toate culorile: *Smithsonit* *Bonamit* Piatra aztecilor
		Sodalit	albastru, cenusiu-albăstrui: *Sodalit* Ditroit
Pirită	culoare galbenă, luciu metalic: *Pirită* Piatra Inca Piatra incasilor	**Spessartin**	portocaliu, rosu închis, galben-portocaliu: *Spessartin* *Granat*
Pirofilit	în mase compacte, semitranslucide, de culoare albă, gălbuie, verzuie: *Agalmatolit* *Pirofilit* Biharit Koreit Pagodit	**Spinel**	toate culorile: *Spinel* (Mineral din grupa *spinelului*; rosu închis): *Spinel* *Spinel rosu* Rubin-balas Rubin-trandafir (Mineral din grupa *spinelului*; rosu deschis: *Spinel rosu* *Spinel* Rubin-spinel
Pirop	rosu, rosu-brun, negru: *Pirop* *Granat*		

	(Mineral din grupa *spinelului*; galben-portocaliu): *Spinel galben* *Spinel* Rubicel (Mineral din grupa *spinelului*; portocaliu) *Spinel portocaliu* *Spinel* Spinel flacără (Mineral din grupa *spinelului*; violet: *Spinel violet* *Spinel* Ametist oriental Almandin-spinel Almandin-rubin (Mineral din grupa *spinelului*; negru): *Spinel negru* *Ceylonit* Candit (Mineral din grupa *spinelului*; brun): *Spinel brun* *Spinel* *Picotit*
	(Mineral din grupa *spinelului*; albastru): *Spinel albastru* *Spinel* Safir-spinel
Spinel	(Mineral din grupa *spinelului*; negru-violet) Pleonast *Spinel negru* *Spinel*
Spodumen	toate culorile: *Spodumen* verde, transparent: *Spodumen verde* Hiddenit Smarald de litiu roz, transparent: *Spodumen roz* Kunzit Ametist de litiu
Staurolit	brun, maclat: *Staurolit* Piatra Crucii Piatră încrucisată Lapis crucifer Piatra de botez de Bâle Piatra de botez de Basel
Stichtit	roz, roz-violet: *Stichtit* Serpentin roz
Sugilit	violet-roziu; translucid, opac: *Sugilit*
Taaffeit	violet: *Taaffeit*
Talc	în mase compacte de culoare albă, alb-verzuie, alb-gălbuie, alb-crem, alb-roziu: *Steatit* *Talc* *Piatră grasă* Saponit Spekstein Masă spumoasă Piatră de săpun (Soapstone) Jad de Manciuria
Thomsonit	alb-roziu, galben-verzui: *Thomsonit* Piatră ochi (Eye stone)
Titanit	galben, galben-brun, galben-roziu: *Titanit* Sfen
Topaz	toate culorile: *Topaz* Crisolit săsesc roz: *Topaz roz* *Topaz* Rubin brazilian
	albastru-verzui deschis: *Topaz albastru* *Topaz* Acvamarin brazilian incolor: *Topaz incolor* *Topaz* Topaz de argint Diamant săsesc Diamantul robilor albastru: *Topaz albastru* *Topaz* Smarald de Brazilia Topaz siberian
Tremolit	alb, alb-verzui, translucid: *Tremolit*
Turcoază	toate culorile: *Turcoază* Piatra sfântă a aztecilor Peruzea Kallait asociată cu oxizi de mangan si/sau fier: *Turcoază matrix* *Turcoază*
Turmalină	(Minerale din grupa *turmalinei* - toate culorile): *Turmalină* zonată cu centrul rosu si zona externă verde: *Turmalină-pepene* *Turmalină* cu centrul rosu si bordura exterioară de culoare neagră: *Turmalină-cap de maur* *Turmalină* albastră închis: *Turmalină albastră* Indicolit Indigolit rosu închis: *Turmalină rosie* Rubellit *Turmalină* roz intens: *Turmalină roz* Apirit *Turmalină* toate culorile, cu efect ochi-de-pisică: *Turmalină ochi-de-pisică* *Turmalină*

	rosie: *Turmalină rosie* *Tubelit* *Turmalină* Rubin de Siberia albastră sau verde: *Turmalină albastră* sau *verde* *Turmalină* Safir brazilian violet: *Turmalină violet* *Turmalină* Siberit galbenă: *Turmalină galbenă* *Turmalină* *Tsilaisit* Peridot de Ceylon rosie: *Turmalină rosie* *Turmalină* Daourit		albastru intens: *Vezuvian albastru* *Vezuvian* Cyprin
Uvarovit	verde: *Uvarovit* Granat	**Zircon**	toate culorile: *Zircon* incolor, transparent: *Zircon incolor* *Zircon* Diamant de Matara Diamant de Ceylon galben: *Zircon galben* *Zircon* *Jargon* rosu: *Zircon rosu* *Zircon* *Hiacint* Jacinth albastru: *Zircon albastru* *Zircon* Acvamarin siamez verde: *Zircon verde* *Zircon* Beccarit brun: *Zircon brun* *Zircon* Malacon alb-albăstrui: *Zircon* *Starlit*
Uvit	galben-brun: *Uvit* *Turmalină brună* *Turmalină* Mg-turmalină		
Varsicit	incolor, verde intens: *Variscit* Utahlit în mase compacte cu structură în benzi de diferite nuante de verde: *Variscit* Trainit		
Vezuvian	verde deschis, verde-gălbui, verde-brun: *Vezuvian* *Idocras* Californit Jad pakistanez Egeran Gema Vezuviului galben: *Vezuvian galben* *Vezuvian* Xantit verde-brun: *Vezuvian verde-brun* *Vezuvian* Viliuit verde: *Vezuvian verde* *Vezuvian* Jad american	**Zoisit**	toate culorile: *Zoisit* (**Zoisit** roz) *Zoisit roz* *Thulit* albastru-violet închis: *Zoisit violet* *Tanzanit* Safir de Meru cenusiu-verzui: *Zoisit* Zoisit de California verde, din Tanzania: *Tanzanit verde* *Zoisit* cu efect ochi-de-pisică: *Zoisit* *Zoisit ochi-de-pisică*

NOTĂ: *Denumirile acceptate pentru varietătile gemologice sunt redate cu caractere italice.*

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În nomenclatura substanţelor minerale naturale, termenul *semipreţios* a fost înlocuit cu cel de *piatră fină* iar expresia **piatră gemă** se utilizează numai pentru substanţe naturale.

Tabel 4
Nomenclatura unor asociaţii minerale şi roci utilizate în gemologie

Substanta	Varietăti gemologice
Argilă silicioasă rosie	Piatră de pipă
Aragonit + calcit	Aragonit italian Onix italian
Calcit + malachit sau azurit	Cerulin
Jasp de Arizona	Zunit
Jasp fin stratificat	Piatră zebrată
Obsidian	Jet de Montana Lignit de Montana *Sticlă vulcanică* Agat de Islanda *Obsidian - fulgi de zăpadă*
Cuart fin granular	*Jasp*
Cuart fin granular	*Jasp multicolor*
Cuart fin granular	*Jasp-porbelan*
Cuart fin granular	*Jasp* *Silex* *Chert*
Elemente rulate de pietris din aluviuni	*Agate de râu*
Tectit	*Tectit* *Australit* *Moldavit* Crisolit de apă Fals crisolit Georgiait

Adjectivele *veritabil, preţios, fin - fină, natural* sau alţi analogi se raportează exclusiv la pietre naturale şi anume: pietre preţioase, pietre fine, pietre de ornament precum şi substanţe organice, cu calităţi de geme. Aceste adjective nu se vor utiliza pentru produsele artificiale.

Nu se utilizează denumirea unui mineral sau al unei pietre-gemă pentru calificarea culorii unei alte pietre (exemplu: spinel-rubin pentru *spinel* de culoare roşie, safir-alexandrit pentru *safir* cu efect "alexandrit" etc.).

Nu se folosesc combinaţii de denumiri de geme care nu au nimic comun între ele. În acest sens, sunt acceptate denumiri ca: *citrin, cuarţ* galben, dar nu sunt acceptate expresii ca topaz-cuarţ sau cuarţ-topaz, citrin-topaz sau topaz-citrin.

Nu se utilizează termeni legaţi de tipul de tăiere-şlefuire (briliant, rozetă, baghetă etc.) fără adăugarea denumirii exacte a pietrei, cu excepţia **diamantelor** tăiate tip briliant. Indicaţiile privind tipul de tăiere-şlefuire trebuie date în forma:
- *safir* tăiat briliant (şi nu safir briliant)
- **diamant** tăiat rozetă
- *smarald* tăiat în formă marchiz
- *smarald* în formă de baghetă
- *rubin* tăiat tip-smarald
- *turmalină* fasonată în formă de baghetă
- *safir* tăiat caboşon

Fenomenele optice speciale, cum sunt efectul "ochi-de-pisică", aventurescenţa, asterismul etc., sunt marcate prin cuvinte compuse asociind fenomenul cu denumirea gemei (exemple: *crisoberil ochi-de-pisică* sau *safir stelat, rubin stelat* etc. Aceeaşi regulă se aplică şi pietrelor sintetice (ex. crisoberil sintetic ochi-de-pisică, rubin sintetic stelat etc.). In afara tăierii şi şlefuirii, gemele şi substanţele organice sunt adesea tratate pentru îmbunătăţirea unor proprietăţi, cum sunt culoarea şi/sau aspectul. Dintre tratamente, trebuie specificate clar următoarele:
- *iradierea:* modificarea culorii prin iradiere ;
- *colorarea artificială:* modificarea culorii prin difuzie-depunere sau cu ajutorul agenţilor coloranţi chimici sau de altă natură;

Tabel 5
Nomenclatura substanțelor de origine organică utilizate în gemologie

Substanta	Varietăți gemologice	Denumire comercială
Ambră	Ambră	*Ambră* Succinit
	Simetit	*Ambră* Simetit
	Bucharamangit	*Ambră* Bucharamangit
	Burmit	*Ambră* Burmit Birmit
	Rumanit	*Chihlimbar* *Ambră* Rumanit Muntenit
Baga	Baga	Baga
Copal	Copal	*Copal*
Coral	Coral	*Coral* Mărgean
	Coral rosu, roz	Coral nobil Corai Coralină
	Coral negru	*Coral negru* Accabar
	Coral (mărgele)	*Coral* Perle de Marea Rosie
Fildes	Fildes	*Fildes* Ivoriu
Gedanit (rășină)	Gedanit	*Gedanit*
Glessit (rășină)	Glessit	*Glessit*
Grandel (dinti de ren)	Grandel	*Grandel*
Jet	Jet Gagat	*Jet* Jais Gagat Ambră neagră Chihlimbar negru
Lemn silicifiat	Lemn silicifiat	*Lemn silicifiat*
Lumasel	Lumasel	*Lumasel* Marmură de scoici
Odontolit (Dinti de mamifere cuaternare)		*Odontolit* *Turcoază falsă* *Imitatie de turcoază*
Perle	Perle	*Perle* (diferentiat - vezi tab. 7 si 8)
Pseudomorfoze de aragonit după cochilii de ammoniți	Ammolit	*Ammolit* *Ammonit*
Retinit (rășină)	Retinit	*Retinit*
Sidef	Sidef	*Sidef* Nacru Camee

NOTĂ: Denumirile comerciale corecte sunt redate cu caractere italice iar cele incorecte, cu caractere normale.

- *tratarea:* obturarea adânciturilor sau cavităţilor externe cu ajutorul materialelor plastice, sticlei sau altor substanţe (minerale sau neminerale).

Informaţiile cu caracter general vor menţiona tratamentele considerate a fi de practică curentă, cum sunt:
- impregnarea unei geme cu un agent incolor, cum ar fi ulei, ceară sau orice altă substanţắ organică incoloră (tratament frecvent în cazul *smaragdelor, jadului,* **turcoazei** etc.);
- tratamentul termic cu efect permanent (de uz curent îndeosebi pentru **corindon, beril, cuarţ, zoisit, turmaline, topaz** etc.);
- schimbarea culorii unui *agat* prin tratament termic sau prin acţiunea unei soluţii colorante.

Documentele comerciale sau certificatele de expertiză gemologică trebuie să conţină cel puţin un comentariu general dacă:
- gemele au fost încălzite înainte şi/sau după tăiere, în scopul ameliorării culorii şi transparenţei;
- gemele au fost impregnate înainte şi/sau după tăiere cu un ulei incolor sau cu răşini naturale sau artificiale incolore în scopul îmbunătăţirii transparenţei.

Se acceptă doar unele denumiri comerciale pentru geme (tabelele 2, 3, 4, 5).

Documentele comerciale nu trebuie să conţină nici o indicaţie legată de originea gemelor respective. În documentele oficiale, toate calificativele unei geme se trec cu caractere de aceeaşi mărime şi culoare ca şi denumirea pietrei. Nu se folosesc prescurtări.

Articolele de bijuterie care conţin atât pietre naturale cat şi pietre artificiale trebuie să menţioneze acest lucru.

Certificatele şi atestatele de laborator trebuie să conţină:
- clasificarea produsului (cf. reglementărilor CIBJO);
- denumirea lui comerciala (cf. Nomenclatorului CIBJO);
- culoarea (în cazul în care Nomenclatorul CIBJO menţionează posibilitatea situaţiei "toate culorile");
- dimensiunile;
- greutatea;
- forma.

În cazul indicării greutăţii unei pietre colorate, în carate (prescurtare internaţională ct), valoarea acesteia trebuie să aibă 2 zecimale după virgulă. Se poate rotunji la zecimala superioară numai dacă a treia zecimală este 9. De asemenea, nu se indică numai greutatea pietrei centrale sau a celor mari.

B. Substanţe organice naturale

Nomenclatura diverselor substanţe organice naturale utilizate în gemologie este prezentată în tabelul 5.

Pe certificatele de expertiză nu se menţionează tratamente de tipul albirii coralului sau fildeşului dar se specifică colorarea artificială.

Reglementările privind nomenclatura perlelor (tabelul 6) sunt cuprinse în Le livre des perles (CIBJO, 1996) şi se referă la următoarele aspecte:
- descrierea exemplarelor de perle se face conform clasificărilor actuale (perle fine, perle de cultură, perle de cultură compuse şi imitaţii de perle);
- in cazul documentelor, pentru denumirile şi caracteristicile perlelor se utilizează caractere de acelaşi tip şi dimensiune;
- obiectele care conţin mai multe categorii de perle, vor menţiona explicit acest lucru;
- atestatele şi certificatele de laborator vor menţiona tipul de perlă, eventual denumirea comercială, culoarea (cu specificaţia dacă este naturală sau artificială), greutatea, dimensiunile, forma; nu este necesara identificarea locului de origine.
- adjectivele *fin, preţios* etc. nu se utilizează decât pentru pentru perle fine (perle, blistere, perle-blister);
- termenul singular de perlă se poate aplica numai perlelor fine;
- expresiile "perlă de Orient" şi "perlă de apă dulce" se utilizează numai pentru perlele naturale;
- nu se utilizează expresia "perlă de Japonia" sau "perlă japoneză" pentru a desemna perlele de cultură produse în Japonia, perlele hemisferice sau imitaţiile de perle;
- perlele de cultură compuse se definesc ca atare.

C. Substanţe minerale artificiale (tabelul 7)

Produsele sintetice sunt întotdeauna desemnate prin termenul *sintetic* sau *artificial* care insoţeşte denumirea pietrei produse artificial (ex.: rubin sintetic, spinel sintetic) (Nickel, 1996).

Tabel 6
Nomenclatura perlelor (cf. CIBJO, 1997)

Categoria	Subcategoria	Tipul
PERLE	Perle marine	Perle - toate culorile Perle de Orient Perle Abalone Blistere, Perle blister Seeds Perle roz, Perle conche
	Perle de apă dulce	Perle - toate culorile Perle de râu Perle mulette Blistere, Perle blister Seeds
PERLE DE CULTURĂ	Perle de cultură marine, cu sau fără nucleu artificial	Perle de cultură Perle de cultură Akoya Perle de cultură din mările sudului Perle de cultură de Tahiti
	Perle de cultură de apă dulce, cu sau fără nucleu artificial	Perle de cultură Perle de cultură Biwa Perle de cultură chinezesti Perle de cultură de apă dulce

O piatră sintetică poate primi denumirea pietrei-gemă căreia ii corespunde prin proprietăţile fizice, chimice şi cristaline cu condiţia ca acesta denumire să fie imediat urmata de menţiunea *sintetic* sau *artificial*. Nu se folosesc alţi termeni decât **sintetic** sau **artificial** pentru produsele obţinute prin cristalizarea sau recristalizarea provocate total sau parţial de către om. Calificativul *sintetic* sau *artificial* poate fi urmat de numele mărcii sau al fabricantului. De ex., nu se folosesc expresii ca:

- smarald "Chatham" sau "Gilson" sau "Linde"

- rubin creaţie Knischka, smarald creat de Inamori sau smarald de sinteză (cultură) Linde;

- rubin de cultură Gilson sau Ramaura etc., nici alţi termeni cum sunt: *producţie, reproducţie, replică* sau *înrudit*.

Se utilizează numai denumiri ca:

- smarald sintetic sau artificial "Chatham", sau smarald sintetic sau artificial "Gilson" sau smarald sintetic sau artificial "Linde" etc.

- rubin sintetic "Knischka" etc.

Nu se utilizeaza denumiri de zone geografice de provenienţă a gemelor, sau numele centrelor de şlefuire sau de export pentru caracterizarea produselor sintetice, artificiale sau de imitaţie.

Produsele artificiale cristaline care nu au echivalent cunoscut in natură sunt întotdeauna denumite de expresia *produs artificial*, chiar dacă poartă o denumire fantezi. De ex.: Fabulit - produs artificial; Titanat de stronţiu - produs artificial; Linobat (niobat de litiu) - produs artificial; YAG (aluminat de ytriu) - produs artificial.

Denumirea fantezii sau de marcă nu trebuie să prezinte similitudine totală sau parţială cu denumirea unei pietre geme sau al unei substanţe organice cu calităţi de geme. Exemplu, nu se folosesc denumiri ca: diamantin, diamlit, diamonair, smaril, emeraldolit etc.

Tabel 7
Substanțe naturale sau artificiale utilizate pentru imitarea gemelor

Gema imitată	Substanța utilizată	Denumire comercială
Acvamarin	Spinel albastru sintetic	Spinel sintetic Acvamarin
Ambră	Fragmente de ambră + liant	Chihlimbaroid - produs artificial Ambroid - produs artificial
Ambră	Fragmente de ambră	Ambră presată - produs artificial Chihlimbar presat - produs artificial
Citrin	Ametist	*Citrin artificial* Topaz auriu Topaz de Madeira Topaz (de) Palmira Topaz cehesc Topaz indian Topaz de Salamanca Topaz spaniol Fals topaz
Cuarț-aventurin	Sticlă-aventurin	*Imitație de aventurin* *Aventurin - produs artificial* Goldfluss
Cuarț verde	Ametist Citrin	*Praziolit - produs artificial* *Cuarț verde - produs artificial*
Diamant	Oxid de calciu și zirconiu	*Djevalit - produs artificial*
Diamant hline	Titanat de stronțiu	*Fabulit - produs artificial* Diagem Symant
Diamant	Sticlă	*Strass - produs artificial* Similidiamant
Diamant incolor, roz sau verde	Granat sintetic, de ythriu și aluminiu	*YAG - produs artificial* Diamonair
Diverse geme	Sticlă	*Sticlă* Pastă Schmelye
Feldspat-aventurin	Sticlă-aventurin	*Imitație de feldspat-aventurin* *Feldspat-aventurin - produs artificial* *Imitație de Piatra Soarelui* *Piatra Soarelui - produs artificial*
Fildeș	Oase animale + clorură de var	*Fildeș artificial*
Granat	Granat sintetic, cu galiu și gadoliniu	*Galliant - produs artificial*
Granat incolor, roz sau verde	Granat sintetic, de ythriu și aluminiu	*YAG - produs artificial* Diamonair
Kunzit	Safir roz sintetic	*Safir roz sintetic* Kunzit roz
Obsidian	Sticlă verde	*Sticlă* Obsidian-smarald
Obsidian	Sticlă verde	*Sticlă* *Helenit - produs artificial*
Opal nobil	Opal comun	*Opal (tratat)* *Opal cameleon - produs artificial* *Cameleon - produs artificial*

Rubin	Corindon roşu sintetic	*Rubin sintetic* Danburit
Rutil	Rutil	*Rutil sintetic* *Titania - produs artificial* Diamonit
Turcoază	Ceramică	*Turcoază falsă* *Imitaţie de turcoază* Turcoază vieneză
Turcoază	Howlit	*Howlit* *Turcoază falsă*
Turcoază	Calcedonie	*Imitaţie de turcoază* *Turcoază falsă* Neoturcoază Neolit Turcoază de Hamburg Turcoază Reese
Zircon albastru	Malacon (zircon brun)	*Zircon (tratat)* Acvamarin siamez Starlit

NOTĂ: Denumirile comerciale corecte sunt redate cu caractere italice iar cele incorecte cu caractere normale.

Termenii *crescut, cultivat* sau *de cultură* nu se folosesc pentru substanţe neorganice.

Pietrele compozite (pietrele compuse, pietrele asamblate) poartă obligatoriu denumirea dublet sau triplet, după caz, urmat de numele componenţilor pietrei, începând cu piatra din partea de deasupra. Exemplu, un dublet format la partea superioară dintr-un granat iar la partea inferioară dintr-o sticlă albastră nu se numeşte "dublet safir" sau "dublet granat" ci "dublet granat-sticlă".

Imitaţiile de minerale nu se definesc prin termeni ca: *reproducţie, replică, re-creaţie, cultură înaltă (haut culture), ştiinţific* etc.

D. Substanţe organice artificiale

Se cunosc o serie de materiale, organice sau minerale, care sunt destinate imitării unor substanţe organice utilizate în gemologie (tabelul 7), îndeosebi chihlimbarul, fildeşul, perlele şi bagaua. Nomenclatura acestora este variată şi conţine, în general, expresia "produs artificial".

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MAJOR AND MINOR ELEMENTS IN PEGMATITE-FORMING MINERALS OF THE GILĂU MOUNTAINS AS METALLOGENETIC INDICATORS

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Key words: Apuseni Mountains. Gilău Mountains. Metallogenetic potential. Geochemistry. Pegmatites. Potassium feldspars. Muscovite. Garnets. Tourmaline.

Abstract: This approach represents a geochemical attempt in order to identify the metallogenetic potential of the Gilău Mountains pegmatites, hosted by medium-grade metamorphic rocks of the Someş Series, east of the Muntele Mare granitoid intrusion. In this respect wet- chemical, electron microprobe and spectral analysis as well have been performed. A comparative evaluation of the geochemical features (major and minor elements) in respect to geochemical data published for the Romanian territory and those published in geological literature from abroad shows that most pegmatites of the Gilău Mountains belong geochemically to the field of *unmineralized (barren) pegmatites* (mica-bearing and feldspars-bearing pegmatites). However, some occurrences from the area fall in a transition field between the barren and the *mineralized pegmatites* (rare elements-bearing pegmatites). This is a specific feature of the Gilău Mountains pegmatites that makes the difference in respect to pegmatites in the rest of the Carpathian pegmatite province. The use of some so-called diagnostic diagrams (Li and Rb in potassium feldspars; phengite: muscovite: annite, Al_{IV} vs. Al_{VI}, ΣY vs. R^{2+}_Y, Li vs. $(Al_{IV}+Al_{VI})$, $C_{Li2O}{}^{Mus}$ vs. T ^0C, Rb vs. K/Rb, $C_{Rb2O}{}^{Mus}$ vs. T ^0C, Li and Rb - in muscovite; MgO: FeO: MnO, pyrope: almandine: spessartine - in garnets; Al:Fe_{tot}: Mg in tourmaline) leads to similar results.

Introduction
Regional setting of pegmatite bodies

In his classification scheme on pegmatites on the Romanian territory, Mărza (1980) considers that all pegmatite occurrences are parts of the so-called *Carpathian Pegmatite province*, that can be reduced to four subprovinces as follows: *Rodna Pegmatite subprovince, Preluca Pegmatite subprovince, Getic Pegmatite subprovince* and *Gilău-Muntele Mare Pegmatite subprovince*. Pegmatite bodies of the Gilău Mountains form part of the Gilău-Muntele Mare Pegmatite subprovince, a more specific part of the *Someşul Rece-Iara valley Pegmatite district*; this one as well as the *Geamăna-Măzăratu Pegmatite district*, represent subdivisions of the subprovince mentioned above. In the first pegmatite district (split by Marza - 1980 in two fields: *Muntele Rece* and *Iara Valley*, respectively), pegmatite bodies are hosted by the medium-grade metamorphic rocks of the Someş Series (group), whereas in the second one pegmatite bodies are located in the medium-grade metamorphic series of Baia de Arieş.

East of the Muntele Mare granitoid intrusion – the study area, in this approach – medium-grade metamorphic series of Someş consists mostly of migmatites, leptynites, gneiss, almandine-disthen-staurolite-sillimanite micaschists, as well as quartzites, amphibolites and accidentaly crystalline limestones. Detailed approach led by some geologists on the lithostratigraphy of this geological area (Borcoş and Borcoş, 1962; Hârtopanu et al., 1982 a-b, 1986 etc.) revealed two lithostratigrapic formations in the Someş Series located east of the granitoids of Muntele Mare: *the lower terrigenous formation* and *the middle formation of quartz-feldspars gneiss*. Dimitrescu (1994) showed the superior position of the so-called *lower terrigenous formation* over the middle formation of quartz-feldspars gneiss; this one was called the *gneiss formation of Corabia* and it is not similar – in the author's opinion – to the middle formation of quartz-feldspars gneiss located west of the Muntele Mare intrusion-forming granitoids.

Typical dikelike and lensoid shapes have been assumed for pegmatites of the Gilău Mountains. Thus, pegmatite lenses are rather small, while simple or ramified veins have lengths of meters to hundreds of meters and thickness ranging between less than a centimeter to 10-20 m.

The mineralogy of pegmatites is simple; these rocks consist mostly of coarse-grained *quartz* (many generations) and *K-feldspars* (generally maximum and intermediate microcline), plus *Ca-Na-feldspars* (albite-low albite and oligoclase) and *muscovite*; as subordinate minerals *biotite, tourmaline* and *garnets* have been noticed. The presence of *beryl, cordierite, staurolite, sillimanite* and *amphyboles* have been notified, too. Pegmatite bodies are ordinarily uniform from wall to wall, both in composition and texture. The simple mineralogy could be the result of metamorphic differentiation or even anatectic process we consider to be responsible for the genesis of pegmatite bodies in the Gilău Mountains.

Finally, in terms of geochemical features, pegmatite bodies in the Someşul Rece-Iara Valley district have a granite-like composition.

Analytical techniques

A geochemical approach on the metallogenetic potential of the Gilău Mountains pegmatite bodies needs as any geochemical approach do - specific analytical techniques for major and minor elements as well. As a result, the following types of analyses have been performed: wet-chemical analysis, electron microprobe analysis (performed on a CAMECA SX 50), spectral analysis (performed on a PGS-2 JENA emission spectrograph and on an optical emission spectrometer with ICP excitation source – ICP-MS). Most of the data performed by the wet-chemical method represent the result of activity carried out by the Geological Institute of Romania in the middle seventies (Iosof et al., 1975; Constantinescu et al., 1976), whereas the electron microprobe analyses have been performed by the author of this paper in the Laboratory of Petrology (University Paris VI-France). The author gratefully thanks Professor Jean-Hugues Thomassin from ESIP Poitiers (France), who provided ICP-MS analysis for lithium and rubidium.

Major and minor elements in minerals as metallogenetic indicator

Potassium feldspars

Barium in feldspars as metallogenetic indicator. The barium bulk composition of potassium feldspars (2305 ppm – electron microprobe analysis) falls in a range values represented by the results published for the potassium feldspars of Bihar Siberia (1900 ppm Ba) and for the microcline of Mamsk-Siberia (3137 ppm Ba), respectively. Moreover, in terms of Gordienko's classification (1976) (in Trueman and Černý, 1982), the barium composition in pegmatite potassium feldspars of the Gilău Mountains plots these rocks in the field of *muscovite-bearing pegmatite provinces*; however, there are samples that plot in the field of *rare elements-bearing pegmatites provinces*, as well.
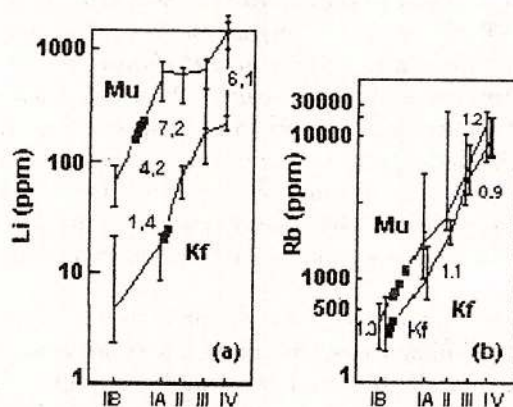
Fig. 1 – Li and Rb in muscovites (Mu) and potassium feldspars (Kf) in different types of pegmatites: rare elements pegmatites from mica-bearing provinces (IA), barren pegmatites from mica-bearing provinces (IB); muscovite+feldspars (+Be, Nb, Ta)-bearing pegmatites (II); spodumene+Li, Be, Ta, (Nb, Sn)-bearing pegmatites (III), spodumene+lepidolite+Li, Cs, Ta, Be (+NB, Sn)-bearing pegmatites (IV) (Trueman and Černý, 1982).

Lithium in feldspars as metallogenetic indicator. The lithium in potassium feldspars bring information on the metallogenetic potential of pegmatites. Thus, the projection of our data on the diagram in Figure 1

shows the belonging of the Gilău Mountains pegmatites to the *mica-bearing pegmatite provinces with a theoretical potential for accumulation of rare elements.*

Rubidium in feldspars as metallogenetic indicator. A comparison of our data on rubidium amounts in potassium feldspars (291 ppm and 364 ppm Rb, respectively) with those published by other geologists shows a medium position of samples from the Gilău Mountains between Gaweda's (1992) data (150 ppm Rb-pegmatites from western Tatra Mountains) and Trumbull's (1995) ones (535 ppm Rb-border zone of a rare metals pegmatite body at Sinceni, Swaziland), respectively. In such a context, it seems interesting to notice the range of 3109 ppm - 1,65 % Rb identified by Černý and Lenton (1995) in the peculiar case of granite pegmatite bodies of Buck and Pegli (Manitoba).

Table 1 $(Rb/K) \times 10^3$ in some potassium feldspars in pegmatites

Occurrences	$(Rb/K) \times 10^3$	Authors
Pegmatite subprovince of Gilău-Muntele Mare		
Ms-87*, Raşca Mare Valley	9.27	
Ms-141*, Iara Valley	5.74	
Pegmatite subprovince of Preluca	4.5	Murariu et al. (1997)
Pegmatite subprovince of Rodna	4.3	Murariu et al. (1997)
Comparative data		
Baikal - Russia		
Ceramic pegmatites	5.2	Manuilova et al. (1966)[1]
Mica-bearing pegmatites	4.1	
Rare metals-bearing pegmatites	14.7	
Siberia - Russia		
Bifeldspars-bearing pegmatites	16.0	Zagorsky and Kuznetzova
Albite-bearing pegmatites	27.7	(1990)[1]
Albite+spodumene-bearing pegmatites	40.1	
Russia		
Muscovite+microcline-bearing pegmatites	0.4	Salyie and Glebovitzky
Oligoclase+microcline-bearing pegmatites	0.4	(1976)[2]
Albite+spodumene-bearing pegmatites	7.5	
Spodumene+lepidolite-bearing pegmatites	10.1	

[1] in Murariu et al. (1997); [2] in Murariu et al. (1998); * Analyses performed on an ICP-MS
(analyst: J.-H. Thomassin, E.S.I.P. Poitiers, France)

Using the Trueman and Černý's (1982) diagram (Fig. 1) we could notice that, in respect of rubidium in potassium feldspars, pegmatites of the Gilău Mountains fall in the *mica-bearing pegmatites* field. Finally, $(Rb/K \times 10^3)$ parameter (Table 1) places the pegmatites of Romania (pegmatite subprovinces of Preluca, Rodna and Gilău-Muntele Mare) between the *mica-bearing* and *feldspars-bearing pegmatites*, respectively, of Russia.

Muscovite

Major elements in muscovite as metallogenetic indicator. The participation of major elements as well as of minor elements in pegmatite muscovite give information on the metallogenetic potential of pegmatites. In terms of major elements, the phengite-muscovite-annite diagram has been used in a first stage. The projection of our data in this diagram reveals that most of muscovite samples plot in the *rare elements-bearing pegmatites field* (Fig. 2); only one sample has been placed in the *muscovite-bearing pegmatite field*.
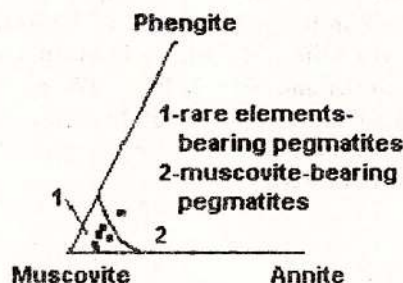
Fig. 2 – Mg:(Al, Fe^{3+}, Ti):(Fe^{2+}, Mn) diagram. 1, rare metals-bearing pegmatites; 2, muscovite-bearing pegmatites (Foster, 1960; in Bailey, 1984).

Our studies on muscovite in the last years (Stumbea, 1997; Stumbea 1998) identified *phengite* and *dioctahedral-trioctahedral*, respectively, substitutions in muscovite. This hypothesis gave us the opportunity to use $Al_{VI}:Al_{IV}$ (Fig. 3) and $\Sigma VI:R^{2+}_{VI}$ (Fig. 4) diagrams that revealed a geochemical intermediate position of muscovite samples, between the *field of rare elements-bearing pegmatites* and that of *muscovite-bearing pegmatites*; to be more specific, the muscovite samples place the pegmatites hosted by metamorphic rocks of the Someş Series in the *field of rare elements and muscovite-bearing pegmatites*.
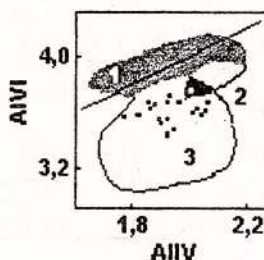
Fig. 3 – $Al_{VI}:Al_{IV}$ diagram for muscovites from rare elements-bearing pegmatites (1); rare elements+muscovite-bearing pegmatites (2); muscovite-bearing pegmatites (3) (Černý, 1982).

Lithium in muscovite as metallogenetic indicator. The bulk composition of lithium in muscovites of a magmatic pegmatite border zone of Manitoba (Canada) is about 604 ppm (Černý and Lenton, 1995), while Morteani et al. (1995) found out a 32-1100 ppm Li range for muscovites of a similar geological setting in Sierras Pampeanas (Argentina). A comparison of these data with our data (54-232 ppm Li with a mean of 137 ppm – emission spectrograph PGS-2 JENA; 38-136ppm Li with a mean of 88 ppm – ICP-MS), as well as the comparison between our data and those specific to metamorphic pegmatites – published by foreign geologists – led to the same conclusion: the pegmatites hosted by medium-grade metamorphic rocks of the Gilău Mountains belong to the *rare elements potentially carrying-barren pegmatites* category; that represents an intermediate field between the *field of barren pegmatites* and that of *rare elements - pegmatites*.

The geochemical relationship between lithium and dioctahedral-trioctahedral aluminium in muscovite, shown in Figure 5, revealed that pegmatites of the Gilău Mountains are affiliated to the *unmineralised pegmatites category*, with one exception sample 116 (Iara Valley) – that has an intermediate position between the *unmineralised* and *mineralised pegmatites fields*. The main results fit the data of Murariu et al. (1997, 1998) concerning the metallogenetic potential of the Preluca and Rodna pegmatite subprovinces.

Using the Trueman and Černý's (1982) diagram (Fig. 1), the affiliation of pegmatites to the *barren pegmatites of mica-bearing provinces category* is obvious; the highest lithium amounts make the passage toward the *barren pegmatites of rare elements-bearing provinces*.
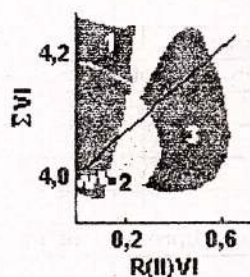
Fig. 4 – ΣY:R^{2+}$_Y$ diagram for muscovites from rare elements-bearing pegmatites (1); rare elements and muscovite-bearing pegmatites (2); muscovite-bearing pegmatites (3) (Černý, 1982).

Fig. 5 – Li vs. (Al$_{VI}$+Al$_{IV}$) diagram. A-unmineralised pegmatites; B-mineralised pegmatites; 1, pegmatites of the Gilău Mts.; 2, pegmatites of the Preluca and Rodna subprovinces; 3, albite+spodumene pegmatites of the Getic subprovince (Conţu field); 4, rare metals-bearing pegmatites from Siberia (Russia); 2, 3, 4, in Murariu et al. (1997).
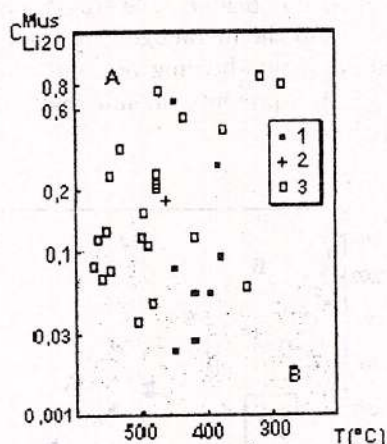
Fig. 6 – C$_{Li2O}$^{Mus}:T (^{0}C) diagram (Talantzev, 1976; in Murariu et al., 1998). A-mineralised pegmatites; B-unmineralised pegmatites: 1, pegmatites from Gilău Mts.; 2, albite+spodumene pegmatites of the Getic subprovince (Conţu field); 3, pegmatites of the Preluca and Rodna subprovinces; 2, 3, in Murariu et al. (1998).

Finally, the C$_{Li2O}$^{Mus}:T(^{0}C) diagram of Talantzev (1976) (Fig. 6) sustains the intermediate position of pegmatites hosted by the medium-grade metamorphic rocks of the Gilău Mountains, between the *unmineralised pegmatites* (five samples of eight) and the *mineralised pegmatites* (three samples of eight) *categories*; our results match those of Murariu et al. (1998) for the rest of Carpathian Pegmatite Province – Romania.

Table 2 $(Rb/K) \times 10^3$ in some muscovites from pegmatites

Carpathian Pegmatite Province	$(Rb/K) \times 10^3$
Pegmatite subprovince of Gilău-Muntele Mare	
Ms-163, Crişeni	1.0
Ms-166, Răşca Mare valley	22.8
Ms-153, Calului valley	9.7
Ms-561, Vinţa valley[1]	4.7
Pegmatite subprovince of Preluca	
Ms-423, Pleşii valley	2.9
Ms-410, Codru Butesii	4.8
Ms-417, Ciungi vein	3.6
Pegmatite subprovince of Rodna[3]	
Ms-101, Intre Rebre	4.1
Ms-105, Scărişoara	4.0
Getic Pegmatite subprovince (pegmatite field of Conţu-Muntele Mic)[3]	
Ms-17, albite+spodumene complex	19.2
Ms-18, quartz+spodumene	8.9
Ms-19, albite+spodumene complex	14.4
Comparative data	
Pegmatite field of Baikal (Manuilova et al., 1966)[3]	
Bifeldspars-bearing pegmatites	7.9
Mica-bearing pegmatites	4.0
Rare metals-bearing pegmatites	24.2
Siberia (Zagorsky and Kuznetzova, 1990)[3]	
Rare metals-bearing pegmatites:	
• two-feldspars	23.5
• albite	37.0
• spodumene and albite	40.1

[1] processed after Constantinescu et al. (1976); [2] in Murariu et al. (1997); [3] in Murariu et al. (1998).

Rubidium in muscovite as metallogenetic indicator. The studies carried out on the relationship between the $(Rb/K) \times 10^3$ parameter in muscovite and the metallogenetic potential of muscovite-carrying pegmatites show higher $(Rb/K) \times 10^3$ values in rare elements-bearing pegmatites and lower ones in unmineralised pegmatites. Working from this principle, Table 2 presents the muscovite $(Rb/K) \times 10^3$ values for different occurrences of pegmatites in Romania and abroad.
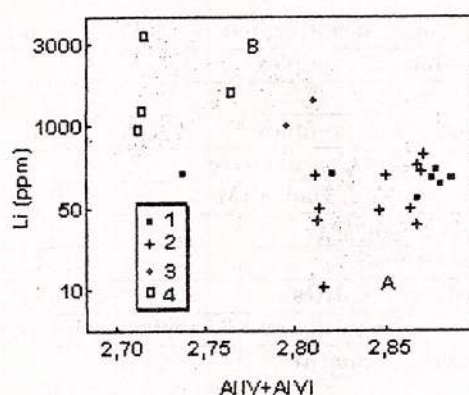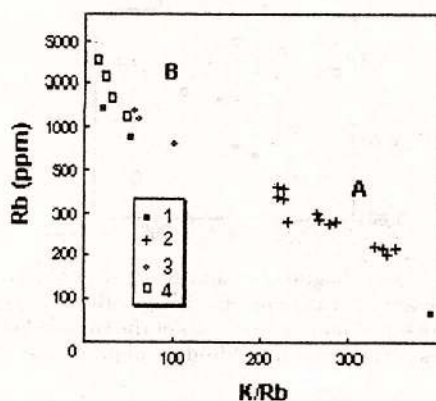

Fig. 7 - Rb:(K/Rb) diagram. A-unmineralised pegmatites; B-mineralised pegmatites; 1, pegmatites of the Gilău Mts.; 2, pegmatites of the Preluca and Rodna subprovinces; 3, albite+spodumene pegmatites of the Getic subprovince (Conţu field); 4, rare metals-bearing pegmatites of Siberia (Russia); 2, 3, 4, in Murariu et al. (1997).

As compared with the data on pegmatite muscovites from abroad, the muscovite of Preluca and Rodna pegmatite subprovinces shows $(Rb/K) \times 10^3$ values specific to *unmineralised pegmatite provinces*, while muscovite samples separated from albite-spodumene pegmatite bodies of Conţu-Negovanu have higher $(Rb/K) \times 10^3$ values, typical of muscovite from *rare elements-bearing pegmatites*. Concerning muscovite of the Gilău-Muntele Mare pegmatite subprovince, the same intermediate geochemical position between muscovite of *barren pegmatites* (Ms-163) and that of *mineralised pegmatites* (Ms-153, Ms-166), respectively, has been revealed.
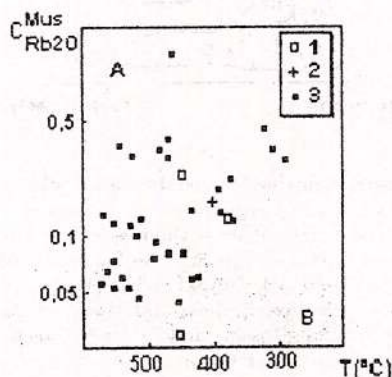
Fig. 8 – $C_{Rb2O}{}^{Mus}$:T(^{0}C) diagram (Talantzev, 1976; in Murariu et al., 1998). A-mineralised pegmatites; B-unmineralised pegmatites; 1, pegmatites of the Gilău Mts.; 2, albite+spodumene pegmatites of the Getic subprovince (Conţu field); 3, pegmatites of the Preluca and Rodna subprovinces; 2, 3, in Murariu et al. (1998).

Similar conclusions could be drawn by using two so-called diagnostic diagrams such as: Rb vs. K/Rb (Fig. 7) and $C_{Rb2O}{}^{Mus}$: T (^{0}C) (Fig. 8). The plot of the geochemical data on the pegmatite muscovite of the Gilău-Muntele Mare subprovince in the two diagrams leads to the same double position of the samples: there are samples that plot in the field of *barren (unmineralised) pegmatites*, but also samples that have geochemical parameters specific to the *field of mineralised pegmatites*. This geochemical behaviour matches to that noticed by Murariu et al. (1998) concerning the muscovite of the Preluca and Rodna pegmatite subprovinces.

Garnets

Major elements in garnets as metallogenetic indicator. The MgO, FeO and MnO amounts in the garnets of the geological study area plot the samples in an interference zone of *muscovite-bearing pegmatites field* and that of *muscovite+rare elements-bearing pegmatites* (Fig. 9); the similar disposition of samples separated from Preluca and Rodna pegmatite subprovinces can also be noticed.
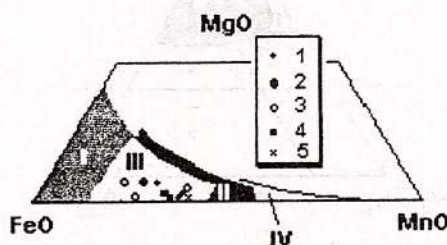
Fig. 9 – MgO:FeO:MnO diagram (Salyie, 1975, in Černý and Hawthorn, 1982); I-muscovite-bearing pegmatites (A-type); II-muscovite-bearing pegmatites (B-type); III-muscovite+rare elements-bearing pegmatites; IV-rare elements-bearing pegmatites. 1, pegmatites hosted by metamorphic rocks (Gilău); 2, pegmatites hosted by granitoid rocks (Vinţa); 3, Rodna pegmatite subprovince; 4, Preluca pegmatite subprovince; 5, Getic pegmatite subprovince.
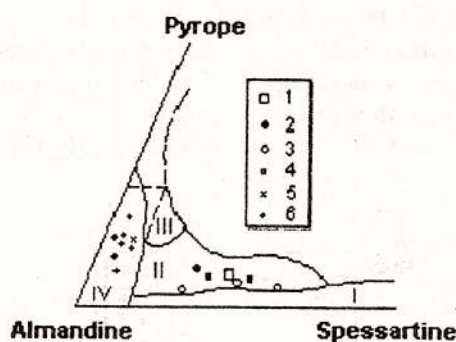
Fig. 10 – Almandine:Spessartine:Pyrope diagram (Sokolov et al., 1962). I-garnets in rare metals-bearing pegmatites; II-garnets in muscovite-bearing pegmatites; III-garnets in pegmatites without mica; IV-garnets in metamorphic rocks (amphibolite facies). 1, pegmatites hosted by metamorphic rocks (Gilău); 2, pegmatites hosted by granitoid rocks (Vinţa); 3, pegmatites hosted by metamorphic rocks (Rodna, Preluca and Getic subprovinces); 4, pegmatites of Northern Karelia (Russia) and Smrček (Czech Rep.); 5, garnets in micaschists of the Gilău Mts.; 6, garnets in metamorphic rocks of the Rodna and Preluca Mts.

On the other hand, the diagram of Figure 10, on which we have plotted the participation of pyrope, almandine and spessartine terms specific to each garnet sample, suggests their affiliation to the *field of mica-bearing subprovinces*; in the last case, as well as *rare and specific elements-bearing pegmatites* position could be noticed, as well.

Lithium in garnets as metallogenetic indicator. As in the case of feldspars and muscovite, the lithium amount of pegmatite garnets (200 ppm, 220 ppm Li) set up our samples in the transition field of *rare elements potentially carrying-barren pegmatites*. In this respect we also present the mean of lithium amount revealed by Mason and Berggren's (1941) research (in Černý and Hawthorne, 1982) for garnets separated from rare elements-bearing pegmatites of Woodgina (Australia): 464 ppm Li.

Tourmaline

Major elements in tourmaline as metallogenetic indicator. The relationship between iron, aluminium and magnesium participation in the tourmaline structure and the metallogenetic potential of tourmaline-carrying pegmatites is revealed by the $Al:Fe_{tot}:Mg$ diagram of Henry and Guidotti (1985) (Fig. 11). In can be seen that in respect to these major elements the pegmatite bodies of the Gilău Mountains fall in the field of *Li-poor granitoids and their associated pegmatites and aplites.*
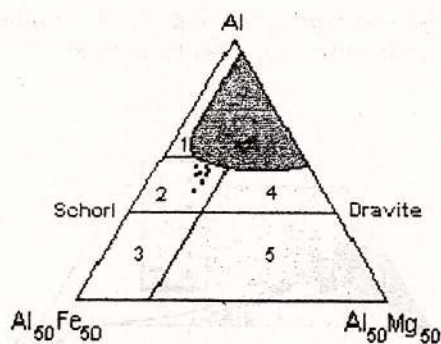
Fig. 11 – $Al:Fe_{tot}:Mg$ diagram (Henry and Guidotti, 1985; in Cavarretta and Puxeddu, 1990). 1, Li-rich granitoid pegmatites and aplites; 2, Li-poor granitoids and their associated pegmatites and aplites; 3, Fe^{3+}-rich quartz-tourmaline rocks (hydrothermally altered granites); 4, metapelites and metapsammites; 5, Fe^{3+}-rich quartz-tourmaline rocks, calc-silicate rocks and metapelites.

Table 3
FeO, Fe_2O_3, MnO and $(Mn/Fe)x10^3$ ratio in pegmatite tourmalines of the Carpathian province

Occurrence	Sample	Fe_2O_3 (%)	FeO (%)	MnO (%)	$(Mn/Fe)x10^3$
Rare metals-bearing pegmatites					
Siberia[1]		3.13	7.80	0.87	81.21
Barren pegmatites					
Gilău	T 7.3	3.36	8.63	0.14	12.40
	T 14.7	3.81	7.02	0.13	11.86
	T 11.19	2.87	10.40	0.06	.4.40
	T 11.26	2.38	12.14	0.11	7.51
	T 16.40	3.61	7.75	0.15	13.41
	T 16.42	3.11	9.53	0.14	11.73
	T-535	3.83	7.27	0.12	10.90
Rodna[2]		2.69	9.54	0.14	11.65
Preluca[1]		6.83	1.53	0.14	18.47
Conţu[1]		5.65	0.95	0.12	19.19

[1] in Murariu et al. (1998); [2] bulk values processed after Murariu et al. (1998).

On the other hand, in Table 3 some $(Mn/Fe x10^3)$ values are presented. One can notice the lower $(Mn/Fe x10^3)$ values for the Gilău-Muntele Mare and Preluca pegmatite subprovinces as compared to the corresponding value in the rare metals-bearing pegmatites of Siberia. The transition features of $(Mn/Fe x10^3)$ parameter in some occurrences in the Preluca Mountains and Conţu (Getic pegmatite subprovince) can be seen as well.

Conclusions

A comparative evaluation of the geochemical features (major and minor elements) shows that pegmatites of the Gilău Mountains mostly belong to the field of *unmineralized (barren) pegmatites* (mica-bearing and feldspars-bearing pegmatites). However, some occurrences fall in a transition field between the unmineralized and the *mineralized pegmatites* (rare elements-bearing pegmatites). This is a specific feature of the Gilău Mountains pegmatites that makes the difference in respect to pegmatites in the rest of the Carpathian pegmatite province.

The use of so-called diagnostic diagrams (Li and Rb in potassium feldspars; phengite:muscovite: annite, Al_{IV} vs. Al_{VI}, ΣY vs. R^{2+}_Y, Li vs. $(Al_{IV}+Al_{VI})$, C_{Li2O}^{Mus} vs. T^0C, Rb vs. K/Rb, C_{Rb2O}^{Mus} vs. T^0C, Li and Rb in muscovite; MgO:FeO:MnO, pyrope:almandine:spessartine – in garnets; $Al:Fe_{tot}:Mg$ – in tourmaline) leads to similar results.

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BROOKITE FROM BĂDEANCA VALLEY, LEAOTA MTS

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Abstract: Evidence of a first well documented brookite occurrence on Purcăreața brook, a left tributary of Bădeanca Valley in Leaota Mts is presented. Brookite occurs as nests within sulphide ores developed in strongly deformed metamorphic rocks on shear zones.

The metamorphic rocks of the Leaota Mts., South Carpathians host numerous occurrences of extremely different chemical and isotopic compositions (see Udubașa, 1988, 1993 for details). The size of the ore bodies is generally small and they are hardly difficult to be mined. However, the genesis of ores was a matter of discussion and both epigenetic (Vlad, Dinică, 1984) and syngenetic (Gurău et al., 1985) models have been advocated. The "mesogenetic", i.e. a shear-zone related model was suggested for most of the ore occurrences in the Leaota Mts (Udubașa et al., 1988, 1993) and the resemblance with the Skandinavian fahlbands cannot be ruled out. On a relatively restricted area (Fig. 1) there exist ores of very different chemical, mineralogical and isotopic compositions, which show various positions in relation to the metamorphic foliations of the host rocks. Hydrothermal alteration is either lacking or of limited development. Several ore types have been recognized in the Leaota Mts., i.e. (1) shear zone related pyrite-pyrrhotite-chalcopyrite ores, (2) vein-like Pb-Zn-Cu-Ag ores, (3) Ni-Co-Ag ores of limited extension, as a rule cutting across the type 1 of ores, (4) Au Pb ores in quartz bodies, (5) U-ores forming lenses along the faults, etc. Small pockets of rutile-pyrrhotite ores scarcely occur in retrogressed gneisses as well as short fluorite veinlets,in brecciated metamorphics (Gurau, 1984).

The occurrence described here is located in the southern part of the Leaota Mts. (Figs. 1 and 2) and differs from the above mentioned types in having uncommon high brookite amounts.

The brookite-bearing occurrence is located on the Purcăreața brook, a left tributary of the Bădeanca Valley (Fig. 2). The host rocks are retrogressed and sheared metamorphics of various composition, i.e. micaschists and gneisses (now seen as chlorite-sericite schists, sometimes with albite porphyroblasts), to which graphite- bearing varieties may associate.

The ore bodies are small sized and very irregularly shaped and consists of iron sulfides (pyrite, pyrrhotite, marcasite), chalcopyrite, sphalerite and subordinate amounts of galena. Magnetite occurs as minute inclusions in pyrite. Rutile and titanite are present as elongated inclusions in micas. Hematite forms fine lamellae in garnets. The gangue minerals are represented by quartz and carbonates, commonly forming rims around the pyrite aggregates. In addition, there were found small pockets of light-brown, fine grained aggregates, which have proved to consists of brookite.

Microscopically, brookite is hardly difficult to identify, first of all because of its extremely fine grain size. In polished section brookite appears as irregular masses of light grey colour with abundant yellowish or grey-greenish or brownish internal reflections. Such features fit neither rutile nor anatase properties. In addition, the X-ray powder diffraction data (Table 1) confirm fairly good the presence of brookite. Brookite forms nearly monomineralic lenses some 0.5 to 2 m in size, in which rarely small euhedral, mostly isometric outlines can be observed. It is finely intergrown with quartz and silicates, sometimes with pyrrhotite and chalcopyrite (Figs. 3 and 4)).
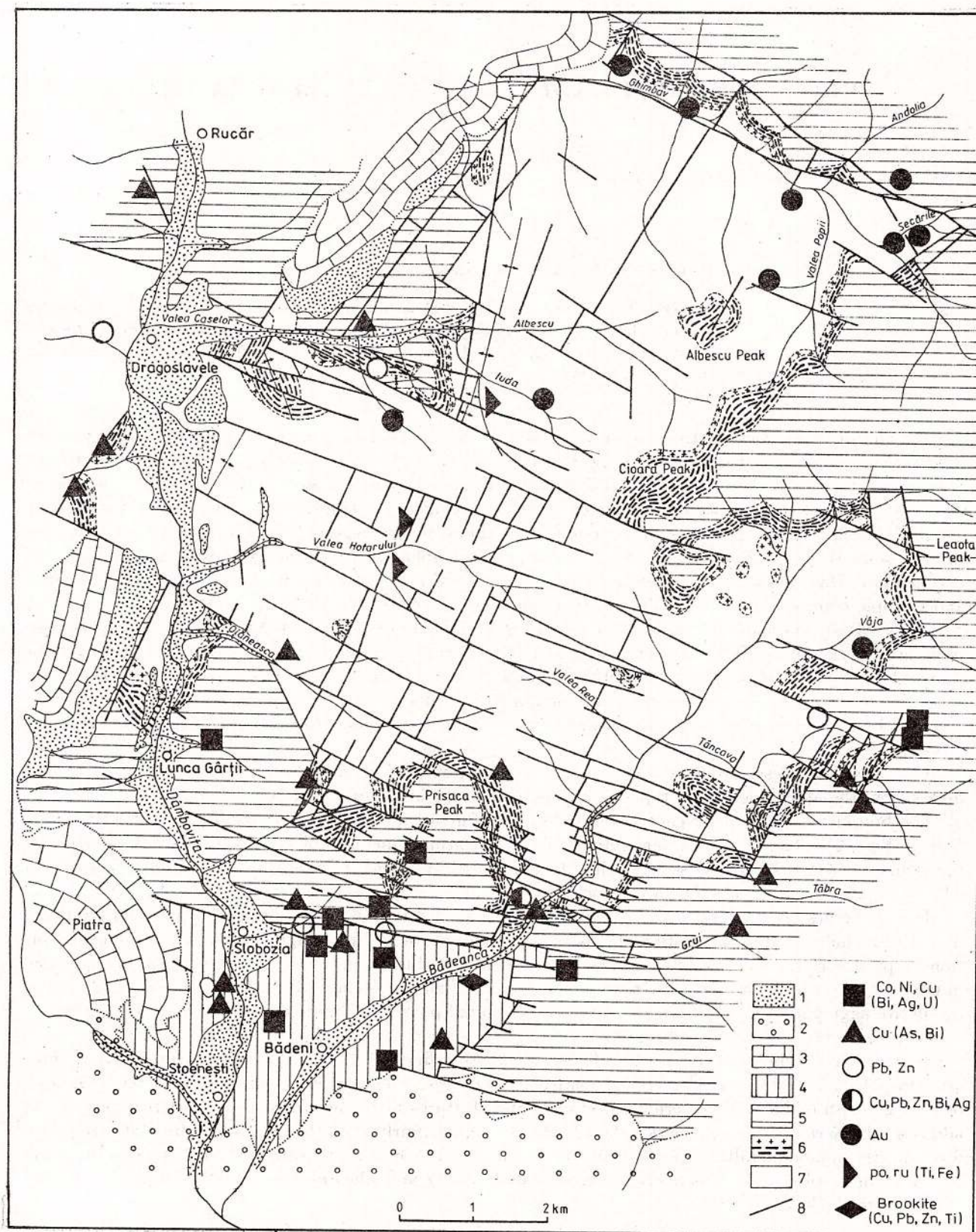
Fig. 1 – Geological sketch map of the Leaota Mountains (based on the geological maps of Gheucă and Dinică, 1986, 1996 simplified; the classification of ore occurrences has been made by Udubaşa, 1988).
1. Quaternary deposits; 2. and 3. Mesozoic sedimentary deposits, mostly conglomerates and limestones, respectively; 4-7. Leaota metamorphic Group (Late Proterozoic?): 4. Călușu or Stoenești or Râușoru Rucărului Formation (Mainly quartz-chlorite-sericite schists, see Fig. 2); 5. Lerești Formation (partly retrogressed micaschists±garnet and albite porphyroblasts, gneisses); 6. Bughea amphibolites and Albești granite - a rock mixture reminiscent of a pseudo "mini greenstone belt"; 7. Voinești Formation (Gneisses, amphibolites ± garnet and pyroxene); 8. Faults.
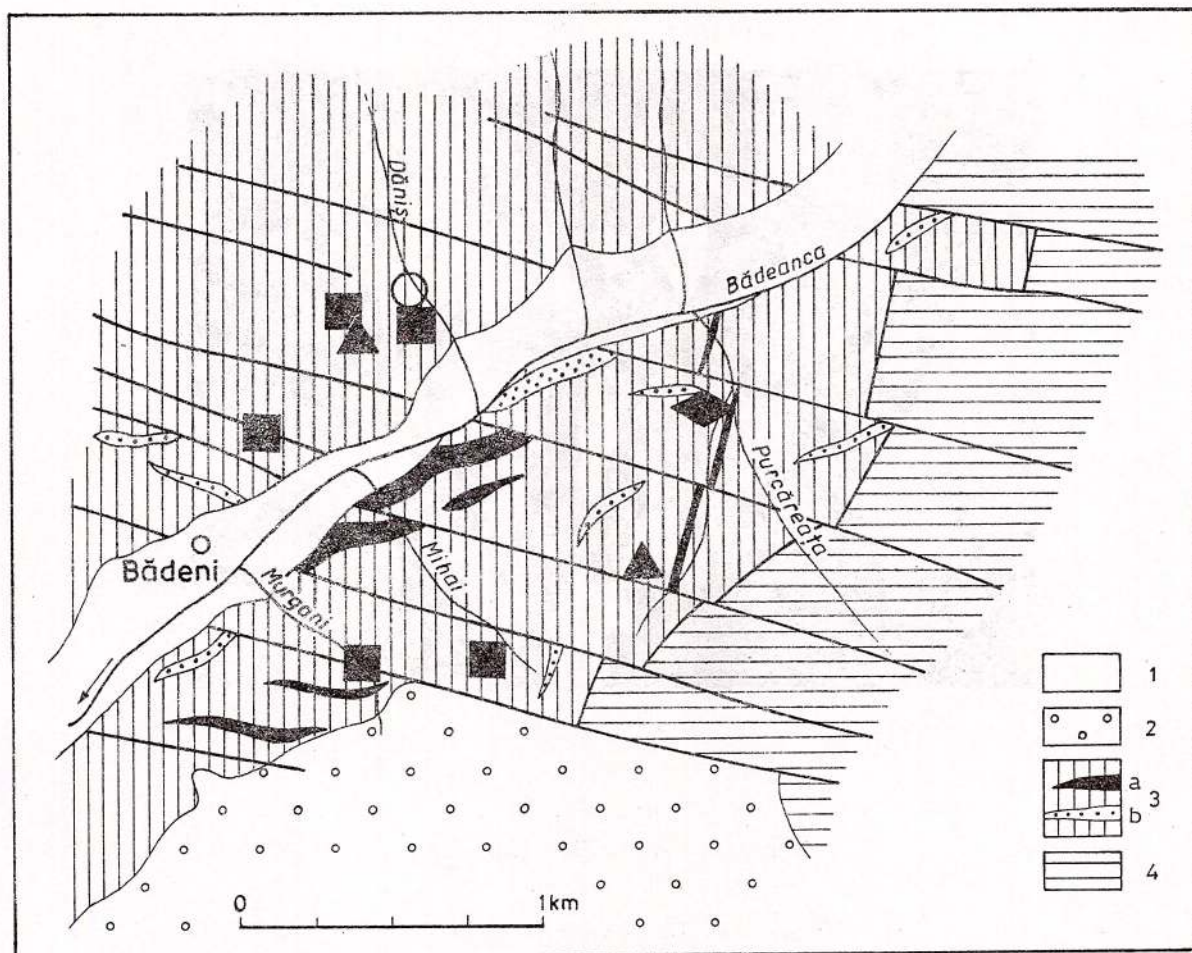
Fig. 2 – Geological map of the surroundings of the Purcăreaţa Brook. 1. Alluvia: 2. Mesozoic conglomerates; 3. "Căluşu Formation, consisting mainly of sericite-chlorite-quartz schists with albite porphyroblasts and subordinate chlorite (a) and acidic (metatuffs) schists (b); 4. Lereşti Formation. For occurrence types see Fig. 1.
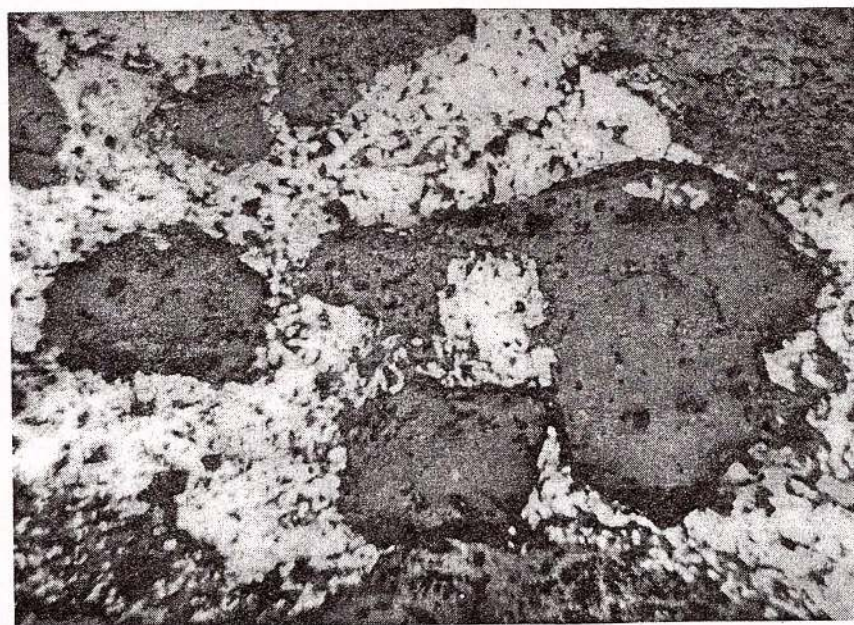
Fig. 3 – Reflected light microphotograph showing a fine aggregate of brookite (whitish) cementing subhedral grains of garnets. X 100.

Fig. 4 – RL microphotograph showing an intergrowth of brookite (greyish-white) and pyrrhotite (white). Oil immersion, x 300.

Table 1
X-ray powder diffraction data

Purcăreaţa brookite		Brookite from Magnet Cove, Arkansas, ASTM 16-617		
d	l	d	l	hkl
3.500	100	3.510	100	120
3.420	12	3.470	80	111
2.900	27	2.900	90	121
2.790	27	2.729	4	200
2.603	12	–		
2.495	11	2.476	25	012
–		2.409	18	201
2.306	11	2.370	6	131
2.340x	5	2.344	4	220
2.330	5	2.332	4	211
2.275	18	2.296	6	040
2.250	5	2.254	8	112
–		2.244	18	022
2.130	7	2.133	16	221
–		1.969	16	032
1.185	21	1.893	30	231
1.850	7	1.851	18	132
–		1.833	4	212
–		1.757	4	240
1.691	3	1.691	20	320
1.661	5	1.662	30	241

Analyst: Iulian Vanghelie, Geological Institute of Romania
DRON diffractometer, CuKα radiation.
Additional peaks at 4.26 and 3.33 (quartz) and 3.01 (calcite).

Comments and conclusions

Brookite is seemingly a rare mineral but it is not easy to identify and could possibly be overlooked. Among the TiO_2 compounds brookite seems to be the lowest PT naturally occurring polymorph, although the relationships among them are quite complex, suggesting that kinetics rather than equilibrium dominates the TiO_2 system (Lindsley, 1976). In addition, the discovery of a new natural polymorph, TiO_2(B) (Banfield et al., 1991) further complicates the things. Anyhow, the abundant brookite in the Purcăreaţa occurrence can be related to the less common mode of formation of such ores, in which the albite-bearing rocks underwent strong deformation. Sodium release from albite decomposition enabled brookite to preferentially form as against the other TiO_2 polymorphs. Such a way to explain brookite abundance in the Purcăreaţa occurrence is thus best explained by using the phase diagram of the TiO_2-Na_2O-H_2O system obtained by Keesmann (Lerz, 1968). The associated calcite show values of $\delta^{13}C$ vs PDB and $\delta^{18}O$ vs PDB of -12.78 and -17.46 $^0/_{00}$, respectively, fairly different as compared to metamorphic (-10 to -15 $^0/_{00}$ $\delta13$ C and about -12 $^0/_{00}$ (18 O) and sedimentary (0 to +5 $^0/_{00}$ (13 C and -2 to -12 $^0/_{00}$ $\delta13$ O) limestones.

The sulphides which occur intimately intergrown with brookite show strongly negative ($\delta^{34}S$ values (Table 2), fitting thus the TT - type of Leaota ores., i.e. the most typically looking shear-related (Udubaşa, 1993, 1998).

Table 2
Sulphur isotope composition of
sulphides associated with brookite

Mineral species	$\delta^{34}S$ $^0/_{00}$	Associated minerals
Phrrhotite	-37.97	Intergrown with garnet and brookite
Pyrite	-24.17	Deformed cubed in graphite-rich rocks
Pyrite	-19.01	Well-developed cubes with strated faces, partly covered by quartz
Spalerite	-6.67	Black and blackish brown in color

Analyst: Filofteia Gaftoi, Geological Institute of Romania Samples analysed at ITIM Cluj

The occurrence on Purcăreaţa brook in the Leaota Mts seems to be the best substantiated as concerns the brookite presence in Romania. Its occurrences at Sasca Montană in Banat, in altered granodiorites (Constantinescu, 1980), in Lower Cambrian metamorphics of the Tulgheş Group (Balintoni and Chiţimuş, 1976) and in Sarmatian and Quaternary gravels in Moldova (Bălan, 1981) have been mentioned without analytical proof.

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CAMIRO 1.0 - THE ROMANIAN CAVE MINERALS DATABASE PROGRAM

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Key words: Computer program. Mineralogical database. Cave minerals. Crystallography. Mineralogy.

Abstract: The present article introduces the Cave Minerals of Romania database (CAMIRO 1.0), a computer-based program that allows cataloging of all known cave mineral species including their main characteristics. CAMIRO 1.0 is a mineralogical database created using Borland(Delphi(4 Professional, an object-oriented, visual-programming environment that allows rapid application development. CAMIRO 1.0 is a collection of geologic, mineralogic, crystallographic, and protection information about cave minerals. It holds and organizes large amounts of information, including photos. Related information (e.g., mineralogical or crystallographic) are grouped together to form records. These records are gathered into several related fields. In order to logically group all necessary fields we have created the following three pages: General data, Mineralogical data, and Crystallographic data. Such a cave minerals database would have many various scientific purposes or it could simply be a quick and easy to surf electronic handbook. With the help of its easyto-excess content, the database could provide cavers with basic information on identifying and describing the mineralogy of most of the strange-looking speleothems.

1. Motivation

Over the last 30 years, several papers and three major books dealing with various aspects of cave minerals worldwide have been published (Moore, 1970; Hill, 1973; Hill, Forti, 1986, 1997; Moore, Sullivan, 1997; Onac, 1999).

In 1973, Hill published the first book describing all the cave minerals found in the United States until that period. Later, Hill and Forti published two editions (1986 and 1997) of Cave Minerals of the World, providing both cavers and professional mineralogists with a considerable amount of information on cave minerals and the speleothems they form.

Advancements in technology (new high-tech X-ray diffraction, SEM and TEM devices, powerful models of ICP-MS) have resulted in an explosion of new mineralogical data included in the last edition of Cave Minerals of the World. However, the last two editions were published 11 years apart, showing that in order to keep up with this exponentially rising knowledge in cave mineralogy a computer- aided database was needed.

There are at least three reasons for creating such a mineralogical electronic database: (1) the data (various information and illustrations) can easily be archived, (2) to update a previous version takes a shorter time and less money than printing a new book edition, and (3) the database can be distributed worldwide so that more cavers and scientists can access it.

2. About CAMIRO 1.0

CAMIRO 1.0 is a mineralogical database created using Borland Delphi 4 Professional edition, an object-oriented, visual-programming environment that allows rapid application development.

CAMIRO 1.0 has the following minimum system requirements:
- IBM PC/PS2 or compatible with 486 based CPU or higher with at least 14MB free on its hard disk.

- Windows 95 or later.
- At least 8MB RAM (16 MB or higher recommended).
- 800x600 or higher monitor resolution.
- High (16 bit) color palette (True color 24 bit recommended).

Fig. 1 — General data page with its fields and records

3. Application description

CAMIRO 1.0 is a collection of geologic, mineralogic, crystallographic, and protection information about cave minerals discovered in Romania. It holds and organizes large amounts of information (including photos), and makes any item immediately accessible. Related information (e.g., mineralogical or crystallographic) are grouped together to form records. These records are divided into several related fields. In order to logically group all necessary fields we have created the following three pages: General data, Mineralogical data, and Crystallographic data.

3.1. General data

This page contains fields such as: Mineral name, Cave name, Other locations, Geographic settings, Geologic settings, Cave climate, Occurrence, First description, References, and Speleothem image (Fig. 1). Some of these fields contain more than one record and therefore need further explanation.

Within the Geographic setting field, information such as cave location and cave numerical code (extracted from the Romanian Cave Index; Goran, 1982) to allow users interested in a certain cave to perform a rapid mineral search. In addition, information such as length and depth of the cave, altitude of the cave entrance, and presence or lack of underground stream was included

The type and age of the host rock that hosts the cave are the main records grouped under the Geologic settings field. If more than one type of rock is present this is mentioned within Others record.

Cave climate, through its main parameters of ventilation type, temperature, and humidity is often responsible for the genesis of some mineral species in the cave environment. Knowing such information, one can better interpret the deposition and stability of minerals.

Under the *Occurrence* field the three dialogue windows are *Speleothems*, *Frequency*, and *Others*. These windows allow the user to find out what types and subtypes of *Speleothems* were identified (according to the

classification proposed by Hill, Forti, 1997) and what is their *Frequency* (i.e., very common, common, rare, and uncommon). If additional remarks can be made under this main field, these comments should be placed in the window called *Others*.

The *First description* field contains two records: *Non-cave occurrence* and *Cave occurrence*. The *Non-cave occurrence* record cites the location of those minerals that were first described outside the cave. The *Cave occurrence* field cites the first cave in which that mineral was·found. When the *Non-cave occurrence* record remains empty, the user should understand that the mineral was first discovered in a cave.

Whenever a common mineral (e.g., calcite, aragonite, gypsum, brushite, etc.) was found in several caves, only that cave where the mineral is best displayed is presented in detail. Other caves were the mineral occurs are listed within the *Other location* field.

Location of certain speleothems within the cave (i.e., well-ventilated passages, aerosols-rich environment, etc.) is sometimes essential when discussing the mineral genesis. For this reason, we believe both cavers and scientists should always record this information in their field book.

Fig. 2 – Mineralogical data page.

3.2. *Mineralogical data*

The page called *Mineralogical data* provides information obtained after observations and laboratory analyses (Fig. 2). Foremost, the *Mineral status* (approved, discredited, or revised by IMA) is presented. The mineral is then placed within the chemical *group* where it belongs. The Chemical formula is given according to Strunz (1982). If the speleothem of a variety of a well-known mineral (e.g., selenite, which is a coarsely crystalline, transparent variety of gypsum) this information is in the *Varieties* field. Cave minerals often do not appear alone but with other minerals formed under the same circumstances. The *Mineral assemblage* field emphasizes what other mineral(s) was/were identified in the composition of the same speleothem. The development of an individual crystal or aggregate of crystals, to produce a particular external shape, is described under the *Habit*. *Color, Luster, Hardness* and *Cleavage* represent the major *Physical properties* of a mineral and are each recorded in a different dialogue window. For those minerals with *Diagnostic features* (e.g., calcite fizzes vigorously in dilute HCl, nitrates have a very bitter, pungent taste, mirabilite forms glassy-clear crystals etc.) a special window was created.

The *Analytical data* field contains an *Identification by* record, listing the main methods used to describe the mineral (X-ray, thermal, IR etc.). In addition, a dialogue window was added in order to specify any other laboratory diagnostic methods.

The *Chemistry* field displays quantitative chemical data provided by various analytic methods (XRF, EDS, ICP-MS, etc.).

The last dialogue window of the *Mineralogical data* page relates to the *Deposition and stability* of the cave minerals. At this location, cavers and scientists will find information on the cave settings under which a particular mineral formed.

Fig. 3 – Crystallographic data page.

3.3. Crystallographic data (Fig. 3)

In the first field of the *Crystallographic data* page users will learn to which of the seven *Crystallographic system* the mineral belongs.

Both *Schoenflies* and *International (Hermann-Mauguin)* notations/symbols are presented under the *Symbol* field.

Two types of data used to describe the axial elements are gathered under the *Cell parameters* field. These include (1) the cell size parameters (a, b, c) and (2) the angles between the crystallographic axes (α, β and γ).

The following four fields bring specific data on the mineral under question: *Size of crystals*, the presence of *Twins* or *Pseudomorphs*, and the most *Common crystallographic forms* (i.e. prisms, rhombohedron etc.). The Load image button can display images of the crystal. This option is normally deactivated in order to increase the application speed.

All results acquired through different optical techniques are grouped under the Microscopy field. Observations made under the polarizing microscope (e.g. refractive indices, twins, cleavage etc.) and with scanning and transmission electron microscopes (crystal fabric and structure, inclusions etc.) are recorded.

3.4. Conservation and Protection

Within each of the three pages a button located in the lower left corner opens the *Conservation and Protection* dialogue window. The purpose of this memo field is to provide a warning signal for cavers on how they should behave when entering a cave that is decorated with speleothems of different mineralogy. To preserve speleothems (minerals) in both wild and show caves, many factors must be considered. For example, when a cave hosts mirabilite speleothems it is absolutely prohibited to camp in their close vicinity.

Mirabilite crystals are highly sensitive to temperature and humidity variations and will quickly dehydrate and disintegrate into a white powder.

4. Conclusions

The CAMIRO 1.0 application, developed using Borland Delphi 4 Professional, is a mineralogical database designed to store a variety of information on all cave minerals described in Romania so far.

Presently, this application represents the first attempt in creating a computer-aided mineralogical database that can be distributed among the speleological community. The intent is to expand it and generate a world-wide electronic catalogue of cave minerals. Such a database would have many various scientific purposes or it could simply be a quick and easy to surf electronic handbook. With the help of its easy-to-access content, the database could provide cavers with basic information on identifying and describing the mineralogy of most of the strange-looking speleothems.

In order to improve the present version of CAMIRO we would appreciate any comments, ideas, and observations. Major input is expected from members of the *Cave Mineralogy Commission* within the International Union of Speleology.

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MORPHOLOGY OF PUMICE CLASTS AND GLASS SHARDS OF THE "RHYODACITIC FORMATION" IN THE GUTÂI MOUNTAINS. ROMANIAN EASTERN CARPATHIANS; INVOLVED PROCESSES

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Key words: Gutâi Mts. Calc-alkaline. "Rhyodacitic Formation". Pumice clasts. Glass shards. Pyroclastic, resedimented volcaniclastics. Magmatic explosions. Welding. Diagenesis.

Abstract: The Gutâi Mts. form complex volcanic structures composed of calc-alkaline acid and intermediary rocks. The "Rhyodacitic Formation" represents the lowermost unit of the volcanic succession, joining volcaniclastics and sedimentary deposits interlayered, spread in time from the Lower Badenian till the Lower Sarmatian. Two units with similar composition have been emphasized, separated into primary, pyroclastic and secondary, resedimented volcaniclastics. The juvenile pyroclasts are represented by: pumice clasts and non-vesicular vitric clasts, glass shards, crystals of plagioclase, quartz, biotite and pyroxene. The mass flow character, as well as the emplacement from suspension preserved the primary morphologies, recording also the emplacement and post emplacement processes. The study of the morphology of pumice clasts and glass shards from the tuffaceous claystones, as well as from the water-settled fallout tuffs and less welded ignimbrites, shows that they have been generated by magmatic explosions involving an acid, highly and heterogeneously vesicular, viscous magma. The highly flattened pumice clasts and glass shards defining a crude bedding suggest the welding of the pumice mass flows and implicitly the hot state deposition and ignimbrite character of the lower unit. An apparent welding, suggested by lower flattening ratios and developed within the resedimented mass flow deposits, resulted during diagenesis and was enhanced by hydrothermal alteration.

Introduction

The Gutâi Mts are part of the Romanian Eastern Carpathians. They form a complex volcanic ediffice composed of acid and intermediary calc-alkaline volcanics, spread in time from the Lower Badenian (15.4±0.6 Ma) till the Upper Pannonian (7,0±0.4 Ma), according to Pecskay et al. (1994, 1995).

The beginning of the volcanic activity is marked by the built up of the "Rhyodacitic Formation", cropping out on the south-western part of Gutâi Mts, between Seini and Firiza (Fig. 1). The "Rhyodacitic Formation" is composed of volcaniclastics of pyroclastic origin interlayered with intra-basinal volcanogenic and non-volcanogenic sedimentary deposits. They have been described by Rădulescu D (1958), Borcos et al. (1970, 1973), Kovacs et al (1989), Fülop et al (1991), who point out the petrographical character and some inffered genetical processes. This paper is focused on the morphology of pumice clasts and glass shards, as main pyroclastic components of the deposits. They offer valuable information about their origin, physical characters of involved magmas, emplacement and post emplacement processes.

Stratigraphical and volcanological background

The "Rhyodacitic Formation" is composed of two stratigraphic units, basically similar from the genetical point of view, but involving different emplacement conditions derived from the subaerial versus subaqueous depositional environment.

Fig. 1 – Simplified geological map of the south-western part of Gutâi Mts. (after Borcoş et al., 1973)

The lower unit, represented by ignimbrites of 15.4±0.6 Ma, lies erosionally over the Paleogene flysch and Lower Badenian sedimentary deposits. It is erosionally overlain by the upper unit, composed of fallout tuffs and resedimented volcaniclastics, interlayered within submarine, deep water claystones and siltstones of Lower Sarmatian age, according to the faunal content (Radulescu S. et al., 1970).

The ignimbrites and the mass flow resedimented volcaniclastics have different internal organization but similar composition: the juvenile clasts of pyroclastic origin are represented by pumice clasts, non- vesicular vitric clasts, glass shards, crystals of plagioclase, quartz, biotite and pyroxene; the xenoliths are represented by alluvial debris of sedimentary and metamorphic rocks and pyroxene andesites, subordinately.

They should have to preserve the primary morphologies of pumice clasts and glass shards because of the mass flow character, but they underwent specific emplacement and post emplacement processes, recorded as secondary morphologies. The water-settled fallout tuffs, as well as the resedimented fallout tuffs associated to the mass flow volcaniclastics, are composed of pumice clasts and a small amount of crystals and glass shards, respectively. They are emplaced from suspension preserving the primary shapes but very often they are overprinted by phyllosilicates, formed during subsequent alteration.

The best source of well-preserved primary morphologies is offered by pumice clasts and glass shards, captured within deep water claystones. They contain different amounts of pumice clasts and ash, heterogeneously distributed within deposits. These pumice clasts and glass shards floated on the sea until their vesicles were filled with water and settled from suspension together with clay pellets, because of the similar hydraulic behaviour.

All the deposits containing abundant pumice clasts and glass shards have been microscopically investigated. The lithological columns of three of the outcrops encapsulating the best preserved morphologies are represented in Figures 2, 3, 4.

Fig. 2 Lithological column of fallout tuffs and associated deposits from Bocilor V. (S1)

Fig. 3 Lithological column of mass flow volcaniclastics and associated deposits from Limpedea V. (S2)

LEGEND

⬭	alluvial debris of sedimentary rocks
⬭	alluvial debris of metamorphic rocks
○	pumice clasts
∼	fiamme, pseudofiamme
•••	lapilli tuff/lapillistone
▨	siltstone
▤	claystone
=	horizontal stratification
∿	hydroplastic deformational structure
∼	slides / slumps
X	gas escape pipes
⎯	sharp limit
---	gradational limit
∿	erosional limit
∼	irregular limit
⋎⋎⋎	unknown limit
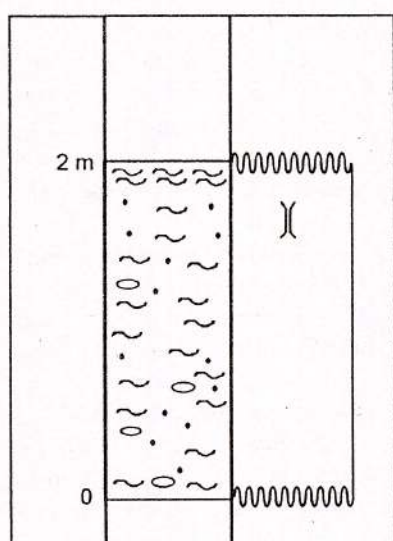
Fig. 4 Lithological column of ignimbrites from Romana V. (S3)

Primary morphology of pumice clasts and glass shards

The microscopical study of the primary morphology is based on rock samples of tuffaceous claystones and resedimented fallout tuffs (Fig. 2), from the western area of outcropping. Few data are based on the ignimbrites from the eastern part (Fig. 4). The study is focused on the morphology of pumice clasts, their vesicularity, the shapes of vesicles and the morphology of glass shards.

The pumice clasts belong to the lapilli and ash grainsizes and the glass shards, representing bubble-wall segments of pumice, are ash components.

Most of the pumice clasts are subequant, slightly elongate, subrounded. Rarely they are subangular. The aspect ratio (length/ height ratio) is about 1./5-2 for the measured pumice clasts (in 18 samples) (Plate I, Fig. 1). The margins of the clasts are very irregular, suggesting they are bounded by rough, ragged surfaces (Plate II, Figs. 1, 3).

The vesicularity (vesicles/compact glass ratio) was estimated at an average of 40-50on 5 microphotos which are relevant from the point of view of the vesicles outlines. However, a wide range of vesicularities has been emphasized, from highly vesiculated (Plate I, Fig. 1) to slightly vesiculated pumice (Plate I, Fig. 4).

Vesicles vary in size and shape. Two main types of shapes have been emphasized: spherical vesicles with 10-20 μm diameter, separated by thin vesicle walls (Plate I, Fig.1) and tubular vesicles with elongate cylindrical shapes, subparallely aligned, imparting a fibrous or woody texture (Plate II, Fig. 1). A wide range of intermediary shapes appears between the two extreme vesicle textures: slightly elongate, ovoid shapes with collapsed walls and coalesced composite vesicles (Plate I, Fig. 3), very elongate shapes, with aspect ratios reaching 10/1 (Plate I, Fig. 2) and distorted vesicles with textures, such as: "vortex pattern" (Plate II, Fig. 3) and folded flow foliation (Plate II, Fig. 4), with the original pore spaces strongly diminished or completely eliminated.

As a whole, pumice has a very heterogeneous vesicle texture (Plate II, Fig.2). Only spheroidal vesicles are considered to be of primary origin, because of the high viscosity of the acid magma (Heiken, Wohletz, 1985). Sometimes the texture shows pockets of large spheroidal to ovoid vesicles and thin, highly elongated vesicles. Spheroidal to ovoid vesicles form clusters surrounding the phenocryst. Examples are given by magnetite (Plate I, Fig.1) and plagioclase phenocrysts included in pumice clasts. Early vesicle growth may begin at phenocryst surfaces acting as bubble nuclei. Vesicle pockets that are radial to the phenocryst have a higher bulk viscosity than the surrounding melt and may resist to deformation by flow. As magma rises, vesiculation begins around the pockets. Closer to the surface, later stage vesicles are sheared into highly elongate tube-like forms as they flow around the competent stronger framework that is created by pockets of spheroidal or ovoid vesicles and phenocrysts.The process takes place prior to eruption, during the laminar flow through the conduit or ring fissure. The distortion of the vesicles resulting in "vortex pattern" and folded flow foliation textures are related to processes developed through magma ascent, conduit abrasion or dynamic stress of cold water-contracted viscous lava, in contact with hot, ductile lava. The last process is responsible for less vesiculated pumice clasts with quench margins (Plate I, Fig. 4).

High pumice vesicularity suggests a high volatile content of the original, viscous magma, involved in explosive eruptions. The heterogeneous vesicle texture is given by the heterogeneous distribution of volatiles in magma, combined with distortions during magma ascent or with the possible interaction with water. The high vesicularity and the relative small amount of phenocrysts indicate rapid rise of magma and release of gases without much volatiles loss during eruption. Such processes are compatible with ring fissure eruptions and ignimbrites generation.

The morphology of the glass shards is given by the bubble-wall segments from which they have been broken. The microscopical study emphasized cuspate, X- and Y-shaped shards, fragments or junctions between vesicles (c, x, y); platy shards, flat or curviplanar (pt), needle-like fragments of the walls separating adjacent large vesicles (n); pumice shards or micropumice, fragments of microvesicular glass (mp) (Plate III, Fig. 1, Fig. 2).

The shards outlines suggest magmatic explosions of highly vesicular magma, generating glass shards typically larger than 50 μm, sometimes as large as 80-100 μm, but finer shards as well. The efficient fragmentation suggests that magmatic disruption has been associated with another mechanism producing the finer shards: the mechanical interaction or grinding of the pumice clasts against each other during eruption or the interaction with water during fragmentation.

Secondary morphology of pumice clasts and glass shards

The secondary morphology derives from the primary morphology, modified, usually flattened during certain emplacement and post emplacement processes. The ignimbrites are the main deposits recording strong flattening of pumice clasts and glass shards (Fig. 4).

Pumice presents a lenticular shape, it is flattened and slightly undulated (Plate IV, Fig. 1, Fig. 2), with ragged terminations; the clasts are moulding phenocrysts edges or they are plastically deformed between two adjacent phenocrysts. The vesicular microtexture is destroyed, the pore spaces are deformed, flattened or completely eliminated. Such pumice clasts are called fiamme (Ross, Smith, 1960). The degree of flattening or the flattening ratio (Fr, according to Petersen, 1979) has been measured in more than 200 samples, collected from outcrops and drill logs, in order to emphasize the areal variation and the variation on thickness.

Glass shards are more or less preserving the primary shapes; very often they are deformed, flattened and sticked together and the micropumice clasts form fine undulated lenses (Plate III, Fig. 3, Fig. 4).

Fiamme and microfiamme are aligned imparting a crude horizontal bedding defined as eutaxitic texture (Smith, 1960) (Plate IV, Fig. 1, Fig. 2). This is the structural feature which indicates the welding, certifying the hot state deposition or the ignimbrite character of pumice rich mass flow deposits. Most of the values of the flattening ratios indicate Fr > 6, corresponding to densely welded ignimbrites (according to Petersen, 1979). An areal assessement of the degree of flattening shows that the densely welded ignimbrites are concentrated in the western part, Seini and Ilba areas and towards east, the degree of flattening decreases. The western part, containing the thickest ignimbrite deposits, shows that welding is continuous on thickness and emphasizes a single cooling unit. The moderate welding has also been determined and very few samples suggest the lack of welding. These data allowed to define the high grade ignimbrites, (sensu Branney, Kokelaar, 1992). The high grade ignimbrites involve the continuum of welding from the syn-depositional agglutination to the post-depositional load compaction, developed at sufficiently high temperature to restrict the extent at a couple of kilometers away from a supposed ring fissure source.

The pumice rich resedimented volcaniclastics, emplaced from mass flows or suspension associated to mass flows, show aligned flattened pumice clasts (Fig. 3), suggesting a horizontal bedding. This fabric is related to the primary, horizontal orientation of the pumice clasts during the laminar flow or during settling from suspension and it is pointed out by diagenetic compaction. This process is enhanced by a pervasive alteration related to the syn-volcanic diagenetic stage, sometimes overprinted by later alterations. The early stage is represented by phyllosilicate alteration of the originally highly porous and permeable pumice rich deposits; the weak assemblage is strongly flattened during load compaction. Foliated lenticular clasts called pseudofiamme (Plate IV, Fig. 3, Fig. 4), tubular pumice clasts and shards are transposed into the bedding-parallel foliation, resembling the eutaxitic texture. This apparent welding has a local character; under the microscope, the essentially non-welded character of deposits is proved by the coexistence of flattened pumice with uncompacted pumice and undeformed glass shards.

A subsequent hydrothermal alteration and the new mineral assemblages change most of the textural features and a clear distinction between welded and non- welded volcaniclastics needs to correlate the microscopical study of morphology with other criteria of separation.

Conclusions

The microscopical study of the pumice rich pyroclastics and resedimented volcaniclastics proves that the primary morphology of pumice clasts and glass shards is a valuable genetical indicator. It suggests that highly and heterogeneously vesicular viscous magma, with a small amount of crystals, was involved in magmatic explosive processes developed with less volatiles loss. Such evolution is suitable for ignimbrites genesis. The history of bubble growth is emphasized and the subsequent deformation during magma ascent is explained on the basis of: shear stress during laminar flow on the access system prior to eruption, abrasion on the conduit/ ring fissure or in the vent during eruption or dinamic stress generated by the interaction of hot lava and water contracted cold lava.

The secondary morphology of pumice clasts and glass shards records emplacement and post emplacement processes. The flattened pumice clasts called fiamme define the eutaxitic texture or welding and certify the ignimbrites. The areal extent of dense welding and its continuity on thickness suggest high grade ignimbrites and their possible ring fissure source location inside the area of outcropping.

Pumice clasts pseudomorphosed by phyllosilicates underwent a diagenetic compaction, defining an apparent welding. The distinction between the real and the apparent welding can be assessed only under

the microscope. An overprinted hydrothermal alteration requests other criteria to separate welding and diagenesis.

Aknowledgements

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PLATES

Plate I

Fig. 1 — magnetite phenocryst and bubbles in a pumice clast; Bocilor Valley, Seini, N+, 30X

Fig. 2 — deformed, elongated vesicles in a pumice clast; Bocilor Valley, Seini, NII, 30X

Fig. 3 — heterogeneously, highly vesiculated pumice; Bocilor Valley, Seini, NII, 30X

Fig. 4 — less vesiculated pumice clast with quench margins; Bocilor Valley, Seini, NII, 30X
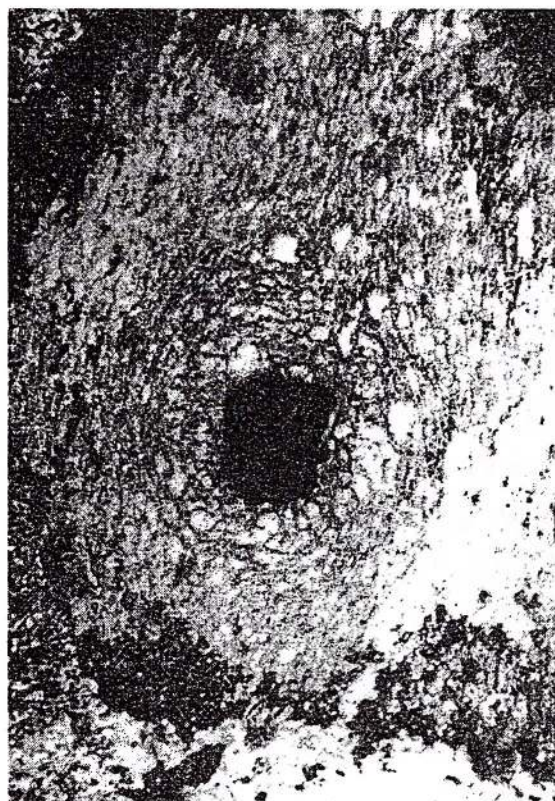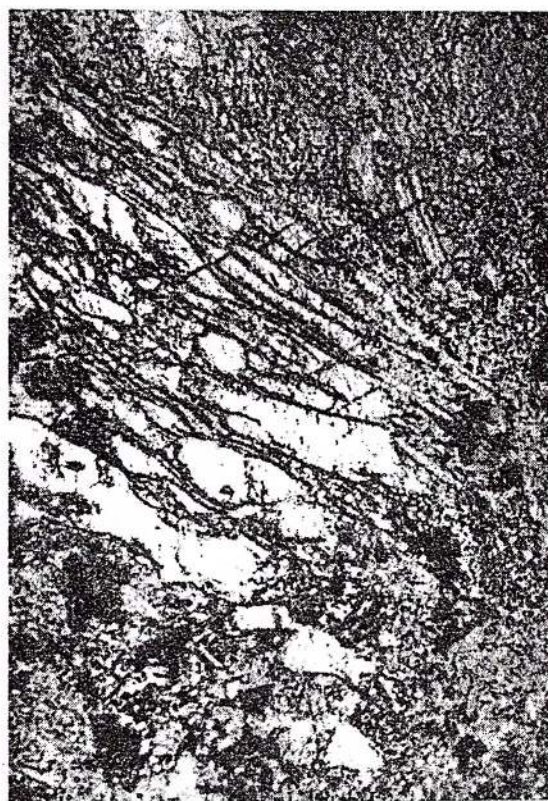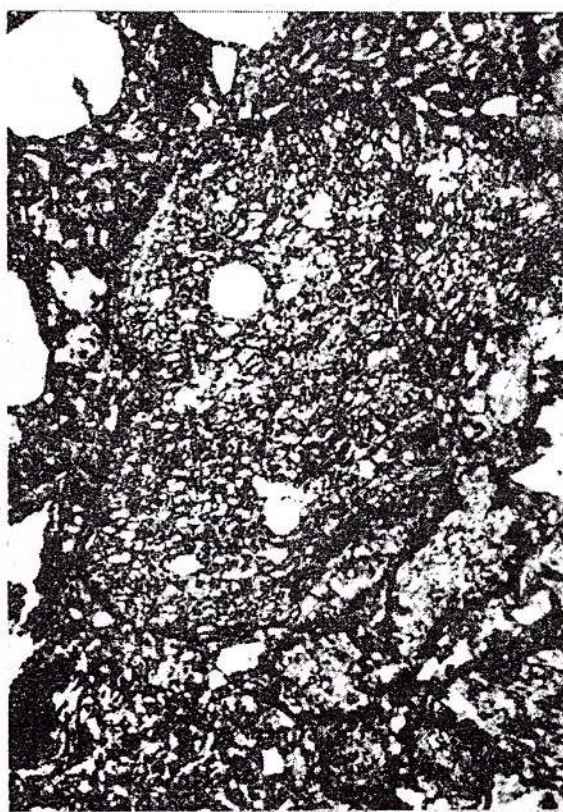
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Plate II

Fig. 1 — deformed, elongated vesicles and fibrous texture in a pumice clast; Toaca Valley, Ilba, NII, 30X

Fig. 2 — heterogeneous vesicle texture in pumice; Bocilor Valley, Seini, NII, 30X

Fig. 3 — "vortex pattern" in a pumice clast; Bocilor Valley, Seini, NII, 30X

Fig. 4 — folded flow foliation of glass in pumice; Bocilor Valley, Seini, NII, 30X
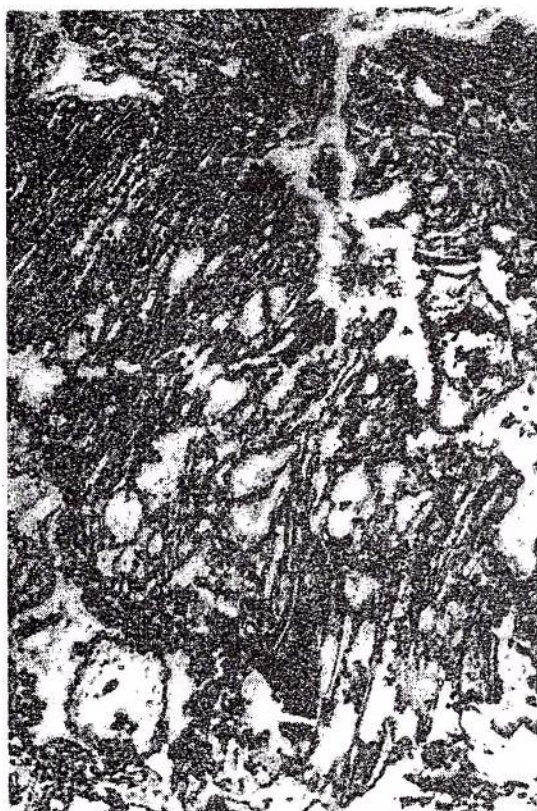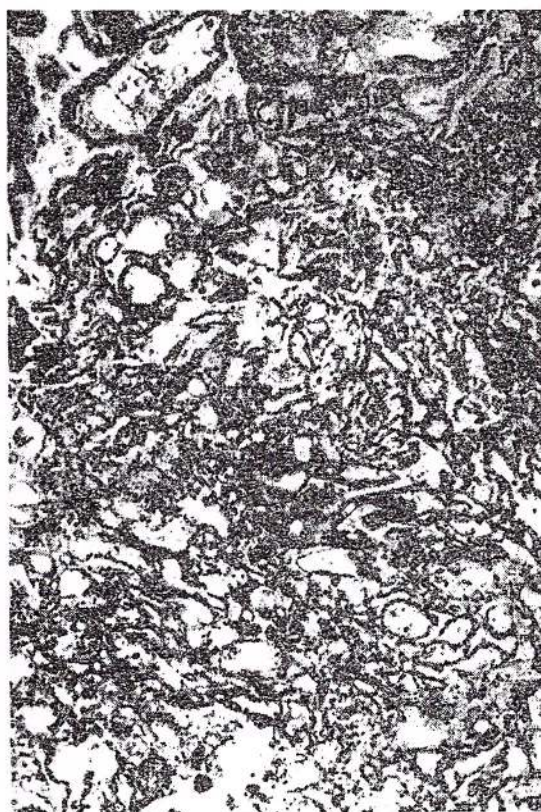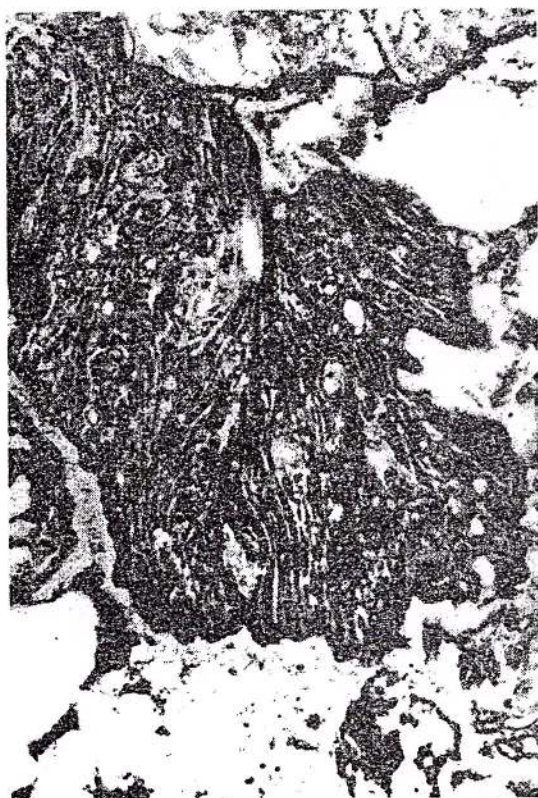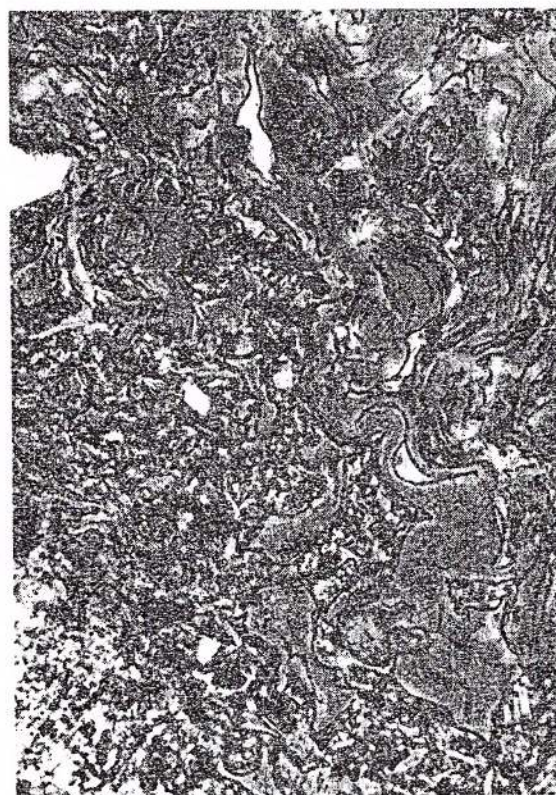
Fig. 1

Fig. 2

Fig. 3

Fig.4

Plate III

Fig. 1 — cuspate (c), needle (n), platy (pt) glass shards in ash; Romana Valley, Firiza, NII, 60X

Fig. 2 — micropumice (mp), X, Y-shaped glass shards (x, y) in ash; RomanaValley, Firiza, NII, 30X

Fig. 3 — microfiamme (mf) in ignimbrite matrix; Viile Racsei, NII, 60X

Fig. 4 — quartz crystal (q) surrounded by microfiamme (mf) in ignimbrite; Lapusna Mare Valley, Baita, NII, 120X
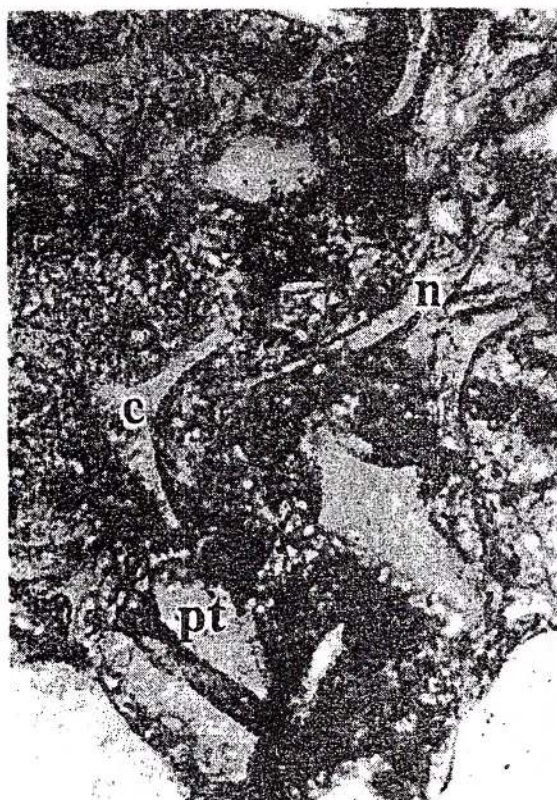
Fig. 1
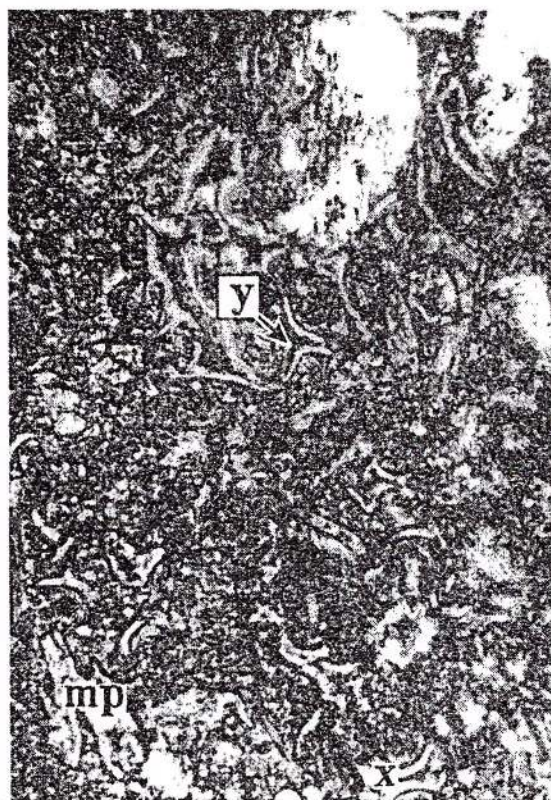
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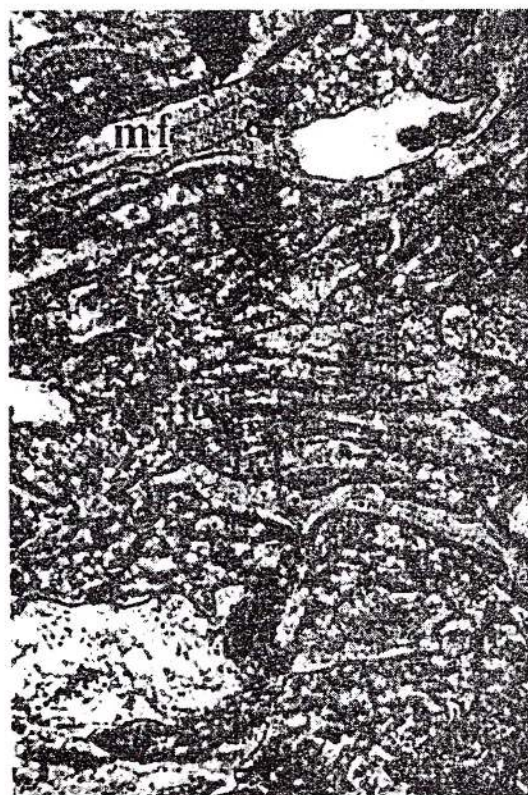
Fig. 3
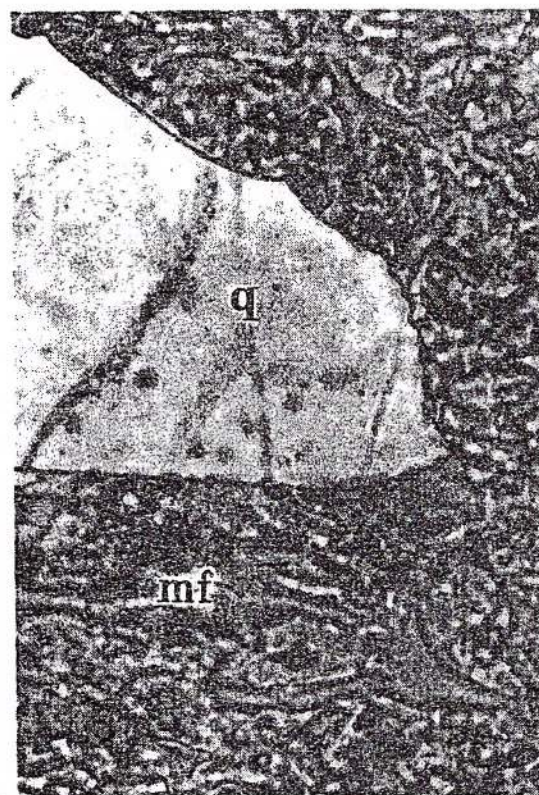
Fig. 4

Plate IV

Fig. 1 — fiamme (f), microfiamme (mf) and quartz (q) in ignimbrite; Viile Racsei, NII, 30X

Fig. 2 — fiamme (f), quartz (q) and matrix (m) in ignimbrite; Dobas valley, Ilba, NII, 30X

Fig. 3 — pseudofiamme (pf), xenoliths (xe), quartz (q) and matrix (m) in mass flow volcaniclastics; Limpedea valley, Baita, N+, 30X

Fig. 4 — pseudofiamme (pf), quartz (q), opaque minerals (o) and matrix (m) in mass flow volcaniclastics; Limpedea valley, Baita, N+, 30X

Particle outlines or textural features have been enhanced in several photographs for clearness.

Fig. 1

Fig.2
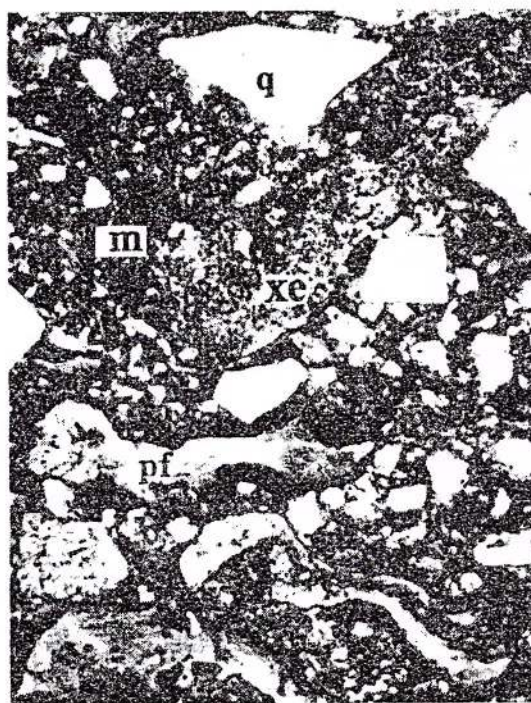
Fig.3
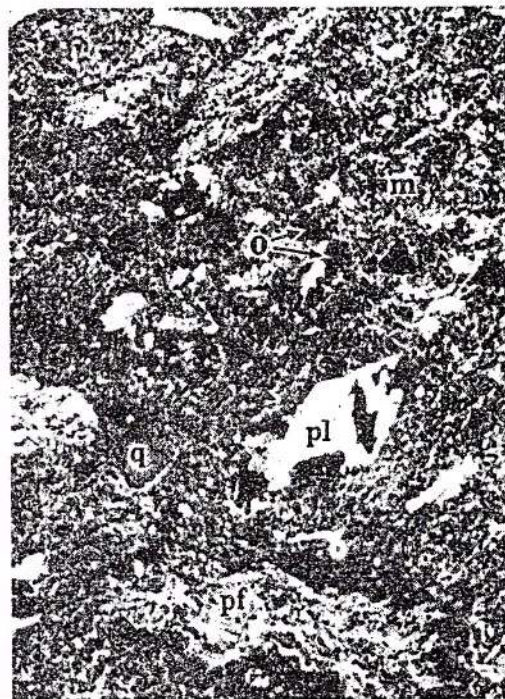
Fig.4

COMPARATIVE ANALYSIS OF THE NEOGENE/QUATERNARY POST-COLLISONAL-RELATED MAGMATISM IN THE BETICS (SE SPAIN) AND EAST CARPATHIANS (ROMANIA): A REVIEW

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Abstract: Neogene volcanic activity in the examined areas - Betics and East Carpathians post-dated continent-continent collision and took place at the inner side (opposite with respect to tectonic transport direction) of the collision-generated orogenic belts. The beginning of volcanism consisted of large-volume silicic explosive eruptions in both areas, although their ages are different: 24-18 Main the Valencia Trough, and 18-14 Main the East Carpathians. The principal calc-alkaline activity developed in both areas between 13 and 7 Ma, being much more extensive in the East Carpathians. In both areas high-K calc-alkaline and shoshonitic compositions characterise, at least partially, the late-stage volcanic products. Coeval alkali- basaltic volcanism occurred in both regions during the Pliocene-Pleistocene interval. The main difference consists of the presence of ultrapotassic volcanism only in the Betics. It is only coeval with the latest calc-alkaline and shoshonitic activity. Geochemical data suggest mantle to be the main common source of magmas, but it appears clear that crust was also involved in their generation. Magmas of different sources underwent a complex interplay of fractional crystallisation, magma mixing and assimilation in crustal magma chambers before reaching the surface. Slab detachment and breakoff mechanisms can be invoked to explain magma generation and relationships between tectonic setting and time-space evolution of calc-alkaline, shoshonitic and alkali-basaltic magmatism in both regions.

1. Introduction

The predominantly calc-alkaline volcanism found in areas of plate convergence considered to belong to one of two basic types: (1) island-arc type, and (2) continental margin (or Andean) type. Their more or less distinct geochemical and petrological features are generally assigned to the different thickness and type of crust belonging to the overriding plate. Fossil continental collision-related volcanic areas do not seem to fit this classification. In many cases they display both "island-arc" and "continental margin" signatures. The Mediterranean area and its extended geologic equivalent - the Tethyian area - display a very complicated situation of convergent plate boundaries as a result of the existence of a number of "microplates" or "plate fragments" assembled during the collision of Eurasia and Africa from Late Mesozoic to Cenozoic.

Time-space relationships and petrological heterogeneity of fossil continental collision-related volcanic are as reflect both the tectonic complexity of the region and its geological history. Thus, a comparative examination of "Tethyan" volcanic areas could provide important insight in the complex geological evolution of this region.

Two Neogene volcanic areas, the Betics in south-eastern Spain and the East Carpathians in Romania, located at the opposite sides of the European Tethys are comparatively examined in this paper. Based on published and unpublished data, the spatial distribution of Neogene volcanics, age and migration of volcanic activity, and the principal petrographical and geochemical features of the rocks in both regions will be reviewed. Both similarities and significant differences between the two areas will especially be emphasised.
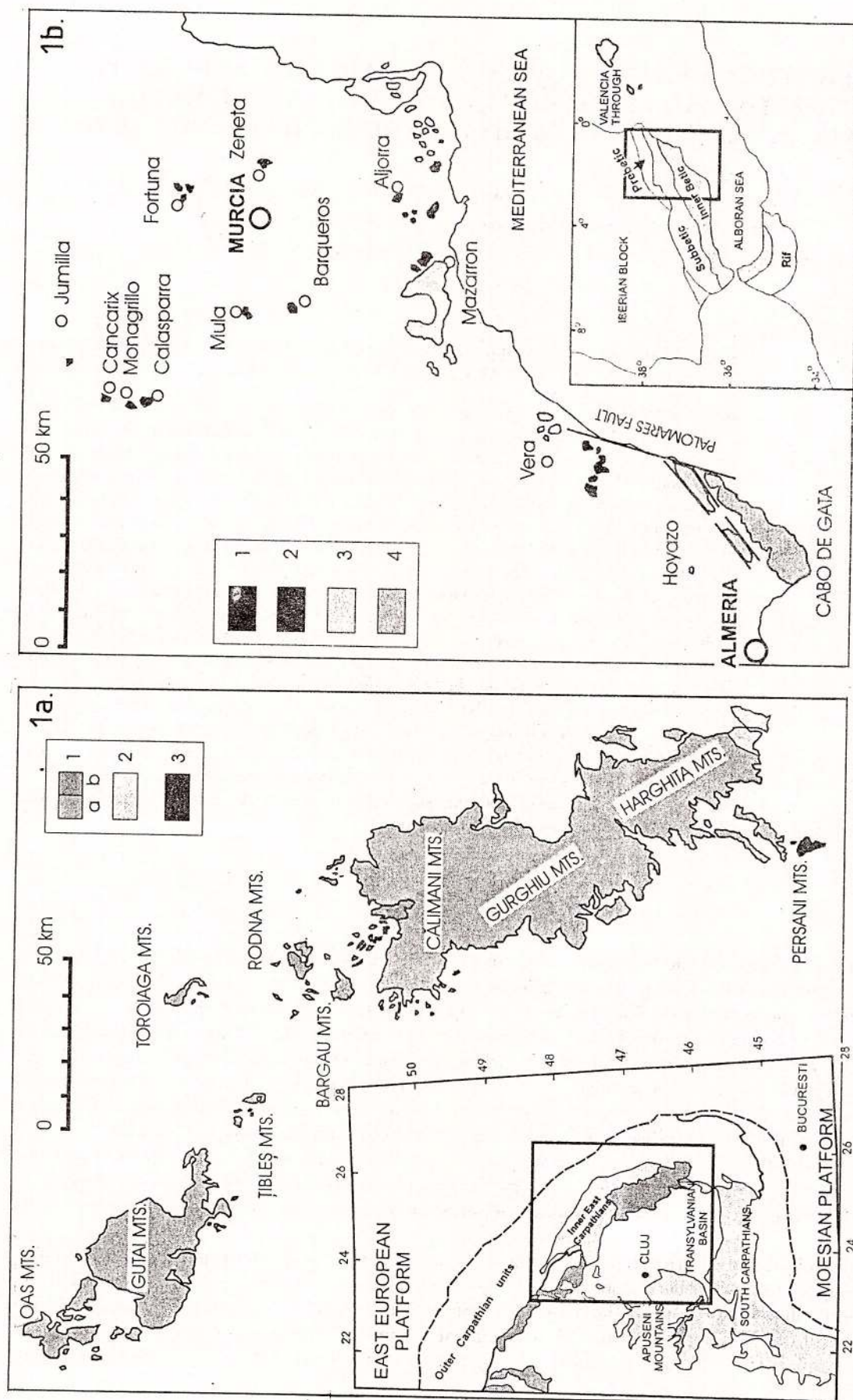
Fig. 1 – Sketches showing the spatial distribution of the Neogene-Quaternary ' volcanic rocks including general geological setting (insets):
1a. East Carpathians, Romania. 1: calc-alkaline; 1a-effusive rocks; 1b-intrusive rocks 2: K-calc-alkaline and shoshonitic; 3: alkali-basaltic
1 b. Betics, SE Spain. 1: calc-alkaline; 2: K-calc-alkaline and shoshonitic; 3: ultrapotassic 4: alkali-basaltic

2. Distribution, age and migration of the Neogene volcanic activity

The Betics and the Carpathians were formed during two main periods of collision during Cretaceous and Lower Miocene (Andrieux et al., 1971; Araña and Vegas, 1974; Weijermans, 1991; Săndulescu, 1984). The Neogene volcanic activity in both areas - the Betics and the East Carpathians - post-dated the continent-continent collision and it took place generally in the inner part (opposite with respect the tectonic transport direction) of the collision- generated orogenic belts characterised by foreland-type thrusting and faulting.

2.1. Betics

The main Neogene calc-alkaline volcanic area is situated on the eastern coastline of Almería, between Cabo de Gata and Carboneras (Fig. 1 a). The volcanics form a 40 km long and 10 km wide chain (Fúster et al., 1965; Araña and Vegas, 1974; López-Ruiz and Rodríguez-Badiola, 1980). A small isolated exposure of high-K volcanics occurs east of the occurrence of calc-alkaline area at Cerro de Hoyazo (Zeck, 1970). Marine geology data suggest a submarine continuation of the calc-alkaline chain more than 60 kms south of Cabo de Gata (García-Rodríguez and Alvárez, 1977) in the Alborán Sea. Further south-eastward, the Alborán island is composed of andesites with tholeiitic affinities (Hernández-Pacheco and Ibarrola, 1970; Molin, 1980). Neogene basaltic dykes with the same tholeiitic features intrude the metamorphic Malaguides units (Torres-Roldán et al., 1986).

Lower Miocene rhyolitic tuffs have been found in the Neogene extensional basins in the inner zone of the Betic belt: (Chauve et al., 1973, de Clércq et al., 1975). Calc-alkaline rhyolitic tuffs of the same age were recognised in the western Betic-Balearic domain, mainly in Mallorca (Alvaro-López et al., 1987, Martí et al.,1992).

Northeast of Cabo de Gata area - close to the Palomares fault - the volcanic rocks form isolated occurrences. In the Vera-Mazarrón area, high-Kcalc-alkaline, shoshonitic, and ultrapotassic rocks appear (Fúster et al., 1967 a; Araña and Vegas, 1974; López-Ruiz and Rodríguez-Badiola, 1980). Several small occurrences of ultrapotassic rocks are scattered over a large area northeast of Vera-Mazarrón, being associated with Neogene sedimentary basins of the Betic and Sub-Betic zones (Fúster et al., 1967 b).

Small-volume alkali-basaltic volcanics are also present near Mazarrón (Rodríguez-Badiola, 1973) and in the Valencia trough (Ancochea, 1984; Martí et al., 1992).

Taking into account that the geotectonic evolution of the Marocco Rif area is comparable to that of the Betic region (Andrieux et al., 1971), it is worth while to mention the presence of the Neogene calc-alkaline, shoshonitic, and alkali-basaltic volcanism on the northern coast of Marroco (Hernández and Bellon, 1985; Hernández et al., 1987; Bakkali et al., 1998).

In the Betic domain, the oldest volcanic activities are located at its extremities (Fig. 2). In the east, in the Balearic extension of the Betic area, large-volume silicic explosive volcanic products were erupted in Aquitanian-Burdigalian times (24-18 Ma). They are probably coeval with the Aquitanian-Burdigalian silicic tuffs present in the Betic domain (Chauve et al., 1973; de Clercq et al., 1975) and in the whole western Mediterranean area (Lorenz, 1984).

The Aquitanian-Burdigalian magmatic activity in the eastern Betic domain has tholeiitic affinity. Its radiometric age was obtained on basic dykes crosscutting the Malaguides and Alpujarrides units (Torres Roldán et al., 1986) and on andesite blocks engulfed in pyroclastic rocks in the Alborán Sea (Bellon, 1981; Hernández et al., 1987; Aparicio et al., 1991).

The wider Neogene volcanic area is situated between Cabo de Gata and Cartagena, but volcanic deposits are also present in the Alborán Sea. The radiometric data in Cabo de Gata rocks indicate a migration of volcanic activity along the chain, from the oldest products in the north-east (15.1 Ma) to the youngest ones located in the south-west (6.7 Ma) (Bellon et al., 1983; Di Battistini et al., 1987). Generally, there is a good agreement between radiometric and biostratigraphic data (Serrano, 1992).

The high-K calc-alkaline and shoshonitic volcanism is scattered over a 200 km long area from Verato Mar Menor displaying K/Ar ages between 8.6-6.8 Ma (Bellon et al., 1983; Nobel et al., 1981).

The ultrapotassic volcanism seems to have been coeval with the Tortonian-Messinian shoshonitic rocks (Nobel et al., 1981; Bellon et al., 1983; Montenat et al., 1975) and with the latest volcanic activity of Cabo de Gata. Minor alkali-basaltic occurrences - northeast of Cartagena - represent the youngest (2.7-2.9 Ma; Bellon et al., 1983) volcanic activity of the Betics. The K/Ar ages of alkali-basaltic volcanics in the Valencia trough and Columbretes zone range between 2.0-0.33 Ma (Sáez-Ridruejo and López-Marinas, 1975; Aparicio
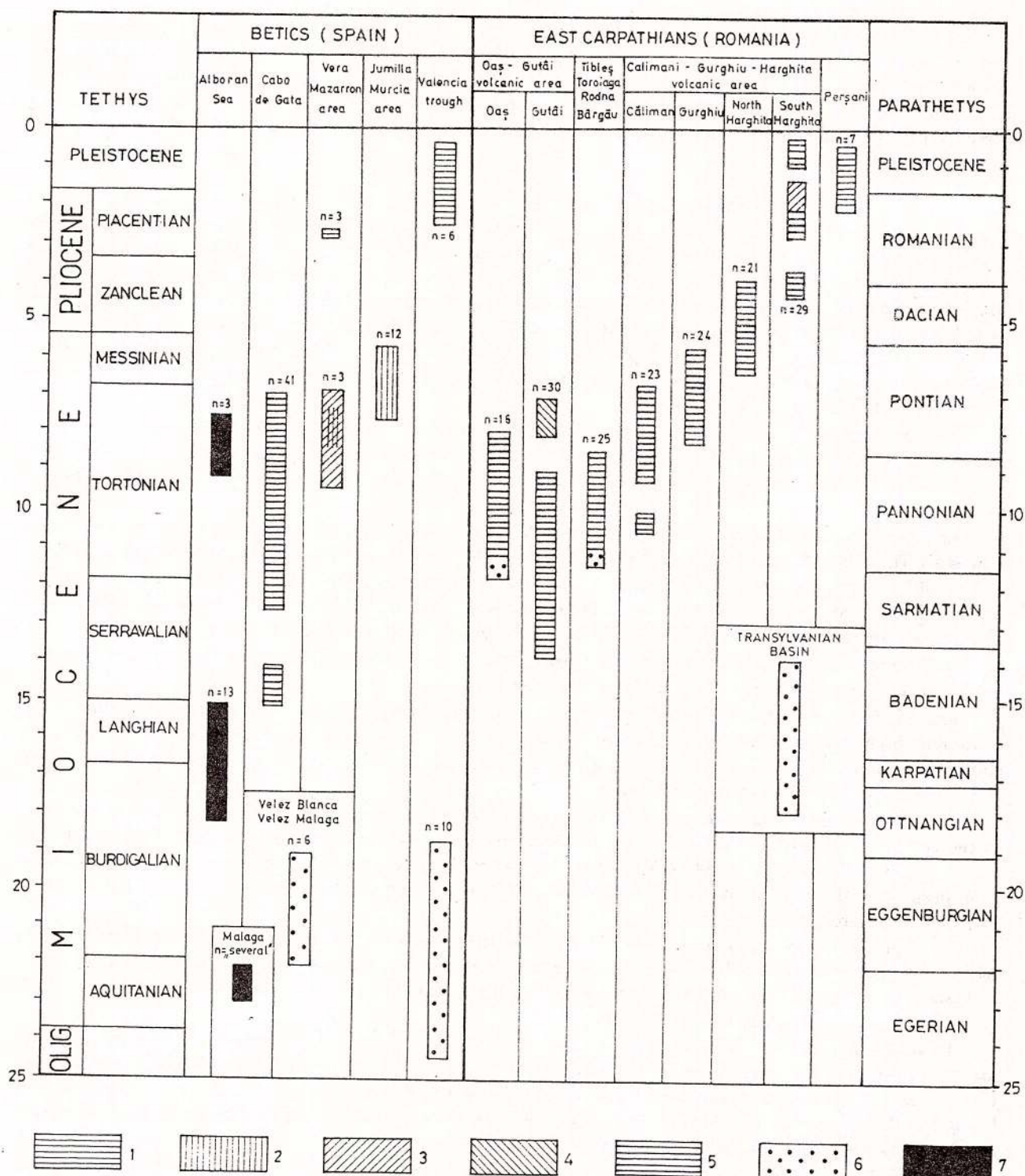
Fig. 2 – Compared time evolution of the Neogene-Quaternary volcanism in the Betics, SE Spain and East Carpathians, Romania. (Chauve et al., 1973, Lorenz, 1984, Torres Roldan et al., 1987, Aparicio et al., 1991, Bellon, 1981, Bellon et al., 1983, Nobel et al., 1981, Pécskay et al., 1995 a, b, Edelstein et al., 1992) 1: alkali-basaltic; 2. ultrapotassic; 3. shoshonitic; 4. basic calc-alkaline; 5. intermediate calc-alkaline; 6. acid calc-alkaline; 7. tholeiitic.

et al. 1991; Martí et al., 1992).

2.2. East Carpathians

The Neogene volcanics associated with the Carpathians are mainly calc-alkaline in character and are distributed along the orogenic arc at its inner side, forming a succession of elongated volcanic areas at the interior of Carpathian arc (Lexa and Konecny, 1974; Szabo et al., 1992; Seghedi et al., 1995) (Fig. 1 a).

Neogene volcanism also occurs in the Apuseni Mts. and mainly along the East Carpathians (Pécskay et al., 1995 a; Roşu et al., 1997; Fig. 1 b). In the East Carpathians Neogene volcanics are clustered in three principal sectors, from north to south: (1) Oaş-Gutâi (OG) area, (2) Ţibleş-Toroiaga-Rodna-Bîrgau (TTRB) area, and (3) Călimani-Gurghiu-Harghita (CGH) volcanic chain (Seghedi et al., 1995). The OG sector is made by calc-alkaline rock assemblages ranging from basalts to rhyolites, forming isolated (in Oaş) or clustered (in Gutai) volcanic edifices. Intrusive bodies of the same age are also present (Pécskay et al., 1995 a). The TTRB sector, also termed "the subvolcanic zone", is characterised by swarms of shallow intrusive bodies. They pierce pre-Cenozoic metamorphic rocks or Upper Cretaceous to Paleogene sedimentary deposits. Their petrography is variable ranging from basaltic andesites to rhyolites (Seghedi et al., 1995). The CGH sector represents the southernmost and longest occurrence area of Neogene volcanics in the whole Carpathians. It consists of a ca. 160 km long continuous volcanic chain with decreasing width, height and volume from north to south. Except for the earliest intrusive stage in the Călimani Mts., effusive-explosive volcanic activity prevailed, building up a chain of adjoining and overlapping composite edifices and well-developed peripheral volcaniclastic aprons (Szakács and Seghedi, 1995).

Apart from the volcanics located in the Carpathian Mountains, large-volume acid pyroclastics of Neogene age are found in the Transylvanian Basin, both in surface outcrops and buried, and in the Moldavian and Moesian Carpathian forelands. Similar large-volume Miocene tuffs are known westwards in the Pannonian basin too.

Small-volume alkali-basaltic volcanics are scattered in the inner areas of the whole Carpathian arc. Such rocks are known in the Perşani Mts. at only 40 km west of the South Harghita calc-alkaline to shoshonitic volcanics (Seghedi et al., 1987, 1995; Downes et al., 1995; Mason et al., 1996). The earliest Neogene volcanic activity occurred in two main stages, that produced mainly volcanoclastics of rhyolitic composition, interbedded within the Miocene basin-filling sedimentary deposits. K/Ar and zircon fission track ages yielded up to now an interval at 13.5-18 Ma, but recently was recognised to be closer to ca. 15 Ma, (Szakács, unpublished data).

The oldest dated volcanic activity in the Gutai Mts. (13.9 Ma, Edelstein et al.,1992) is roughly coeval with the Upper Badenian rhyolitic tuffs in the Transylvanian Basin. Thus, a continuation of acid explosive volcanism with the dacitic-andesitic volcanism occurring at the southern part of Gutâi Mts. could be assumed. The early stage of volcanic activity in the Gutâi Mts. lasted from 13.9 to 12.1 Ma (Upper Badenian and Lower-Middle Sarmatian). The most acid-dacitic-volcanics from the southern Gutâi Mts. are among the oldest ones. Roughly coeval calc-alkaline volcanic activity developed in the Gutâi (2nd stage) and Oaş Mts. during the Pannonian, with ca. 1 million year more in the Oaş Mts. (from 11.2 to 8.0 Ma) than in the Gutâi Mts. (11.6-9.0 Ma), continuing in Lower Pontian (Pécskay et al., 1995). The oldest rocks in the Oaş Mts. are rhyolitic in composition and are located at their southern edge. This second-stage volcanism in the Gutâi Mts. occurred across a wide area, mostly situated northward with respect to the first-stage products. The third-stage of the Neogene volcanic activity of the OG sector occurred during the Pontian (8.1-7.0 Ma), only in the southern part of Gutai Mts. and it is represented by a number of shallow basic intrusions (Pécskay et al., 1995 a, Edelstein et al., 1994).

The intrusive magmatism of the TTRB sector ("the subvolcanic zone") can be considered as being roughly coeval with both Oaş and second-stage Gutâi volcanism. The oldest intrusions are the most acid ones here, too; this is especially evident in the Rodna Mts (Pécskay et al., 1995 a).

The CGH sector was the site of a typical along-arc-migrating volcanism during the Neogene. A large number of K/Ar ages are available for this region (Rădulescu et al., 1972; Michailova et al., 1983; Peltz et al., 1987; Pécskay et al., 1995 a). The earliest magmatic events in the Călimani Mts. were intrusive, being coeval (10.6-9.5 Ma) with the "subvolcanic zone" and its prolongation. The volcanic activity spans from 9.3 to 6.7 Ma, with a dacitic episode as the oldest manifestation. The overall younger age of the volcanism in the Harghita Mts. with respect to both Călimani and Gurghiu is well-documented (Fig. 2). Furthermore, age differences are found between North Harghita (6.3-3.9 Ma) and South Harghita (4.4-0.2 Ma) segments. The northernmost volcanic edifice of South Harghita was contemporaneously active with

North Harghita volcanoes, while the next South Harghita edifice started to be built up after a time gap of almost 1 Ma. Each volcanic edifice in South Harghita is progressively younger toward south. The youngest volcanics have been erupted at ca. 35-42 Ka (Moriya et al., 1996). In the Perşani Mts. of the southern East Carpathians, Upper Pliocene-Pleistocene (2.2-0.35 Ma; Casta, 1980; Mihaila and Kreutzer, 1981; Downes et al., 1995) alkali-basaltic volcanism developed contemporaneously with the youngest volcanic activity in South Harghita.

2.3. Comparative remarks

A comparison between the time-space evolution of the Neogene volcanism in the Betic sand East Carpathians shows some important similarities:

- The beginning of the Neogene volcanic activity was characterised by the eruption of large-volume acidic pyroclastic rocks in both areas, but the ages are different: at ca. 15 Ma in the East Carpathians and 24-18 Ma in Valencia trough and all over the western Mediterranean;
- The main calc-alkaline volcanic activity developed in both areas between 13-7 Ma, being much more extended and voluminous in the East Carpathians;
- In both areas almost at the end of calc-alkaline activity there is a high-K and shoshonitic volcanism;
- Coeval alkali-basaltic volcanism occurred in both areas during the Pliocene-Pleistocene interval.

The differences are mainly related to the presence of ultrapotassic volcanism in the Betics, coeval with the latest calc-alkaline and shoshonitic activity. This kind of volcanic activity did not develop in the East Carpathians. Another important difference consists in the presence of widespread tholeiitic volcanic activity in the Alborán area covering a large time interval. Such kind of volcanism is also lacking in the East Carpathians.

3. Petrology

3.1. Betics

In the Betics the calc-alkaline volcanic rocks are dominated by andesites, with minor basaltic andesites, dacites and rhyolites (López-Ruiz and Rodríguez-Badiola, 1980, 1984; Toscani et al., 1990; Fernández-Soler, 1992; Zeck et al., 1998; Benito et al., 1999). Almost all the rocks display porphyritic texture with glassy to microcrystalline matrix. Plagioclase is the most important phenocryst mineral, present in all rock-types but its composition is variable (An=94-49). Clinopyroxene and in places olivine are present in basaltic andesites. The andesites contain mainly orthopyroxene and amphibole-hornblende or cummingtonite (Fernández-Soler, 1992). Clinopyroxene and biotite are less abundant. The dacites contain additional quartz as compared to the andesites, being richer in amphibole, with less ortho- and clinopyroxene. In the rhyolites the plagioclase, quartz, biotite, amphibole and K-feldspar are the main phenocrysts. Rhyolites containing orthopyroxene have also been encountered. Ubiquitous is magnetite and ilmenite. Minerals show a wider ange of compositions for all phenocryst phases (López-Ruiz and Rodríguez-Badiola, 1980; Toscani et al., 1990; Fernández-Soler, 1992). Accumulations of crystal clots (plagioclase and mafic minerals) were for med mainly in acid andesites and dacites, which also contain crustal xenoliths (Sánchez-Cela, 1968; Bordet, 1985).

The high-K calc-alkaline volcanics represented by K-andesites, K-dacites and shoshonitic rocks - banakites and latites - show a porphyritic texture with glassy to hypocrystalline matrix (Rodríguez-Badiola, 1973; López-Ruiz and Rodríguez-Badiola, 1980). The less acid rocks contain plagioclase, orthopyroxene, amphibole, while in the more acid types prevalent quartz and biotite are added to these minerals. Only the shoshonitic rocks contain sanidine. The common feature of all these rocks is the irrelatively large amount of cordierite, garnet, sillimanite and andalusite of xenocrystic origin. Primary magmatic cordierite and garnet xenocrysts (restites) have also been mentioned (López-Ruiz and Rodríguez-Badiola, 1980; Zeck, 1969, 1970; Munsgaard, 1984). Zeck (1992) also described the presence of crustal quartz-gabbroic and basaltoid xenoliths. Plagioclase-biotite-clinopyroxene-glass association forms crystal clots accumulations in these rocks too.

The ultrapotassic rocks are lamproites and display variable textures ranging from holocrystalline to porphyritic with glassy matrix. The main mineral phases are olivine, phlogopite, clinopyroxene, and variable contents of sanidine, orthopyroxene, leucite, richterite, biotite and calcite. Apatite, rutile and spinels are the most frequent accessory minerals (Fúster et al., 1967; López-Ruiz and Rodríguez-Badiola, 1980; Venturelli et al., 1984). The different relations of phlogopite and biotite (Fúster, 1956; Venturelli et al., 1991) and the presence of shoshonitic xenoliths suggest important mixing processes between shoshonitic and lamproitic
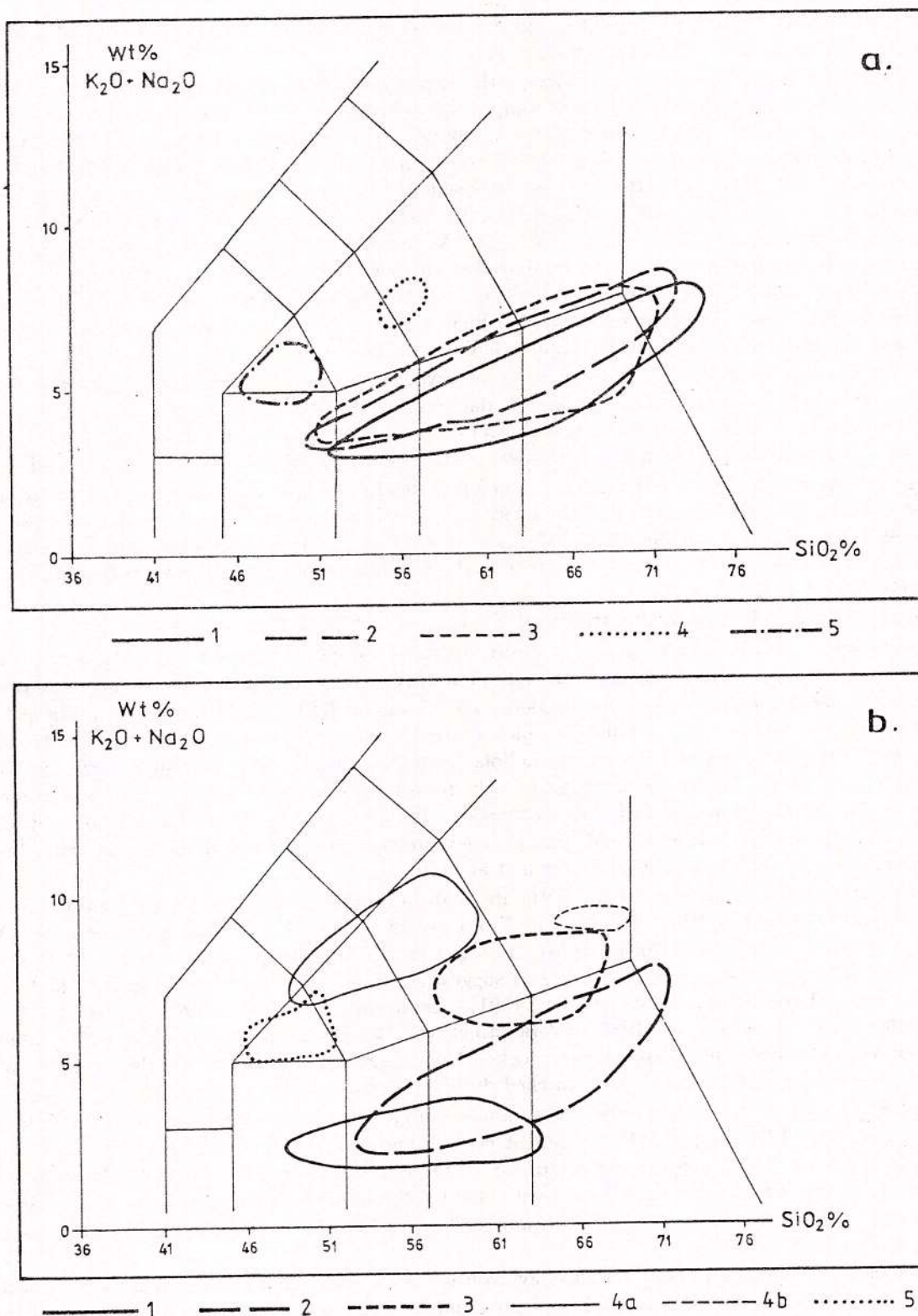
Fig. 3 – Fields of the different groups of volcanics in the TAS diagram (Lopez-Ruiz and Rodriguez-Badiolla, 1980, 1984; Toscani et al., 1990; Fernandez-Soler, 1992; Zeck, 1970, 1992; Munsgaard, 1984; Venturelli et al., 1984; Brandle et al., 1984; Seghedi et al., 1987, 1995; Mason et al., 1996; Downes et al., 1995):
3a. East Carpathians: 1: Oaş-Gutâi (CA), 2: subvolcanic zone (CA), 3: Călimani-Gurghiu-Harghita (CA), 4: Harghita (SH), 5. Perşani (AB).
3b. Betics: 1: Alboran (TH & CA), 2. Cabo de Gata (CA), 3: Vera-Mazarron (K-CA & SH), 4 a: Jumillia-Murcia (UK) 4 b: Vera-Mazarron (UK), 5: Vera-Mazarron (AB).

magmas (Zeck, 1992). Peridotites (dunites and harzburgites) and some crustal rocks were also found as xenoliths (Fúster et al., 1967; Venturelli et al., 1984).

The alkali-basalts have porphyritic textures with microcrystalline to cryptocrystalline matrix. Olivine, augite and plagioclase are the main crystal components. Accessory Fe-Ti oxides are also present. The rocks are rich in xenolithic peridotites, dunites, harzburgites, clinopyroxenites (in places with interstitial plagioclase, kaersutite, phlogopite), quartz-felds pargranulites (with sillimanite, spinel, garnet) and albitic schists (Sagredo, 1972, 1973, 1976; Boivin, 1982; Vielzeuf, 1983). Major element data (Hernandez Pacheco and Ibarrola, 1970; López-Ruiz and Rodríguez-Badiola, 1980; Di-Batistini, 1987; Bordet, 1985; Toscani et al., 1990; Cunningham et al., 1990; Nixon et al., 1984; Venturelli et al., 1988, 1991; Fernández-Soler, 1992; Munskaard, 1984; Aparicio et al., 1991) were plotted in the TAS (Le Maitre et al., 1989) (Fig. 3 a, b) and K_2O-SiO_2 (Pecerillo and Taylor, 1976) diagrams (Fig. 4 a, b). High-silica andesites (58-61 % SiO_2) are the most abundant rock type. Low MgO content and high CaO and Na_2O is obvious mainly in calc-alkaline rhyolites and dacites (López-Ruiz and Rodríguez-Badiola, 1980).

Three associations with different trends can be observed in the K_2O-SiO_2 diagram: (1) Cabo de Gata rocks form medium-K basaltic andesites to high-K dacites and rhyolites; (2) a steeper trend of high-K and shoshonitic rocks from Vera-Mazarrón area; (3) Alborán volcanics trend in the direction of the tholeiitic suite. Acid rocks from Valencia trough are situated at the limit of the high-K and shoshonitic fields.

The ultrapotassic rocks in the TAS diagram cover a large field ranging from trachybasalts to trachydacites. The most basic rocks occuring north and the most acid ones in the south (Fig. 3 a). Almost always the K_2O content is over 2.5 % in the high-K and shoshonitic rocks and, of course, in all the ultrapotassic rocks. The young basalts from Vera-Mazzaron are a plot in the trachybasaltic field of the TAS diagram (Brändle et al., 1984) (Fig. 3 a).

A general overview of the available REE data (Toscani et al., 1990; Fernández-Soler, 1992) indicates a trend of enrichment of LREE from basaltic andesites to rhyolites, which suggests differentiation processes. Some minor negative Eu anomalies suggest the retention of plagioclase during fractional crystallization.

The high-K and shoshonitic rocks from the Betics show a similar REE distribution pattern, but at higher values; they are also enriched in compatible or incompatible trace elements as compared with calc-alkaline rocks (Zeck, 1970; López-Ruiz and Rodríguez-Badiola, 1980; Munskaard, 1984; Martin Escorza and López-Ruiz, 1988, Benito et al., 1999). The lamproitic rocks from the Betic area have very high contents of Ni, Cr, Ba, Ce, Th, Zr as compared with the moderate or low contents of Nb, Y, V, Sc (López-Ruiz and Rodríguez-Badiola, 1980; 1984; Venturelli, 1984). They are strongly enriched in LREE too and displays light Eu anomalies (Nixon et al., 1984; Venturelli et al., 1991 a).

$^{87}Sr/^{86}Sr$ and εN disotopic data for the Betic area indicate different variation ranges for Cabo de Gata calc-alkaline rocks (εNd=-6.4; $^{87}Sr/^{86}Sr$=0.7079-0.7156) and for the high-K and shoshonitic rocks from Vera-Mazarrón (εNd=-10; $^{87}Sr/^{86}Sr$=0.7094-0.7176) (Hertogen et al., 1985, 1988; Toscani et al., 1991) (Fig. 6 a, b). The $\delta^{18}O$ isotopic data (+9.5 to 20.3 $^0/_{00}$) suggest an enrichment from calc-alkaline to high-K and shoshonitic rocks (López-Ruiz and Wasserman, 1991). Lamproitic rocks are more enriched in $\delta^{18}O$ and follow another trend. Munsgaard's (1984) and Benito et al. (1999) data show even higher $\delta^{18}O$ values for Hoyazo and Vera-Mazarrón high-K-shoshonitic rocks. They suggested that the $\delta^{18}O$ inherited the isotopic signature of the source and further on was enriched during the interaction with the crust.

Nd and Sr isotopic data for lamproitic rocks indicate an enriched source for these rocks which follow a strong and long-term LREE and LILE enrichment (Powell and Bell, 1970; Nelson et al., 1986; Venturelli et al., 1991) (Fig. 6 a, b). A general increase of $^{87}Sr/^{86}Sr$ ratio from north to south can also be observed (Nelson et al., 1986). Pb isotopic data for the same lamproites show that the rocks most closely resemble pelagic oceanic sediments (Nelson et al., 1986; Sun, 1980). $^{87}Sr/^{86}Sr$ for the Mazarrón alkali-basalts are of 0.7040 (Hertogen et al., 1985).

The Sr/Ca-Ba/Ca diagram (Fig. 5 a) displays volcanic rocks belonging to the main volcanic edifices: Cabo de Gata, Los Frailes, Rodalquilar, Las Negras and Carboneras. The diagram suggests differences between different volcanic areas interpreted as different degree of partial melting and crystal fractionation processes of a common mantle-derived magma, and probably various small-scale mixing. The more acid rocks are suggested to result either by fractional crystallization processes or via crustal anatexy. The volcanic rocks from Carboneras reveal a higher degree of partial melting (15 %) than those from Las Negras, Rodalquilar, Los Frailes and Cabo de Gata suggesting progressively lower degrees of partial melting of the same source from north to south or, alternatively, more complex mixing processes. Based on the distribution of compatible to incompatible elements, Fernández-Soler (1992) also suggests about 15 % of partial melting of primitive

mantle for the Cabo de Gata rocks. The andesites and basaltic andesites are among the latest products in each volcanic area and their plots are closer to "the partial melting line" suggesting that these volcanic products are closer to the parental magma composition.

The Hoyazo-Mazarrón volcanics present a scattered plot and they are projected together with acid dacites-rhyolites from Cabo de Gata area, covering also the field of the lamproitic rocks. It is difficult to interpret adequately the position of lamproitic rocks in the diagram but - presuming their mantle source - a very low degree of partial melting of a highly metasomatised source can be assumed.

The projection of the Balearic Lower Miocene acid rocks suggests their origin by crustal partial melting. The diagram suggests the same initial mantle source for Cabo de Gata and Hoyazo-Mazarrón volcanic products and a different source for the lamproitic rocks (enriched mantle) and acid Lower Miocene rocks in the Valencia trough (lower crust).

3.2. East Carpathians

The calc-alkaline magmatism of the East Carpathians is dominated by andesites, with minor basalts, basaltic-andesites, dacites and rhyolites (Seghedi et al., 1995). Explosive volcanics in the Transylvanian Basin are mostly rhyolitic containing plagioclase, quartz, biotite and minor amphibole, pyroxene and K-feldspar as crystalloclastic phases (Szakács, unpublished data). The only known rhyolite lavas in the Oaş Mts. are slightly porphyritic with plagioclase and biotite phenocrysts in a mostly glassy matrix. The subvolcanic rhyolites in the Rodna Mts. show similar petrographic features except for their microcrystalline matrix. Based on their mafic phenocryst assemblages, several types of dacites have been recognised: with orthopyroxene; with amphibole and pyroxene; with amphibole, biotite and with biotite, amphibole, quartz, orthopyroxene, clinopyroxene (olivine). This latter variety obviously suggests magma mixing processes (Seghedi et al., 1995; Mason et al., 1995, 1996).

There are many types of andesites of which two pyroxene- , two pyroxene and amphibole-, and amphibole-bearing rocks are the most frequent. In the South Harghita Mts. particular andesite varieties with amphibole and biotite or with amphibole, pyroxene, biotite and quartz phenocrysts, suggesting magma mixing processes, can be encountered. Almandine garnet is also present in some amphibole-pyroxene andesites in the Rodna, Călimani and Gurghiu Mts. Basaltic andesites are present in almost all the areas. They mainly contain clinopyroxene, olivine and orthopyroxene as the principal mafic minerals. Basalts, with phenocryst assemblage including clinopyroxene orolivine-clinopyroxene as mafic phases, have been found only in the Călimani, Rodna, and Bârgau Mts. Some amphibole-bearing basalts crop out in the Călimani Mts. (Seghedi et al., 1995, Mason et al., 1996). The most important accessory minerals in the calc-alkaline rock types are magnetite and ilmenite; in the acid rocks zircon, apatite and allanite are also present. Glomerophiric aggregates of plagioclase, amphibole pyroxene are sporadically present, especially in amphibole-bearing acid andesites.

Small volumes of shoshonitic rocks are present only in the southernmost part of the South Harghita Mts. Besides plagioclase and sanidine, they contain two pyroxenes, amphibole, biotite, and small quantities of both olivine and quartz. This non-equilibrium mineral assemblage suggests mixing processes between an acid and a basic magma (Seghedi et al., 1995; Mason et al., 1995, 1996).

TAS diagram for the rocks of the East Carpathians (Seghedi et al., 1995, Mason et al., 1995, 1996) shows the wide spectrum of types ranging from basalts to rhyolites (Fig. 4). In the K_2O-SiO_2 diagram the rocks cover mainly the "middle-K" field, but "high-K" types are present as well. In the South Harghita an along-the-arc transition from "middle-K" to "high-K" rocks and the presence of shoshonites have been observed (Seghedi et al., 1986, 1987).

With few exceptions, the Perşani basalts fall in the trachybasaltic field (Peltz and Bratosin, 1986; Downes et al., 1995). The East Carpathian alkali-basalts are very close to OIB, but have higher contents of K, Ba, Pb (Downes et al., 1995).

Enrichment in LREE suggests fractional crystallisation processes (Seghedi et al., 1995, Mason et al., 1995, 1996). HREE are less fractionated with the exception of the South Harghita rocks which show an increased depletion along the arc (Peccerillo and Taylor, 1976 b; Seghedi et al., 1987). The South Harghita shoshonitic rocks are strongly enriched in Sr, Ba, Cr, Ni, V and LREE with respect to calc-alkaline rocks (Seghedi et al., 1987; Mason et al., 1996)).

Nd and Sr isotopic ratios of the calc-alkaline rocks in the East Carpathians are plotted closer to the MORB field and are scattered enough (especially $^{87}Sr/^{86}Sr$) to suggest widespread contamination processes, through assimilation in upper crustal magma chambers (Mason et al., 1996). The East Carpathian alkali-basalts have $^{87}Sr/^{86}Sr$ ratios in the range of 0.7035-0.7044 (Peltz et al., 1987; Downes et al., 1995), very
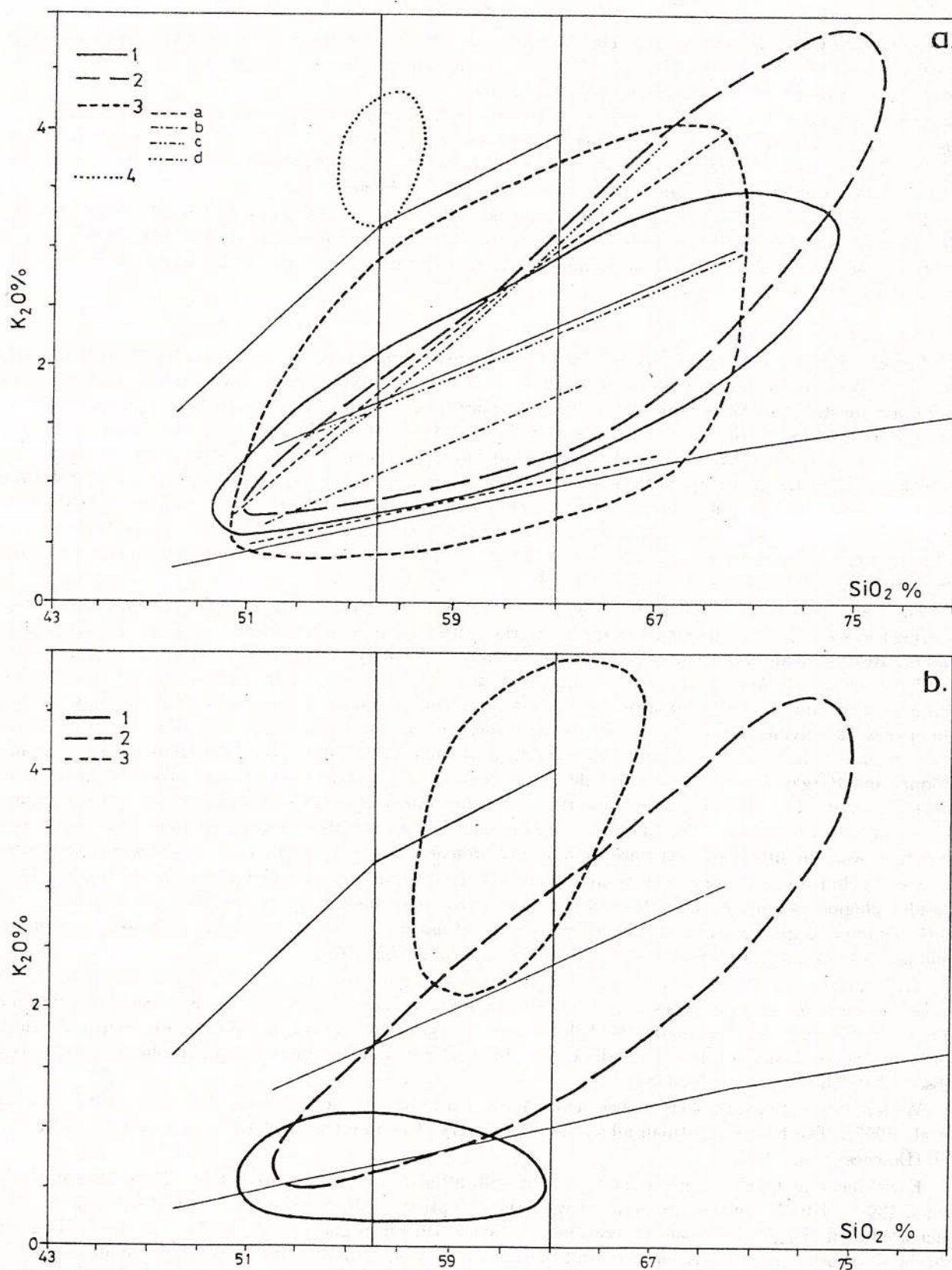
Fig. 4 – Fields of the different groups of volcanic rocks in the SiO_2-K_2O diagram (Lopez-Ruiz and Rodriguez-Badiolla, 1980, 1984; Toscani et al., 1990; Fernandez-Soler, 1992; Zeck, 1970, 1992; Munsgaard, 1984; Venturelli et al., 1984, Brandle et al., 1984; Seghedi et al., 1987, 1995; Mason et al., 1996; Downes et al., 1995): 4 a. East Carpathians: 1: O aş-Gutâi (CA), 2: Subvolcanic zone (CA), 3: Călimani-Gurghiu-Harghita (CA); 3 a - Călimani; 3 b - Gurghiu; 3 c - North Harghita; 3 d - South Harghita, 4: South Harghita (SH), 4 b. Betics: 1: Alboran (TH & CA), 2. Cabo de Gata (CA), 3: Vera-Mazarron (K-CA & SH).
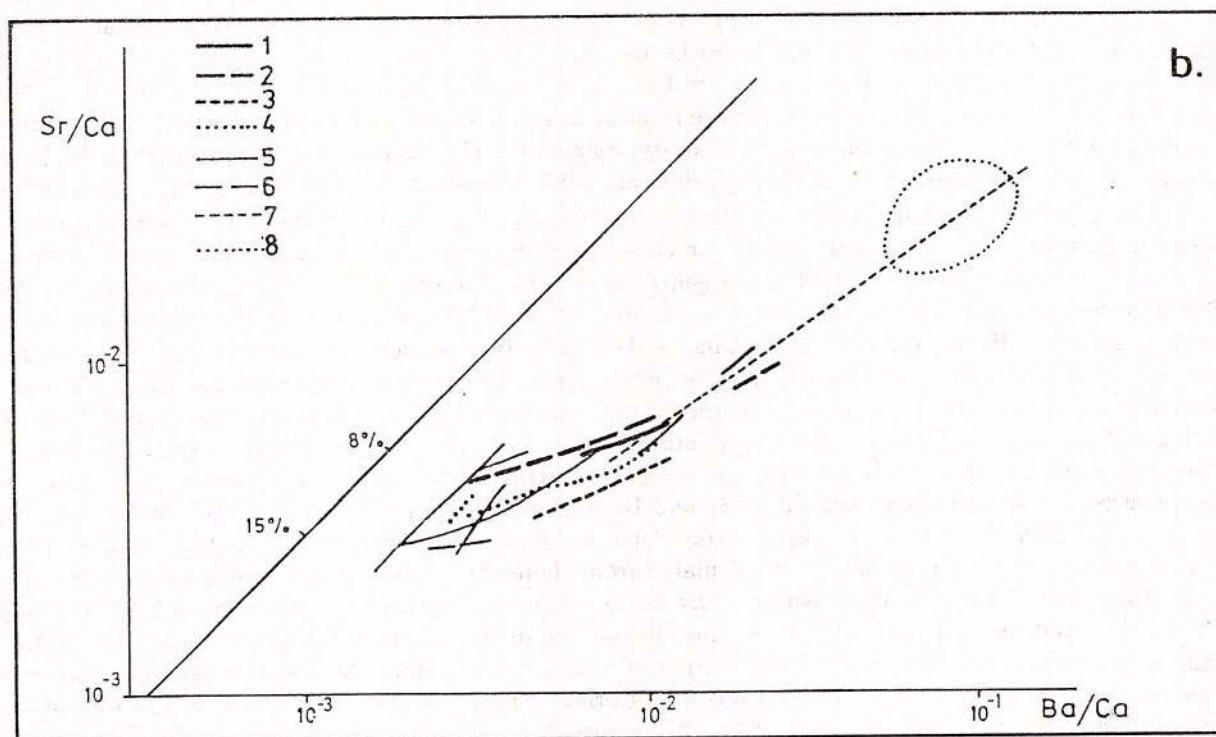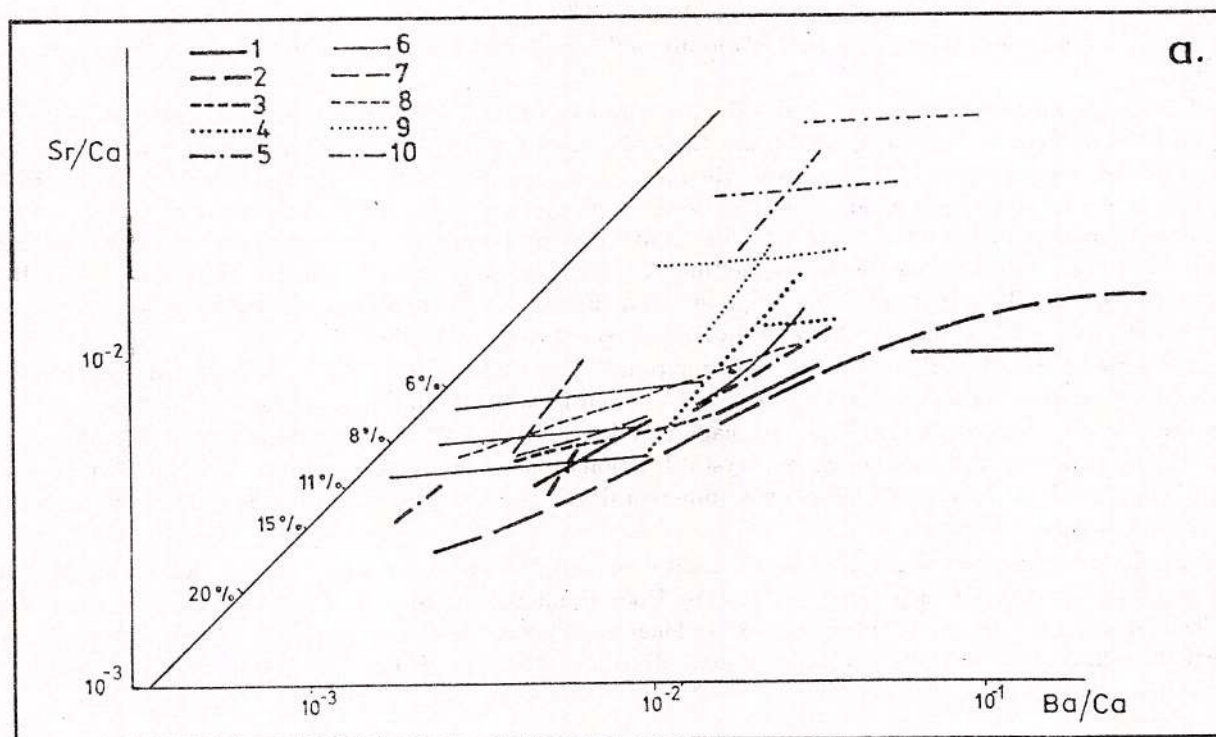
Fig. 5 – Distribution trends of different groups in the Ba/Ca-Sr/Ca diagram (Lopez-Ruiz and Rodriguez-Badiolla, 1980, 1984; Toscani et al., 1990; Fernandez-Soler, 1992; Zeck, 1970, 1992; Munsgaard, 1984; Venturelli et al., 1984; Brandle et al., 1984; Seghedi et al., 1987, 1995; Mason et al., 1996; Downes et al., 1995):
5 a. East Carpathians: CA: 1. Oaş, 2 Gutâi, 3. Ţibleş, 4. Toroiaga, 5. Rodna, 6. Călimani, 7. Gurghiu, 8. North Harghita, 9. South Harghita; 10. K-CA & SH: South Harghita.
5b. Betics: CA: 1. Cabo de Gatà, 2. Los Frailes, 3. Rodalquilar, 4. Las Negras, 5. Carboneras, 6. Nijar. 7. K-CA & SH: Vera-Mazarron. 8. UK: Jumilla-Murcia.

similar to that of the same rock types in the Betics. δ^{18} C values in the CGH chain cover a wide range (5.1-8.6 %), similar to values for typical island arc and continental margin arc volcanic rocks (Mason et al., 1996).

The comparative distribution of chemical composition of volcanic rocks from different studied areas in the Sr/Ca-Ba/Ca diagram (Fig. 5 b) establishes the Călimani volcanic rocks as originating by partial melting of a depleted mantle source. In other areas, the most basic rocks plot at a certain distance from the "partial melting line". A relatively constant degree of partial melting (8-15 %) of the slightly enriched source can be estimated for most of the areas, except for the South Harghita segment, which suggests, according to this diagram, a much lower degree of partial melting (2-4 %). However, in the South Harghita samples, K/Rb increases, but Rb/Ba is reduced, which suggests that the unusual chemistry is not controlled only by melt extraction processes, but also by the fluid metasomatism (Mason et al., 1998).

Along the Ba/Ca line there are two different trends: (1) Starting from rhyolites and/or dacites, firstly erupted, followed by andesites, basaltic andesites or even basalts (Rodna Mts.) suggest a "mixing line" for the Oaş, Gutâi (oldest rocks), Tibleş, Toroiaga and Rodna rocks; (2) The trends from basaltic andesites followed by andesites and dacites suggest crystal fractionation processes in the Gutâi, Tibleş, Călimani and North Harghita Mts. Mixing of magmas with different degree of partial melting are suggested in the Gurghiu and South Harghita Mts.

The diagram suggests slightly different mantle sources, which underwent different degrees of partial melting, characteristic of each area. In the Oaş, Rodna and Bârgau Mts. the mantle-source magmas was underwent mixing with crustal magmas. In the longer-lived volcanic structures of the Gutâi, Călimani and North Harghita Mts. important fractional crystallization processes also occur (Mason et al., 1995, 1996; Seghedi et al., 1995).

3.3. Comparative remarks

The major element diagrams from the Betics and East Carpathians (Figs. 3, 4) show that andesites in both regions are the most abundant rock type. The younger alkali-basalts plot very similar in both regions. On the other hand, the shoshonitic rocks are more acid in the Betics than in the East Carpathians and ultrapotassic rocks are present only in the Betic area. In both Betic and East Carpathian areas the trace element contents of calc-alkaline rocks are more or less similar with other subduction-related volcanics displaying both continental margin-and island-arc-type signatures (López-Ruiz and Rodríguez-Badiola, 1980; Fernández-Soler, 1992; Peltz et al., 1973; Seghedi et al., 1987, Seghedi et al., 1995, Mason et al., 1995, 1996).

Modern geochemical studies based mainly on trace element and isotope geochemistry try to detect the relative importance of the main petrogenetic processes (partial melting, fractional crystallization, wall-rock assimilation, magma mixing) involved in the generation of the observed rock suites. In this study, besides other data we used the Ba/Sr-Ca/Sr diagram (Onuma et al., 1983) (Fig. 5 a, b) as a common base of comparison for the Betics and East Carpathians. This diagram considers the different evolution of large divalent cations Ca^{2+}, Sr^{2+}, Ba^{2+} with different behaviour in igneous processes (partial melting, fractional crystallization) controlled by the crystal structure of mineral phases in silicate melts. Lower degrees of partial melting will increase the amount of the larger cations Sr and Ba in the melt because they do not participate in the major mineral phases (olivine, orthopyroxene, clinopyroxene and garnet) involved in the process. A higher degree of partial melting will dilute Sr and Ba contents in the melt. Sr/Ca-Ba/Ca systematic can be represented by a line with a slope of 45^0, considered as hypothetical "partial melting line". The starting point is represented by a primitive melt calculated from chondritic values, that is generally considered as representing primitive mantle composition. Any melts originating in this kind of source will be projected along the "partial melting line" with increasing distance from the origin as the degree of partial melting progressively decreases. The crystal fractionation of clinopyroxene, plagioclase and amphibole in magma chambers will change the Sr/Ca and Ba/Ca ratios of primary magmas. The derivatives are lined up in the order of progressively more evolved terms: basalt-andesite-dacite-rhyolite. The increase of Ba/Ca ratio will allow a distribution on a line at a low angle to the X-axis, controlled by the precipitated minerals; it is considered as "the fractional crystallization line" which might also be called as "the mixing line" (Fig. 5) when a mantle-derived magma is mixed with a crust-derived magma, mainly where the volcanoes are located on thick continental crust (Onuma et al., 1983).

The diagrams show remarkable similarities of the distribution pattern of the data: the Cabo de Gata calc-alkaline rocks present almost the same trend as the Călimani, Gurghiu and North Harghita volcanics of the East Carpathians.
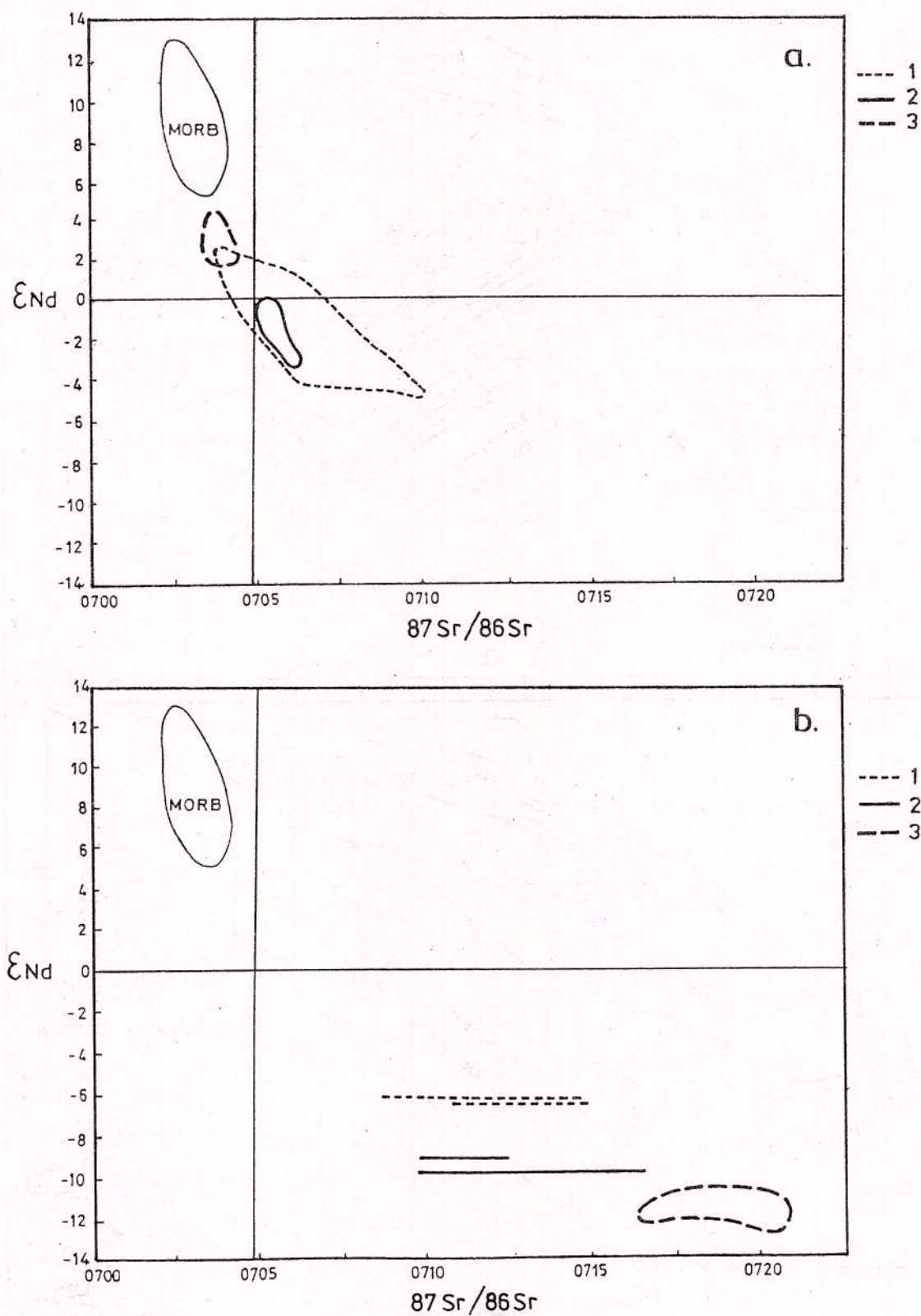
Fig. 6 – Plot of Nd and Sr isotopic data. MORB field is shown (Hertogen et al, 1985, 1988; Toscani et al., 1981; Munskaard, 1984; Nelson et al., 1986; Downes et al., 1995; Mason et al., 1996; Seghedi et al., 1995)
6a. East Carpathians: 1. Călimani-Gurghiu-Harghita (CA), 2. South Harghita (SH), 3. Perşani (AB)
6b. Betics: 1. Cabo de Gata (CA), 2. Vera-Mazarron (K-CA & SH), 3. Vera-Mazarron & Jumilla-Murcia (UK).
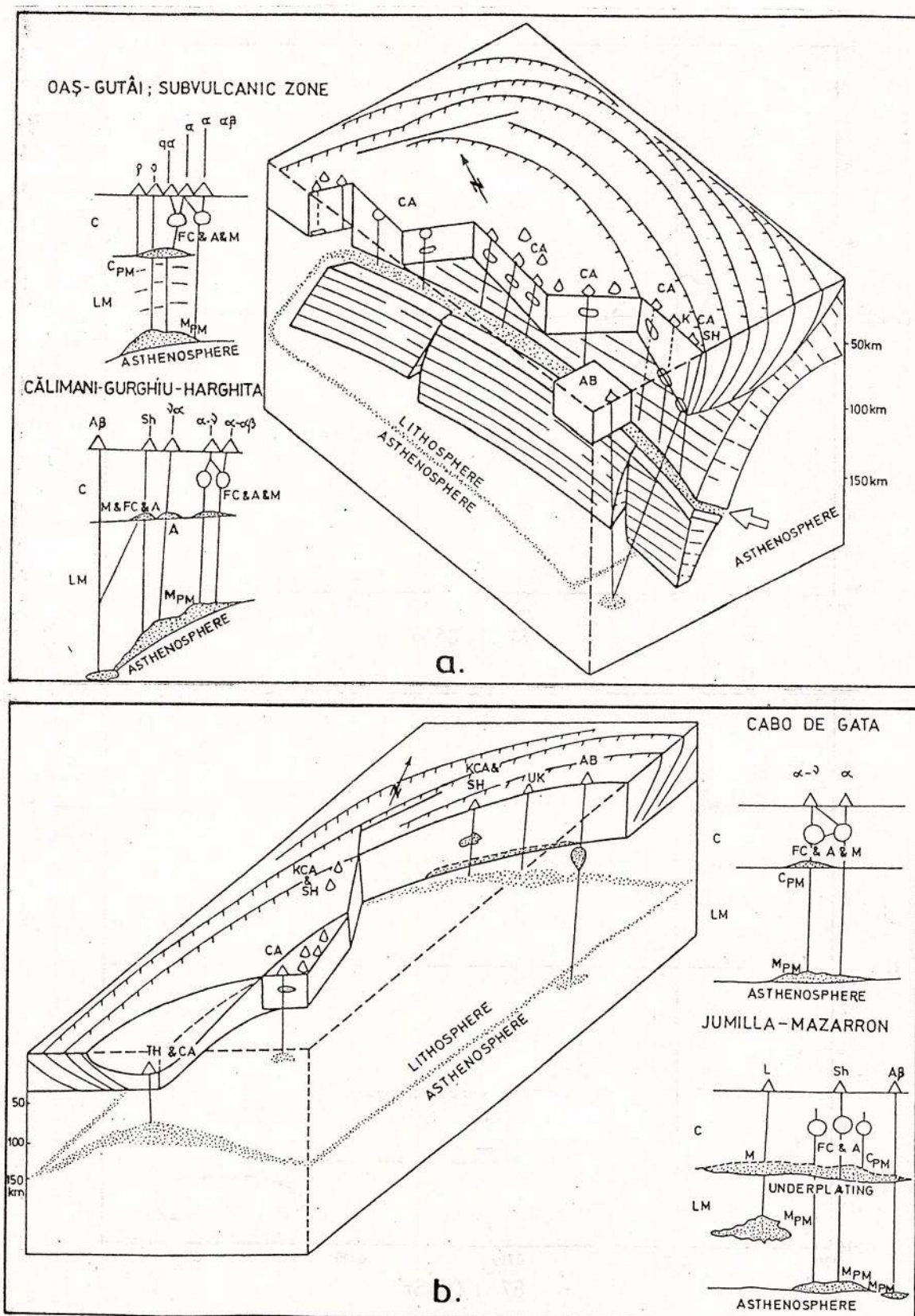
Fig. 7 – Models suggesting inferred relationships between magmatism and its major geotectonic environment in the East Carpathians (7 a) and Betics (7 b).

LM-lithospheric mantle, C-crust, MPM-mantle partial melting, CPM-crustal partial melting, M-magma mixing, FC-fractional crystallisation, A-assimilation, Calc-alkaline rocks, KCA-high-K calc-alkaline rocks, SH-shoshonitic rocks, AB-alkali-basaltic rocks, L-lamproitic (ultrapotassic) rocks.

The upper mantle is the main magma source in both areas. Metasomatised mantle (subduction-related enrichment) is the most common source of calc-alkaline magmas in both regions, except for the Călimani Mts. (East Carpathians), where a primitive asthenospheric mantle-source can be inferred. The degree of subduction-related enrichment is higher in the Betics. Crustal sources are involved for early acid magmatism in both areas as well as for minor volumes of acidic magmas in the northern part of the East Carpathians. Asthenospheric mantle is the primary source for alkali basalts in both regions. The ultrapotassic rocks in the Betics derived from a strongly depleted lithospheric mantle source, previously subjected to an important enrichment event.

Shallow magma chamber processes (assimilation-fractional crystallization) played an important role in both Betics and East Carpathians during the petrogenesis of calc-alkaline, high-K calc-alkaline and shoshonitic suites. Crustal assimilation is important especially in the East Carpathians, but it is also present in the Betics. It is mostly a consequence of long-term storage of calc-alkaline magmas in shallow magma chambers (Mason et al., 1996; Benito et al., 1999).

Mixing of magmas of different sources and/or various stages of differentiation is common in plate-convergence-related volcanics. In our case, several types of magma mixing processes can be pointed out: (1) between mantle-derived calc-alkaline magmas and crustal magmas in deep-seated magma chambers, in both regions; (2) between mantle-source ultrapotassic magmas and crustal-source magmas, at crustal levels, in the Betics; (3) between unevolved mantle-source melts and differentiated ones of the same origin, in shallow magma chambers, mostly in the East Carpathians; (4) between mantle-derived calc-alkaline magmas of different degrees of differentiation, in shallow magma chambers, in both regions.

4. Geotectonic constraints

4.1. Betics

The first proposed subduction-based models (Araña and Vegas, 1974; López-Ruiz and Rodríguez Badiola, 1980) do not explain completely the distribution of volcanic activity in the Betic area. The Moho geometry of the Alborán Sea and related Betic and Rifean areas, as it appears from tomographic studies (Blanco and Spackman, 1993), suggests a delamination model, envisaged for collision zones (Platt and Vissers, 1984, Platt et al., 1996; Doblas and Oyarzun, 1989; Zeck, 1998). According to these models, the delamination of the mantle part of the lithosphere was followed by extensional collapse, from Early to Middle Miocene, of the Alborán Basin, accompanied by calc-alkaline to shoshonitic volcanism.

The generation of calc-alkaline magmas is directly related to the heating effect of the rising asthenosphere, which tends to replace the lithospheric roots (Zeck et al., 1996, 1998; Benito et al., 1999). The hydrated overlying mantle during earlier oceanic subduction may generate calc-alkaline magmas. The enhanced heat-flow will generate lower crustal melting due to underplating processes, leading to shoshonitic magmatism. The generation of ultrapotassic magmatism can be related to right-lateral transtensional movements around 7 Ma. The relaxation of lithosphere may be responsible for low degree decompression melting of the metasomatic layer of the upper part of the lithospheric mantle and production of ultrapotassic magmas. Mixing with crustal magmas generated the large spectrum of Spanish lamproites. The small-volume alkali-basaltic rocks can be generated by decompressional melting of an asthenospheric material.

4.2. East Carpathians

The East Carpathian volcanic chain led to the first applications of the plate tectonic concept in Romania (Roman, 1970; Rădulescu and Săndulescu, 1973; Boccaletti et al., 1973; Bleahu et al., 1973), which did not properly explain the time-space distribution and complex petrogenetic processes. The genesis of calc-alkaline volcanism in the East Carpathians resulted during continental collision of the Eurasian block with the Tisia block (Csontos, 1995). The magmatic rocks in the Gutâi-Călimani sectors, with generally coeval magmatic activity and linear distribution along the folded arc, resulted during subductional roll-back processes and after the descending slab bent almost to vertical along the whole arc segment (Seghedi et al., 1998). The south-eastern end of the magmatic range (the Călimani-Gurghiu-Harghita volcanic chain), displaying obvious along-range migration (10-0.2 Ma), is the result of the gradual south-eastward propagating downward breakoff of the subducted part of the Eurasian plate lithosphere (Mason et al., 1998, Seghedi et al., 1998). The small-volume Persani Mts. alkali-basaltic rocks are likely related to an asthenospheric material rise and further decompressional melting.

4.3. General and comparative remarks

Some general remarks can be drawn when comparing the overall geotectonic setting and evolution of the Neogene magmatism in the Betics and East Carpathians. Similarities include several important features. Although located at its opposite sides, both volcanic areas evolved within the framework of the same Tethysian domain. Plate-convergence-related tectonic setting, as a result of Lower Miocene compressive tectonic phases, characterises both areas. Another common feature is that the Neogene volcanic activity post-dates continent-continent collision and took place at the inner part of the collision-generated orogenic belt.

Significant differences between the two are as can also be pointed out. The relative proportion of the basic types of rock suites are different. They are mostly calc-alkaline, but important volumes of K-rich rocks, ranging from high-K calc-alkaline to ultrapotassic, are present in the Betics, while only minor volumes of K-rich components, spanning a narrower range (from high-K calc-alkaline to shoshonitic) are found in the East Carpathians. The spatial distribution of rock suites is also different in the two regions: the K-rich associations tend to be distributed further from, and parallel to the main collisional belt in the Betics, while in the East Carpathians they are restricted to the chain-terminus segment.

Although most of the magmatism related to continental collisional setting, such as in the Betics and East Carpathians, bears strong "subduction signature", it seems that the principal processes leading to the actual generation of the calc-alkaline magmatic arcs are much more complex than a simple subduction model, involving slab detachment and breakoff mechanisms. Hydration of the lithospheric mantle by subductional processes is a necessary, but not sufficient condition for calc-alkaline magmatism. Asthenospheric upwelling carrying extra-heat into the breakoff and/or detachment window is as essential process as the prior subduction itself. Asthenospheric rise and further decompressional melting can be responsible for the generation of late alkali-basaltic volcanism.

5. Conclusions

The beginning of volcanism in both regions involved large-volume silicic explosive eruptions, but their ages are different: 24-18 Ma in the Valencia Trough, and 18-14 Ma in the East Carpathians. The principal calc-alkaline activity in both are as developed between 13 and 7 Ma, being much more extended in the East Carpathians. In both are as high-K calc-alkaline and shoshonitic compositions characterise, at least partially, the late-stage volcanic products. Coeval alkali-basaltic volcanism occurred in both regions during the Pliocene-Pleistocene interval. The main difference consists in the presence of ultrapotassic volcanism in the Betics. It is only coeval with the latest calc-alkaline and shoshonitic volcanism. The geochemical data suggest mantle to be the main common source of magmas, but it is obvious that crustal melts have also been involved. Magmas of different sources underwent a complex interplay of fractional crystallisation, magma mixing and assimilation in crustal magma chambers before reaching the surface. Slab detachment and breakoff mechanisms are invoked to explain the generation, and relationships between tectonic setting and time-space evolution of calc-alkaline, shoshonitic and alkali-basaltic magmatism in both regions.

Aknowledgements

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PURIFICATION OF QURTZ BY THERMAL AND CHEMICAL TREATMENTS

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Abstract: Thermal and thermochemical treatments were applied in some laboratory researches on the purification of quartz from some Romanian metamorphic quartz deposits. The results obtained from these researches are not conclusive. The aim of this paper is to verify the efficiency of these treatments. Quartz samples from three deposits (Uricani, Ilova and Vârciorova) were used. The processing flowsheet comprises two steps: a) pretreatment step (crushing, screening, magnetic separation) for the liberation of mineral inclusions and for the separation of purer products; b) thermal (decrepitation) and thermochemical treatment step followed by screening for the purification of quartz. The decrepitation of quartz (at 600 ^{0}C or 900 ^{0}C, with or without NaCl) does not significantly change the chemical composition or grain size of the quartz but significantly enhances the grinding of quartz as a result of the structural transformations produced in the quartz mass. The hot HCl treatment of the grinded-decrepited quartz significantly lowers only the content of Fe and to a lesser extent the content of Ca. Thermochemical treatment of quartz is a very expensive purification method and produces only a partial purification of some of the impurities present in quartz (Fe and Ca).

High purity quartz

There is a rapidly growing demand for sources of exceptionally high purity quartz, particularly with respect to very low levels of metal impurities. Such high purity quartz is needed to prepare quartz frequency and timing control devices for electronic applications, as high purity raw materials for optical fibres, to prepare fused quartz optical grade glass such as for halogen, vapour lamps and to prepare crucibles and other quartz apparatus for making high purity silicon crystals for transistors, integrated circuits and other electronic and semi-conducting devices such as photovoltaic cells.

There is an extremely limited supply, far less than required for the above needs, of naturally occurring quartz crystals and quartz of sufficient purity. In fact, there is a U.S.A. company monopoly (Unimin Co.) worldwide, even European companies being some of the main end-users (Philips, Osram etc).

The specifications for high purity quartz are presented in Table 1 (from Lorenz & Gwosdz, 1999, pp. 30). The grain size of these products ranges between 0.075 mm and 0.3 mm.

The product corresponding to IOTA - Standard is used in the manufacture of quartz tubing for halogen and high-intensity discharge lights. The products corresponding to IOTA-4 and IOTA-6 are used in the manufacture of semiconductor quartz glass, such as CZ crucibles, diffusion tubes, quartz rods and ingots.

Chemical processes for purifying quartz

Quartz impurities are Al, Fe, Ca, Mg, Na, K, Ti, Li; they are usually present as: a) loosely associated minerals; b) mineral fragments which are chemically and physically bonded to the quartz crystals at their surface; c) minerals occluded within the grains; d) interstitial ions substituting for Si in the quartz lattice itself. Grinding and physical separation techniques remove the majority of physically associated impurities but are not effective in removing chemically bonded impurities and occluded or interstitial impurities.

Table 1
Specifications for high purity quartz for fused quartz*

Element	IOTA standard		IOTA - 4		IOTA - 6	
	Mean	Max.	Mean	Max.	Mean	Max.
Al	15.2	22.0	7.9	10.0	7.9	9.5
Fe	0.3	1.5	0.6	1.0	0.2	0.3
Ca	0.4	1.5	0.6	1.0	0.5	0.7
Na	0.9	1.5	1.0	1.03	0.1	0.2
K	0.7	1.5	0.4	1.0	0.1	0.2
Li	0.7	1.5	0.2	1.0	0.2	0.3
B	0.08	0.10	0.04	0.05	0.03	0.04

* Products of Unimin, North Carolina, U.S.A

Chemical processes for purifying quartz are focused mainly on the acid dissolution of impurities, including admixed minerals, other than quartz, and quartz particles having relatively high levels of lattice impurities. A preliminary purification stage, concerning the use of inorganic (HCl, H_2SO_4) or organic (oxalic, formic) acids, could be applicable to the dissolution of external impurities (Papanikolau, 1987; Loritsch, 1989; Seki, 1990). For further reduction of the impurities, HF, alone or mixed with other mineral acids (nitric, hydrofluorsillic), is the preferred reagent in the state of the art chemical beneficiation technologies (Lindemann, 1990; Osakeyhtio, 1976). During processing with HF, quartz particles are etched, preferentially along the grain boundaries, for example along the boundaries between twin crystals. In this case, grain boundaries are to be understood to mean the boundaries between the crystallites from which the sand particles are formed. The impurities become accessible because they have been found to be present on grain boundaries. Metal compounds are dissolved amongst others (even inert compounds are substantially etched away).

During grinding quartz breakage takes place preferentially along the impurities and gas nuclei which are consequently exposed and can be chemically treated. Besides, small gas bubbles, which are not located at the surface or along the grain boundaries, are also removed very effectively.

By etching, a crystal aggregate is formed having an irregular weak structure. Upon heating to temperature above 700^0C (calcination) the pressure of the remaining small gas nuclei or fluid inclusions increases to such an extent that the structure bursts and the gas is set free.

The success of such an acid treatment is based on the ability of HF or HF mixtures to reduce the impurities related to the quartz with comparatively small dissolution losses of the quartz itself. It is estimated that, in some cases, for the sufficient removal of the impurities it is necessary to etch at least 40% by weight of the starting material. This happens because the process relies upon different rates of dissolution as between quartz and the various impurities attributable to differences in their chemical and physical properties. For example, most feldspars and iron silicates are more soluble than quartz. Minerals having a slower rate of dissolution than quartz include garnet, zircon, albite and beryl.

Techniques for more efficient removal of gases, solids and liquids existing in quartz as inclusions or interstitial impurities have been developed, adopting a racially different approach than that of the prior art. Instead of using leaching to destroy the impurities, leaching can be used to create a size differential between relatively impure particulate materials and the desirable higher purity or high-grade quartz product, enabling separation by screening, air classification or other size classification techniques. Furthermore, the above processes, by establishing a size differential between a) quartz and the more or less soluble admixed minerals and b) quartz having high levels of lattice impurities and the desirable higher purity or high grade quartz, seem to succeed where the prior art fails, i.e. in elimination of both the less soluble admixed impurities and the quartz fractions with high lattice impurity levels (Jung, 1989).

Previous investigations on Romanian quartz

Until the middle of the 8th decade of the last century only the quartz accumulations used in the glass and fine ceramics industries, such as the Tertiary quartz sands and locally some pre-Alpine metamorphic quartz bodies, were better known. Recent studies aiming to improve the degree of knowledge and evaluation of the

non-metallic mineral resources potential, carried out by I.G.R., extended the area of economic interest to the whole inventory of quartz accumulations, according to genetic criteria. The most important achievements are referring to the new possibilities of re-evaluation of the synmetamorphic quartz which proved to be an useful raw material for the production of synthetic quartz crystals for the electronic industry (Udubaşa et al., 1986, 1987, 1991, 1997). The pure synthetic quartz crystals obtained in the laboratory attest the economic importance of some quartz accumulations (Hobiţa, Nemanu and Uricani).

Some technological researches on laboratory and pilot scale were carried out on the quartz samples from metamorphic deposits (Maschek 1980, 1986; Maschek et al 1996; Pozinărea et al 1980, 1981, 1990; Togan et al 1979). The applied technologies comprise mechanical operations (crushing, screening, grinding, magnetic separation), thermal treatment (calcination, decrepitation) and thermochemical treatments (in alcaline and/or hot acid media). But the obtained results are not conclusive. An accurate analysis of the efficiency of these technologies is not possible for the following reasons: complete chemical analyses of all obtained products are not determined; the chemical methods used for determining the contents of the impurities were not precise for the contents of very low level (ppm); lack of the complete balances a.s.o.

For an accurate evaluation of the technologies, especially of thermal and thermochemical treatments, laboratory researches on some samples of metamorphic quartz were carried out.

Sample characterisation

Quartz samples were hand-picked from three main deposits of metamorphic quartz (Uricanj, Ilova, Vărciorova). The samples were characterised from the grain size, chemical and mineralogical point of view.

The dimensions of quartz fragments from the samples range between 50 mm and 150 mm.

The microscopic study of metamorphic quartz revealed the existence of at least two quartz generations belonging to two different metamorphic moments. The first quartz generation occurs as irregular, large grains. Optically, it displays a slight bi-axiallity, having an optic angle of 5-10^0 and an undulatory extinction. The surface of the grains shows inclusions more frequently than the quartz of the second generation. The second generation, that is the recrystallized quartz, is almost euhedrally developed and shows polygonal shapes resulting in mosaic-like structures. The grain surface is limpid, without inclusions. It is uniaxial positive. The undulatory extinction of the quartz grain is generally subparallel to (0001) and it is the result of the heterogeneous shearing along this plane during the deformation. The increasing degree of deformation leads to the development of some discreet kink bands, more accurately defined than the undulatory extinction zones. Their optical orientation differs as compared to the unaffected parts of the grains.

Under the microscope the inclusions in quartz occur as parallel trails and include very small quartz inclusions, with a parallel optical orientation. The abundance of the fluid inclusions suggests a fluid-rich regime during crystal growth at the peak of the metamorphism. They are represented by the earliest unoriented inclusions. The secondary inclusions display an almost parallel arrangement, related to the post-crystallisation process. These planes with inclusions occur in the thin section as linear trails, intersecting each other at angles of 90^0, 60^0 or 45^0.

The electron microprobe investigations carried out on the quartz from metamorphic accumulations pointed out the very rare presence of mineral inclusions from micrometer sizes up to 1 mm. Among them biotite-phlogopite, specific to both types of quartz, and beryl should be mentioned.

From the processing point of view the main remarks of the mineralogical study are as follows: mineral (solid) inclusions are rare and situated between the quartz grains; feldspars (sericitized), clay minerals, calcite, limonite, goethite, pyrite, muscovite, rutile are present together with quartz; fluid inclusions are numerous, especially of small sizes; fluid inclusions are oriented and grouped; there are two types of quartz grains - large grains (1-3 mm) and small grains (< 0.05 mm); the large grains contain numerous small fluid inclusions and are fissured; the small quartz grains do not contain fluid inclusions and are not fissured; the crushing of fluid inclusions could be done only by very fine grinding (< 20 μm).

From the above remarks it is evident that pure quartz is very difficult to obtain from the crude quartz. Although the mineral (solid) inclusions could be released by a coarse grinding their separation (from quartz)
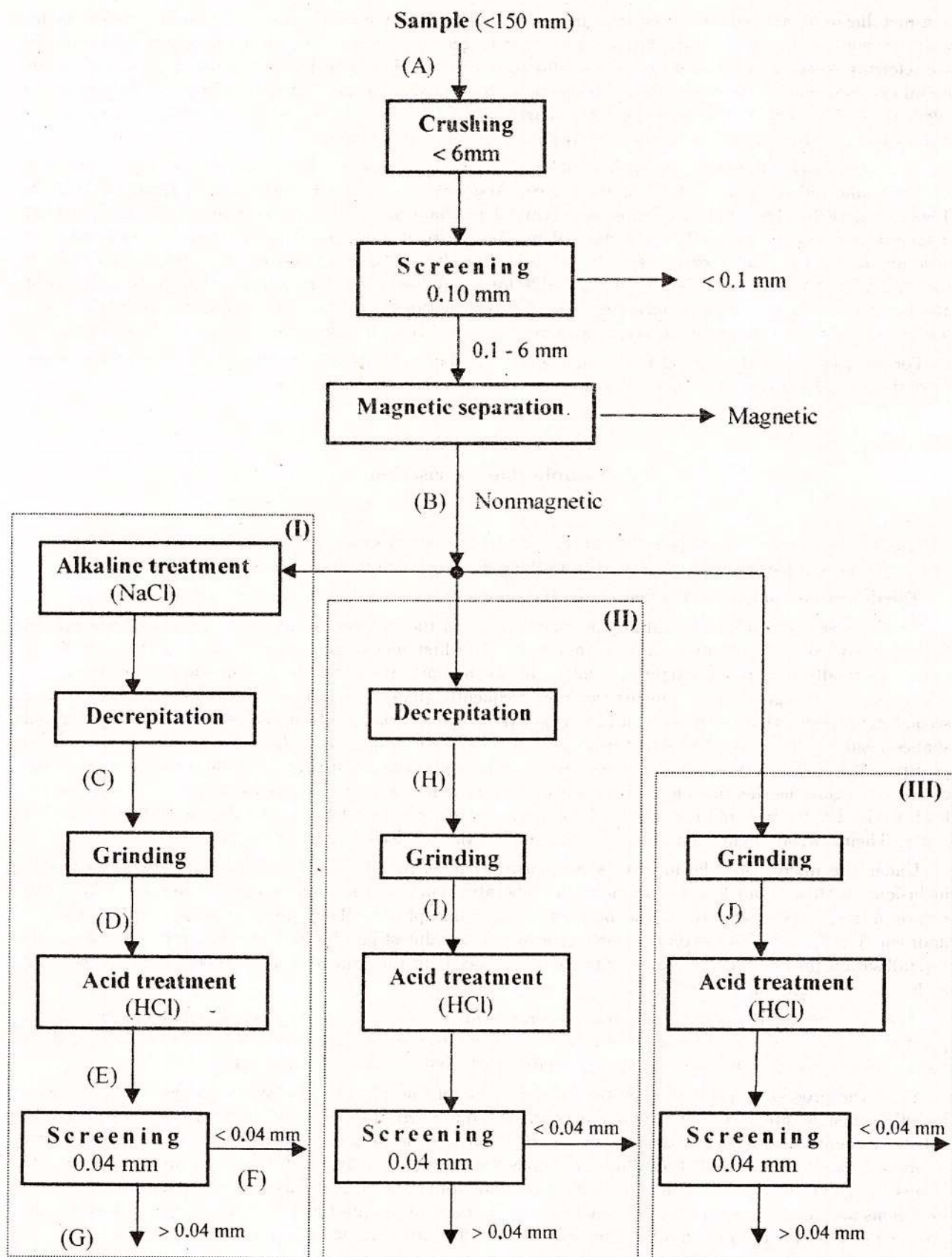
Fig. 1 – Technological flowsheet for processing of quartz samples.

by classical processing methods is rather difficult. However, a very fine grinding is necessary for destroying the fluid inclusions.

Sample processing

The technological flowsheet for processing the samples is presented in Figure 1. For the elaboration of this flowsheet, taking into account the mineralogical observations, it is necessary to bear in mind the following ideas: the crushing of the samples has to be done so as to produce a pollution in a far less degree; the grinding of the samples has to be done without any pollution; by crushing and grinding a complete liberation of the mineral (solid) inclusions has to be done; as the mineral inclusions have a different (smaller) strength than that of quartz, a selective crushing is produced during the crushing and grinding operations; the crushed products could be divided by screening into grain sizes whose content of impurities varies with grain size (the bigger the grain size the smaller the contents of impurities); every grain size has to be separately processed; the finer grain sizes having the highest contents of impurities could be neglected for processing; the magnetic separation is a compulsory purification method to extract the polluting grains (steel grains from crushing equipment) as well as grains of weakly magnetic minerals.

The processing flowsheet comprises two steps: a) a pretreatment step (crushing, screening, magnetic separation) for the liberation of mineral inclusions and separation of the purer products; b) thermochemical treatment of the nonmagnetic product for purification of quartz.

The pretreatment step comprises the following operations: sample crushing, in steps, less than 6 mm; screening the crushed product (<6 mm) at 0.1 mm and avoiding the fraction <0.1 mm; magnetic separation in a strong field (1.5 Tesla) of fraction 0.1-6 mm and avoiding of the magnetic product. The thermochemical step comprises the following operations: calcination at 600 ^{0}C or 900 ^{0}C; cooling in water; grinding; hot HCl treatment; cooling in air; filtration; neutralisation; washing; screening at 0.04 mm.

Thermal and thermochemical treatment was carried out in three variants. The second variant (II) differs from the first variant (I) by the lack of alkaline treatment. The third variant (III) differs from the first variant by the lack of alkaline treatment and the thermal treatment (decrepitation).

The alkaline treatment was carried out by maintaining the nonmagnetic product in a concentrated solution of NaCl during 30 minutes (the ratio liquid:solid being 5:1).

The decrepitation was carried out into two steps. In the first step (calcination) the quartz was heated, for 1 hour, at a temperature of 600 ^{0}C (reached after 30 minutes) or of 900 ^{0}C (reached after 45 minutes), with or without NaCl. In the second step the calcined quartz was suddenly cooled in water.

The grinding was carried out in a vibratory agate mill under the same conditions for all variants (quantity of quartz, quantity of balls, duration).

The acid treatment was carried out in a hot HCl solution (having a concentration of 33 %) at a temperature of 90 ^{0}C during 4 hours (liquid:solid ratio of 4:1).

Product characterisation

All products obtained were characterised from the granulometric and chemical point of view. The grain size analysis was carried out by wet screening. The contents of impurities (Al, Fe, Ca, Mg, Na, K, Mn) were determined by atomic absorption spectrophotometry.

Results

The grain size distribution, massic distribution as well as the contents of impurities of the main products obtained are presented in Table 2, for each of the three samples.

The grain size curves of the nonmagnetic product (before and after grinding) and the decrepitated product (before and after comminution) for each sample are presented in Figures 2-4.

The solubilisation degrees of the impurities by hot HCl treatment for each sample (variant I) are presented in Table 3.
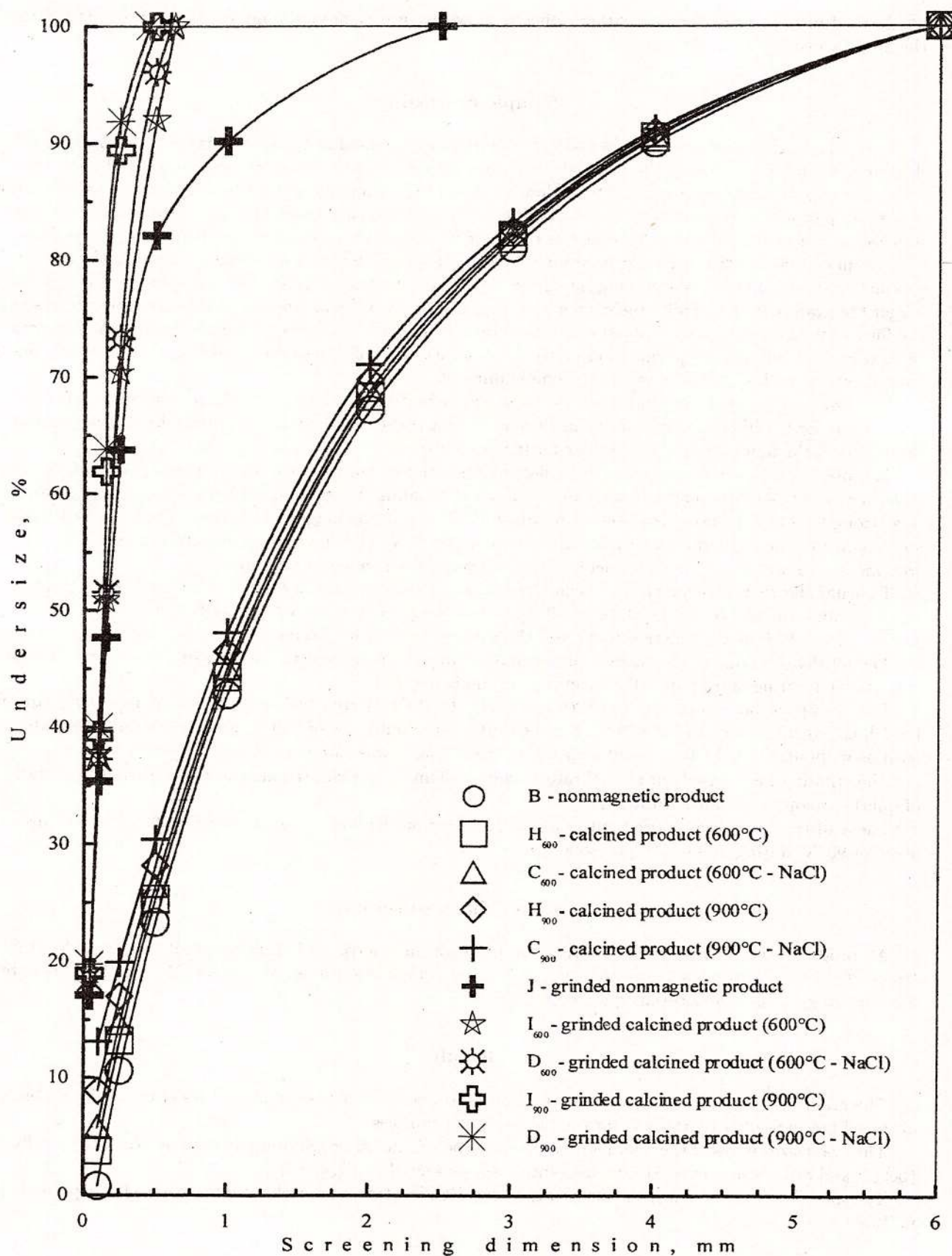
Fig. 2 – Grain size curves of the obtained products from quartz sample of Uricani.

Table no. 2.
Contents of impurities of the most important products obtained.

Product symbol (fig. 1)	Grain size, mm	Massic distribution, %	Content, ppm							
			Al	Fe	Ca	Mg	Na	K	Mn	Total
URICANI										
A	< 100	100.0	131	320	45	18.5	28.5	32.0	6.0	581.0
B	0.1 - 6	91.9	128	243	45	17.9	30.1	33.9	7.0	504.9
C$_{600}$	< 6	91.9	127	242	36	17.7	30.1	33.8	6.9	493.5
C$_{900}$	< 6	91.9	125	239	35	17.2	29.8	33.8	6.8	486.6
E$_{600}$	< 0.6	91.9	116	182	21	12.4	27.1	28.1	6.6	393.2
E$_{900}$	< 0,45	91,9	114	179	19	11.5	27.0	28.0	6.5	385.0
F$_{600}$	< 0.04	16.6	179	650	49	33.2	49.0	50.6	15.5	1026.3
F$_{900}$	< 0,04	17.0	206	646	59	35.7	48.6	58.4	15.3	1069.0
G$_{600}$	0.04-0.6	75.3	102	79	15	7.8	22.3	23.2	4.6	253.9
G$_{900}$	0.04-0.45	74.9	93	73	10	6.0	22.1	21.1	4.5	229.7
I$_{600}$	< 0.6	61.9	127	242	37	17.8	30.0	33.7	6.9	494.4
I$_{900}$	< 0.5	91.9	125	240	36	17.6	29.9	33.6	6.9	489.0
J	< 2.5	91.9	128	243	44	18.0	30.0	33.8	7.0	503.8
ILOVA										
A	< 100	100.0	172	289	96	32	80	48	4.5	721.5
B	0.1 - 6	89.1	174	211	94	25	78	50	4.5	636.5
C$_{600}$	< 6	89.1	169	207	72	20	76	48	4.2	596.2
C$_{900}$	< 6	89.1	167	208	70	20	74	45	4.2	588.2
E$_{600}$	< 1.5	89.1	156	155	43	14	69	40	4.0	481.0
E$_{900}$	< 0.6	89.1	150	154	40	14	67	37	4.0	466.0
F$_{600}$	< 0.04	12.5	309	596	46	26	100	114	10.0	1201.0
F$_{900}$	< 0.04	15,0	270	610	60	33	94	96	15.0	1178.0
G$_{600}$	0,04-1.5	76.6	131	83	39	12	64	28	3.0	360.0
G$_{900}$	0,04-0.6	74.1	126	62	36	10	62	25	2.0	323.0
I$_{600}$	< 1.5	89.1	170	208	92	23	75	48	4.3	620.3
I$_{900}$	< 0.6	89,1	169	207	90	23	73	46	4.3	612.3
J	< 2.5	89.1	172	209	94	24	78	49	4.3	630.3
VÂRCIOROVA										
A	< 100	100.0	134	334	91	21	57	40	7.0	684.0
B	0,1 - 6	92.2	138	250	96	23	58	36	6.8	607.8
C$_{600}$	< 6	92.2	135	247	94	21	55	34	6.5	592.5
C$_{900}$	< 6	92.2	136	248	95	22	56	35	6.6	598.6
E$_{600}$	< 1.5	92.2	125	185	55	15	50	28	6.2	464.2
E$_{900}$	< 0.6	92.2	125	185	55	15	50	28	6.2	464.2
F$_{600}$	< 0.04	15.8	236	806	67	38	55	43	20.9	1265.9
F$_{900}$	< 0.04	15.8	275	830	82	48	74	58	24.8	1391.8
G$_{600}$	0,04-1.5	76.4	102	57	53	10	49	25	3.1	299.1
G$_{900}$	0.04-0.6	76.4	94	52	50	8	45	22	2.3	273.3
I$_{600}$	< 1.5	92.2	137	248	95	22	56	35	6.7	599.7
I$_{900}$	< 0.6	92.2	136	246	94	21	55	34	6.7	592.7
J	< 2.5	92.2	138	249	96	23	57	35	6.8	604.8

Table no. 3.
Solubilisation degree of impurities from decrepitated product (D) by acid treatement

Sample	Calcined temperature, °C	Solubilisation degree, %						
		Al	Fe	Ca	Mg	Na	K	Mn
Uricani	600	7.3	24.8	41.7	29.9	9.0	16.9	4.3
	900	9.1	25.1	45.7	33.1	9.4	17.2	4.4
Ilova	600	7.7	29.1	40.3	30.0	9.3	16.7	4.8
	900	10.1	26.0	42.9	30.0	9.5	17.8	4.8
Varciorova	600	7.4	25.1	41.5	29.6	9.1	17.4	4.6
	900	8.1	25.4	42.1	31.8	10.7	20.0	6.1

Discussion

The total content of impurities of each sample is relatively low but varies from one sample to another increasing in the following order: Uricani (581 ppm); Varciorova (684 ppm); Ilova (721.5 ppm). In every sample the contents of impurity is decreasing in the following order: Fe (289-334 ppm); Al (131-172 ppm); Ca (45-96 ppm); Na (28.5-80 ppm); K (32-48 ppm); Mg (18.5-32 ppm); Mn (4.5-7 ppm). The sample of Uricani has the lowest contents of Al, Ca, Mg, Na, K; the sample of Ilova has the lowest contents of Fe and Mn and the highest contents of Al, Ca, Mg, Na, K; the sample of Varciorova has the highest contents of Fe and Mn.

Although the three samples were picked up from different deposits - but of the same genetic type- they have a similar behaviour from the technological point of view.

The crushing and the grinding of quartz fragments are necessary for the following three reasons: the desassociation of mineral inclusions from quartz; the destroying of fluid inclusions; to meet the custom requirements for grain sizes of purified quartz. The crushing of fragments is carried out on the surfaces of minimum resistance such as: interfaces (contact surfaces) between quartz and mineral inclusions; fissures from the quartz mass; the concentration zones of fluid inclusions. During the crushing a concentration of quartz grains by selective crushing is produced as a consequence of different grindability of quartz and the other associated minerals (easier to grind and having a finer grain size so they concentrate in the finer fractions). The concentration efficiency is determined by the ratio between the grinding degree of fractions and the association degree between quartz and association minerals; this efficiency becomes maximum when the grinding degree is similar to the intergrowth degree. By screening the crushed (grinded) product at a certain dimension (usually low) one can obtain as oversize a product with impurity content lower than the sample. The experimental results obtained for the three samples led to the conclusion that the samples have to be crushed in steps under 6 mm and screened at 0.1 mm. The undersize was thrown out as an useless product.

The oversize (grain size 0.1-6 mm) was purified by dry magnetic separation in strong field (1.5 Tesla). Two products were obtained, namely: nonmagnetic product (further processed); magnetic product (thrown product). The nonmagnetic product represents 89.1-92.2 % from the mass of the processed samples (Table 1). The total content of impurities of this product is as follows: 504.9 ppm (Uricani sample); 607.8 ppm (Varciorova sample); 636.5 ppm (Ilova sample). The proportion of lowering of the total content of impurities is of 21.4 % (Ilova), of 20.1 % (Uricani), of 18.1 % (Varciorova). The total content of impurities of the nonmagnetic product is lower than that of the sample as a consequence of the lower iron content (the contents of the others impurities are similar with those of the sample). The proportion of lowering of the iron content is, as follows: 35 % (Ilova); 31 % (Varciorova); 30.2 % (Uricani).

The nonmagnetic product was further processed by three technological variants, as follow: I) alkaline treatment-decrepitation-grinding; II) decrepitation-grinding; III) grinding.

The influence of decrepitation on the grain size of the obtained products can be determined from the shape of grain size curves of the following products: nonmagnetic product - before (B) and after (J) grinding; decrepitated product (at 600°C or 900°C) - before (H_{600}, H_{900}) and after (I_{600}, I_{900}) grinding; decrepitated (after NaCl treatment) product at 600°C or 900°C - before (C_{600}, C_{900}) and after (D_{600}, D_{900}) grinding. The grain sizes of these products are presented in Figures 2-4. By examining these curves the following remarks can be made: decrepitation does not significantly change the grain size of the quartz (the grain size curves of the quartz -before and after heating at 600°C or 900°C- are very near); alkaline treatment (with NaCl)

before heating does not significantly influence the decrepitation process; increasing the heating temperature from 600°C to 900°C influences to a little extend the grain size of the decrepitated product; decrepitation enhances grinding (the grain size of the grinded calcined product is finer than that of the grinded-noncalcined product, the higher the calcination temperature the finer the grain size of the grinded product). From these remarks the following conclusion can be drawn: **the decrepitation of quartz does not significantly change its grain size but enhances its grinding, as a result of the advanced fissuration of the quartz mass.**

The influence of decrepitation on the contents of impurities of the decrepitated quartz can be determined by examining the contents of impurities of the following products: nonmagnetic product -before (B) and after (J) grinding; grinded-decrepited product (I_{600}, I_{900}); decrepited product, after alkaline treatment and calcination at 600 °C or 900 °C (C_{600}, C_{900}). The contents of impurities of these products are presented in Table 2. As it is seen, **the decrepitation -even if it is preceded by alkaline treatment- does not significantly influence the contents of impurities of the decrepitated products**, with the exception of Ca content which is slowly lowered (from 45 ppm to 36 ppm in the case of Uricani sample or from 94 ppm to 71 ppm in the case of Ilova sample). The total content of impurities of the nonmagnetic product obtained from Uricani sample slowly decreases by decrepitation from 505 ppm to 494 ppm or 488 ppm (when decrepitation is preceded by alkaline treatment). **The raising of the calcination temperature from 600 °C to 900 °C does not significantly change the total content of impurities of the decrepited product in case of the Uricani sample.** In case of the nonmagnetic product from Ilova sample, its total content of impurities lowers by decrepitation at 600 °C from 630-636 ppm to 620 ppm or to 596 ppm when decrepitation is preceded by alkaline treatment; when the decrepitation is carried out at 900 °C, the total content of impurities decreases to 612 ppm or to 596 ppm (when the decrepitation is preceded by alkaline treatment). In case of the nonmagnetic product from Vârciorova sample, the total content of impurities decreases by decrepitation from 605-608 ppm to 593-600 ppm; this decrease is not significant and is not influenced by both the calcination temperature and the alkaline treatment.

From the above statements one can conclude that **the decrepitation of the nonmagnetic product (at 600 °C or 900 °C) does not significantly change the chemical composition or grain size of the nonmagnetic product but significantly improves the grinding of this product as a result of the advanced fissuration produced in the quartz mass.**

The solubilisation degree of the impurities from the grinded-decrepited product (D) by hot HCl treatment at 600 °C or 900 °C is presented in Table 3. One can notice that the solubilisation degree is little influenced by the calcination temperature but it varies from one impurity to another decreasing in the following order: 41.5- 45.7 % for Ca; 29.6-33.1 % for Mg; 24.8-29.1 % for Fe; 16.7-20 % for K; 9-10.7 % for Na; 7.3-10.1 % for Al; 4.3-6.1 % for Mn.

In case of the Uricani sample, the total content of impurities of the grinded- calcined product (D) decreases by the acid treatment from 493.5 ppm to 393.2 ppm - at a calcination temperature of 600 °C - or from 486.6 ppm to 385 ppm - at a calcination temperature of 900 °C. The most important decrease of content - of 60 ppm - is in case of Fe (from 242 ppm to 182 ppm at a calcination temperature of 600 °C or from 239 ppm to 179 ppm at a calcination temperature of 900 °C). For the other impurities, the decrease is, as follows: of 15 (16) ppm for Ca; of 11 ppm for Al; of 5.3 (5.7) ppm for Mg; of 5.7 ppm for K; of 2.8 (3.3) ppm for Na; of 0.3 ppm for Mn.

In case of the Ilova sample, the total content of impurities of the grinded-calcined product (D) decreases by the acid treatment from 596.2 ppm to 491 ppm - at a calcination temperature of 600 °C- or from 588.2 ppm to 466 ppm - at a calcination temperature of 900 °C. The most important decrease of content - of 52 (54) ppm - is in case of Fe (from 207 ppm to 155 ppm at a calcination temperature of 600 °C or from 208 ppm to 154 ppm at a calcination temperature of 900 °C). For the other impurities, the decrease is, as follows: of 29 (30) ppm for Ca; of 14 (17) ppm for Al; of 8 ppm for K; of 7 ppm for Na; of 6 ppm for Mg; of 0.2 ppm for Mn.

In case of the Vârciorova sample, the total content of impurities of the grinded-calcined product (D) decreases by the acid treatment from 592.5 ppm to 464.2 ppm - at a calcination temperature of 600 °C- or from 598.6 ppm to 464.2 ppm - at a calcination temperature of 900 °C. The most important decrease of content - of 62 (63) ppm - is in case of Fe (from 247 ppm to 185 ppm at a calcination temperature of 600 °C or from 248 ppm to 185 ppm at a calcination temperature of 900 °C). For the other impurities, the decrease is, as follows: of 39 (40) ppm for Ca; of 10 (11) ppm for Al; of 6 (7) ppm for Mg and K; of 5 (6) ppm for Na; of 0.3 (0.4) ppm for Mn.
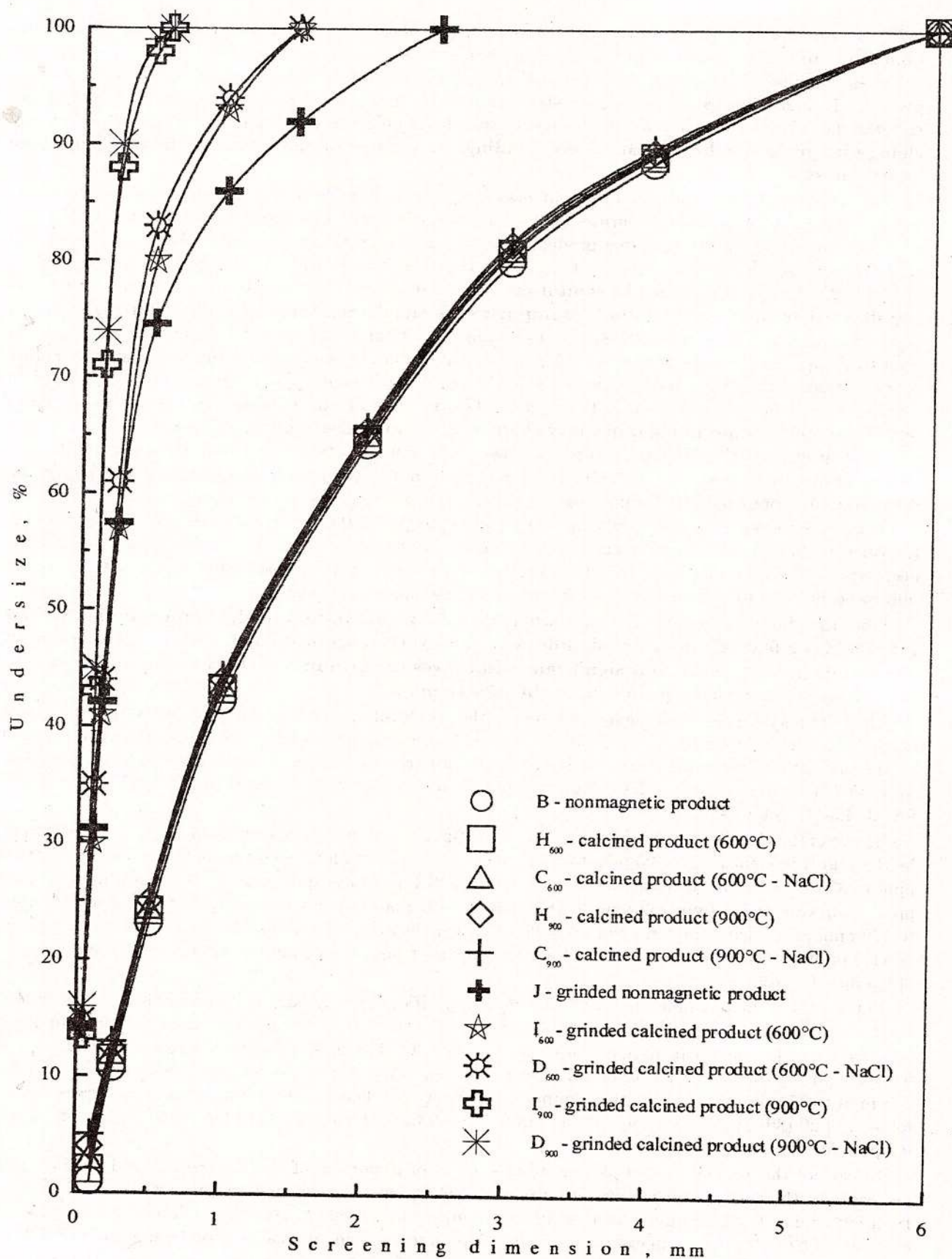
Fig. 3 – Grain size curves of the products obtained from quartz sample of Ilova.

Legend:

○   B - nonmagnetic product

□ H_{600} - calcined product (600°C)

△ C_{600} - calcined product (600°C - NaCl)

◇ H_{900} - calcined product (900°C)

$+$ C_{900} - calcined product (900°C - NaCl)

✚   J - grinded nonmagnetic product

✩ I_{600} - grinded calcined product (600°C)

✷ D_{600} - grinded calcined product (600°C - NaCl)

✤ I_{900} - grinded calcined product (900°C)

✳ D_{900} - grinded calcined product (900°C - NaCl)
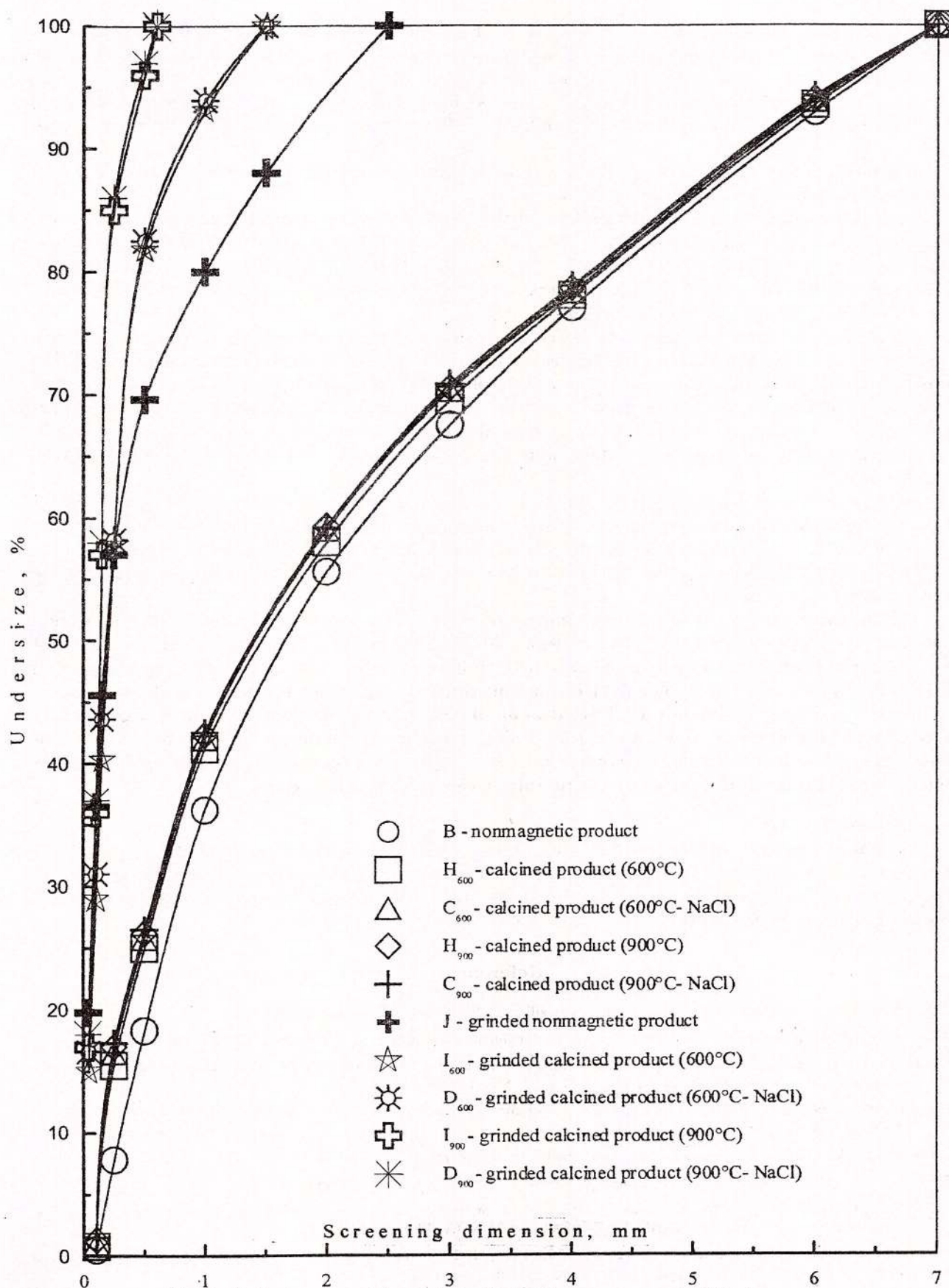
Fig. 4 – Grain size curves of the products obtained from quartz sample of Vârciorova.

○ B - nonmagnetic product

□ H_{600} - calcined product (600°C)

△ C_{600} - calcined product (600°C- NaCl)

◇ H_{900} - calcined product (900°C)

+ C_{900} - calcined product (900°C- NaCl)

✚ J - grinded nonmagnetic product

☆ I_{600} - grinded calcined product (600°C)

☼ D_{600} - grinded calcined product (600°C- NaCl)

✚ I_{900} - grinded calcined product (900°C)

✳ D_{900} - grinded calcined product (900°C- NaCl)

Screening dimension, mm

Undersize, %

From the above statements it can be concluded that by hot HCl treatment of the grinded-calcined product (D) the total content of impurities of this product decreases by over 100 ppm. The most important decreases were observed for Fe (52-63 ppm) and Ca (15-40 ppm), for the rest of the impurities the decrease is at most 17 ppm. The important decreases of Fe and Ca contents can be explained by the fact that these two chemical elements are present as mineral forms soluble in the hot HCl (oxides and/or hydroxides of Fe, Ca carbonate etc).

The total content of impurities of the chemically purified product (E) is, as follows: 393 (385) ppm (Uricani); 464 ppm (Vârciorova); 481 (468) ppm (Ilova).

From this product, by avoiding of the fine fraction (< 0.04 mm) by volumetric screening at 0.04 mm having a high content of impurities (1026-1392 ppm), one can obtain a product (G -fraction > 0.04 mm) with a total content of impurities, as follows: 254 (230) ppm (Uricani); 299 (273) ppm (Vârciorova); 360 (323) ppm (Ilova). The yield of this product, according to the sample mass, is as follows: ≈ 75 % (Uricani); ≈ 74.1 (76.6) % (Ilova); 76.4 % (Vârciorova).

Finally, from the metamorphic quartz of Uricani, Ilova and Vârciorova deposits it is possible to obtain a quartz product having the following characteristics: the massic yield of 74-76 %; the grain size between 0.04 mm and 0.5 (1.5) mm; the total content of impurities of 236-360 ppm (93-131 ppm Al, 52-63 ppm Fe, 22-64 ppm Na, 10-53 ppm Ca, 21-28 ppm K, 6-12 ppm Mg, 2-5 ppm Mn). The technology for the obtaining of this product is complex and comprises the mechanical operations (crushing, grinding, screening, magnetic separation), thermal operations (calcination, decrepitation) and thermochemical treatment (with cool NaCl and hot HCl).

But this product is not a high purity quartz as its total content of impurities (230-360 ppm) is higher than the maximum content accepted for the high purity quartz (100 ppm). Moreover, the calcination of quartz at 600 ^{0}C or 900 ^{0}C produces the transformation of α-quartz to β-quartz (useless for producing the synthetic quartz). Additionally, this technology is very expensive and pollutant; therefore its application on the industrial scale is prohibitive.

The researches carried out elucidate two important aspects of the quartz purification by thermochemical way, namely: a) decrepitation; b) treatment with cold NaCl and hot HCl. **The decrepitation does not significantly contribute to the purification of quartz even in case of the NaCl treatment of quartz before decrepitation; the only important contribution of decrepitation is the enhancing of quartz grinding. The hot HCl treatment of the grinded-decrepited quartz significantly lowers only the content of Fe and in a smaller measure the content of Ca. It follows that the thermochemical treatment of quartz is a very expensive purification method and produces only a partial purification of some of the impurities present in quartz.**

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Recenzii - Book rewiews – Buchbesprechung - Analyse d'ouverage

V. I. Kvasnita, N. N. Zinciuk, V. I. Koptil - Tipomorfismul microcristalelor de diamant (Tipomorfizm mikrokristallov almaza). Editura Nedra, Moscova, 1999, 224 p., peste 100 fotografii alb/negru (majoritatea imagini SEM).

Alături de nenumăratele cărţi şi lucrări despre diamant, cartea colegilor de la Kiev vine cu un element nou de cunoaştere, i.e. tipomorfismul diamantelor, care pune în evidenţă relaţia reciprocă dintre proprietăţile acestui mineral, în special dintre morfologia microcristalelor (până la 0.5 mm) şi condiţiile de formare. Necesitatea unui aştfel de studiu a fost indusă şi de creşterea numărului de tipuri genetice de ocurenţe de diamant. Pe lângă descoperirea unor noi arii cu kimberlite diamantifere (China, Australia, Belamorsk, Canada), în ultimele decenii au fost identificate diamante în roci metamorfice de presiune inaltă (Kazahstan, China, Norvegia), în zone de impact (Ries/Germania, Ukraina), în chondritele din meteoriţi. Apariţia diamantului în lamproite este de asemenea de dată recentă.

Fiecare tip genetic de diamante este prezentat în detaliu, cu numeroase microfotografii de calitate, uneori incluzând şi mineralele asociate, e.g. grafitul şi granatul din metamorfite, forme rare de cub sau cuboid, uneori de culori neobişnuite (violet), la diamantele din aluviuni (Ukraina), forme "lamelare" reprezentand creşterea spiralată-stratificată a diamantelor din rocile de impact, concreşteri particulare de diamant/grafit (zona Tunguska), etc.

În final se fac consideraţii privind cristalogeneza diamantului, legătura dintre tipomorfismul diamantelor şi prognoza, relaţia paramorfă diamant/lonsdaleit (în special în rocile de impact), semnificaţia tipomorfă a conţinutului de azot. a culorii si luminiscenţei, precum şi a spectrelor de rezonanţă electronică paramagnetică la diamantele cu sursă în manta (kimberlite) etc.

Cartea se incheie cu o bibliografie consistentă (peste 250 titluri) atât din literatura "vestică", cât şi cea "estică". Mai putin obişnuită este traducerea titlului revistelor ruseşti în limba engleza, ceea ce le face greu de identificat pentru un necunoscător al limbii ruse. De asemenea, traducerea engleză este puţin deficitară, dar textul rămâne în general inteligibil. Evaluarea "realităţii" exprimării şi sensului este uşurată însă tocmai de textul bilingv (rusa şi engleza), chiar la explicaţia figurilor. De remarcat incă odată calitatea excelentă a fotografiilor SEM. Cartea este valoroasă şi extrem de utilă; ea se recomandă pentru orice bibliotecă de geologie.

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