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DITRĂU ALKALINE MASSIF MAPS–HYPOTHESIS–REFERENCES

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Abstract. Located in the Eastern Carpathians, the western extremity of the Cristallino-Mesozoic Zone, bounded by Rebra Group and Series of Tulgheș, DAM has attracted the attention of scientists since 1859, when it was discovered by F. Herbich. Interest has gone from petrographic diversity (the presence in massive of the calco-alkaline series: granites, granodiorites, diorites, syenitoides, aplites, albitites, alongside a number of alkaline pregnant rocks with nepheline syenites, essexites, alkali gabbros, foidal monzonites) and a structural complexity.
With an almost circular section and a diameter of about 15 km, the massive mapping revealed its ring structure, from outside to inside of the alkaline to/and calco-alkaline facies. Located at the intersection of major crustal fractures, G8 and G9–G4, repeated intrusions have generated a specific thermal contact aureole, in the mass of the Tulgheș Series. Progressively, the list of identified mineral-petrographic level and metallogenetic one was enriched gradually, reaching today more than 300 species. The internal fractures that affected the massif were ways of accessing the late magmas that became veins (aplites, lamprophyres–vogesites, kersantites, spessartites, camptonites, odinites, carbonatites). Metallogenic differentiation has enriched the petrographic framework and led, through specific paragenesis (molybdenum, and with REE to ore fields: ***Jolotca*** fields (pyrite, chalcopyrite, sphalerite, pyrrhotite, molybdenite), oxides (Ti, Fe, Th, Nb) and phosphates (monazite-Ce), ***Hereb*** (molybdenite, pyrite, sphalerite and galena) together with REE), ***Aurora*** (molybdenite, pyrite, sphalerite and galena) together with REE), ***Belcina*** (sphalerite, galena, arsenopyrite, pyrite, molybdenite), xenotime (with Th and REE), siderite, fluorapatite, chlorite, calcite, quartz, rutile, anatase), etc. Geochemical footprint throughout the Massif, is Ti, Nb, Zr, V, Th, Mo, Fe, Pb, Zn, P, REE). The age of the DAM, considered by *A. Streckeisen*, 160 m.y. it was reconsidered by many authors by using modern methods of investigation (K/Ar and 40Ar/39Ar = 165–160 m.y.; nepheline sienites = biotite–180 m.y.; nepheline = 210–230 m.y.; ultramafites = 230 m.y.; U–Pb zircon = 229 m.y.). The findings of researchers from a period so long find themselves in very different cartographic representations, at larger scales or smaller. A synthesis of these sketches and geological maps, structural, metallogenetic ones confirms the diversity aspects of petrogenesis. Various models have been elaborated and belong to *A. Streckeisen, Foldvari, A. Streckeisen* & *J.C. Huntziker, Al. Codarcea* & *V. Ianovici, N. Anastasiu* & *E. Constantinescu, I. Balintoni, D. Zincenco, G. Jakab, E. Pal-Molnar, A. Fall, O. Iancu, G. Săbău* & *E. Negulescu*. There are also presented the maps of the massive, at different scales that have been published in the works mentioned in the bibliographic list. Finally, the main points of view on the genesis of the massif are listed (Ianovici (1929–1932), Codarcea *et al*. (1958), Streckeisen (1960), Anastasiu & Constantinescu (1980), Jakab (1998), Iancu (2010), Morogan (2000), Dallmeyer (1997), Fall (2006), Pál-Molnár (2000). The references list at the end of the paper was desired to be a complete one and groups the specialists who worked in the DAM and had published results.

Keywords: *research history, maps, hypothesis, references, East Carpathians.*

Résumé. Situé dans les Carpates Orientales à l'extrémité occidentale de la zone Cristallino-Mésozoïque, délimitée par le Groupe Rebra et la Série de Tulgheș, le DAM continue à attirer l'attention des scientifiques depuis 1859, quand il a été découvert par F. Herbich. Son intérêt concerne tant sa diversité pétrographique (la présence de la série calco-alcaline avec des granites, granodiorites, diorites, syénites, aplites, albitites; ainsi que de celle alcalines avec des syénites à la néphéline, des essexites, des gabbros alcalins et des monzonites) que sa complexité structurelle. Avec une coupe presque circulaire d'un diamètre d'environ 15 km, la cartographie du DAM a révélé sa structure en anneau, de l'extérieur à l'intérieur, du faciès alcalin à celui calco-alcalin. Situé à l'intersection des principales fractures de la croûte, G8 et G9–G4, les intrusions répétées ont généré une auréole de contact thermique spécifique, au sein de la série Tulgheș. Progressivement, la liste des minéraux identifiés dans des roches et des minerais a progressivement été enrichie, atteignant aujourd'hui plus de 300 espèces. Les fractures internes qui ont affecté le DAM ont constitué les voies d'accès des magmas qui ont généré les filons d'aujourd'hui (aplites, lamprophyres–vogesites, kersantites, spessartites, camptonites, odinites, carbonatites).

La différenciation métallogénique a enrichi le cadre pétrographique et a conduit, par la paragenèse spécifique (molybdène et REE), aux divers champs de minerais: champs de ***Jolotca*** (pyrite, chalcopyrite, sphalérite, pyrrhotite, molybdénite), des oxydes (Ti, Fe, Th, Nb) et des phosphates (monazite-Ce), ***Hereb*** (molybdénite, pyrite, sphalerite et galène) avec REE), ***Aurora*** (molybdénite, pyrite, sphalérite et galène) avec REE, ***Belcina*** (sphalérite, galène, arsénopyrite, pyrite, molybdénite), xénotime (avec Th et REE), sidérite, fluor-apatite, chlorite, calcite, quartz, rutile, anatase) etc. L'empreinte géochimique dans le DAM est Ti, Nb, Zr, V, Th, Mo, Fe, Pb, Zn, P, REE). L'âge du DAM, considéré par A. Streckeisen à 160 millions d'années (m.a.), a été reconsidéré par de nombreux auteurs en utilisant des méthodes modernes d'investigation (K / Ar et 40Ar / 39Ar = 165–160 m.a.; nepheline sienites = biotite–180 m.a.; nepheline = 210–230 m.a.; ultramafites = 230 m.a.; U–Pb zircon = 229 m.a.). Les résultats des chercheurs au cours d'une si longue période se retrouvent dans des nombreuses représentations cartographiques à des échelles très variés. Une synthèse de ces croquis, ainsi que des cartes géologiques, structurelles et métallogénétiques, confirme la diversité pétrogénétique. Les divers modèles ont été élaborés par: *A. Streckeisen, Foldvari, A. Streckeisen et J.C. Huntziker, Al. Codarcea et V. Ianovici, N. Anastasiu et E. Constantinescu, I. Balintoni, D. Zincenco, G. Jakab, E. Pál-Molnár, A. Fall, O. Iancu, G.Săbău et E. Negulescu*. La liste des références bibliographiques, à la fin de cet article, se veut complète et indique les groupes de spécialistes qui ont travaillé dans le DAM et qui ont publié leurs recherches.

Mots-clés: *histoire de la recherche, cartes, ipothèse, références, Carpates Orientales.*

INTRODUCTION

The alkaline massif of Ditrău, unique in Romania by size and petrographical variety, lies in the central part of the East Carpathians, on the inner border of Mesozoic Crystalline Zone, within in Tulghes Group. Since 1859, when it was discovered by *F. Herbich*, the massif constituted the object of study for many geologists, who contributed to its mineralogical, petrographical, chemical, structural and economic potential knowledge.

The Ditrău massif has an autochtonous, intrusive character and its tendency of enrooting has been proved by petrographic, mineralogic and geophysical data. It constitutes a multistage magmatic intrusive of shallow crustal character. The intrusive body penetrated the crystalline schists of the Tulgheş Group (Bucovian Nappe of the Median Dacides). Its petrographic heterogeneity and petrochemical incompatibilities, that is occurrence of supersaturated rocks (granitoides) besides nonsaturated rocks (foidic syenites) suggest the existence of two deep magmatic sources.

The massif was discovered in 1859 by F. Herbich and soon visited by many eminent geologists: Koch (1877–1880), Berwerth (1905), Mauritz (1910–1925), Ianovici (1929, 1932–1968), Streckeisen (1931–1938, 1952–1954, 1960, 1974), Codarcea, Codarcea M. D., Ianovici (1958), Rădulescu (1956), Anastasiu, Constantinescu (1974–1984), Zincenco (1975), Jakab (1982).

In the following, we will present a summary of the main conclusions drawn from the published papers on Tectostructural location, Mineralogy, Petrography, Veins, Structure, Geochemistry, Age, Thermal contact aureole, Metallogeny–ore deposits, Maps, Genetical ipothesis.

GEOLOGICAL SETTING

Tectostructural location; the crystalline series basement: Ditrău Alkaline Massif is considered a laccolith with concentric pattern (inner nefeline syenites, outer granite and alkali-syenite rocks). Codarcea *et al.* (1958) estimated that the fluidal structure is a relict situated in the upper part/ apex of a batholit which altered metasomatically the surrounding crystalline schists. At various stages of investigation, A. Streckeisen (1952/1954) explained the massif occurrence by Daly's theory of limestone syntextis but has eventually gave up, accepting a magmatic origin accompanied by mylonitization and metasomatism.

According to absolute age determinations, the intrusion took place during Jurassic times, but recently Săbău (2017) show 235 m.y. (Upper Triassic).

Anastasiu and Constantinescu (1984) stated that polystage distribution and consolidation of the Ditrău massif have been controlled by crustal fractures and mobility of the structural compartments limited by them. Geophysical evidence (e.g. gravimetric anomalies, geophysical deep sounding) indicated the existence of a maximum line which marks, at the limit between crystalline schists and the Neogene volcanic chain, a continental crustal fracture type. Its petrographic heterogeneity and petrochemical incompatibilities, that is occurrence of supersaturated rocks (granitoides) besides nonsaturated rocks (foidic syenites) suggest the existence of two deep magmatic sources.

The Ditrău massif has an autochtonous, intrusive character and its tendency of enrooting has been proved by petrographic, mineralogic and geophysical data. It constitutes a multistage magmatic intrusive of shallow crustal character. The intrusive body penetred the crystalline schists of the Tulgheş Group (Bucovian Nappe of the Median Dacides).

But, about the DAM position in relation to the Crystalline Mesozoic Area of the Eastern Carpathians there are different view points (Fig. 1):

Bercia I. *et al*., 1971: DAM is placed in the meso–Cretaceous Rodna-Mestecăniș overthrust, with Rebra–Barnar, Tulgheș and Izvoru Mureș crystalline Series, around.

Streckeisen A. & Huntziker J. C., 1974: Tulgheș Series and Rarău overthrust, older the ADM.

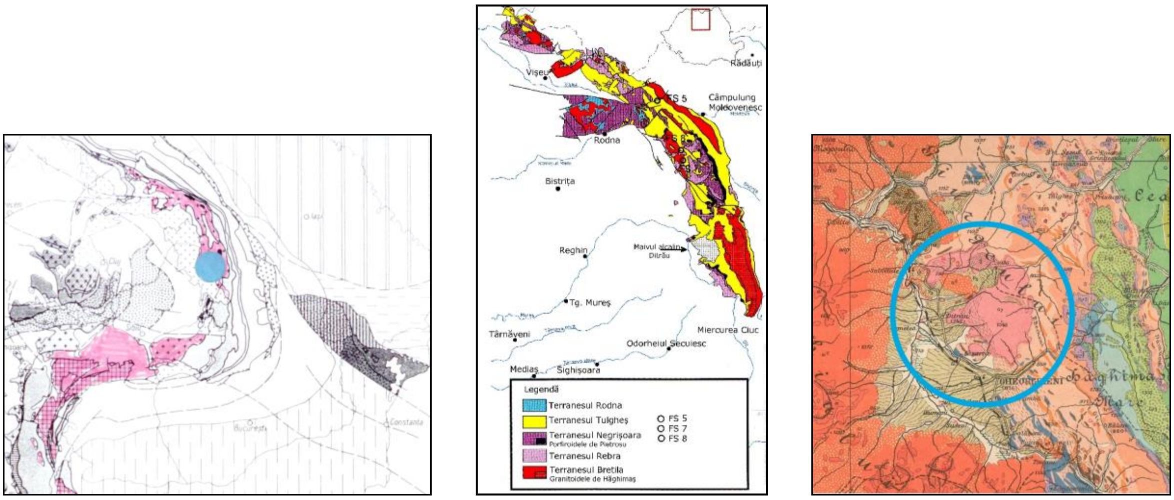
Săndulescu M., 1975: within meso-Cretaceous Bucovinian overthrust (Tulgheș, Rebra-Barnar and Bretila–Rarău Series.

Mureșan M., 1976, 1983: Mestecăniș meso-Cretaceous overthrust.

Zincenco D & Catrinel Papadopol, 1978: Rebra Series, Pietrosu Formation, Tulgheș Series, and Rarău gneisses Serie (within meso-Cretaceous sub-Bucovinian overthrust).

Balintoni I., 1981: Tulgheș Series, Negrișoara Series, Tulgeș Series, Mândra Formation, Rarău Series. (Fig. 1).

Fall A., 2006: ADM occurs within a rift related continental province, and covers 800 km^2; the massif cuts the Pre-Alpine metamorphic rocks of the Bucovina nappe system near the Neogene-Quaternary volcanic arc of the Călimani–Gurghiu–Harghita Mountain chain.



a. **b.** **c.**

Figure. 1. Location of DAM on Romania tectonically sketch (by Săndulescu, 1984) (**a**), related to Crystalline Mesozoic Zone map (by Balintonii apud Iancu, 2010) (**b**), and on a segment from Romanian Geological Map, scale: 1: 1 000 000 – IGR (**c**).

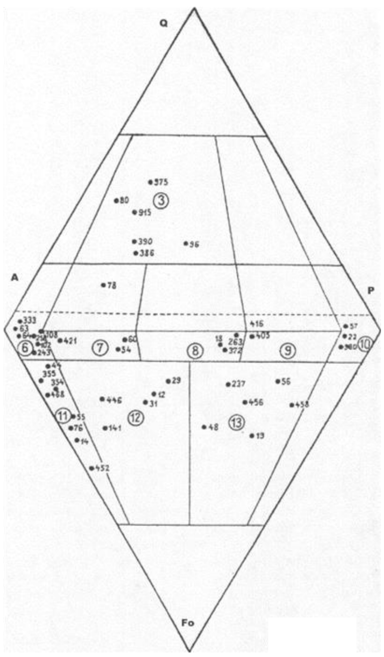
Mineralogy: According to Constantinescu & Anastasiu (2004) the main rock forming minerals are: a) salic minerals: orthoclase, microcline, albite, oligoclase, andesine, nepheline, cancrinite, sodalite, very rare quartz; b) femic minerals: ferro-hornblende, biotite, Ti-augite, diopsidic augite, seldom olivine; c) accessory minerals: apatite, titanite, ilmenite, allanite-(Y), epidote, etc. phlogopite, kaersutite, pargasite, hastingsite, riebeckite-arfvedsonite scapolite, pectolite, analcime, natrolite, wairackite, calcite, dolomite, ankerite.

More than 200 new minerals were, by Paulina Hârtopanu (2013), recently identified, many of them being first occurrences in Romania. The rare element minerals belong to the following classes, in the predominant order: I. LREE(Y)-carbonates; II. Nb, Ta, REE(Y), Ti, Zr, Th, U-oxides III.REE(Y)-Phosphates; IV. REE-(Y), Th, Zr, Pb-Silicates. Among silicates, the following minerals occur in DAIC, specially in Jolotca area: allanite-(Ce), thorite, thorogummite, cerite-(Ce), chevkinite-(Ce), törnebohmite-(Ce), stillwellite-(Ce), tritomite-(Ce), britholite-(Ce) and Th-zircon. The allanite-(Ce) belong to silicates class together with dollaseite-(Ce) (?), thorite, thorogummite, chevkinite-(Ce), törnebohmite-(Ce), cerite-(Ce), stillwellite-(Ce), tritomite-(Ce), britholite-(Ce) and zircon.

Petrography: The massif of Ditrău consists of a large variety of rocks (hornblendites, alkalifeldspar, syenites, monzodiorites, essexites, nepheline syenites, granites and alkali granites) their composition comprising, in various contents, mineral characteristic for alkaline bodies. Structural features of the rocks are due to their degree of crystallinity and to the frequent transitions between the coarse, medium and micro-crystalline facies. Almost regardless of the petrographic type, the rocks show both massive and oriented fabric. (Constantinescu & Anastasiu, 2000) (Fig. 2 and 3).

Pál Molnár (2000), classified the rocks of the dioritic group as: a) Meladiorites, including meladiorites with oriented texture, meladiorites with non-oriented texture and "foliate-like" meladiorites; b) Diorites, including diorites with oriented texture, diorites with non-oriented texture, diorites with feldspar schlieren and diorites with feldspar aggregates; c) Leucodiorites, including leucodiorites with oriented texture; leucodiorites with non-oriented texture.


a.



b.

Figure 2. a) Outcrop in the Güdücz complex (white nepheline syenites and alkaline gabbros are clearly visible, foto by *Iancu*, 2010'. **b)**The modal analysis (in QAPF diagram): 3, granites; 6, alkali-feldspar syenites with foides; 7, foidic syenites; 8, foidic monzonites; 9, monzonites with foides; 10, foidic diorites; 11, foidic syenites (nephelinic); 12, foidic monzosyenites; 13, essexites (after Anastasiu & Constantinescu, 1979, 1994).

Figure 3. The main type of rocks from DAM: 1, hornblendite; 2, diorite; 3, syenite; 4, granite; 5, oriented nephelin syenite; 6, nepheline syenite; 7, essexite: 8, monzodiorite; 9, syenite with paragonite; Jo–Jolotca, He–Hereb.

Veins: A lot of veins (dykes) cross the igneous rocks, from lamprophyres to aplites, like that: tinguaite, camtonites, spessartites, monchiquites, vogesites, microdiorites, nepheline syenites, carbonatites (Streckeisen, 1974; Jakab, 1998).

From a petrographical point of view, the vein rocks may be classified in *felsic facies* – leucosyenites, porphyritic and bostonitic microsyenites, foidic syenites and microsyenites, tinguaites, alkali granites, aplites and *mafic facies* – various lamprophyres (vogesites, kersantites, spessartites, camptonites, odinites) phonolite.

A part of the vein rocks are represented by *monomineralic* aggregates such as albitites, epidotites, carbonate veins, or correspond to *simple assemblages*, e.g., sodalite and biotite.

The bulk mineralogical composition of the vein rocks reflects a tight connection with the rocks of the main massif. Their structural diversity (e.g., microcrystalline, medium grained and seldom pegmatoid facies), reflects the cooling conditions of the parental magma and sketch the temporal extension of the magmatic processes. The veins are an expression of (1) the disjunctive tectonics manifested prior to their emplacement and (2) the existence within the massif of “S”-type planes, with a visible directional continuity (Anastasiu, Constantinescu, 1980).

Structure: Din PH-2013: The massif presents a distinct ring structure (Streckeisen, 1960). The outer ring is formed by alkali-granites, alkali-syenites and nepheline-syenites, essexites, generally red in color, with gradual transitions between these rocks. The intermediate ring-dyke consists of foliated, sometimes schistose essexites which are banded by alkali-syenites being cut by nepheline-syenite veins by which they have been hybridised and metasomatically transformed. The large body of Ditrau essexites (nepheline gabbros) of both rings contain small lenses of ultrabasites at several places and show a gradual transition to the alkali syenites. The central stock (6 km in diameter) is formed by white, coarse grained nepheline syenites with abundant cancrinite and primary calcite. Abundant sodalite is found in veinlets or penetrating the rock and replacing the nepheline. Smaller masses of white nepheline-syenite with cancrinite and sodalite occurr at several places in the intermediate and outer ring-dykes up to the contact and even in the immediate contact aureole. The lamprophyres (camptonites and spessartites) dykes cut sharply the rocks of the outer and intermediate rings but are lacking in the central stock. Aplitic and pegmatitic rocks are frequent especially in the white nepheline syenites to which they show gradual transitions. At several places, sodalite and cancrinite-sodalite-nepheline syenite pegmatites can be found; such rocks were termed “ditroites” by Streckeisen (1960). Also, the tinguaites (alkali feldspars, nepheline and alkali pyroxenes and amphiboles) rich in cancrinite are specially frequent in the central stock. Small veins of diverse carbonates are found in various rocks described above.

Geochemistry: Generally, the rocks show enrichment in Ca, Na, Fe, Ti, P, Zr, CO2, Cl and F indicating that these rocks represent a transition from alkaline to peralkaline character (or from miaskitic to agpaitic) (Hârtopanu, 2013).

Age: Ditrău Alkaline Massif – 160 m.y. (Streckeisen and Hunziker, 1974).

Pall-2015: The ultramafic rocks were the earliest components, emplaced at 216–237 m.y., although their age overlaps that of the gabbros (234 m.y.). The nepheline syenites and granites are somewhat younger (216–232 m.y. and 196–217 m.y. respectively). Original dating was by K/Ar on hornblende, biotite, nepheline and feldspar separates, (Pál-Molnár and Árva-Sós, 1995) and a mid- to late-Triassic age of the early components was subsequently confirmed by additional $^{40}Ar/^{39}Ar$ hornblende ages of 231 m.y. and 227 m.y. for gabbro and diorite, respectively (Dallmeyer *et al*., 1997). A mantle origin for the mafic and ultramafic bodies was inferred by Kräutner and Bindea (1998) and Morogan *et al*. (2000).

Pál-Molnár and Árva-Sós (1995) obtained similar ages for the earlier intrusions but obtained nepheline ages of about 210–230 m.y. and biotite ages of about 180 m.y. for the nepheline syenites. The ultramafic rocks have been dated at about 230 m.y., the gabbros, diorites, monzodiorites, monzonites, syenites and granites are about 215 m.y., and the nepheline syenites have ages of about 165–160 m.y., all determined using K/Ar and $^{40}Ar/^{39}Ar$ chronology (Bagdasarian, 1972; Streckeisen and Hunziker, 1974 Dallmeyer *et al*., 1997; Kräutner and Bindea, 1998 (Fall *et al*., 2006).

The DAM formed during the Variscan orogeny. The precise U-Pb zircon age of 229.6+1.5/-1.7 m.y. determined by Pană *et al*. (2000) for the Ditrău syenite matches within error the hornblende $^{40}Ar/^{39}Ar$ dates obtained by Dallmeyer *et al*. (1997) from the diorite complex and hints to a relative short magmatic evolution of the DAM, within the Ladinian time (Mid-Triassic).

Thermal contact aureola: The DAM has a thermal contact zone with hornfels, larger than 50–70 m, but much more 1 – 2 km with influence of thermal metamorphism (andalusite, corundum, spinel, alkali amphibole, chloritoid, second biotite) which affected Tulgheș Group (Streckeisen & Huntziker, 1974, Jakab, 1998, Hârtopanu *et al*., 2000).

Metalogeny, ore deposits: The first informations concerning the mineralizations belong to Ianovici (1933, 1938), who describes occurrences of sphalerite, galena, pyrite, chalcopyrite and goethite localized in the valley of Jolotca, and to Panto (1942), who described pyrite, chalcopyrite, sphalerite.

Other minerals have been identified by Koch (1886) – orthite, Zepharovich (1859) – pyrochlore, Stanciu (1955) – baddeleyte; Codarcea *et al*. (1958) – rhönite, xenotime, molybdenite, Jakab, Garbaşevschi (1975) – arsenopyrite.

The petrogenetical and structural study of the mineralisation (Constantinescu *et al*., 1981) pointed out two characteristics which are in a sense similar to the situations described for the vein rocks:

1) the existence of multiple generations of minerals (e.g., pyrite-1, pyrite-2; orthite-1, orthite-2); (Fig. 4);

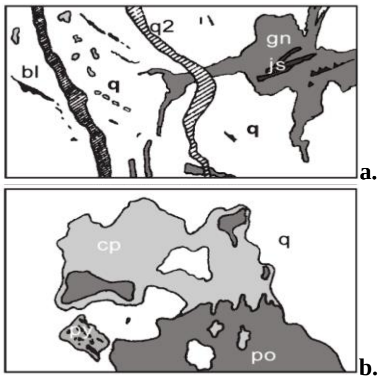


Figure 4. Spatial relationships between the minerals constituting the mineralization **a)** cp, chalcopyrite; gn, galena; bl, sphalerite; js, joseite; q, quartz. **b)** py, pyrite; cp, chalcopyrite; po, pyrrhotite; q, quartz. (after Constantinescu. & Anastasiu, 1981)

2) the existence of breccification structures signifying the tight relationship between breccias and mineralisation; similarly, for the vein rocks a relationship between deformation and recrystallisation could be described, suggesting the role played by the recrystallization processes in the attainment of the present mineralogical relations. Such a conclusion may direct the prospecting works toward areas with known post-magmatic deformations, a plausible host for the reconcentration of the mineralization.

The ore deposits occur as EW/40–60 N vein sets (isolated, complex and branching discontinuously) and impregnations; they are spatially related to lamprophyre and albitite dykes.

The main metallic elements concentrated within the massif – Zr, Ti, Nb, V, Th, Mo, REE, Fe, Pb, Zn, P – belong to both structural levels (Fig. 5 and 6):

1) the "primary" formation – segregation or magmatic dissemination – includes two distinct parageneses:

a) Zr-P-Nb-Ti-REE minerals: zircon, apatite, ilmenite, orthite, xenotime, pyrochlore, niobite, garnet and Pb, Zn, Mo, Fe, Cu, Sb sulfides (goldbearing pyrite, sphalerite, galena, molybdenite), oxides (ilmenite, magnetite), xenotime, parisite and bastnäsite, pyrrhotine, rohnite, marcasite, bismuthite, joseite, tetradymite, macinawite, cubanite, etc) related to syenitoides and foidic syenites, located in Aurora, Hereb, Várbükk, Balas Lorincz areas (Iakab, 1982).

2) postmagmatic formation with pneumatolitic-hydrothermal features and with veins with distinct mineralogy in the two distinct compartments:

a) in the Jolotca-Tarniţa area, the Mo-REE-Ti-Nb-Fe-(Pb, Zn) molybdenite, xenotime, loparite, monazite, ilmenite, concentrated in veins (Constantinescu *et al*.,1981);

b) in the southern area – the Belcina valley basin – Th-V-REE-Zr-F-Mo minerals are concentrated: pyrochlore, bastnäsite, thorite, xenotime, niobotantalite, zircon, fluorite and Pb, Zn, Cu, Mo, Fe sulfides.

The mineralogical, petrographical, petrochemical and structural investigations rise the metallogenetic potential of the massif and enhance the possibilities for exploiting the rocks. The quality of hornblendites was emphasized for their Fe, P, Ti contents and that of the foidic syenites for their Al contents and for their usage in the ceramic industry. We also established the metallogenetic indicators used to orient the geological explorations.

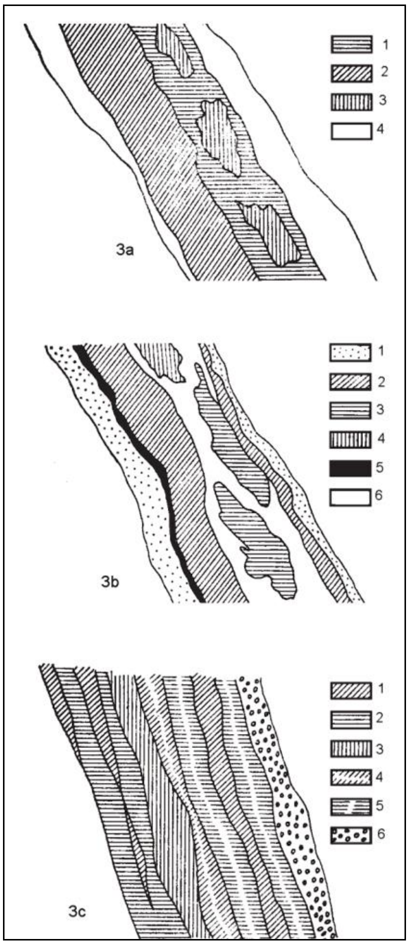


Figure 5. Structures and textures of the mineralization from Ditrău - Jolotca sector. **3a**: 1, monazite; 2, pyrite; 3, ilmenite; 4, carbonates. **3b**: 1, quartz; 2, pyrite; 3, monazite; 4, ilmenite and chalcopyrite; 5, molybdenite; 6, carbonates. **3c**: 1, pyrite; 2, monazite and orthite; 3, orthite; 4, pyrite, ilmenite and sphalerite; 5, monazite and orthite nests within carbonates; 6, mylonitic zone with monazite showing brittle deformation. (after Constantinescu & Anastasiu, 1981).

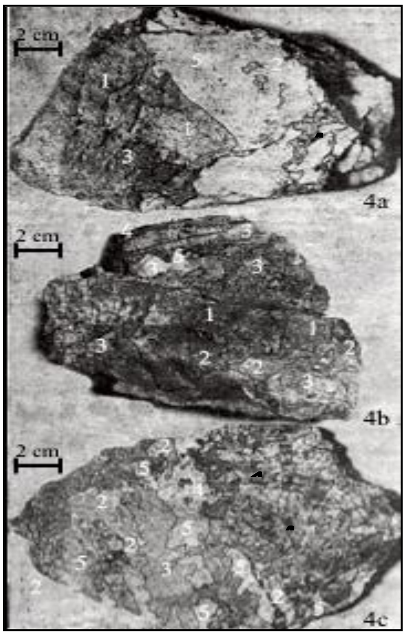


Figure 6. Characteristic mineral associations in the alkaline massif of Ditrău – Jolotca sector. **4a, 4b**: 1, ilmenite; 2, pyrite; 3, monazite; 4, orthite; 5, carbonates; 6, chlorites. **4c**: 1, ilmenite; 2, pyrite; 3, carbonates; 4, chlorites; 5, sphalerite; 6, molybdenite.

They contain molybdenite, pyrite, galena, sphalerite, ilmenite, magnetite, rutile, monasite, tapiolite, columbite, parisite, also xenotime, orthite, bastnasite, chalcopyrite, pyrrhotine, rohnite, marcasite, bismuthite, joseite, tetradymite, macinawite, cubanite, etc. The main character is molybdenic common sulfides; the Ti-Nb associations that is ilmenite-magnetite, rutile, tapiolite and columbite is of less important significance. The Mo-sulphide minerallization is associated with carbonatic-albitic rocks whereas the Ti-Nb minerallization with carbonatic gangue. (Constantinescu & Anastasiu, 1981; Anastasiu *et al*., 1994).

All this aspects of the mineralisation formed during the main (pneumatolitic and hydrothermal) stages, indicate a sequential formation. This is pointed out by the presence of several mineral generations and by the existence of important discontinuities marked by brecciation intervals.

The REE mineralisation (Nb-Th minerals) can be considered genetically affiliated to the alkaline rocks, the mineralogical and geochemical data showing a common geochemical trend for OIB setting of the REE, Ca and Nb with Th. (Constantinescu & Anastasiu, 2000; see Paulina Hârtopanu (2013), too).

MAPS

The main maps of the DAM published in specialty magazines are playable in the original figures 7–22.

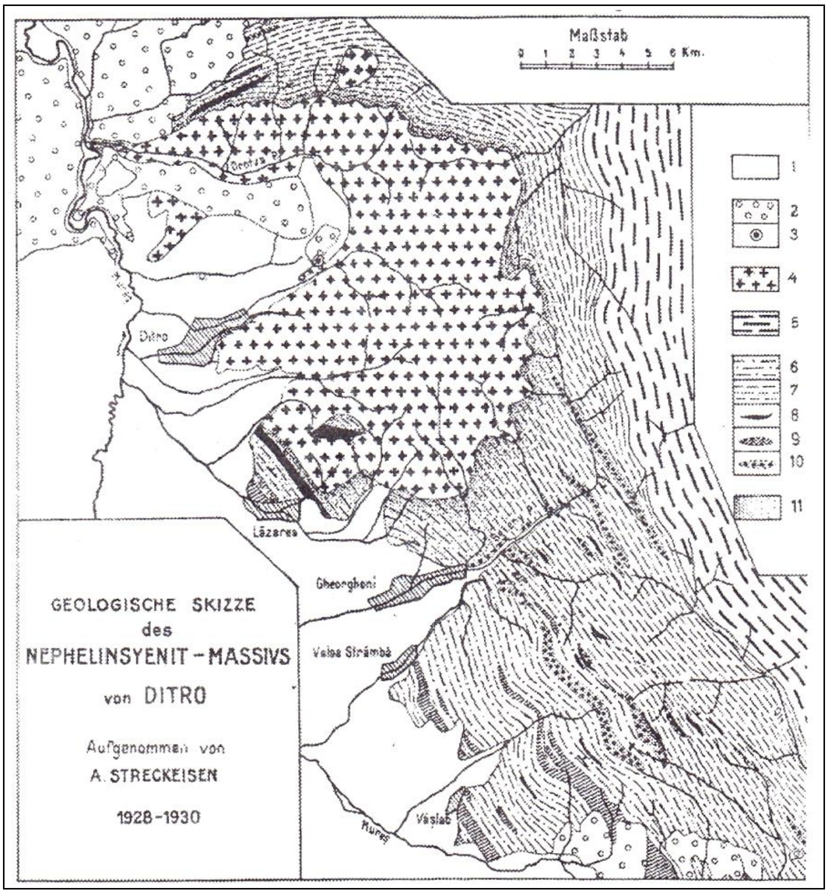


Figure. 7. Geological sketch map of the DAM, A. Streckeisen, 1928–1930.

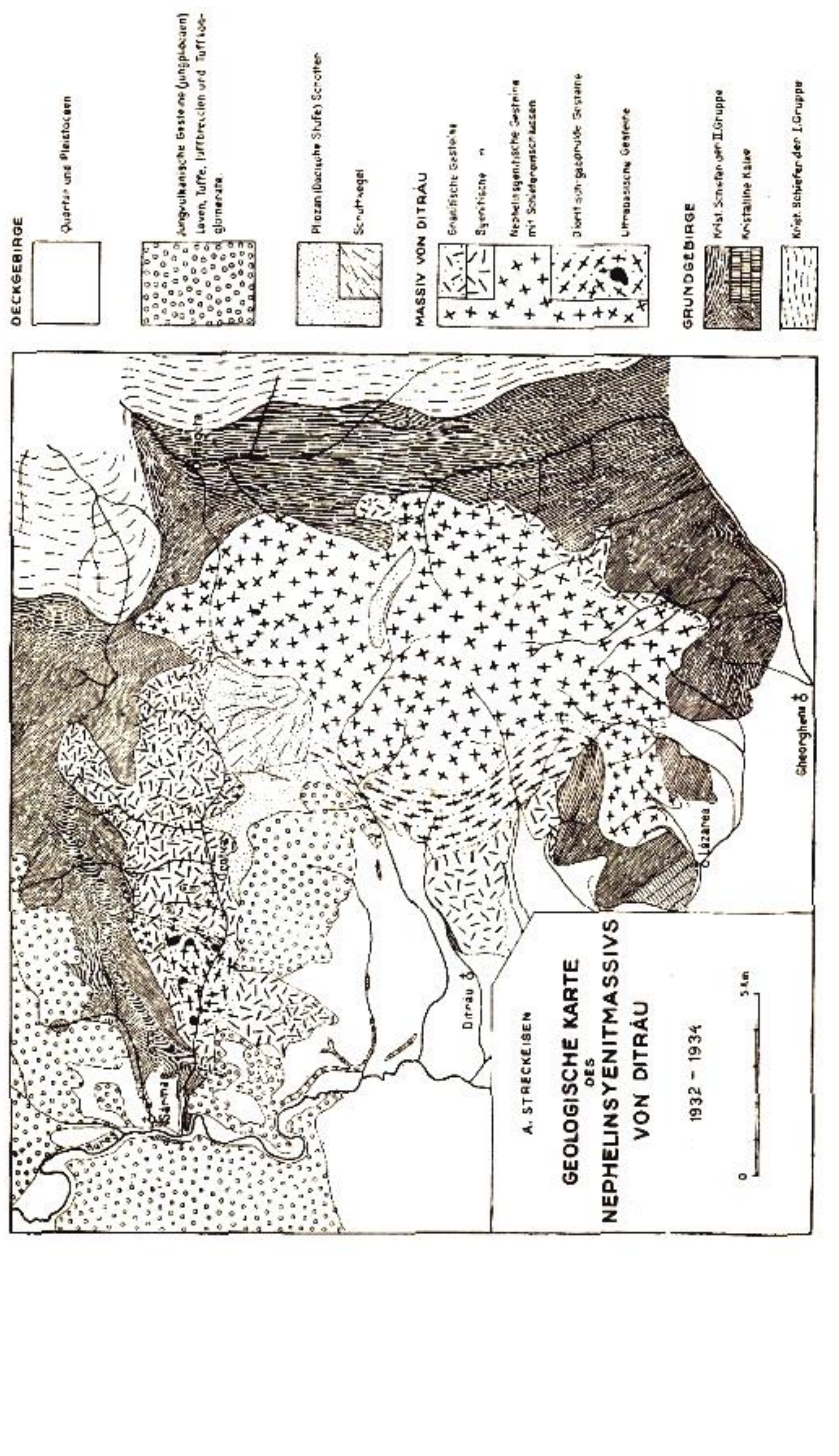


Figure 8. Geological sketch map of the DAM, A. Streckeisen, 1932–1934.

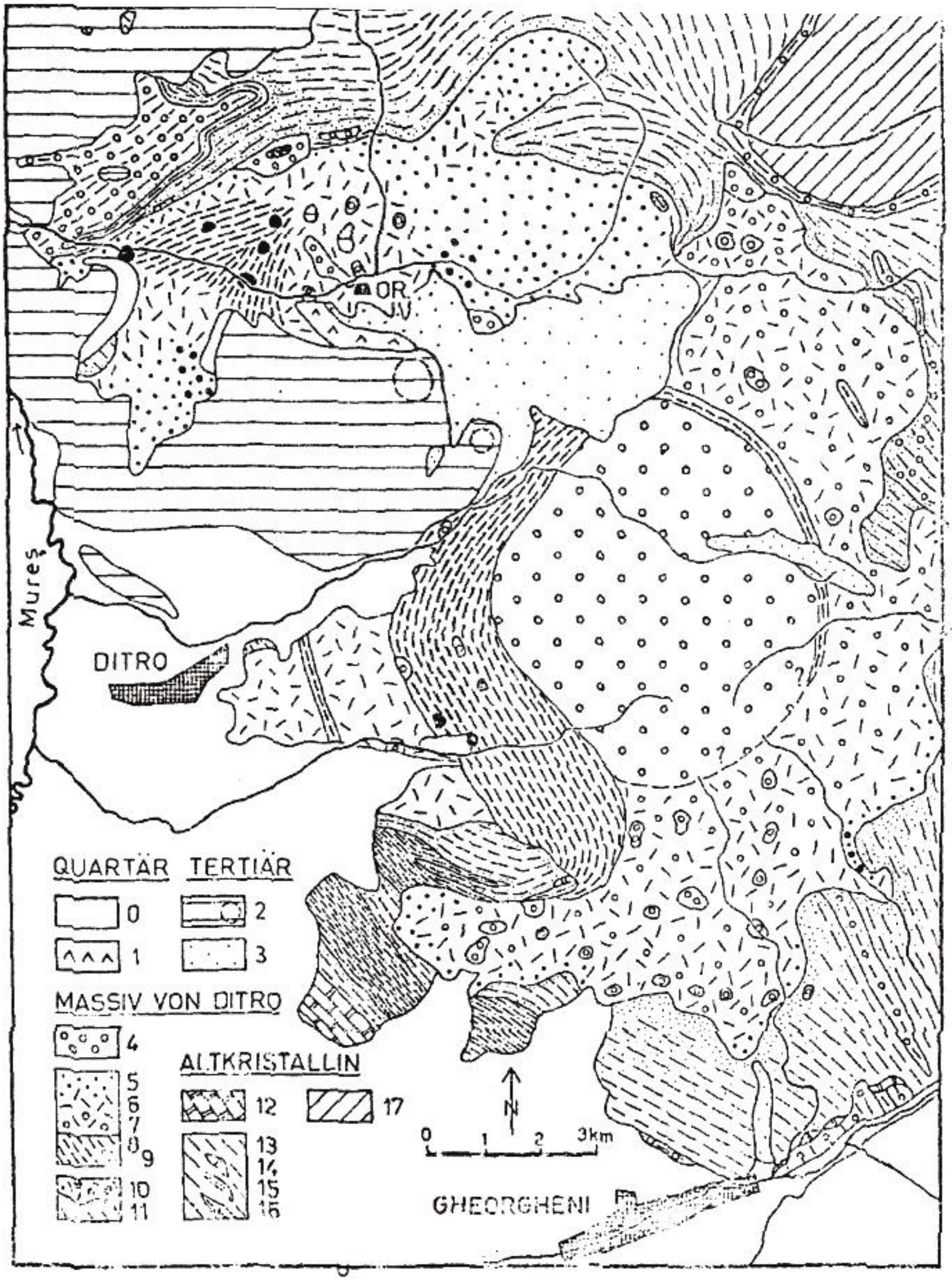


Figure 9. Geological sketch map of the DAM, original Foldvari, 1946.

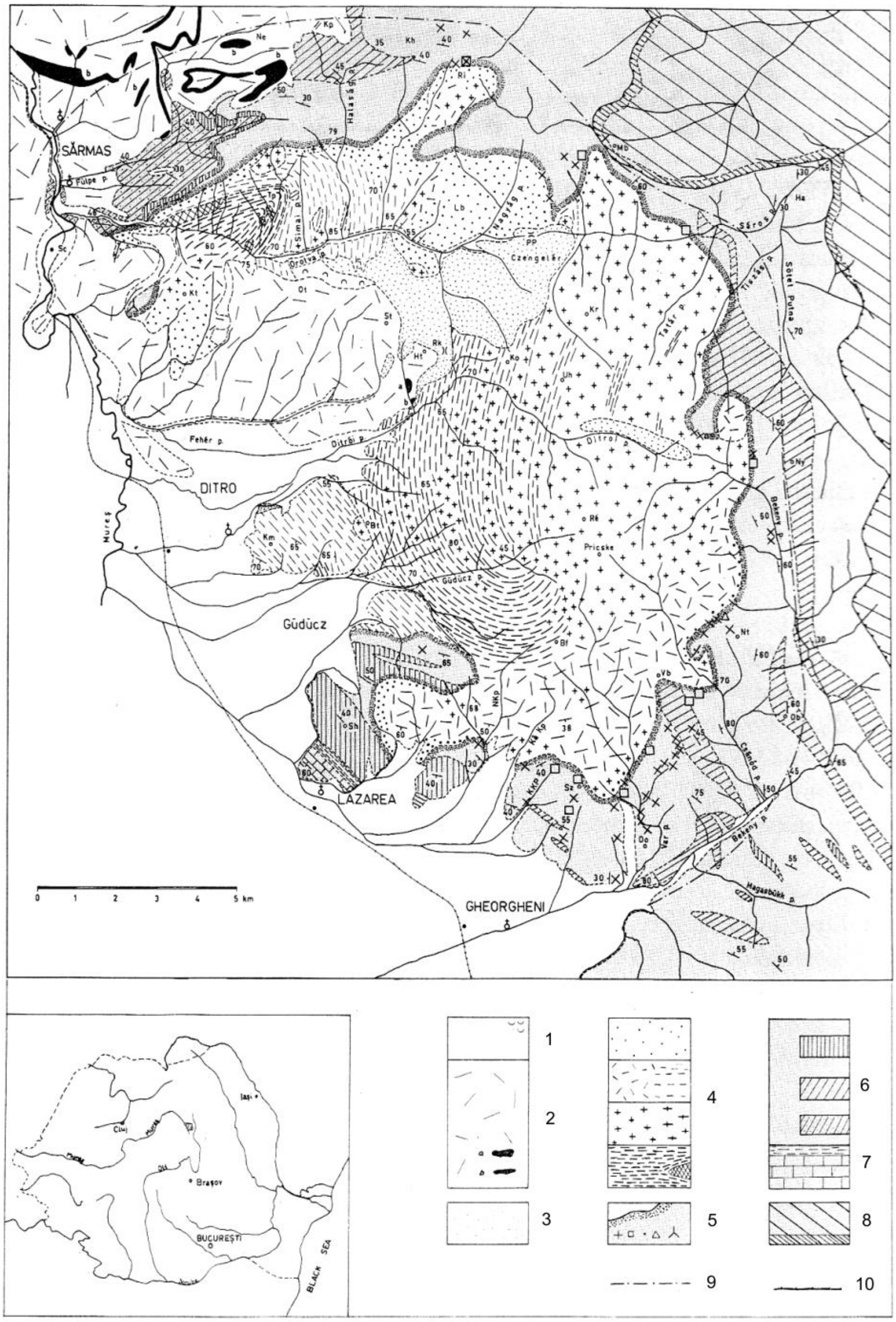


Figure 10. Geological sketch map of the DAM, A. Streckeisen & J.C. Huntziker, 1974. Cuaternary; 2, pyroclastics; 3, gravels-Upper Pliocene; 4, Ditro Rocks. 5, thermal contact aureole. 6, epizonal Tulgheş Series; 7, mesozonal Bistriţa-Barnar series; 8, Rarău series; 9, outer limit of contact aureole; 10, thrust plane of the Rarău gneisse nappe.

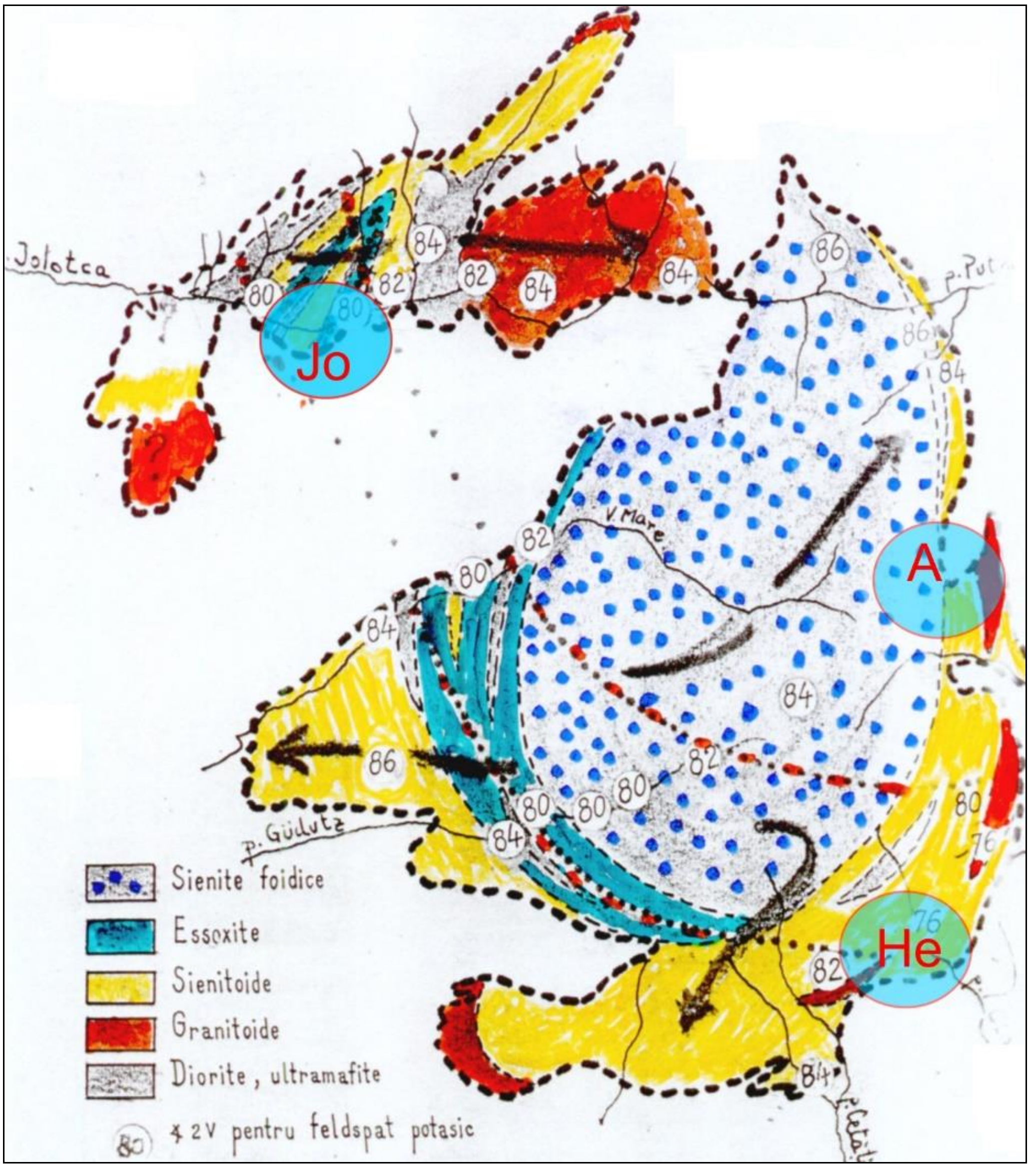


Figure 11. Geological sketch map of the DAM showing 2Va value distribution for the K-feldspars, Jo–Jolotca, A–Aurora, He–Hereb, from Anastasiu & Constantinescu, 1978/1981.

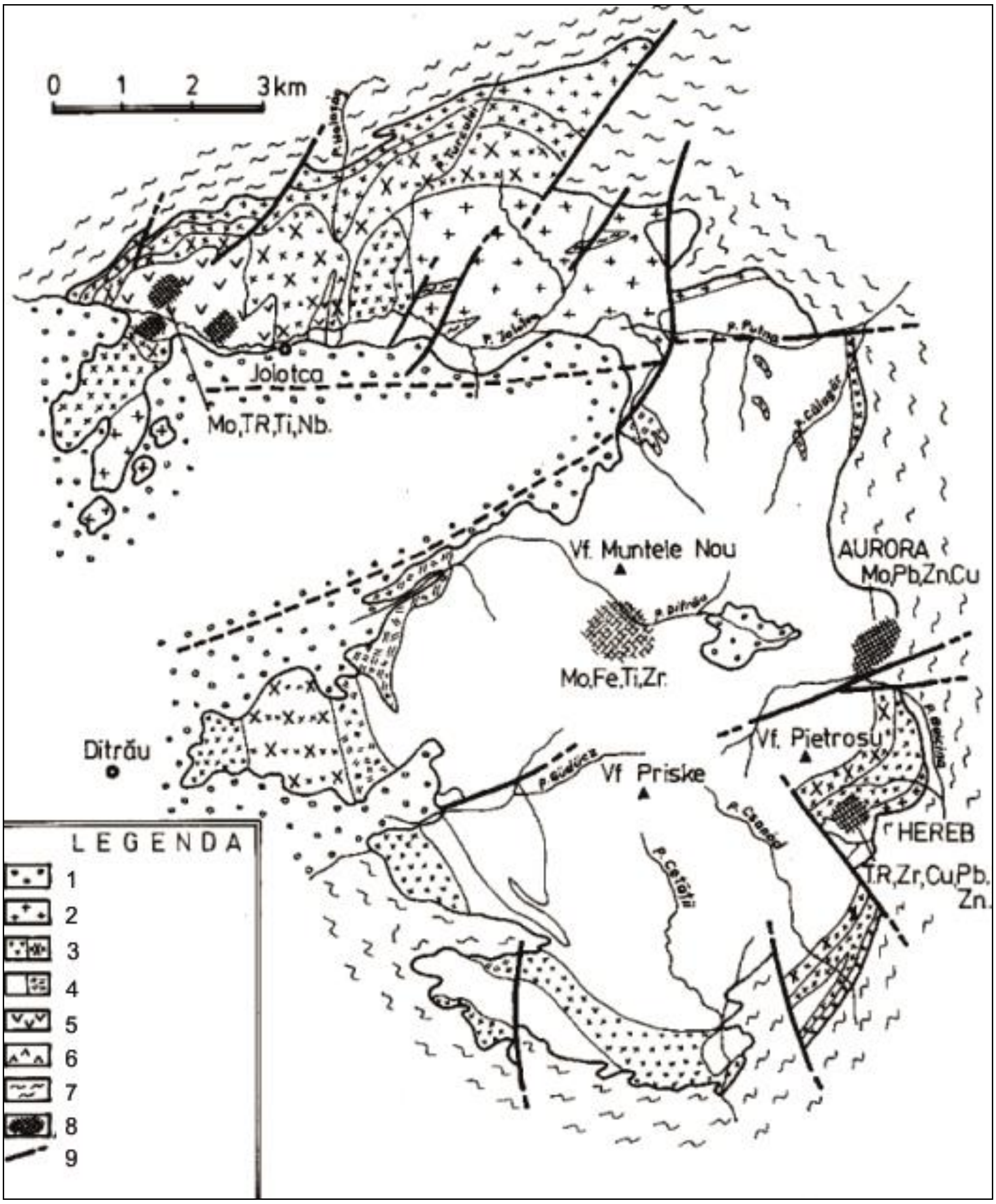


Figure 12. Geological sketch map of the DAM with mineralizations location (Jolotca, Muntele Nou, Aurora, Hereb), after Constantinescu, Anastasiu, Pop, Garbasevschi, 1983: 1, Quaternary; 2, granitoides; 3, syenitoides; 4,. foidic rocks (nepheline syuenites, essexites); 5, diorites; 6,maphytes (hornblendites); 7, metamorphites (Rebra, Tulgheș Series); 8, ore deposits; 9, fault.

.

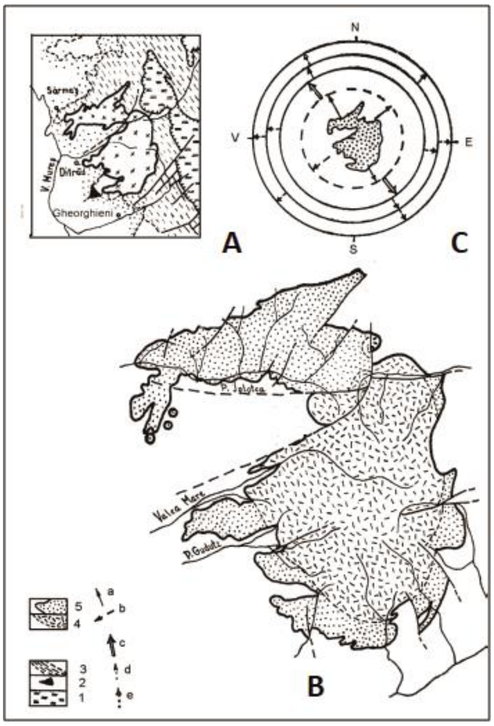


Figure. 13. The tectostructural position and the structure of the DAM: 1, Rebra-Barnar Series, 2, Rarău-Bretila Series, 3, Tulgheş Series, 4, central zone with foidic rocks, 5, marginal zone; **a**) G8 crustal fracture strike, **b**) the fault strikes in Tulgheş Series, **c**) the joint strikes in contact zone, **d**) the joint strikes in the northern compartment, **e**) the joint strikes in the central-southern compartment (after Anastasiu & Constantinescu, 1982).

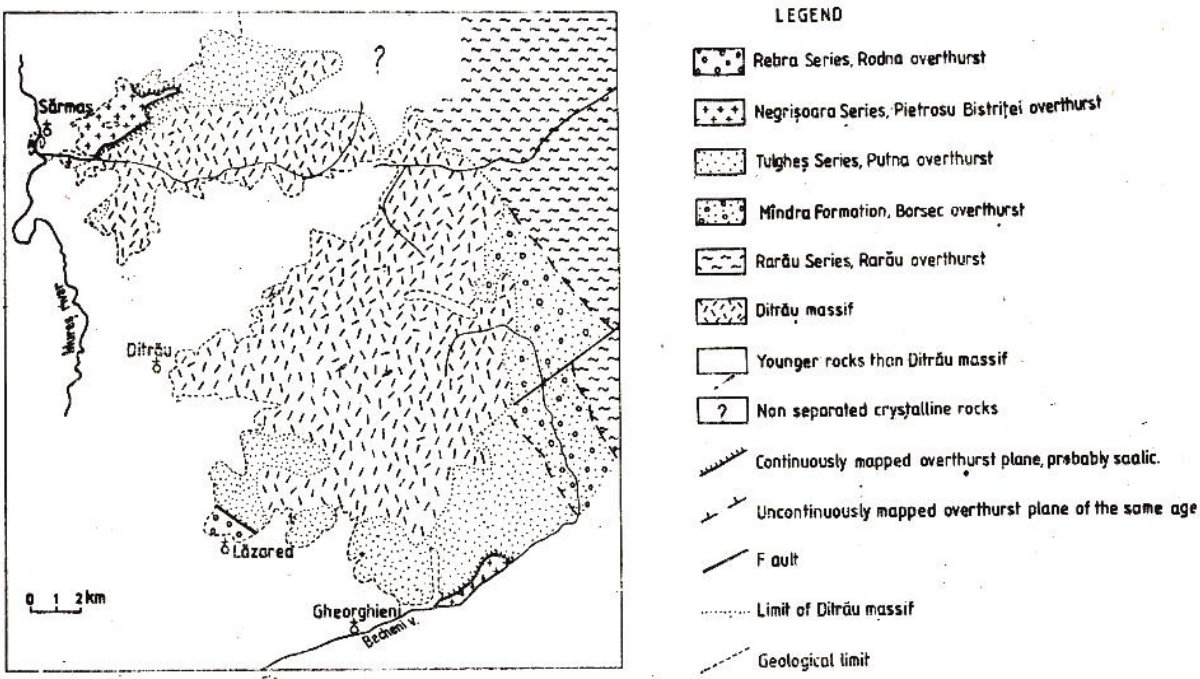


Figure. 14. Structural sketch map of the crystalline rocks around the DAM. The limits between the Tulgheș Series, Negrișoara and Rebra Series; after I. Balintoni, 1981

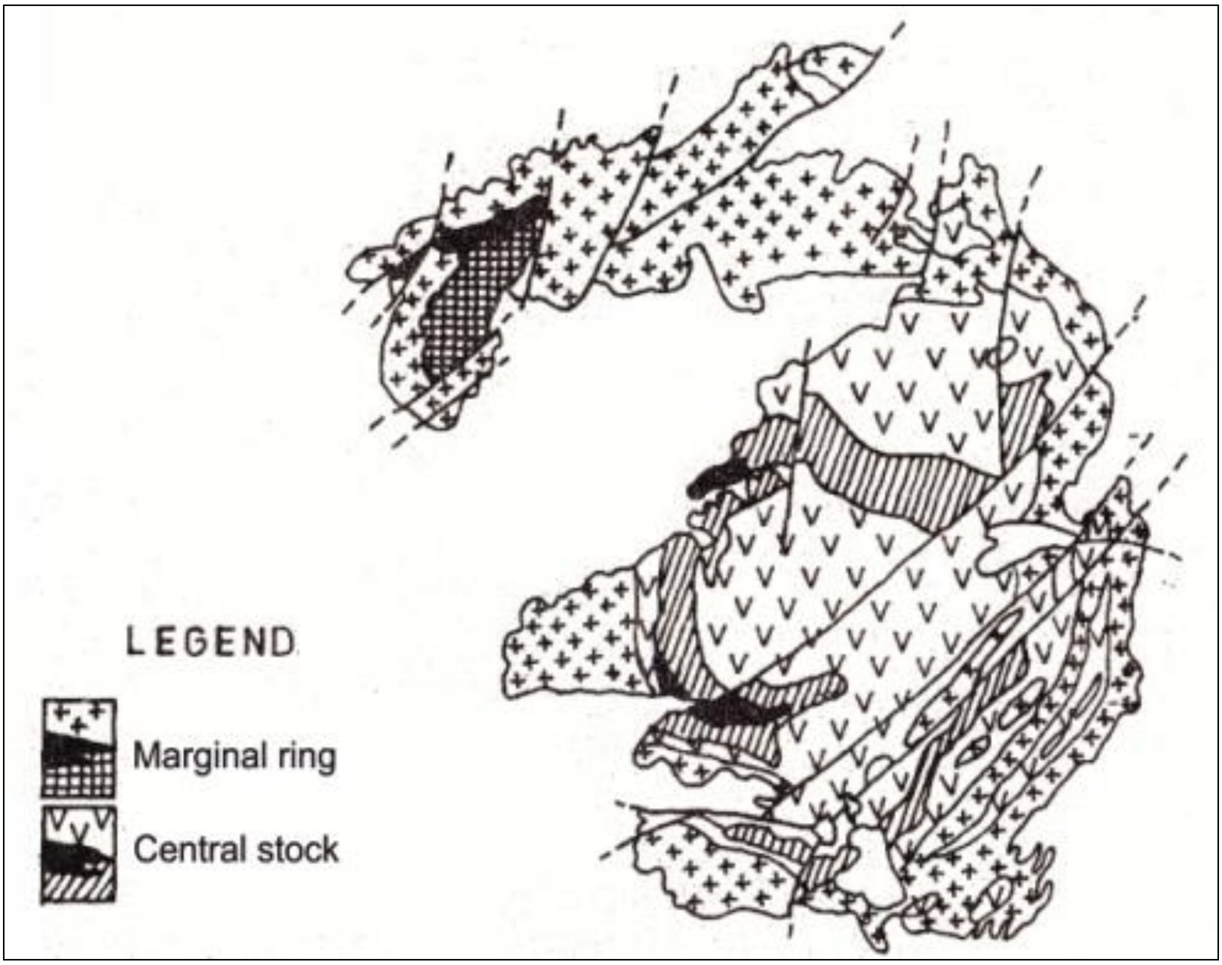


Figure. 15. DAM sketch with ring and stock petrographically associations (after Zincenco, 1980).

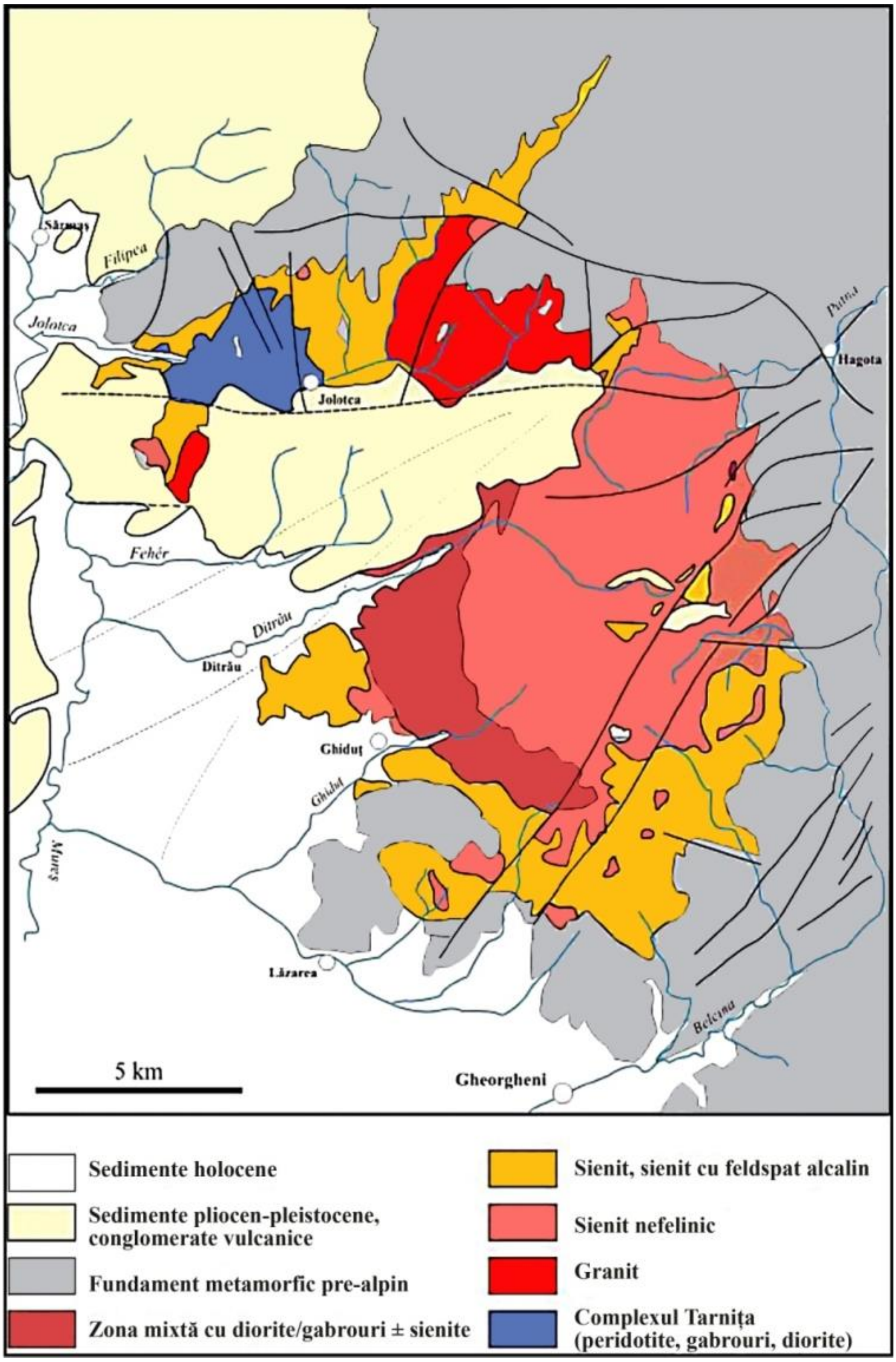


Figure 16. Geological sketch map of the DAM, after Pál–Molnár, 2010.

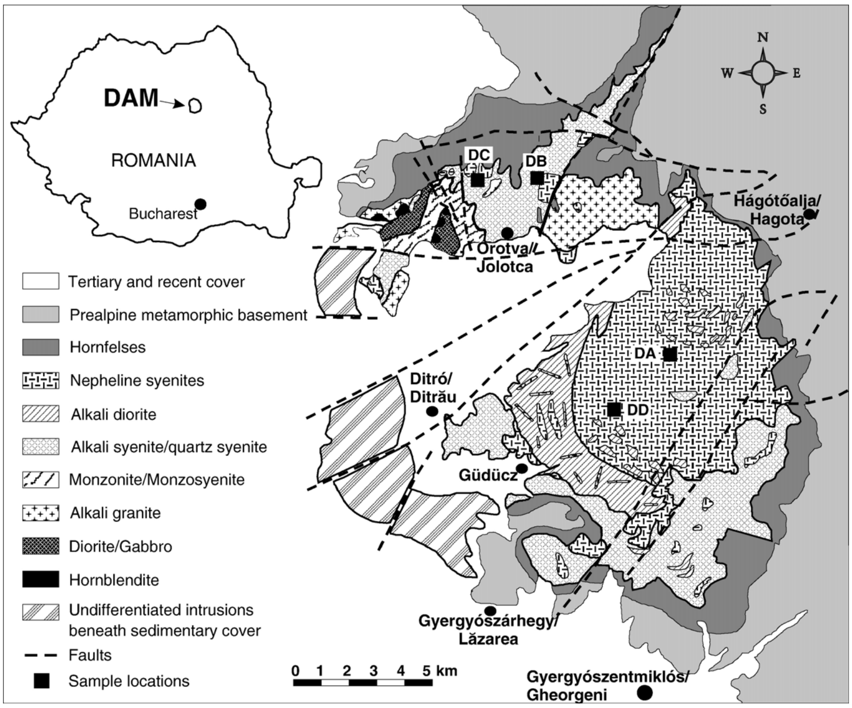


Figure 17. Location map and geology of the DAM, with the sample locations: DA–11 samples; DB–2 samples; DC–2 samples, DD–3 samples. (modified from Kräutner and Bindea, 1998), after Fall *et al*., 2006.

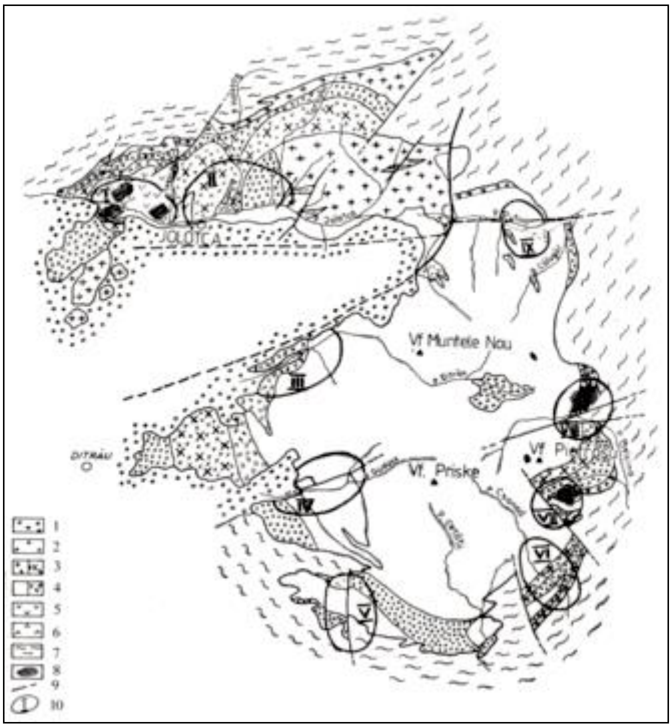


Figure 18. Geological sketch of the DAM (scale 1:1.000.000). 1, cover deposits; 2, granitoide complex; 3, syenitoide complex: syenites, monzonites; 4, foidic rock complex: foidic syenites, essexites; 5, diorite complex; 6, ultramafic and mafic complex; 7, Rebra series, Tulgheş series; 8, mineralized zones; 9, fault; 10, vein fields (I–IX). (after Anastasiu & Constantinescu, 1984).

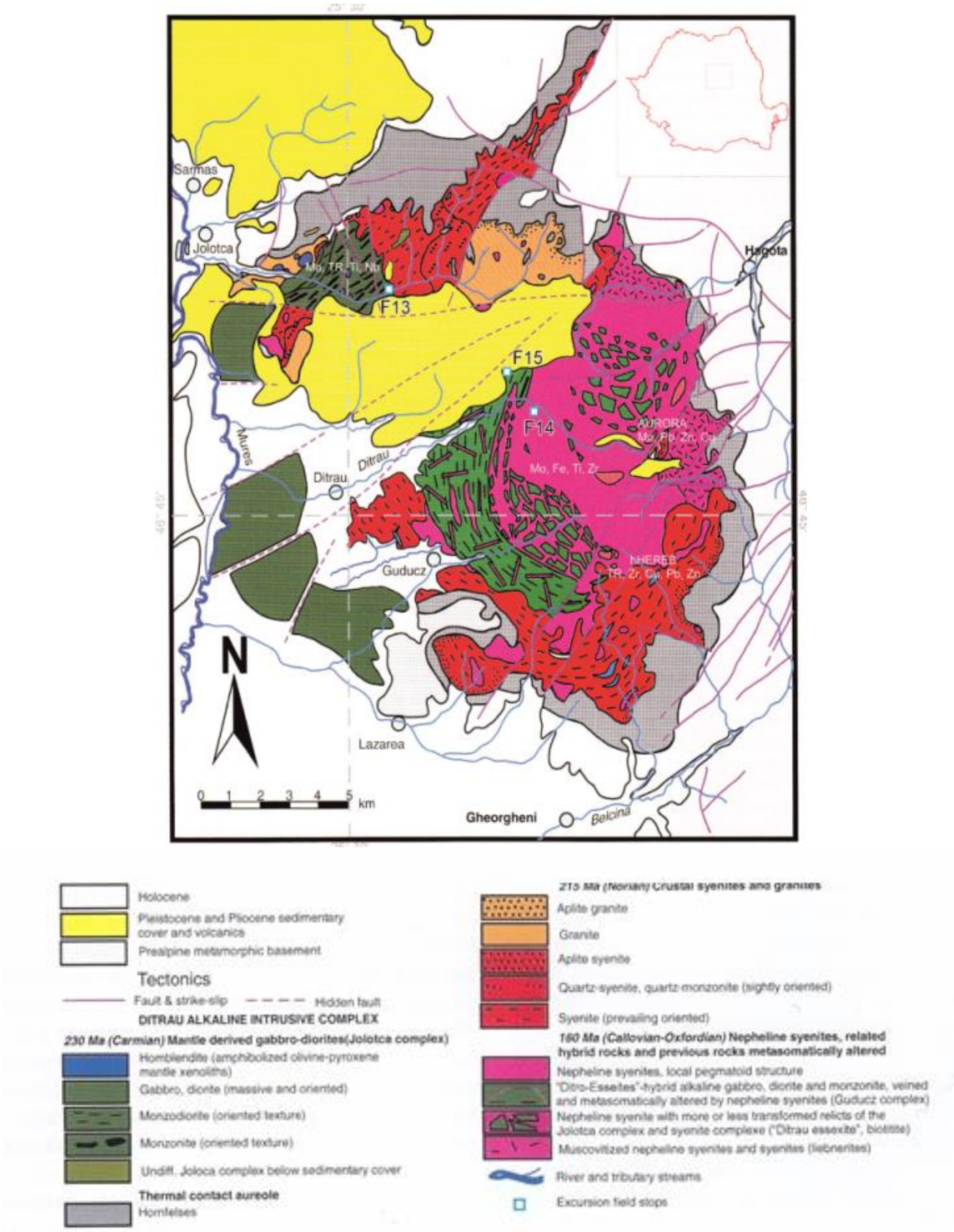


Figure 19. Geological sketch map of the DAM, O. Iancu, 2010, modified from Krautner & Bindea.

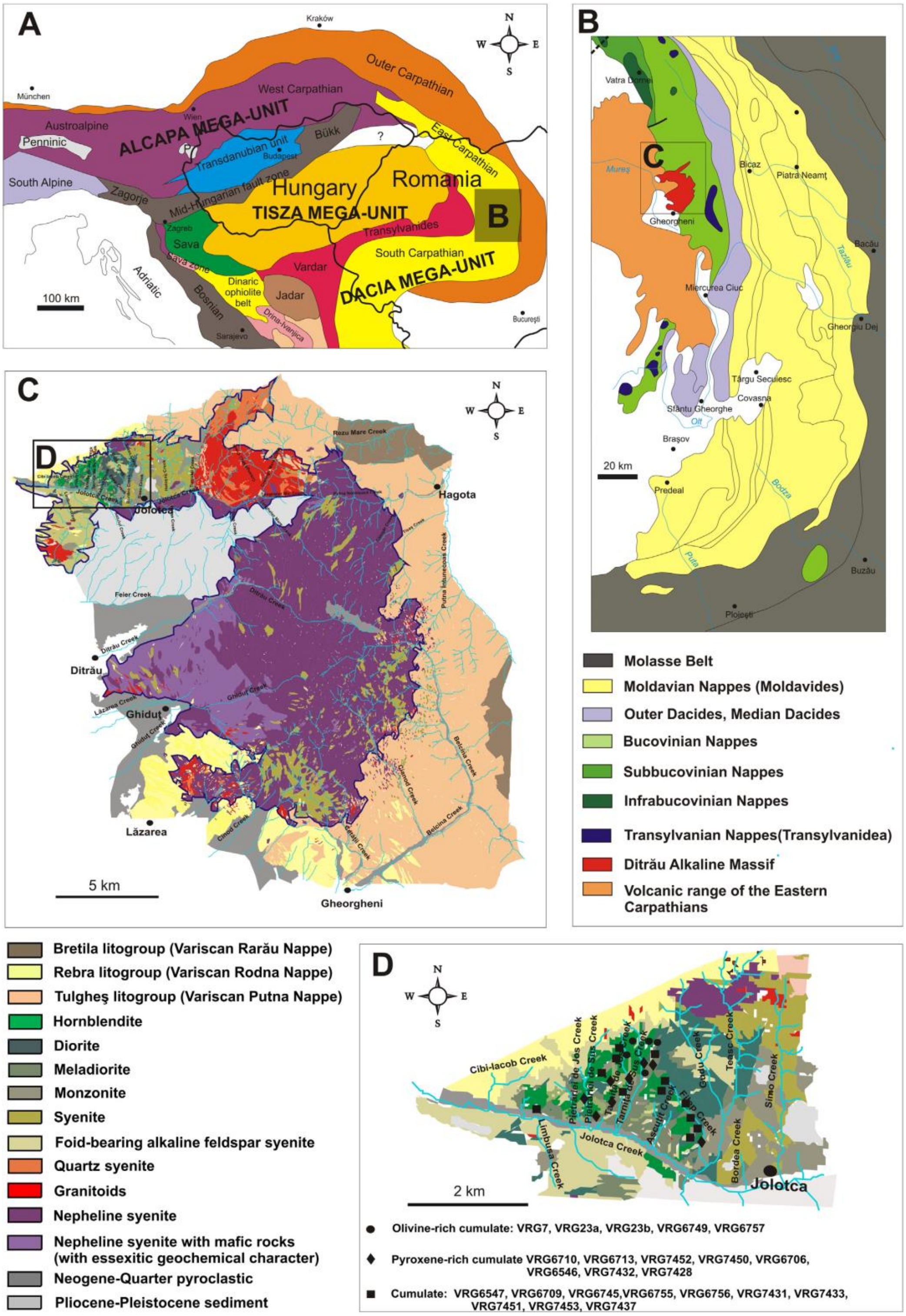


Figure 20. Geological sketch map of DAM, Pál–Molnár *et al*., 2015. (A) Location of the DAM in the structural system of the Alpine–Carpathian–Dinaric region (Pál-Molnár, 2010a). (B) Alpine structural units of the Eastern Carpathians (Săndulescu *et al*., 1981, modified). (C) Schematic geological map of the DAM (Batki *et al*., 2014). (D) Sample locations in the northern part of the DAM the same legend as in figure C.

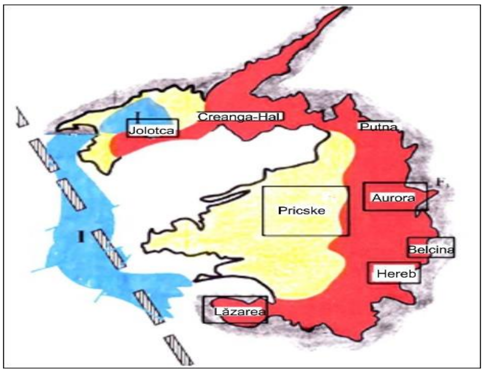


Figure 21. The schematic geological map of the DAM with mineralization areas: hornblendite-diorite complex (blue), red syenite (red), white nepheline syenite (yellow), Tulghes Group (grey), G8 = crustal fracture (hachure interrupted line); G. Jakab, 1998.

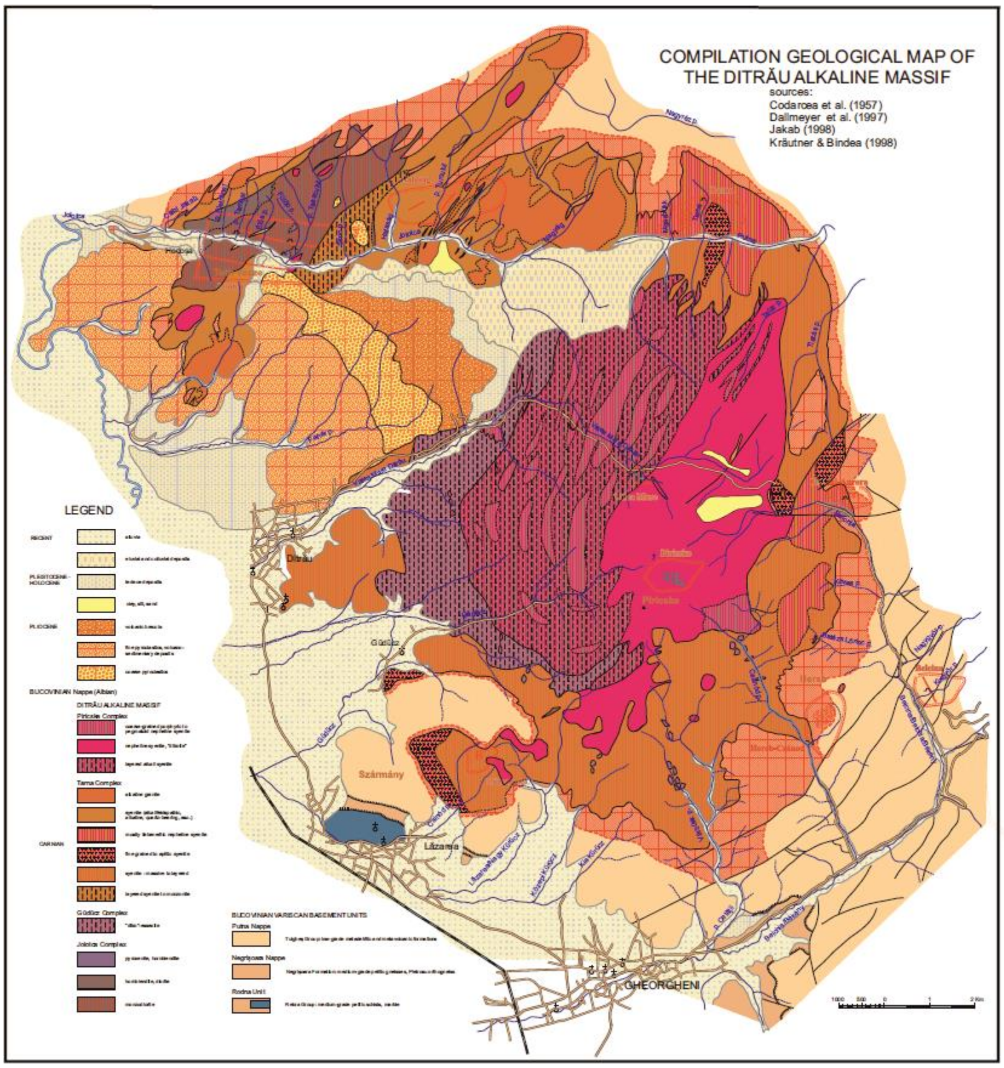


Figure 22. Compilation geological sketch map of the DAM, after Săbău & Negulescu, 2015.

GENETICAL HYPOTHESIS

According to Ianovici (1929–1932) the Ditrău alkaline rocks are the result of phenomena of magmatic differentiation and assimilation of quartzites and adjacent limestones, respectively. The massif is described as a laccolith with a concentrical structure, its margins consisting of granites and alkali-syenites and its central parts of nepheline syenites.

Codarcea, Codarcea M.D. & Ianovici (1958) explained the fluidal texture of the massif as a replica, in the apical part, of batholit which altered by metamorphosis the crystalline schists of the Tulgheş Series (amphibolites, micaschists, phyllites).

At various stages of the investigation, **Streckeisen** explains the formation of the massif by Daly's theory of limestone synthesis but finally abandoned this idea and accepted a magmatic origin, accompanied by widespread hybridization phenomena and metasomatic changes (for many reasons: sharp contact, thermal contact aureole, dike rocks, structure of the massif); according to determinations, the intusion occurred in the Jurassic time. Streckeisen (1960) explained the genesis of the massif by an origin through magmatic differentiation of an alkali syenite parental magma. Streckeisen & Hunziker (1974) presented a chronology of the magmatic events, suggesting early intrusion of the gabbros and diorites, followed by the syenites, nepheline syenites and granites culminating with emplacement of lamprophyric dykes, although without discussing the source of the magmas.

According to **Anastasiu & Constantinescu** the polystage distribution and the consolidation of the Ditrău massif within the tectostructural space of the East Carpathians were controlled by crustal fractures and the mobility of the structural compartments limited by them. The geophysical data point out, on the basis of the gravimetric anomalies (Socolescu *et al*., 1975) and of the geophysical deep sounding (Rădulescu *et al*., 1976), the existence of a maximum line which marks, at the limit between the Crystalline-Mesozoic zone and the Neogene volcanic chain, a continental crustal fracture type. The Ditrău massif has an autochthonous, intrusive character and its tendency of enrootment has been proved by petrological, mineralogical or geophysical arguments. It constitutes a multistage magmatic intrusion in a superior level of the earth's crust. Its petrographic heterogeneity and the petrochemical incompatibilities – the presence of the supersaturated rocks, granitoides, beside the nonsaturated ones (foidic syenites) – point to the existence of two deep magmatic sources.

Anastasiu & Constantinescu (1982) considered a magmatic derivation with two principal rock suites, one generated from a mantle-derived basic magma, and the other from a felsic alkaline magma formed through partial melting of crustal rocks with low silica content.

Iancu, 2010: The Mesozoic Ditrău Alkaline Massif (DAM), unique in Romania by size and petrographical variety, is emplaced within the metamorphic basement rocks at the interior of the Eastern Carpathians. The DAM is an intermediate size massif (about 800 km^2) and exhibits an eccentric ring structure in which the more basic rocks tend to lie to the west, with an arcuate zone of syenitic rocks extending from the far north to the southeast, and a large area dominated by nepheline syenite on the eastern side.

Geological location, age, tectonic setting The DAM is considered to represent an intrusion body with a internal zonal structure, which was emplaced into pre-Alpine metamorphic rocks of the Bucovinian nappe complex close the Neogene-Quaternary volcanic arc of the Călimani–Gurghiu–Harghita Mountain chain (Ianovici, 1938; Kräutner& Bindea, 1998). The massif lies at the inner border of Mesozoic crystalline zone, within Tulgheş Group (Tulgheş Terrane according to Balintoni *et al*., 2009) (see the introductory chapter).

The alkaline massif of Ditrău has an intrusive character and its trend of enrootment has been proved by petrologic and geophysical arguments, too. It constitutes a multistage magmatic intrusion in a high level of the Earth's crust (Constantinescu & Anastasiu, 2004).

Morogan *et al*. (2000) suggested that the whole complex have originated from basanitic magmas with OIB- character, generated by low degrees of melting of asthenospheric garnet lherzolite. However, the general dominance of amphibole among the ferromagnesian minerals points to the relatively hydrous nature of the Ditrău magmas and leads to the speculation that the primitive melts may have been modified by passage through hydrated (possibly amphibole-bearing) lithospheric rocks; the multistage intrusions were caused by a longlived mantle plume, and attribute an important role to assimilation and fractionation.

Based on detailed geochemical data, according to **Dallmeyer** *et al*. (1997), the intrusion of the Ditrău Alkaline Massif was associated with mantle-plume activity which predated Jurassic rifting within the Eastern Carpathian Orogen. On the basis of KAr and 39Ar/40Ar data Kräutner & Bindea (1998) dated the DAM emplacement. Pană *et al*. (2000) performed a precise U-Pb zircon dating of the syenite phase from the Ditrău Massif.

Pál-Molnár (2000) suggested a two-stage model with the emplacement of ultramafic rocks in the mid-Triassic into the lower crust, with formation of nepheline syenite by fractionation and formation of granites by fractionation and assimilation of silica-rich country rocks. A second stage (Middle-Jurassic/Lower Cretaceous) involved the emplacement of syenites and diorites.

Starting with the early studies by Herbich (1859) the massif has been the subject of many investigations. However, because of its structural complexity and wide petrographic variability the petrogenesis is still not completely understood, and several petrologic interpretations have been proposed. Streckeisen initially explained the genesis of the massif according to Daly's limestone assimilation theory and later by an origin through magmatic differentiation of alkali syenite parent magma (Streckeisen, 1938, 1960). Anastasiu and Constantinescu (1982) considered a magmatic derivation with two principal rock suites, one generated from a mantle-derived basic magma, and the other from a felsic alkaline magma formed through partial melting of silicapoor crustal rocks. More recently, Kräutner & Bindea (1995, 1998) concluded that the complex formed by three main stages in the Triassic and Jurassic:

a) emplacement of a mantle derived gabbro-dioritic magma into the lower crust;

b) emplacement of the gabbrodioritic mass into the crust in a subsolidus stage, magma mixing with a crustal syenitic magma produced a variety of hybrid rocks;

c) mantle derived nepheline syenite-magma, formed by partial melting, intruded into the Triassic massif, followed by local hydrothermal alteration and mineralization.

REFERENCES

Anastasiu, N., Constantinescu, E., 1975. *Observaţii mineralogice în rocile sienitice din Masivul Ditrău.* Com. Geol., Sesiune festivă, Decembrie, 1975, 17–18.

Anastasiu, N., Constantinescu, E., 1976. *Feldspaţii potasici din Masivul alcalin de la Ditrău* (*K-feldspars from Ditrău alkaline Massif*). D. S. Inst. Geol. Geof., LVIV, 13–36.

Anastasiu, N., Constantinescu, E., 1976. *Observaţii mineralogice asupra rocilor alcaline din Masivul Ditrău* (*Mineralogy of alkaline rocks from Ditrău alkaline Massif*), Comunicări de Geologie, TUB, 77–85.

Anastasiu, N., Constantinescu, E., 1978. *Feldspaţii alcalini din Masivul alcalin de la Ditrău.* D. S. Inst. Geol. Geof., LXIV/1, 13–36.

Anastasiu, N., Constantinescu, E., 1979. *Structure and petrogenesis of the alkaline Massif of Ditrău.* Unpub. Geol. Report, IPEG "Harghita", Miercurea-Ciuc, Archives (in Romanian).

Anastasiu, N., Constantinescu, E., 1980. *Structura Masivulul alcalin de la Ditrău* (*Structure of Ditrău alkaline Massif)*, Anal. Univ. Bucureşti, XXIX, 3–22.

Anastasiu, N., Constantinescu, E., 1981. *Feldspaţii plagioclazi din Masivul alcalin de la Ditrău* (*Plagioclase feldspars from Ditrău alkaline Massif*). St. cerc. geol., Academia Română, 26/1, 83–95.

Anastasiu, N., Constantinescu, E., 1982. *Tectonostructural position of the foidic rocks in the Romanian Carpathians.* Rév. Roum. Géol., Géoph., Géogr., Academia Română, 26, 33–45.

Anastasiu, N., Constantinescu, E., 1983. *Criterii petrografice pentru conturarea câmpurilor filoniene în Masivul alcalin de la Ditrău, Carpaţii Orientali* (*Petrographical criteria for vein fields identifying in the East Carpathians*). Simpozionul Geologic de la Gheorgheni, Vol. special, 3–13.

Anastasiu, N., Constantinescu, E., 1984. *Contributions a la connaissance pedologique et structurale du Massif alcalin de Ditrău – implications metallogenetiques.* Anal. Univ. Bucureşti, XXXIII, 43–49.

Anastasiu, N., Constantinescu, E., 1994. *The alkaline Massif of Ditrău: A petrogenetical retrospective view.* Anal. Univ. Bucureşti, XIV, Suppl.

Anastasiu, N., Constantinescu, E., 1994. *The alkaline massif of Ditrău: A petrogenetical retrospective view.* Anal. Univ. Bucureşti, XLIII, 1–2.

Anastasiu, N., Constantinescu, E., 1999. *Contributions to the petrological and structural knowledge of the Ditrău alkaline Massif – Metalogentic implications. Mineralogy and the system of earth sciences.* Imperial College Press, Londra, 239–244.

Anastasiu, N., Constantinescu, E., Garbaşevschi, N., Gyula, J., 1983. *Petrografia şi petrogeneza rocilor filoniene din Masivul alcalin de la Ditrău* (*Petrography and petrogenessis of vein rocks from Ditrău alkaline Massif*). St. cerc. geol., Academia Română, 28, 17–23.

Anastasiu, N., Constantinescu, E., Garbaşevschi, N., Gyula, J., 1983. *Structural control of vein setting in the alkaline Massif of Ditrău*, Anal. Univ. Bucureşti, XXXII, 1–22.

Anastasiu, N., Garbaşevschi, N., Gyula, J., Vlad, Ş., 1994. *Mesosoic rift related magmatism/metallogeny at Ditrău.* In Borcoş M. & Vlad Ş., (eds): *Plate tectonics and metallogeny in the East Carpathians and Apuseni Mts*, June 7–19, 1994, Bucharest, Geological Institute of Romania, Field trip guide, IGCP Project No. 356, 11–13.

Apostol, A., Szasz, M., 1985. *Aspecte privind valorificarea în perspectivă a zăcământului de molibden şi magnetit de la Jolotca.* Ministerul Minelor, Petrolului şi Geologiei, Bucureşti, Mine, Petrol şi Gaze, XXXVI/3, 128–132.

Bagdasarian, G.P., 1972. *On the absolute age of some igneous and metamorphic rocks from the Ditrău alkaline Massif and Banat Mountains, Romania.* St. cerc. geol., geof., geogr., seria Geologie, Academia Română, 17/1, 13–21 (in Romanian).

Balintoni, I., 1981. *The importance of the Ditrău alkaline Massif emplacement moment for dating of the basement overthrusts in the Eastern Carpathians.* Rév. Roum. Géol., Géoph., Géogr., serie Géologie, 25, 89–94.

Balla, T., Căruntu, C., Gyula, J., Peter, J., 1991. *Privire critică asupra concepţiilor referitoare la geneza unor roci filoniene felsice din Masivul Ditrău.* Lucrările Seminarului Geologic "Grigore Cobălcescu", Univ. Iaşi, III, 133–140.

Bercia, I., *et al.*, 1971. Geological Report, Arch. IGG and ANRM, Bucureşti.

Bercia, I., Kräutner, H., Mureşan, M., 1976. *Pre-Mesozoic metamorphites of the East Carpathians*. An. Inst. Geol. Geof., L, 37–70.

Bindea, G., 1993. *Coexisting albite and oligoclase in some rocks of Ditrău alcaline Massif.* Rom. J. of Mineralogy, IGG, Bucureşti, 76, Suppl. 1, 9–10.

Bindea, G., 1995. *Igneous history and structure of the Ditrău Massif*, Rom. J. of Mineralogy, IGR, Bucureşti, **77,** Suppl. 1, 9.

Bindea, G., Kräutner, H., Lorincz, E., Runceanu, M., 1995. *The metamorphic host rocks in the northern part of the Ditrău alkaline Massif*, Rom. J. of Mineralogy, IGR, Bucureşti, **77**, Suppl. 1, 10.

Botezatu, R., Calotă, C., 1979. *Ipoteză asupra sursei anomaliei magnetice produsă de Masivul de roci alcaline de la Ditrău rezultată din aplicarea unui procedeu de analiză spectrală*, St. cerc. geofiz., Academia Română, **17/1,** 47–66.

Codarcea, A., Codarcea, D.M., Ianovici, V., 1957. *Structura geologică a masivului de roci alcaline de la Ditrău* (*Geological structure of alkaline rocks from the Ditrău Massif)*, Bul. şt. Acad. Rom., Secţia Geologie şi Geografie, II/3–4, 385–446.

Codarcea, A., Ianovici, V., Iova, I., Lupan, S., Papacostea, C., 1958. *Elemente rare în Masivul de la Ditrău.* Com. Acad., VIII/3, 321–328.

Constantinescu, E., Anastasiu, N., 1978. *Chemical-mineralogical investigations on Triassic-Lower Cretaceous sedimentary rocks between the Nera and Radimna Valley.* Acad. Rom., Rev. Roum. Géol., 22, 121–127.

Constantinescu, E., Anastasiu, N., 1979. *Nepheline du massif alcalin de Ditrău*, Anal. Univ. Bucureşti, XXVIII, 15–27.

Constantinescu, E., Anastasiu, N., 1984. *Contributions a la connaissance petrographique et structurale du masif alcalin de Ditrău - importance metallogeenique*, Anal. Univ. Bucureşti, XXXIII, 43–49.

Constantinescu, E., Anastasiu, N., 1999. *The alkaline massif of Ditrău: A mineralogical approach.* Mineralogy, Petrology, Metallogeny and Geochemistry International Symposium, 15–17 Oct. 1999, Anal. Univ. Bucuresti, vol. abstracte, XLVIII.

Constantinescu, E., Anastasiu, N., 2004. *The Massif of Ditrău*: *A mineralogical and petrological approach at Dan Giuşcă centenary*, Rom. J. of Petrology, IGR Bucureşti,79, Suppl.,11–12.

Constantinescu, E., Anastasiu, N., Pop, N., Garbaşevschi, N., 1983. *Contributions à la connaisance des aspects paragénétiques de la minéralisation associée au Massif alcalin de Ditrău.* An. Inst. Geol., LXII, 91–101.

Constantinescu, E., Anastasiu, N., Pop, N., Garbaşevschi N., 1981. *Les caracteres texturales et paragenetique de la mineralisation du masif alcalin de Ditrău*, Anal. Univ. Bucureşti, XXXI, 23–32.

Constantinescu, E., Anastasiu, N., Pop, N., Garbaşevschi, N., 1982. *Contributions a la connaisance des aspects paragénétiques du massif alcalin de Ditrău*, Travaux 12[eme] Congr. Asoc. Géol. Carp.-Balc., Bucharest.

Cristescu, T., Strugaru, T., Neacşu, F., 1982. *Consideraţii ale prospecţiunii geofizice privind unele aspecte structurale şi metalogenetice în cadrul Masivului alcalin de la Ditrău, Carpaţii Orientali*, *formaţiuni endogene*. I.P.E.G. Harghita, Gheorgheni, 304–318.

Dallmeyer, R.D., Kräutner, H.G., Neubauer, F., 1997. *Middle-late Triassic 40Ar/39Ar hornblende ages for early intrusions within the Ditrău alkaline Massif, Romania*: *implications for Alpine rifting in the Carpathian orogen.* Geologica Carpathica, 48, 347–352.

Damian, Gh., Pop, N., Garbaşevschi, N., 1988. *A new lead and bismuth sulpho-telluride identified at Jolotca–Ditrău*, Acad. Rom., Rev. Roum. Géol., 32, 3–8.

Damian, Gh., Pop N., Garbaşevschi, N., 1992. *Sur la presence de la lillianite dans les mineralisations de Jolotca–Ditrău.* IGG, Bucureşti, Rom. J. of Mineralogy, 75, 87–90.

Ene, I., Rusu, C., Niţulescu, I., Ion, D., 1996. *Valorificarea sienitului nefelinic din zona Ditrău.* An. Inst. Geol., Bucureşti, 69/1, 112–113.

Fall A., Bodnar, R.J., Szabó, Cs., Pál-Molnár, E., 2007. *Fluid evolution in the nepheline syenites of the Ditrău alkaline Massif, Transylvania, Romania.* Lithos, 95, 331–345.

Gohn, E., Isvoreanu, I., Scurtu, S., Heredea, N., 1973. *Cercetarea aeroradiometrică a Masivului Ditrău şi a formaţiunilor adiacente.* Acad. Rom., St. cerc. geofiz., 11/1, 3–11.

Hârtopanu, P., Bermanec, V., Udubaşa, G., Melgarejo, J.C., 2000. *Monazite and allanite from the Ditrău alkaline Massif, East Carpathians, Romania.* An. Inst. Geol., 72–41.

Hârtopanu, P., Udubaşa, G., Hârtopanu, I., 2003. *Some old and new minerals from the Ditrău alklaline Massif and their genetical implication*, Anniversary Symposium, Petrology – global context, 4[th] April 2003.

Heredea, N., *1985. Radiometric Investigations in Precambrian Problems from Al Homura Zone, The Arabic Republic of Yemen.* Academia Română, Rev. Roum. Géoph., **29**, 65.

Heredea, N., Strugaru, T., Neacşu, F., Teulea, Gh., 1988. G*eological elements in the Ditrău Massif deduced from the natural gamma-radioactivity measurements.* Acad. Rom., Rev. Roum. Géoph., 32, 102–102.

Hîrtopanu, P., 2006a. *One hundred minerals for one hundred years (dedicated to the Centennial of the Geological institute of Romania).* 3[rd] Conference on Mineral Sciences in the Carpathians, Miskolc Hungary, Acta Min. Petr. Univ. Szeged, Hungary, Abstr. Series, 5, 86.

Hîrtopanu, P., Andersen, J., Fairhurst, R., Gyula, J., 2013., *Allanite-(Ce) and its associations, from the Ditrău alkaline intrusive Massif, East Carpathians, Romania.* Proc. Rom. Acad., Series B, Chemistry, Life Sciences and Geosciences, 15/1, 59–74.

Hîrtopanu, P., Anderson, C. J., Fairhurst, J. R., 2010. *Nb, Ta, Ree (Y), Ti, Zr, Th, U and Te Rare element minerals within the Ditrău alkaline intrusive complex, Eastern Carpathians, Romania.* In Szákall S. & Kristály F. (ed.), Mineralogy of Szekelyland, Eastern Transylvania, Romania, Csik County Nature And Conservation Society, Sfântu Gheorghe-Miercurea Ciuc-Târgu Mureș, pp. 89–128

Hîrtopanu P., Bermanec V., Udubaşa Gh., Melgarejo J., 2000. *Monazite and allanite from the Ditrău alkaline Massiff, East Carpathians, Romania.* An. Inst. Geol., 72, 41.

Hîrtopanu, P., Fairhurst, J. R., Jakab G., Andersen C. J., 2015. *Niobian rutile and its associations at Jolotca, Ditrau alkaline intrusive massif, East Carpathians, Romania.* Proc. Rom. Acad., Series B, Chemistry, Life Sciences and Geosciences, 17/1, 39–55.

Hîrtopanu, P., Udubaşa, Gh., 2003. *Mineralogy of a "sacred monster": the Ditrău alkaline Massif, East Carpathians (Romania).* Stud. Univ. Babeş-Bolyai, Spec. issue, Cluj-Napoca, pp. 47.

Hîrtopanu, P. & Udubaşa, G., 2004. *REE-bearing minerals at Ditrău*. Rom. J. of Mineral., 82, 184–187.

Jakab, Gyula, 1975. *Consideraţii asupra poziţiei spaţiale a Masivului alcalin de la Ditrău.* D. S. Inst. Geol. Geof., LXII, 93–98.

Jakab, Gyula, 1986. *Geochemical data on the different origin of the phases of syenitic intrusion in the Ditrău alkaline Massif.* D. S. Inst. Geol. Geof., 70-71/1, 363–372.

Jakab, Gyula, 1996. *Petrogenesis of the alkaline Massif of Ditrău.* Anal. Univ. "Al.I. Cuza", Geologie, XlII, Supl., 95–99.

Jakab, Gyula, 1998. *Geologia Masivului alcalin de la Ditrău (Geology of alkaline Massif from Ditrău).* Pallas-Akademia, Miercurea-Ciuc, 298 pp. (in Romanian).

Jakab, Gyula, 1976. *Consideraţii asupra poziţiei spaţiale a Masivului alcalin de la Ditrău (Carpaţii Orientali).* D. S. Inst. Geol. Geofiz., LXII/1, 93–98.

Jakab, Gyula. 1982. *Studiu mineralogic şi geochimic al mineralizaţiilor metalifere dintre Voşlobeni şi Corbu.* Rezumat teză de doctorat, Universitatea "Al. I. Cuza" din Iaşi, 25 pp.

Jakab, Gyula, 1982. *Unele aspecte privind fenomenele postmagmatice în Masivul alcalin de la Ditrău, Carpaţii Orientali,* formaţiuni endogene, I.P.E.G. Harghita, Gheorgheni, 35–41.

Jakab, Gyula, Căruntu, C., Salagran, M., Pantelică, A. (1988), *Aspecte mineralogice şi geochimice ale zirconiului din Masivul alcalin de la Ditrău.* Lucrările Seminarului Geologic "Grigore Cobălcescu", Univ. "Al. I. Cuza" din Iaşi, 2, 226–233.

Jakab, Gyula, Căruntu, C., Szikszai, L. (1988), *Zeoliţi în Masivul Ditrău (Carpaţii Orientali).* Lucrările Seminarului Geologic "Grigore Cobălcescu", Univ. "Al. I. Cuza" din Iaşi, 2,193–196.

Jakab, Gyula, Garbaşevschi, N. (1977), *Consideration on the pyrite from the Jolotca vein mineralisation (Eastern Carpathians).* D. S. Inst. Geol. Geofiz., 63, 13–25 (in Romanian).

Jakab, Gyula, Mînzatu, S., 1983. *L'etude des grenats du Massif syenitique de Ditrău (Roumanie).* An. Inst. Geol., LXII, 37–44.

Jakab, Gyula, Peter, Jozefa, Olti, Kalman, 1982. *Originea biotitelor din zona Masivului Ditrău şi câteva criterii de departajare a acestora, Carpaţii Orientali, formaţiuni endogene.* I.P.E.G. Harghita, Gheorgheni, 42–47.

Jakab, Gyula, Urcan, T., 1982. *Date inedite asupra fluorinei şi nathonitului din Masivul alcalin de la Ditrău (Carpaţii Orientali).* Lucrările Seminarului Geologic "Grigore Cobălcescu" 1981, Univ. "Al. I. Cuza" din Iaşi, I, 57–65.

Ianovici, V., 1929. *Studiul Masivului sienitic de la Ditrău, Regiunea Jolotca, Districtul Ciuc.*, Teză de doctorat, Universitatea din Iaşi.

Ianovici, V., 1931. *Le granite alcalin provenant de Megasbukk (Făgeţelul Înalt), Ditrău, District Ciuc (Transylvanie).* Ann. Sci. Univ. Jassy, Imprimeria Naţională, Iaşi, XVIII/1-2, 113–117 .

Ianovici, V., 1931. *Gabbro olivine provenant de Pr. Jolotca, Ditrău, District Ciuc.* Ann. Sci. Univ. Jassy, Imprimeria Naţională, Iaşi, XVIII/1-2, 107–112.

Ianovici, V., 1932. *Gabbro á olivine provenant de Pr. Jolotca, Ditrău, District Ciuc.* Ann. Sci. Univ. Jassy, 18, 107–112.

Ianovici, V., 1933. *Étude sur le massif syénitique de Ditrău, Région Jolotca, District Ciuc (Transylvanie)*. Rev. Muz. Geol. Mineral., Univ. Cluj, 4/2, 1–53.

Ianovici, V., 1938. *Considérations sur la consolidation du massif syénitique de Ditrău en relation avec la tectonique de la region.* C.R. Acad. Sci. Roum, II/6, 689–694.

Ianovici, V. (1938), *Etude minéralogique du gisement métallifere de Pr. Baia, Ditrău, District Ciuc (Transylvanie),* Ann. Sci. Univ. Jassy, XXIV/2, 438–456.

Ianovici V., Ionescu J., 1964. *Contribuţii la cunoşterea mineralogică a masivului de roci alcaline de la Ditrău – România*. Acad. Rom., St. cerc. geol., 9/2, 417– 430.

Ianovici, V., Ionescu, J., 1965. *Contribution a la connaisance mineralogique du massif des roches alcalines de Ditrău – Roumanie.* Rev. Roum. Géol., Géoph., Géogr., ser. Géol, 9/1, 439–456.

Ianovici, V., Ionescu, J., 1972. *Contribuţii la mineralogia masivului alcalin de la Ditrău*. *I. Amfibolii*. Acad. Rom., St. cerc., XIV/2.

Ianovici V., Constantinescu E., Anastasiu N., 1984. *Petrochimia lamprofirelor din Masivul alcalin de la Ditrău*. Acad. Rom., St. cerc. geol., geofiz., geogr., geologie, 29, 5–17.

Ion, A., 2012. *Determination of uranium, thorium and potassium contents in rock samples from Ditrău alkaline massif using gamma-ray spectrometry*. IGG, Rom. J. of Mineral Deposits, 85(2), 81–85.

Ionescu, J., 1959. *Sienitul nefelinic de la Ditrău, o nouă materie primă pentru ceramică şi sticlă.* Com. Acad. Rom., I/ 10, 1075–1081.

Ionescu, J., 1960. *Folosirea sienitului alcalin de la Ditrău la fabricarea porţelanului.* Com. Acad. Rom., X/1, 69–80.

Ionescu, J., 1963. *Studiul valorificării sienitelor alcaline nefelinice de la Ditrău ca înlocuitor al feldspatului în industria ceramică.* Acad. Rom., St. cerc. geol., VIII/4, 553–601.

Ionescu, J., 1965). *Study on the utilization of the alkaline syenites from Ditrău as feldspar* substitute *in the ceramics industry.* Acad. Rom., Rev. Roum. Géol., 9/2, 247–257.

Kräutner, H.G., Bindea, G., 1995. The *Ditrău alkaline intrusive complex and its geological environment.* Rom. J. of Mineralogy, 77/3, 1–44.

Kräutner, H.G., Bindea, G., 1998. *Timing of the Ditrău alkaline intrusive complex (Eastern Carpathians, Romania).* Slovak Geological Magazine, 4, 213–221.

Mauritz, B., 1912. *Adatok a gyergyó-ditrói szienittömzs kémiai viszonyainak ismeretéhez (Data for the knowledge of chemistry of the Ditrău syenite Massif).* Matematikai Természettudományi Értesítő, 30, 607–631 (in Hungarian).

Mauritz, B., Vendl, M., Harwood, H.F., 1925. *A ditrói szienit további petrokémiai vizsgálata (Further petrochemical examination of the Ditrău syenite.* Matematikai Természettudományi Értesítő, 41, 61–73 (in Hungarian).

Mînzatu, S., Gyula, J., 1986. *Aureole de contact du Massif alcalin de Ditrău dans la zone de Lăzarea (Carpathes Orientales).* D. S. Inst. Geol. Geof., 70-71/1, 69–80.

Molnar, E., 2000. *Hornblendites and fiorites of the Ditro syenite Massif.* University Szeged, 172 pp. ISBN 963-482-424-2.

Morogan, V., Upton, B.G.J., Fitton, J.G., 2000. *The petrology of the Ditrău alkaline complex, Eastern Carpathians.* Mineralogy and Petrology, 69, 227–265.

Mureşan, M., 1983. *Relations entre le Massif alcalin de Ditrău et les nappes de chariage des Carpates Orientales.* An. Inst. Geol., LX, 159–167.

Pál-Molnár, E., 1992. *Petrographical characteristics of Ditró (Orotva) hornblendites, Eastern Charpatians, Transylvania (Romania): A preliminary description.* Acta Mineralogica-Petrographica, 33, 67–80.

Pál-Molnár, E., 1994. *A Ditrói Szienitmasszivum kialakulása a földtani megismerés tükreben (Formation of the Ditrău syenite Massif in view of geological aspects).* A Magyar Tudomanyos Akademia Szegedi Akademiai Bizottsaganak Kiadvanyai, Szeged, 85 p. (in Hungarian).

Pál-Molnár, E., 2000. *Hornblendites and diorites of the Ditrău syenite Massif.* Department of Mineralogy, Geochemistry and Petrology, University of Szeged (Ed.), Szeged, 172 pp.

Pál-Molnár, E., 2010. *Rock-forming minerals of the Ditrău alkaline Massif.* In: Szakáll S. & Kristály F. (eds.), Mineralogy of Székelyland, Eastern Transylvania, Romania, Csík Mureş, 63–88.

Pál-Molnár, E., Anikó Batki, Enikő Almási, Balázs Kiss, Brian G.J. Upton, Gregor Markl Nicholas Odling, Szabolcs Harangi, 2015. *Origin of mafic and ultramafic cumulates from the Ditrău alkaline Massif, Romania.* Lithos, 239, 1–18.

Pál-Molnár, E., Árva-Sós E., 1995. *K/Ar radiometric dating on rocks from the northern part of the Ditrău syenite Massif and its petrogenetic implications.* Acta Mineralogica-Petrographica, 36, 101–116.

Pană, D., Balintoni, I., Heaman, L., 2000. *Precise* U-Pb *zircon dating of the syenite phase from the Ditrău alkaline igneous complex*, Stud. Univ. Babes-Bolyai, Geologia, 65/1, 79–89.

Panto (1941–1942), *Orotva Ore prospect near Ditro (Transylvania*), An. Inst. Geol., Publ. Hung., II.

Postolache, A., Postolache, C., Mocanu, V., 1988. S*tructural aspects of the Ditrău alkaline Massif by gravity and magnetic information.* Acad. Rom., Rev. Roum. Géoph., 32, 97.

Postolache, C., 1997. S*tructura de adâncime a Masivului alcalin Ditrău dedusă din date geofizice.* Rezumat teză de doctorat, Universitatea din Bucureşti, 38 pp.

Rădulescu, D., 1956. *Monazitul de la Ditrău*. Manuscriptum. Arch. Mineralogy Dept. University of Bucharest.

Reinhard, M., 1911. *Vârsta intruziunii sienitului nefelinic de la Ditrău (Transilvania).* D. S. Inst. Geol. Rom., II, 102–105.

Robu, L., Robu, N., Stelea, G., Vanghelie, I., 1995. *Chemical and structural considerations of ca-amphibole and biotite from the northern part of the Ditrău alkaline Massif (Romania).* IGR, Bucureşti, Rom. J. of Mineralogy, 77/1, Suppl., 40–41.

Robu, N., Robu, L., 1992. *Acccesory minerals in the alkaline rocks of Ditrău (East Carpathians): petrogenetic implications.* IGG, Bucureşti, Rom. J. of Mineralogy, 75/1, Suppl., 39–40.

Săbău, G., Negulescu, E., 2015. *Late Stage HFSE-Enrichment in the Ditrău Alkaline Complex, East Carpathians*. Goldschmidt Conf. Prague, Cz. PPT.

Săbău, G., Negulescu, E., 2017. *Reconsiderări temporale în unități de soclu din România – consecințe geotectonice.* Conf. GG, CNGR-Romanian Academy (oral presentation), 40 p.

Săndulescu, M., 1975. *Essai de synthèse structurale des Carpathes*. B.S.G.F. (7), XVII/3, 299–358.

Stoian, A., Iacoban, I., Vasilescu, V., 1962. *Prepararea sienitelor de la Ditrău.* Institutul de Cercetări Miniere, Bucureşti, St. cerc. miniere, 294–295.

Stoian, A., Rohr, L., Vicol, C., 1974. *Înnobilarea sienitelor de la Ditrău pentru utilizarea în industria sticlei şi ceramicii.* Ministerul Minelor, Bucureşti, Rev. Minelor, XXV/5.

Streckeisen, A., 1934. *Sur la tectonique des Carpathes Meridionales.* An. Inst. Geol., 16, 327–418 (in French, with English abstract).

Streckeisen, A., 1938. *Das Nephelinsyenit-Massiv von Ditró (Rumänien) als Beispiel einer kombinierten Differentiation und Assimilation.*Verhandlungen der Schweiz. Naturforschenden Gesellschaft, 119, 159–161.

Streckeisen, A., 1952. *Das Nephelin syenit-Massiv von Ditro (Siebenburgen).* I. Teil, Schweiz. Min. Petrogr. Mitteilungen, 32, 251–308.

Streckeisen, A., 1954. *Das Nephelinsyenit-Massiv von Ditro (Siebenburgen).* II. Teil, Schweiz. Min. Petrogr. Mitteilungen, 34, 336–409.

Streckeisen, A., 1960. *On the structure and origin of the nephelinesyenite complex of Ditro (Transylvania, Romania).* Rep. 21th IGC., 13, 228–238.

Streckeisen, A., Hunziker, J.C., 1974. *On the origin of the Nephelin syenit Massif of Ditro (Transylvania, Romania).* Schweiz. Min. Petrogr. Mitteilungen, 54, 59–77.

Strugaru, T., Heredea, N., Hannich, D., Zorilescu, V., 1985. *New considerations regarding geological significance of geophysical regional data in the zone of alkaline Massif from Ditrău.* Acad. Rom., Rev. Roum. Géoph., 29, 71.

Strugaru, T., Heredea, N., Hannich, D., Zorilescu, V., 1987. *Noi consideraţii privind semnificaţia geologică a datelor geofizice regionale în zona Masivului alcalin de la Ditrău.* Acad. Rom., St. cerc. geofiz., 25, 70–77.

Visarion, M., 1963. *Cercetări geofizice pentru roci ultrabazice în Regiunea Jolotca (Ditrău)*, Com. Geol. Acad. Rom., 111–122.

Zincenco, D., Papadopol, C., 1978. Geological Report, Arch. IGG and ANRM, București.

CHARACTERISATION OF GAS HYDRATES AND FREE GAS OCCURRENCES IN THE NORTH-WESTERN BLACK SEA

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Abstract. A dense set of reflection seismic data offshore Romania provides evidence that gas hydrate occurrences and gas seeps found outside the gas hydrate stability zone are associated with gas produced by microbial methanogenesis and thermal cracking of oil. Gas hydrate and free gas occur in the deepsea fan complex of the Danube. Here, channel-levee systems offer pathways for the migration and accumulation of gas. They represent more-or-less closed systems under lithologic and stratigraphic control. Sealing is provided by condensed sections, relatively impermeable layers of fine-grained hemipelagic deposits which delimitate the systems at their top and base. Within the systems, migration is facilitated by the relatively coarse channel-fill deposits and overbank strata. Special features in this environment are multiple (up to quadruple) BSRs whereby the uppermost marks the present base of the gas hydrates stability zone. They are interpreted as geophysical expressions of the hydrate stability zones of different gas compositions. It is suggested that higher hydrocarbons may ascent via deep-seated faults from the Oligocene Histra Formation underlying the study area. They probably enter the channel-levee system by diffusion and through fissures. Thermal modelling indicates that multiple BSRs are probably not relict features related to an increase in bottom water temperature after the flooding of the Black Sea about 7100 yr BP. Heat transfer into the subbottom at the multiple BSR location is a long lasting process which is not yet completed.

Keywords: *Black Sea, Danube deepsea fan complex, gas hydrate, gas seeps, gas hydrate stability zone, multiple BSRs*

Résumé. Un important set de données sismiques réflexion au large de la Roumanie montre que les occurrences d'hydrate de gaz et les gas-seeps détectés à l'extérieur de la zone de stabilité d'hydrate de gaz sont associés au gaz produit par méthanogénèse microbienne et craquage thermique du pétrole. L'hydrate de gaz et le gaz libre sont présents dans l'éventail de mer profonde du Danube. Ici, les systèmes de levées de canaux offrent des voies pour la migration et l'accumulation de gaz. Ils représentent des systèmes plus ou moins fermés sous contrôle lithologique et stratigraphique. L'étanchéité est assurée par des sections plus denses, par des couches relativement imperméables de dépôts hémipélagiques à granulation fine qui délimitent les systèmes à leur sommet et à leur base. Dans les systèmes, la migration est facilitée par les dépôts relativement grossiers de remplissage de chenaux et les couches des berges. Les caractéristiques spéciales de cet environnement sont des BSR multiples (jusqu'à quadruple), le plus haut marquant la base actuelle de la zone de stabilité des hydrates de gaz. Elles sont interprétées comme des expressions géophysiques des zones de stabilité des hydrates de différentes compositions de gaz. Il est suggéré que les hydrocarbures supérieurs peuvent remonter via des failles profondes à partir de la Formation Histria d'age Oligocène sous-jacente à la zone d'étude. Ils entrent probablement dans le système de canaux-levées par diffusion et par des fissures. La modélisation thermique indique que les BSR multiples ne sont probablement pas des éléments reliques liées à une augmentation de la température de l'eau de fond après l'inondation de la mer Noire vers 7100 ans BP. Le transfert de chaleur dans le sous-sol à l'emplacement des BSR multiples est un processus de durée qui n'est pas encore terminé.

Mots-clés: *Mer Noire, l'éventail de mer profonde du Danube, hydrates de gaz, gaz-seeps, zone de stabilité d'hydrate de gaz, BSR multiples*

1. INTRODUCTION

Gas hydrates are solid, ice-like non-stochiometric crystalline solids consisting of water molecule cages stabilized by enclosed low molecular-weight gas molecules, notably methane (Sloan 1990). Their stability is controlled by the prevailing pressure, temperature, water chemistry, gas composition, and gas concentration (Sloan 1990). Most of the gas hydrate found worldwide is derived almost entirely from bacterially generated methane, although in a few cases (e.g., in the Gulf of Mexico and offshore Guatemala), the gas is of thermogenic origin (Kvenvolden *et al*. 1984). Methane hydrates are supposed to be of socio-economic relevance; this is because: (1) a large volume of gas is captured in gas hydrates (1 m^3 of gas hydrate = 164 m^3 of methane at STP), thus forming the largest natural gas reservoir (Kvenvolden 1993; MacDonald 1990) and (2) they are climatically highly relevant as methane is a much more effective greenhouse gas than CO_2 and when released to the atmosphere as a result of destabilization of gas hydrates, it may contribute to global warming (e.g., Haq 1998; MacDonald 1990; Shine 1990; Kennett *et al*. 2000; Dickens 2001, 2003). Gas hydrates may also represent a potential geohazard on continental slopes because when rapidly dissociated, they can trigger large sediment failures on the seafloor (e.g., McIver 1982; Kayen & Lee 1993; Minert *et al*. 1998; Paull *et al*. 2000).

The semi-enclosed Black Sea is a potential candidate for free gas and gas hydrate accumulation on account of its anoxic water regime which favours the preservation of organic matter in the sediments (the chemocline lies at 110–140 m depth). Regions outside the stability field of gas hydrates, namely the shelf and upper slope, show a high gas content in the sediments. These areas are, as in the southeastern Black Sea (Ergun *et al*. 2002), characterised seismically by extensive acoustic blanking and by numerous methane seeps (Polikarpov *et al*. 1992; Luth *et al*. 1999; Kutas *et al*. 2002, Naudts *et al*., 2006, Popescu *et al*. 2007). The prevailing *P–T* conditions in the Black Sea suggest that gas hydrates are stable below a water depth of 700 m. Here, they have been recovered in surface samples at different locations (Yefremova & Zhizhchenko 1974; Ginsburg *et al*. 1990; Limonov *et al*. 1994; Ivanov *et al*. 1998). They contain mainly methane (99.1–99.9%, Soloviev & Ginsburg 1994; Ginsburg & Soloviev 1998; Ivanov *et al*. 1998) and their isotopic composition points to a biogenic origin.

A conventional research tool to detect and quantify the amount of free gas and gas hydrate present in sediments is seismic techniques. Hydrates are indicated seismically by a bottom simulating reflector (BSR) which marks the thermobaric base of the gas hydrate stability zone (BGHSZ). This reflector results from the large acoustic impedance contrast between high-velocity gas hydrate-cemented sediments and low-velocity sediments containing free gas beneath (Stoll & Bryan 1979; Hyndman & Spence 1992). However, the BSR is caused primarily by gas and not gas hydrate (Holbrook *et al*. 1996).

To study the characteristics of gas hydrates in the northwestern Black Sea, we used a dataset of 87 multi-channel reflection seismic lines acquired by TOTAL offshore Romania in the years 1994 and 2001 (Fig. 1). The tracks form a grid over an area of 13,500 km^2 with a line spacing of 3 to 3.5 km and a total length of 6,500 km. The second dataset consists of seismic profiles obtained by the University of Hamburg during the GHOSTDABS cruise of 2001 (Lüdmann *et al.* 2004). BSRs recorded in our seismic data serve as an indirect indicator for gas hydrate occurrence in the sedimentary column. Our study area lies approximately 130 km offshore Romania at water depths ranging from 100 to 1,800 m. Here, the sedimentary system is represented largely by the Danube deepsea fan which started to develop about 900 ka (kyr BP) (e.g., Wong *et al*. 1994; Winguth *et al*. 2000; Popescu *et al*. 2001, 2004). The patchy distribution of gas hydrates in the western Black Sea suggests that the primary condition for BSR occurrence, namely a high impedance contrast at the base of the gas hydrate zone (BGHZ), is satisfied only locally. The reflection coefficient is largely a function of the amount of gas hydrate above the BGHZ and of free gas below, with the concentration of free gas being probably the deciding factor (Holbrook *et al*. 1996). The patchy regional distribution of the BSR implies patchy, localized concentrations in free gas below the BGHZ. To better understand the mechanism of this free gas enrichment pattern, we shall now examine the structural and geological framework of the gas hydrate occurrences.

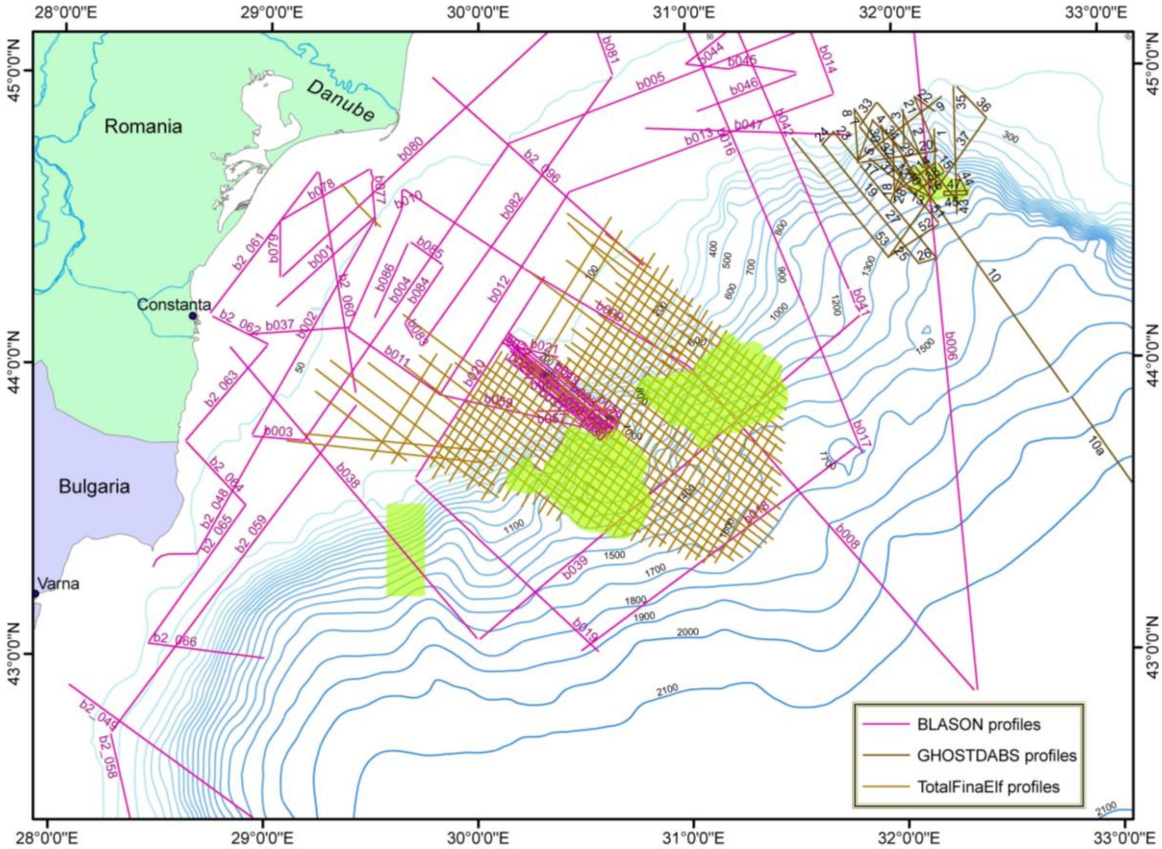

Figure 1. Map showing our study area on the continental margin off Romania and localization of seismic lines. Green mark areas of BSR occurrence. (Lüdmann *et al*., 2005, Popescu *et al*., 2006 and this study).

2. STRUCTURAL AND GEOLOGICAL BACKGROUND

The Black Sea opened as a back-arc basin from the Late Cretaceous to the Eocene (Letouzey 1977; Dercourt *et al*. 1986; Zonenshain & Le Pichon 1986; Görür 1988). It can be divided into two extensional sub-basins, namely the Western and Eastern Black Sea Basins which are separated by an uplifted basement block, the Andrusov Ridge (Finetti *et al*. 1988; Robinson *et al*. 1996). Major tectonic units in the study area are, from north to south: the East European platform, Scythian platform, pre-Dobrogean Depression, North Dobrogea Orogen, and Central- and South Dobrogea (as parts of Moesian platform). They are separated by prominent NW-SE to WNW-ESE trending strike-slip faults (Fig. 1). Most of these units are offshore extensions of onshore structures. The development of the Western Black Sea Basin began in Albian-Cenomanian times (Finetti *et al*., 1988; Görür 1988; Artyushkov 1992) during a N-S extensional phase and a subsequent E-W extensional phase (Dinu *et al*. 2005). Offshore, the tectonic movements resulted in the development of a large half-graben (the Histra Depression) visible in the northwestern part of the study area (Fig. 1). During the Neogene, this depression experienced an extension accompanied by gravitational faulting, the most tectonically active period being the Pontian (Dinu *et al*. 2002). In the following discussions, we shall use the geochronology of the Eastern Parastethys, including the stages of Badenian (Middle Miocene), Sarmatian (Late Miocene), Meotian–Pontian (Latest Miocene) and Dacian–Romanian (Pliocene).

The continental margin of Romania is marked by a thick sedimentary pile (ca. 10 km), of which the post-tectonic Cenozoic section found almost over the entire shelf is for our discussions the most relevant (see Bancila *et al.*, 1997, and Dinu *et al.*, 2002, 2005 for details). Note the diffuse reflection pattern throughout the sedimentary column interpreted to be a result of gas accumulation. Cenozoic sedimentation on this continental margin was mainly controlled by subsidence and sea-level fluctuations. A major sea-level drop at the Eocene/Oligocene boundary led to widespread erosion on the shelf and extensive transport of sediments into the deepsea basin (Dinu *et al.* 2005). The sea level rose subsequently in the Oligocene and silciclastic sediments, dominated by the bituminous shales of the Histria Formation, accumulated on the margin. These shales are the main source rock for offshore hydrocarbons (Dinu *et al*. 2005). They might have also played an important role in the formation of gas hydrates on the slope (see later discussions). While the Sarmatian section is dominated by marls and limestones, the Pontian is characterised by massive deltaic and deep-water argillaceous sands (Ţambrea *et al*., 2000). During Dacian to Quaternary times, the sedimentation rate increased and the deposits are dominated by an alternation of deltaic shales, marls and sands. The Danube deepsea fan complex developed ca. 900 ka (Winguth *et al*. 2000). It consists of a succession of stacked channel-levee systems which extend from the lower slope to the abyssal plain (>2,000 m water depth), covering an area about 150 km in the NW–SE direction and up to 200 km in the NE–SW direction. The slope gradient changes from 1:50 on the upper continental slope to 1:1,000 in the deep basin. Details on the evolution of the deepsea fan complex can be found in Wong *et al*. (1994), Winguth *et al*. (2000) and Popescu *et al*. (2001, 2004).

3. RESULTS

3.1. SEISMIC SEQUENCES

Three major seismic sequences where mapped by interpolation of the stratigraphy derived from shelf boreholes (unpublished data, *PETROM*) into the study area, namely base of the Pontian, Dacian and Romanian/Quaternary respectively (Fig. 2, A–C). The Pontian is composed of well-stratified continuous reflectors of high amplitude on the shelf which transit basinward into an overall chaotic reflection pattern that could be related to extensive mass wasting. Its thickness decreases from 2.5 s TWT on the shelf to about 800 ms TWT at the slope. The Dacian is notably thinner; it reaches only 150 ms on the continental slope. Its internal configuration consists of sub-parallel reflectors of high amplitude, indicating a change to quieter depositional conditions. The transition from the Dacian to the Romanian and Quaternary is seismically difficult to recognize on the slope. The latter succession here is dominated by the Danube deepsea channel-levee system deposited during phases of relatively sea-level lowstand and has a thickness of 2.5–2.0 s TWT. According to Wong *et al.* (1994) and Winguth *et al.* (2001), it can be subdivided into 8 sequences. Gas hydrates are found in the younger sequences 5–8.

3.2. FACIES DISTRIBUTION

The facies distribution of the Quaternary slope deposits mapped corresponds well with published results (Wong *et al.* 1994; Winguth *et al.* 2000; Popescu *et al.* 2001). We recognized facies types associated with deepsea fan complexes such as the levee, overbank, and HAR (high-amplitude reflector) facies in the channel-levee systems as well as HARPs (high-amplitude reflection packages) and mass wasting facies (namely slides, slumps and debris flows) elsewhere. The top of the sequences mapped was marked by a condensed section deposited during a relative sea-level highstand. It consists of well-stratified hemipelagic deposits that thicken basinward. BSRs marking the BGHSZ are confined to the channel-levee and overbank facies of the major systems (Fig. 2D). Where only minor channel-levees with little or no free gas exist, a BSR is missing. Deposits of the youngest sequence (sequence 8, Late Weichselian lowstand) are located within or above the GHSZ.

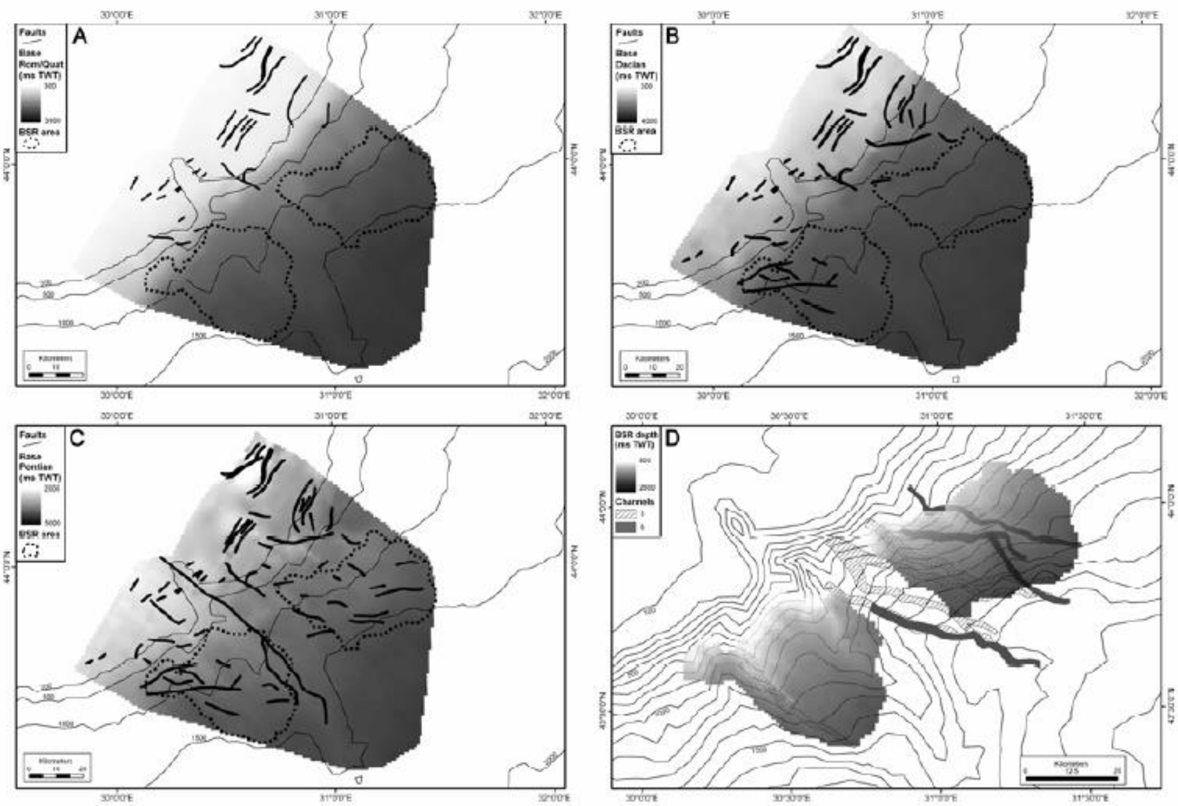

Figure 2. Maps A–C show the base of the Romanian-Quaternary, Dacian and Pontian respectively. In addition, the fault system mapped and the areas of BSR occurrence (bounded by dotted lines) are shown. Map D gives the channels mapped in sequences 5 and 6 as well as the depth to the BSR in ms two-way travel time.

3.3. TECTONIC FRAMEWORK

Faults derived from our seismic data in the study area with ages corresponding to the base of the Pontian, Dacian and Romanian/Quaternary are shown in Figure 2 (A–C). They are probably related to the gas hydrate development observed but are difficult to trace from the shelf onto the slope because of widespread masking at the shelf edge due to the occurrence of extensive gas-bearing sediments. Maximum fault activity took place during the Pontian which might be related to the last stage of Tertiary deformations in the Carpathians, namely the Late Miocene to Pliocene NW–SE to N–S shortening in the East Carpathians (Csontos 1995). The dominant fault trends are NNW–SSE and ENE–WSW, marking normal faults with both synthetic and antithetic character. Particularly significant is the NW–SE directed dextral strike-slip fault which terminates basinward in a horsetail splay near the continental rise (Fig. 2C). It marks the offshore continuation of the prominent Peceneaga-Camena Fault which separates the North Dobrogrea Orogen from the Moesian Platform (Dinu *et al*. 2005) (Fig. 1). The Viteaz Canyon incising the shelf deposits is developed over this fault which acts as a zone of weakness. With the transition to the Dacian, activities along this fault ceased. However, penetration of the Dacian strata by this fault, especially on the shelf, could not be completely excluded because of the low data resolution. From the Pontian to the Romanian/Quaternary, fault activity migrated landward and the dominant trend remained NNE–SSW, while the ENE–WSW direction became unimportant. Many of the faults mapped are deep-seated (pre-Oligocene) and may represent reactivated older structures. Many Pontian faults are found in areas of BSR occurrence and are noticeably absent between and basinward of these areas (Fig. 2C). There are no major post-Pontian faults (Fig. 2, A and B).

3.4. GAS HYDRATES AND FREE GAS OCCURRENCE

Gas hydrate can form where the prevailing *P–T* conditions lie within its phase equilibrium field. In the Black Sea, these conditions occur generally below a water depth of about 700 m. However, the distribution of BSRs is patchy, suggesting that gas hydrates occur only locally off southwest Crimea (Lüdmann *et al*. 2004) and offshore Romania (Ion *et al*. 2002; Popescu *et al*. 2006) (Fig. 1, inset). These occurrences are associated with major channel-levee systems of the Dnieper and Danube rivers respectively. In the Ukrainian sector, the gas hydrates occupy a connected area of ca. 805 km^2 in a water depth range of 700–1,350 m (Lüdmann *et al*. 2004). In the Romanian sector, the hydrates are found in two areas covering a total of about 2,900 km^2 (Fig. 1 and 2D) with water depths ranging from 650 to 1,450 m in our study area, but extends to >1,900 m in the adjacent environs (Popescu *et al*. 2006). Seismic line 17 shows a typical example of a BSR (Figs. 1 and 3) with the following reflection characteristics: (1) It has a high reflection coefficient, reaching up to 50 % of that of the seafloor. (2) It is characterized by a polarity opposite to that of the seafloor reflector. (3) It mimics the topography of the seafloor and may in places cross-cut the original stratification (Hyndman & Spence 1992).

The northeastern gas hydrate area of the Danube fan is marked by double BSRs, both of which show the same seismic characteristics. The upper BSR represents the present BGHSZ (Figs. 1 and 3). The double BSRs recognized in our data and the multiple BSRs reported by Popescu *et al.* (2006) are restricted to the overbank deposits of the topographically-low Danube channel-levee systems.

Extensive acoustic masking, an indicator for free gas occurrences, was observed in all sequences mapped. In the Pontian deposits, this masking is related to faults occurring around as well as near the top of the succession. Romanian to Quaternary strata show widespread blanking near the shelf edge and occasionally at the channel-levees on the slope. Both areas are also marked by BSR occurrence.

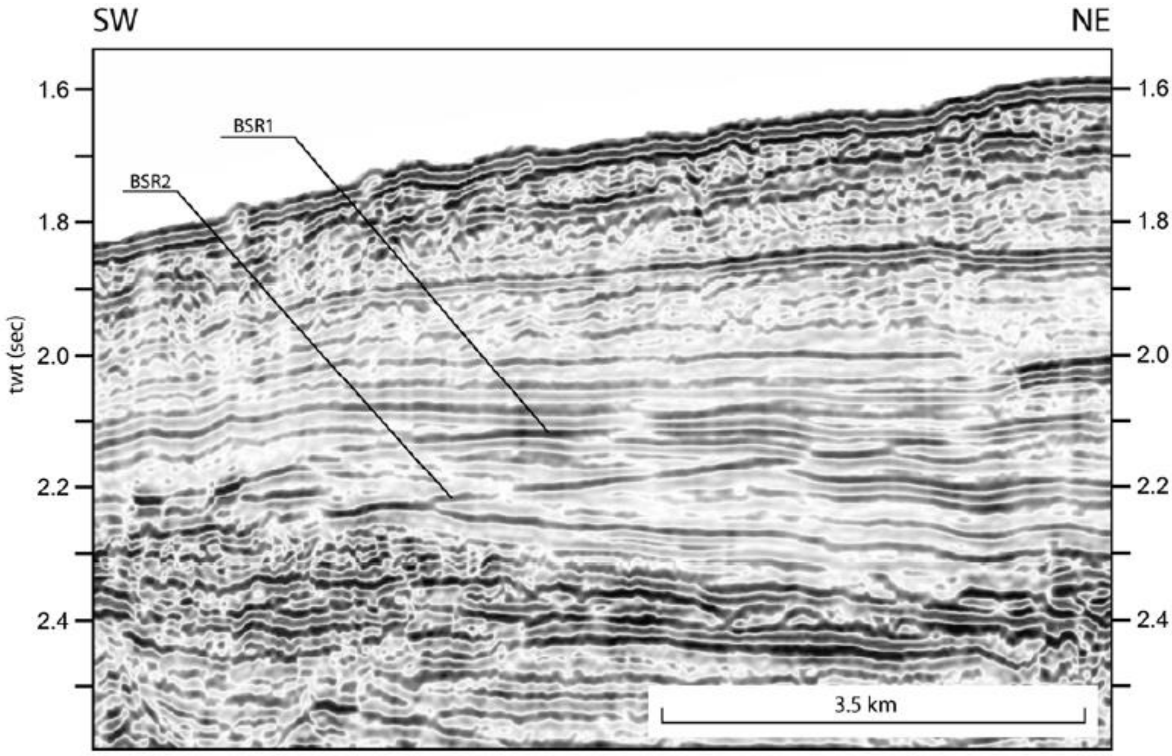

Figure 3. Part of seismic line 17 showing BSR1 which marks the base of the methane hydrate stability zone and BSR2, the stability zone of a mixture of methane and higher homologues.

3.5. MULTIPLE BSR'S

A phenomenon typical for the Romanian sector is the occurrence of multiple BSR's. Popescu *et al.* (2006) have determined several locations at the continental slope off Romania where a quadruple to double BSR occurs. In our study area, a double BSR is found in its northeastern part (Fig. 1 and 2D). The multiple BSRs could be either interpreted as relict features attributed to changes in bottom water temperature of the Black Sea or as expressions of the BGSHZ with different gas composition (Popescu *et al.* 2006). The first hypothesis favoured by Popescu *et al*. (2006) is related to sea-level rise and climate change. The response of GHZ in the Black Sea to the Holocene temperature rise was modelled by Poort *et al*. (2005). The abrupt flooding 7,100 yr BP by the injection of warm Mediterranean waters led to a significant change in *P-T* conditions, resulting in a reduction of the GHZ of about 15–62 % (Poort *et al*. 2005). They assumed that specifically, the increase in bottom water temperature and higher temperatures at the BGHSZ over-compensate the pressure increase due to a larger water volume. Taking the example of Popescu *et al*. (2006; their Fig. 2, profile b039-GI), here, at 1,600 m water depth BSR 4 lies 495 mbsf and BSR 1 (the present BGHSZ) is located at 349 mbsf ($v_{p,\text{ water}}$ = 1,500 m/s and $v_{p,\text{ sediment}}$ = 1,700 m/s). Assuming a present salinity of 22.3 ‰, an average sediment density of 1.6 g/cm^3 and a bottom temperature of 8.85°C, the computed thermal gradient is 31°C/km using the experimental thermobaric stability conditions for the methane-seawater system of Dickens and Quinby-Hunt (1994). Applying the same input parameters, BSR 4 could then be explained by a former bottom temperature of 5.3°C or a drop of 3.55°C, respectively. This calculated temperature difference of 3.55°C lies within the range of 5.5 to 2°C proposed by Poort *et al*. (2005) for a change in bottom water temperature compared to the present value in their model.

According to the above assumptions, multiple BSRs could theoretically represent former locations of the BGHSZ corresponding to different bottom water temperatures as postulated by Popescu *et al*. (2006). However, it remains unclear why the gas hydrate has not dissociated outside the present GHSZ, and why generally only one BSR occurs, but locally 4, 3 or 2 BSRs exist. Furthermore, equally puzzling would be the fact that multiple BSRs have not been observed in the Dnieper Canyon area (Lüdmann *et al*. 2004), although the Holocene bottom temperature fluctuations should have left their imprint on all gas hydrate systems in the Black Sea. In addition, the above calculation does not include the increase in pressure due to the Holocene sea-level rise. This increase would act against the upward shift of the BGHSZ associated with the Holocene temperature increase. Assuming that pressure fluctuations act instantaneously, changes in bottom temperature would leave their imprint much more slowly in comparison. An open question is therefore the time span needed to heat a sedimentary column of 349 m (depth to BSR 1) by about 3.55°C. In other words, would the scenario given by Popescu *et al*. (2006) be realistic.

In an attempt to answer this question, we applied the formula of Carslaw and Jaegger (1959) to model the effect of past temperature changes, where the temperature *T* at any depth *z* due to such a change is given by:

$$T = T_0 + gz + T_1 \cdot \left[erf\left(\frac{z}{\sqrt[2]{s \cdot t_1}}\right) - erf\left(\frac{z}{\sqrt[2]{s \cdot t_2}}\right) \right]$$

T_0 is the bottom temperature (8.85 °C at present), T_1 the temperature increase (+3.55°C), *s* the diffusivity (marine sediment: 0.3 mm^2/s on average after Shusaku *et al.* 1999; pure methane hydrate: 0.32 mm^2/s after Turner *et al*. 2005), and t_1 and t_2 are the end and starting points of the climate change, respectively. With this formula, we can now compute the time necessary for the heat transfer that shifted BSR 4 (495 mbsf) to its present location (349 mbsf). Figure 6 shows the computed values for a diffusivity of 0.31 mm^2/s. It suggests that since the flooding of the Black Sea (7,100 yr BP), the temperature at BSR 1 rose only by 2.76°C, even if we assume an unrealistic high bottom water increase of 8°C. If we take into account the additional effect of the Holocene sea-level rise of about

120 m (e.g., Ryan *et al*. 2003, Winguth *et al*. 2000), then the temperature increase amounts to 4°C instead of 3.55°C at BSR 1. Under more realistic conditions represented by the curve of T_1 = 5 °C, a 4 °C or 3.55°C higher temperature at BSR1 are reached after 100 and 50 kyr, respectively (Fig. 6). Our results imply that climate-induced heating (or cooling) of the subbottom layers is a slow process. Despite the fact that gas hydrate increases the thermal diffusivity compared to water-saturated sediments (Waite *et al*. 2007). BSR 4 is very likely not a paleo-feature as proposed by Popescu *et al*. (2006); moreover, the GHSZ is at present not yet in thermal equilibrium with the prevalent ambient conditions after the Holocene bottom temperature rise and flooding of the Black Sea.

4. DISCUSSIONS

BSRs are found in the northwestern Black Sea only rarely and in association with certain depo-environments. Their occurrence is controlled mainly by the amount of free gas below the BGHSZ, and is hence dependent on processes which favour the accumulation of free gas. For the Dnieper Canyon, the decisive process is mud diapirism below the BSR area, which results in rupture of the upper sediment layers, producing small faults and fractures along which gas and fluids can ascent and accumulate below the GHSZ (Lüdmann *et al*. 2005). Offshore Romania, it is the combined effect of lithology and stratigrahy which capture free gas in the major channel-levees of the Danube deepsea fan complex (Fig. 4; Popescu *et al*. 2006).

As an alternative interpretation, we suggest that the multiple BSRs in the Black Sea are related to differences in gas composition (e.g. methane and 26.0–28.3 % ethane). Each major channel-levee acts as a closed system sealed at the base and top by impermeable layers, namely the condensed sections deposited during sea-level highstands. The channels are orientated perpendicular to the continental margin and in the direction of the bottom gradient (Fig. 2D). Free gas and fluids can migrate upslope within the coarser channel-fill sediments characterized by high-amplitude reflections (HAR). As they reach a certain concentration in the upper channels, migration into the overbank deposits takes place. Where the channel-levee system penetrates the GHZ, fluids and free gas are captured below the BGHSZ and cannot migrate farther upwards. This may increase the pressure locally and the gas and fluids can spread laterally into the overbank deposits, where the BSR is generally well-expressed (Fig. 4).

We suggest that two processes contribute to gas hydrate accumulation on the slope off Romania. As Tréhu *et al*. (2006) reported for the Hydrate Ridge, (1) microbial methane is generated by *in situ* methanogenesis; and (2) it is transported upwards with a significant amount of thermogenic hydrocarbons from deeper sources *via* permeable stratigrahic layers and/or along faults. A major hydrocarbon source rock in the study area is bituminous shales of the Oligocene Histra Formation (Dinu *et al*. 2005). Deep-seated Pontian to Dacian faults (Figs. 2C and 5) provided pathways for the ascent of wet hydrocarbons. These gases could have entered the channel-levee systems by diffusion or along minor faults or cracks. From there, they migrate upslope as a mixture with the lighter methane as free gas or in solution. During the ascent of the mixture, fractionation separates the hydrocarbons in accordance with their stability conditions. Hereby the lighter and smaller methane molecules migrate faster and may reach areas where the stability conditions for methane and water are satisfied.

Multiple BSRs with often a different number of BSRs occur in three separate channel-levee systems. This difference in BSR multiplicity may be a result of different gas mixtures in the systems. Kruglyakova *et al*. (2004) reported the occurrence of methane homologues for gas seeps, gas hydrates and breccia of mud diapirs. The lack of a hydrocarbon-bearing formation in the Dnieper Canyon area could be the cause of the absence of multiple BSRs.

The gas seeps concentrated on the shelf edge off Romania could be related to gas enrichment in the subsurface layers. Profile 33 shows extensive acoustic masking due to free gas (Fig. 7). These gas accumulations may originate from gas which migrated unhampered through channel-levees of the older sequences 3–4 because they are situated below the BGHSZ. The gas could therefore follow the dip of the channel-levee to the break point of the shelf edge, where the layers become horizontal (Fig. 7, grey arrows). This process may have also played an important role when, after flooding of the Black Sea, the GHSZ started to shrink and gas hydrate dissociation produced a large amount of free gas. Part of this gas may have formed new gas hydrates, but may have also migrated farther upslope to the shelf break where the channel-levees terminate. This process might still be continuing because the present BGSZ has not yet reached thermal equilibrium (see discussion before). At the shelf edge, a vertical gas flux as indicated in Fig. 4 (grey arrows) could not be excluded; here, faults may provide additional pathways.

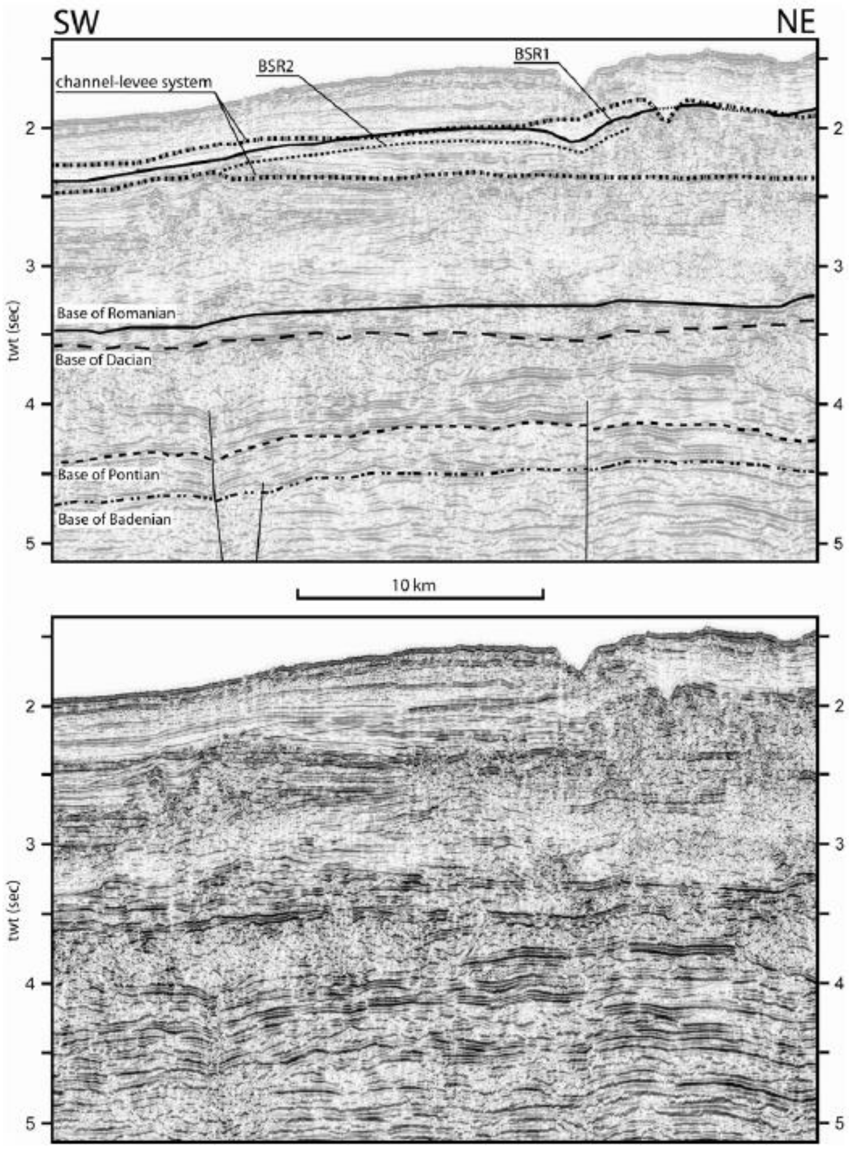

Figure 4. Part of profile 17 showing that the BSR is confined to the channel-levee and overbank deposits. Note the diffuse reflection pattern throughout the sedimentary column which is interpreted to be a result of gas accumulations.

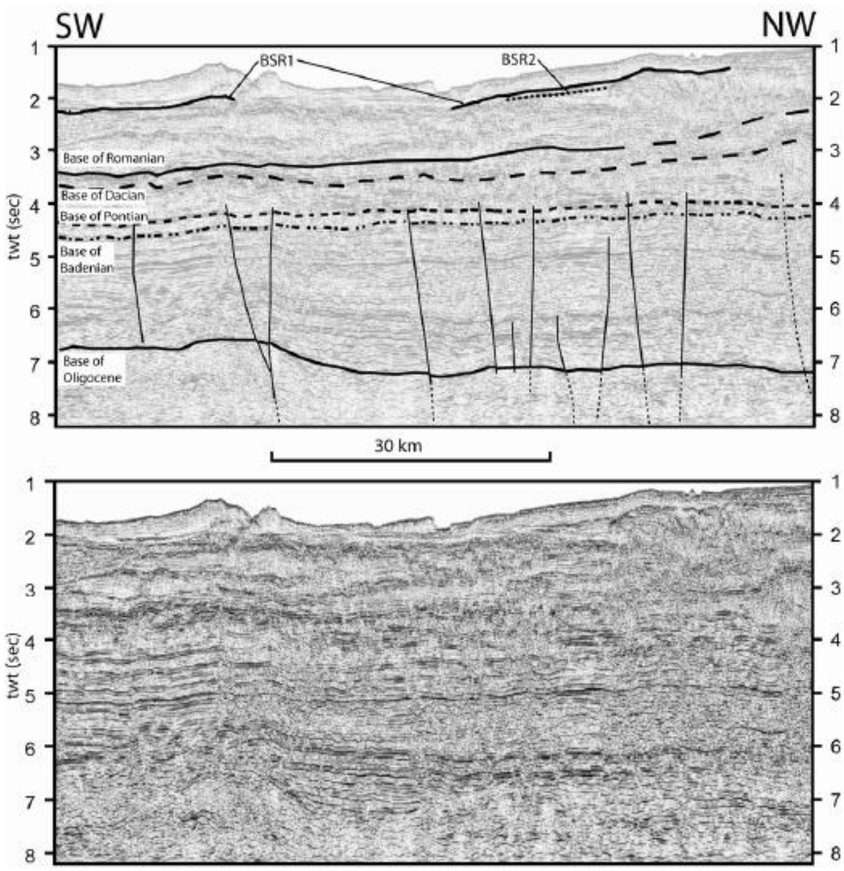

Figure 5. Part of profile 20 which crosses the 2 BSR areas. Deep-seated faults which penetrate the base of the Pontian are also shown. Note the diffuse reflection pattern throughout the sedimentary column which is interpreted to be a result of gas accumulations.

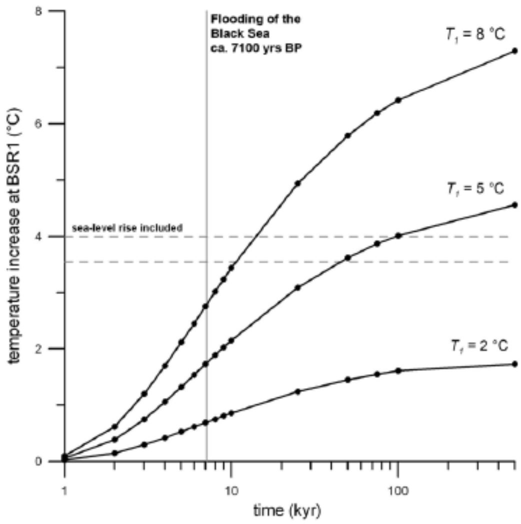

Figure 6. Diagram showing the time span needed for the transfer of heat from the seafloor at 1,600 m water depth to the present BSR location at about 349 mbsf. Simulated are an increase in bottom water temperature of 2, 5 and 8°C respectively. The dashed lines indicate temperatures of 3.55 and 4.0°C needed to shift BSR 4 (495 mbsf) to its present position at BSR 1 (see text for further discussions).

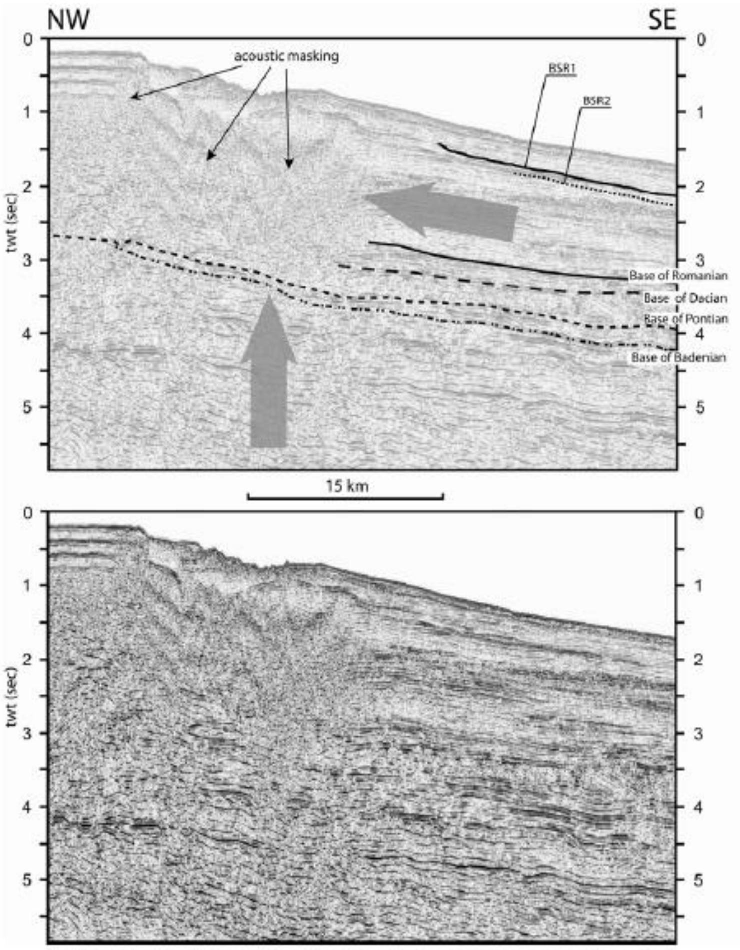

Figure 7. Part of profile 33 which shows areas of gas accumulation near the shelf edge indicated by extensive acoustic masking. Grey arrows show possible migration paths of free gas.

5. CONCLUSIONS

Our study shows that a BSR occurs only locally in the western Black Sea, namely at the continental margin of Romania and near the Dnieper Canyon southwest of the Crimea Peninsula. The associated gas hydrate accumulations are probably characterised by a higher free gas content below the BGHZ compared to the surrounding areas. In the Ukrainian sector, the surplus in free gas might have been derived from mud diapirs which penetrated the sedimentary column below the BGHSZ (Lüdmann *et al*. 2005). The top of the diapirs are characterized by extensive fracturing, allowing fluids to ascent and accumulate beneath the GHSZ. In the Romanian sector, the free gas flux is controlled by the specific lithostratigrahy of the channel-levee system of the Danube River. The coarse channel deposits provide excellent migration paths and the low-permeability condensed sections overlying the channel-levees and the GSHZ function as a perfect seal. In addition, numerous faults in this area allow the ascent of thermogenic gas from deeply-buried oil-bearing subbottom layers into the channels of the deepsea fan system.

Multiple BSRs which occur only in the Romanian sector probably represent boundaries of GHSZs containing different mixtures of methane and higher homologues. The latter originated from leaky Oligocene oil reservoirs, and migrated along deep-seated faults into the channels of the Danube deep-sea fan system. The alternative explanation, namely that the multiple BSRs are relicts of the former GHSZ under different *P–T* conditions, seems less likely. For example, the time required to produce a 5°C decrease in temperature at the present BSR position would be about 50 kyr. We suggest that the influence of temperature fluctuations might be only relevant near the upper slope where the GHSZ pinches out and heat could propagate much more rapidly into the subbottom.

To summarize, gas hydrates and free gas accumulations off Romania are characterised by a complex interplay of the lithology of the host sediments, stratigraphic background and local tectonic pattern.

REFERENCES

Artyushkov, E. V., 1992. *Role of crustal stretching on subsidence of continental crust*. Tectonophysics, 215, 187–207.

Bancilă, I., Neagu, T., Muţiu, R., Dragastan, O., 1997. *Jurassic–Cretaceous stratigraphy and tectonic framework of the Romanian Black Sea offshore*. Rev. Roum. Géol., 41, 65–76.

Carslaw, H.S., Jaeger, J.C., 1959. *Conduction of Heat in Solids*, 2nd edn. Clarendon Press, Oxford.

Csontos, L., 1995. *Tertiary tectonic evolution of the Intra-Carpathian area: a review*. Acta Vulcanol., 7, 1–13.

Dercourt, J., Zonenshain, L.P., Ricou, L.-E., Kazmin, V.G., Le Pichon, X., Knipper, A.L., Grandjacquet, C., Sbortshikov, I.M., Geyssant, J., Lepvrier, C., Pechersky, D.H., Boulin, J., Sibuet, J.-C., Savostin, L.A., Sorokhtin, O., Westphal M., Bazhenov, M.L., Lauer, J.P., Biju-Duval, B., 1986. *Geophysical evolution of the Tethys belt from the Atlantic to the Pamirs since the Lias.* Tectonophysics, 123, 241–315.

Dickens, G.R., 2001. *Modelling the global carbon cycle with a gas hydrate capacitor: significance for the latest Paleocene thermal maximum*. In: Paull, C.K., Dillon, W.P. (Eds.), Natural Gas Hydrates: Occurrence, Distribution, and Detection. Am. Geol Union Geophys. Mono. 124, 3–18.

Dickens, G.R., 2003. *Rethinking the global carbon cycle with a large, dynamic and microbially mediated gas hydrate capacitor*. Earth Planet Sc. Lett., 213, 169–183.

Dinu, C., Wong, H. K., Ţambrea, D., 2002: *Stratigraphic and tectonic syntheses of the Romanian Black Sea shelf and correlation with major land structures*. Bucharest Geoscience Forum, Special Volume No. 2, 101–117.

Dinu, C., Wong, H. K., Tembrea, D., Matenco, L., 2005: *Stratigraphic and structural characteristics of the Romanian Black Sea shelf*. Tectonophysics, 410, 417–435.

Finetti, I., Bricchi, G., Del Ben, A., Pipan, M., Xuan, Z., 1988. *Geophysical study of the Black Sea.* Bolletino di Geofisica Teorica ed Applicata, 30(117-118), 197–324.

Ginsburg, G.D., Kremlev, A.N., Grigor'ev, M.N., Larkin, G.V., Pavlenkin, A.D., Saltykova, N.A., 1990. *Filtrogenic gas hydrates in the Black Sea (twenty-first voyage of the research vessel "Evpatoriya").* Soviet Geology and Geophysics (geolgiya I Geofizika), 31(3), Allerton Press, 8–16.

Görür, N., 1988. *Timing of the opening of the Black Sea basin*. Tectonophysics 147, 247–262.

Haq, B.U. 1998 *Gas hydrates: greenhouse nightmare? Energy panacea or pipe dream?* GSA Today, 8(11), 1–6.

Holbrook, W.S., Hoskin, H., Wood, W.T., Stephen, R.A., Lizarralde, D., *ODP Leg 164 Shipboard Scientific Party (1996) Methane hydrate and free gas on the Blake Ridge from vertical seismic profiling*. Science, 273, 1840–1843.

Hyndman, R.D., Davis, E.E., 1992. *A mechanism fort the formation of methane hydrate and seafloor bottom-simulating reflectors by vertical fluid expulsion*. J. Geophys. Res. 97(B5), 7025–7041.

Hyndman, R.D., Spence, G.D., 1992. *A seismic study of methane hydrate marine bottom simulating reflectors*. J. Geophys. Res. 97(5), 6683–6698.

Ion, G., Lericolais, G., Nouzé, H., Panin, N., Ion, E., 2002: *Seismoacoustic evidence of gases in sedimentary edifices of the palaeo-Danube realm.* CIESM Workshop Series 17, 91–95.

Ivanov, M.K., Limonov, A.F., Woodside, J.M., 1998. *Extensive deep fluid flux through the sea floor on the Crimean continental margin (Black Sea).* In: Henriet, J.-P., Mienert, J. (Eds.), Gas hydrates: relevance to world margin stability and climate change. Geological Society, Special Publication 137, 195–213.

Kayan, R. E., Lee, H. J., 1991: *Pleistocene slope instability of gas hydrate-laden sediment on the Beaufort Sea margin*. Mar. Geotechnol., 10, 125–141.

Kruglyakova, R.P., Byakov Y.A., Kruglyakova M.V., Chalenko, L.A., Shevtsova, N.T, 2004. *Natural oil and gas seeps on the Black Sea floor*. Geo-Mar- Lett., 24: 150–162.

Kutas R.I., Rusakov O.M., Kobolev V.P., (2002) *Gas seeps in northwestern Black Sea: geological and geophysical studies*. Russian Geology and Geophysics, 43(7), 698–705.

Letouzey, J., B. Biju-Duval, A. Dorkel, R. Gonnard, K. Kristchev, L. Montadert, O. Sungurlu, 1977. *The Black Sea: A marginal basin - Geophysical and geological data*. In Biju-Duval, B., Montadert L. (Eds.), International Symposium on the structural history of the Mediterranean basins. Split. Paris, 363–376.

Limonov, A.F., Woodside, J.M., Ivanov, M.K., 1994. *Mud volcanism in the Mediterranean and Black Seas and shallow structure of the Eratosthenes Seamount. Initial results of the geological and geophysical investigations during the Third UNESCO-ESF "Training-Through-Research" cruise of RV Gelendzhik (June-July 1993)*, UNESCO Rep Mar Sci 64.

Lüdmann, T., Wong, H.K., Konerding, P., Zillmer, M., Petersen, J., and Ernst, F., 2004. *Heat flow and quantity of methane deduced from a gas hydrate field in the vicinity of the Dnieper Canyon, northwestern Black Sea*: Geo-Marine Letters, 24, 182–193.

Luth, C., Luth, U., Gebruk, A.V., Thiel, H., 1999. *Methane gas seeps along the oxic/anoxic gradient in the Black Sea: manifestations, biogenic sediment compounds and preliminary results on benthic ecology*. Mar. Ecol., 20(3-4), 221–249.

MacDonald, D. T., 1990. *The future of methane as an energy resource*. Ann. Rev. Energy, 15, 53–83.

McIver, R. D., 1982. *Role of naturally occurring gas hydrates in sediment transport*. AAPG Bull., 66, 789–792.

Naudts, L., Greinert, J., Artemov, J., Staelens, P., Poort, P., Van Rensbergen, P. and De Batist, M., 2006. *Geological and morphological setting of 2778 methane seeps in the Dnepr paleo-delta, northwestern Black Sea*. Mar. Geol., 227, 177–199.

Polikarpov, G.G., Egorov, V.N., Gulin, S.B., Gulin, M.B., Stokozov, N.A., 1992. *Gas sseps from the bottom of the Black Sea – a new object of molismology*. In: Polikarpov, G.G. (Ed.), Molismology of the Black Sea. Nauka, Kiev, 10–28. (in Russian)

Popescu, I., De Batist, M., Lericolais, G., Nouzé, H., Poort, J., Panin, N., Versteeg, W., Gillet, H., 2006. *Multiple BSRs in the Black Sea related to deep-sea fan architecture*: Mar. Geol., 227, 163–176.

Popescu, I., Lericolais, G., Panin, N., Wong, H.K., Droz, L., 2001. *Late Quaternary channel avulsions on the Danube deep-sea fan*. Mar. Geol., 173, 25–37.

Robinson, A.G., Rudat, J.H., Banks, C.J., Wiles, R.L.F., 1996: *Petroleum geology of the Black Sea.* Mar. Petrol. Geol. 2(13), 195–223.

Ryan, W.B.F., Major, C.O., Lericolais, G., Goldstein, S.L., 2003. *Catastrophic flooding of the Black Sea*. Annu. Rev. Earth Planet. Sc., 31(1), 525–554.

Sloan, E. D., 1990. *Clathrate Hydrates of Natural Gas*. 641, Marcel Dekker, New York.

Soloviev, V., Ginsburg, G.D., 1994. *Formation of submarine gas hydrates.* Bull. Geol. Soc. Denmark, 41(1), 86–94.

Stoll, R.D., Bryan, G.M., 1979. *Physical properties of sediment containing gas hydrates*. J. Geophys. Res., 84, 1629–1634.

Shusaku, G., Mastaka, K., Makotu, J., Osamu, M., 1999. *Thermal diffusivity estimation of marine sediment and its application by the long-term temperature data*. Geophysical. Expl., 53(3), 119–213, in Japanese.

Ţambrea, D., Şindila, V., Olaru, R., 2000. *The Pontian from the Romanian continental shelf of the Black Sea*. Romanian Oil J., 7(1), 9–20.

Turner, D.J., Kumar, P., Sloan, E.D., 2005. *A new technique for hydrate thermal diffusivity measurements.* Int. J. Thermophys., 26(6), 1681–1691.

Waite, W.F., Stern, L.A., Kirby, S.H., Winters, W.J., Mason, D.H., 2007. *Simultaneous determination of thermal conductivity, thermal diffusivity and specific heat in sI methane hydrate.* Geophys. J. Int., 169(2), 767–774.

Winguth, C., Wong, H.K., Panin, N., Dinu, C., Georgescu, P., Ungureanu, G., Krugliakov, V.V., Podshuveit, V., 2000. *Upper Quaternary water level history and sedimentation in the northwestern Black Sea*. Mar. Geol., 167, 127–146.

Wong, H. K., Panin, N., Dinu, C., Georgescu, P. Rahn, C., 1994. *Morphology and post-Chaudian (Late Pleistocene) evolution of the submarine Danube fan complex*. Terra Nova, 6, 502–511.

Yefremova, A.G., Zhizhchenko, B.P., 1974. *Occurrence of crystal hydrates of gas in sediments of the modern marine basins*. Doklady Akademii Nauk SSSR, 214, 1179–1181.

Zonenshain, L.P., Le Pichon X., 1986. *Deep basins of the Black Sea and Caspian Sea as remnants of Mesozoic back-arc basins*. Tectonophysics, 123, 181–211.

COMPARATIVE ANALYSIS OF THE EGGSHELL BIOMINERALIZATION IN MODERN BIRDS AND MEGALOOLITHID EGGS FROM THE MAASTRICHTIAN OF THE HAŢEG BASIN. ABNORMAL SHELL UNITS LINKED TO DIAGENESIS IN THE FOSSIL EGGSHELLS

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Résumé: Les œufs de dinosaures de type mégaloolithide, fréquents dans plusieurs sites de Maastrichtien du Bassin de Hațeg, et sujet de nombreux articles dédiés aux caractéristiques des œufs et des coquilles et de la taphonomie, sont examinés ici du point de vue des aspects ultrastructurales de la microscopie électronique à balayage (MEB), par comparaison aux coquilles d'œufs de certains oiseaux modernes. L'objectif principal de cette étude est d'interpréter la biominéralisation dans la coquille d'œuf mégaloolithide, en comparant le développement des cristaux de calcite dans la matrice organique de la membrane (*membrana testacea*) et le progrès de calcification dans les deux parties principales de la coquille dure : la couche mamillaire et la palissade dans la coquille d'œuf de l'oiseau. L'étude révèle des similitudes entre la coquille de l'oiseau et celle mégaloolithide, dans le procès de calcification des fibres organiques dans la membrane de la coquille et de développement des cristaux de calcite des centres de nucléation à la base de la couche mamillaire. L'étude révèle également des différences significatives entre les modifications diagenétiques des coquilles d'œufs de *Megaloolithus siruguei* des deux sites investiguées, Tuştea et Livezi ; tandis que les coquilles d'œufs de Tuştea préservent même des structures organiques perminéralisées, celles de Livezi sont fortement modifiées par la recristallisation, qui semble être à l'origine des structures anormales de la coquille. L'analyse élémentaire EDS indique une variation similaire de contenu et de poids per cent des plus communs éléments (C, O, Ca) dans la membrane et la coquille, aussi dans les œufs de poule que dans ceux de type mégaloolithide de Tuştea.

Mots-clés: *coquille d'œuf de dinosaure,* Megaloolithus siruguei*, biominéralisation, oiseaux modernes, structures anomales de la coquille, diagenèse.*

INTRODUCTION

The comparative studies between living and fossil organisms are essential in interpreting the anatomy and the physiology of the soft parts of fossils and, on this basis, the environmental conditions in which the organisms from the past lived. The eggshells, as the bones and other skeletal forms, are the result of the physiological processes in the organisms between the organic and mineral components, under genetic control, being thus relevant for the evolutionary history of the groups, and consequently, with a taxonomic and phylogenetic significance (Grellet-Tinner, 2000). The complex processes which lead to the crystal growth in the eggshells are investigated by different methods: light and electron microscopy, biochemical, crystallographic and crystallochemical, the most elaborated studies involving all or most of these (Chien *et al*., 2008). Among these methods, the scanning electron microscopy (SEM) on fracture eggshell surfaces, presents very detailed, three-dimensional views, which allow the recognition of the intimate processes taking place within the organic matrix in successive stages of biomineralization (Nys & Guyot, 2011).

This is also the aim of this comparative study, based on SEM analysis between some modern birds, mostly domestic ones, and *Megaloolithus siruguei*, the common dinosaur oospecies in the Maastrichtian of the Haţeg Basin and the only one in the region for which several places of incubation are known (Grigorescu *et al*., 2010).

The SEM comparative studies on birds and dinosaurs eggshell microstructure and ultrastructure, much developed in the last two decades, envisage also the understanding of the reproductive system in dinosaurs, on the other hand of the diagenetic processes during the taphonomic processes of some dinosaur eggs.

STRUCTURE AND FORMATION OF THE AVIAN EGGSHELL

STRUCTURE OF THE EGGSHELL

The sauropsid (reptile and birds) eggshell generally consists of individual shell units, vertically divided in four parts, each displaying different microstructural aspects: the shell membrane (*membrana testacea)*, the mammillary layer, the continuous layer, usually the thickest one, and the organic cuticle and the *external zone*, not present in all the eggshell types, covered by the cuticle. The shell units are separated from place to place by pores which enable the gas exchange for the embryo (Fig. 1).

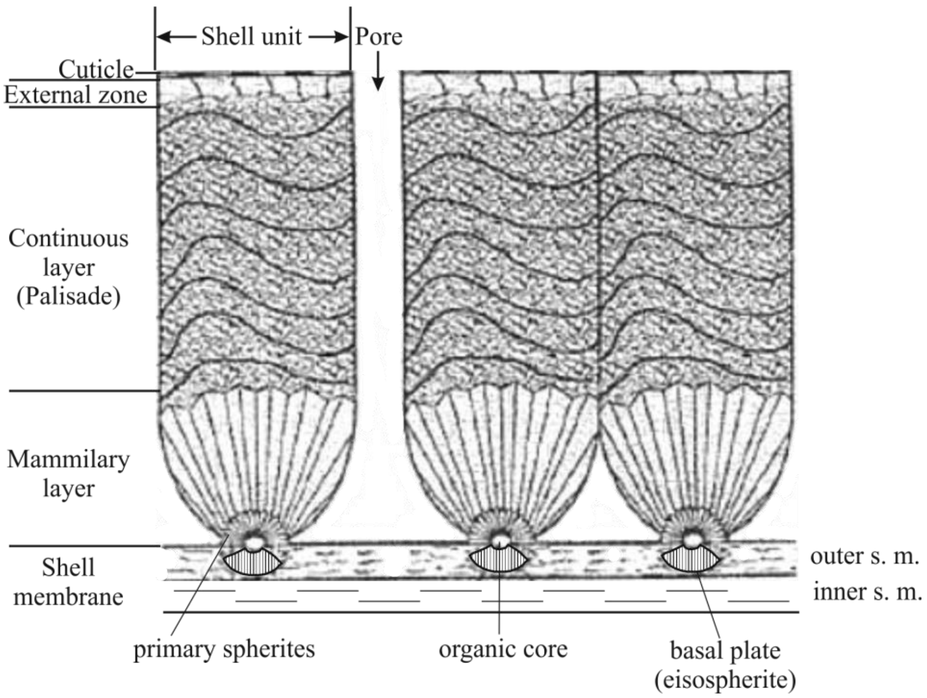

Figure 1. Schematic structure of the amniotic vertebrate eggshell (after Grellet-Tinner, 2000, with changes: *continuous layer* instead of squamatic layer, *external zone* instead of third layer).

The membrana testacea (MT) is composed of two juxtaposed layers of interlacing collagen filament-like structures. The outer part of the MT serves as nucleation centre for the growth of the calcium carbonate eggshell units. In the initial stage, the crystal nuclei occur as seeds within the protein fibers, from the amorphous calcium carbonate which progressively transforms into calcite crystals (Rodriguez-Navarro *et al*., 2015) . The proliferation of the process generates small bodies of calcite at the base of the mammillary layer (*basal caps* or *eisospherites*) (Mikhailov, 1997). Due to its dominant organic composition, MT is rarely preserved in fossil eggshells which were exposed, even for short time to the oxidizing atmospheric condition (Grellet-Tinner, 2000).

The mammillary layer represents the base of the mineral part of the eggshell. It has a conical shape and is composed of acicular calcite crystals, polygonal in cross section, that radiate from the nucleation center (*organic core)*. In birds (as in most theropod dinosaurs), the radiating structure does not continue into the overlying layer, a distinct boundary separating these two parts of the eggshell (Mikhailov, 1997, p. 12).

The continuous layer (with uniform microstructure and squamatic ultrastructure). It is named *palisade* layer by modern bird oologists (Nys & Guyot, 2011).

The external zone has a prismatic or homogenous crystalline structure**,** different from the structure of the continuous (palisade) layer.

THE EGGSHELL BASIC TYPES

Three basic eggshell types are recognized in dinosaurs and birds, based on ultastructural characteristics: *Dinosauroid – spherulitic*, *Dinosauroid – prismatic*, and *Ornithoid*. According to the microstructural aspects, among which the morphology of the shell units, the structure of the pore system, eight distinct structural morphotypes and a problematic one are distinguished by Mikhailov *et al*. (1996). The morphotypes are more or less clearly correlated with different taxonomic groups (Fig. 2).

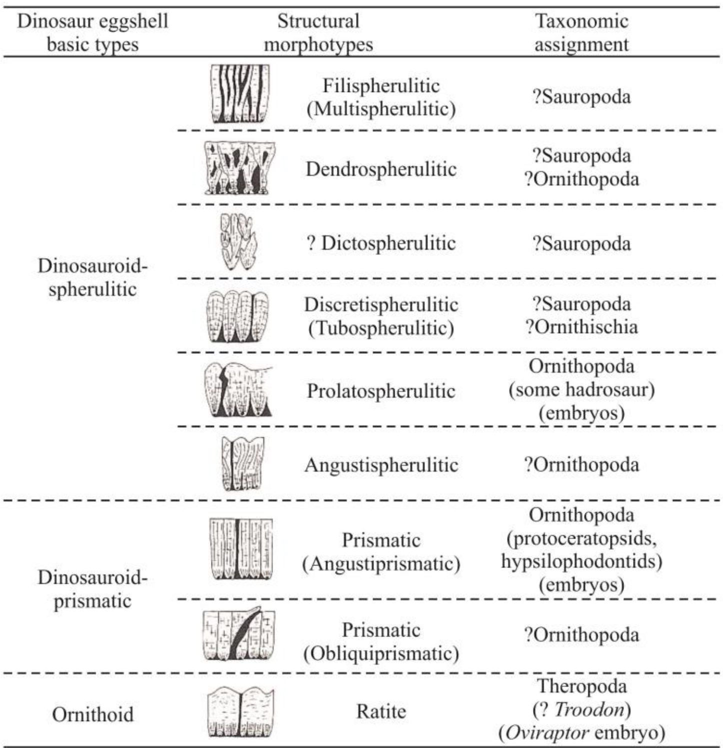

Figure 2. Basic eggshell types in birds and dinosaurs (from Mikhailov *et al*., 1996).

The Dinosauroid – spherulitic basic type exhibits on the entire eggshell thickness an ultrastructure composed of units which are sometimes coalescent, with indistinct boundaries among them, discernible only in polarized light. This type characterizes the non-theropod dinosaurs. Six morphotypes belong to this basic type: *Filispherulitic*, *Dendrospherulitic*, *Dictospherulitic*, *Discretispherulitic* (*Tubospherulitic*), *Prolato-spherulitic*, and *Angustispherulitic*. All these morphotypes are assigned to sauropods and ornithopods.

Megaloolithus siruguei, discussed in this paper and, generally the Megaloolithidae oofamily corresponds to the *Discretispherulitic* (*Tubospherulitic*) morphotype.

The Dinosauroid – prismatic basic type presents shell units with two parts, not clearly separated. The lower part (mammilla) has a radial-tabular ultrastructure, while the upper part is more homogenous with a quasi-tabular ultrastructure (Fig. 2). This type includes two structural morphotypes: *Angustiprismatic* and *Obliquiprismatic*, characteristic to ornithischian dinosaurs (ornithopods, protoceratopsians).

The Ornithoid type also exhibits two parts, but distinctly separated. The mammilla presents radial or radial-tabular ultrastructures, while the upper part is homogenous with squamatic ultrastructure. Below the mammilla, a compact basal plate group (*eisospherite*) is frequently developed. The external zone is present only in the avian eggshell (Fig. 2). This type is characteristic to birds and theropod dinosaurs (Mikhailov, 1997).

THE EGG FORMATION

The bird eggshell, and generally the amniotic eggshell, represents a composite structure of organic matrix (collagen) and mineral (calcium carbonate). The entire process of egg formation in birds is developed in sequential stages in the oviduct, following the transition through its different regions, each of them having a specific role (Nys *et al*., 2004; Nys & Guyot, 2011). The process starts from the maturation of the *oocytes* (immature ova or egg cells) released from the follicle in the ovary. From the thousands of oocytes present in the ovary at hatch, only one reaches maturation within 24-hour period. The yolk mass of a maturated oocyte is captured by the *infundibulum* where it gets the first egg membrane. Next, in the *magnum*, layers of albumen are laid down, the shell membrane (*membrana testacea*) is added in the *isthmus*, and finally, the calcification takes place in the *uterus*, by the shell gland. From the *uterus* the egg covered by the solid shell passes *to the vagina* and is evacuated through the *cloaca* for the incubation (Fig. 3) (Nys & Guyot, 2011).

MATERIALS AND METHODS

The bird eggshells studied in this paper come from commercial eggs (chicken) respectively from private aviary (duck, goose, turkey, pigeon, ostrich) while the megaloolithid eggshells come from two localities which provided dinosaur egg remains, Tuștea and Livezi. The bird eggshell fragments were cleaned for 3 minutes in the UZDN ultrasonic bath at 22 kHz, 25µA with distilled water. The samples were coated with Au at the Quorum Q300TD equipment, for 30 seconds at 20µA. The dinosaur eggshells were kept in perhydrol for 30 minutes to 24 hours, depending on the quantity and cementation degree of the attached clastic residues, then cleaned in the ultrasonic bath with perhydrol for 3 minutes and coated with Au for 30 seconds at 20µA. After the evaporation of the perhydrol, each sample fragment was broken to obtain a fresh radial fracture. The fracture samples of both bird and megaloolithid eggshells were examined using a Hitachi TM 3030 Tabletop and a ZEISS Merlin Gemini II scanning electron microscope (SEM). Pore openings and channels were measured with SEM. Analytical conditions for images were: acceleration voltage 1keV to 5keV, beam current 56-500pA on uncoated samples.

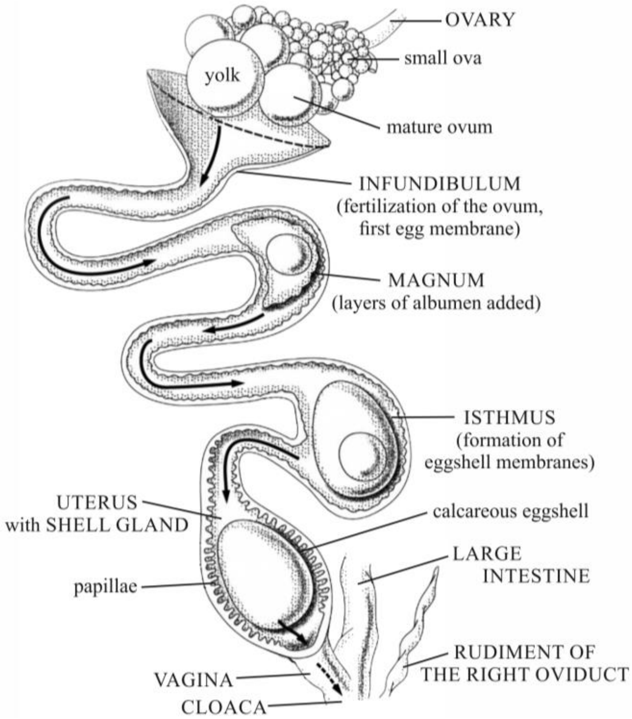

Figure 3. Sequences of the egg formation in the bird oviduct organs (after Gill, 2007).

For the comparative elemental analysis by Energy dispersive X-ray spectroscopy (EDS) we used megaloolithid eggshells from the Tuștea incubation site in which the SEM figures show a minimal diagenetic alteration, respectively chicken eggshells fractured from commercial eggs. The comparison was made at the two main levels of the eggshell, the membrane (54 spectra for the megaloolithid eggshells, respectively 53 for the chicken) and the hard shell (310 megaloolithid spectra vs. 32 for the chicken). Additional 25 spectra were made in the ostrich eggshell: 6 in the membrane and 19 in shell.

The chemical composition was determined using a Zeiss Merlin Gemini II with an Oxford Instruments EDS X MAX 50 spectrometer. The EDS condition: acceleration voltage 15keV, beam current 1nA, coated with gold.

Nomenclature and terminology for eggshell microstructure used are based on Mikhailov (1997) and Chien *et al*. (2008).

Note: The megaloolithid eggshells are inventoried at the University of Bucharest, Faculty of Geology and Geophysics (FGGUB). The SEM catalogue number is provided in the figure captions. **Abbreviation:** CPR – bird eggshell; MTC – megallolithid eggshell from Tuștea; MLC – megallolithid eggshell from Livezi.

COMPARATIVE ANALYSIS OF THE EGGSHELL ULTRASTRUCTURES IN SOME EXTANT BIRDS AND *MEGALOOLITHUS SIRUGUEI* FROM HAȚEG BASIN

In spite of the great taxonomic diversity of the birds, also reflected in the size and the external characters of the eggs, the eggshell of all the birds belong to the same *ornithoid basic type*. Contrary, the dinosaurs are divided in three structural basic types, including the ornithoid basic type, to which the theropod dinosaurs belong, the other two basic types being the dinosauroid–spherulitic and dinosauroid–prismatic (Mikhailov, 1997). The megaloolithid eggs, by far the most numerous in what regards the number of oospecies (around 20), correspond to the dinosauoroid–spherulitic basic type.

In both birds and megaloolithids the lower part of the eggshell is similarly built, whereas the layered structure of the upper part is present only in birds (Fig. 4).

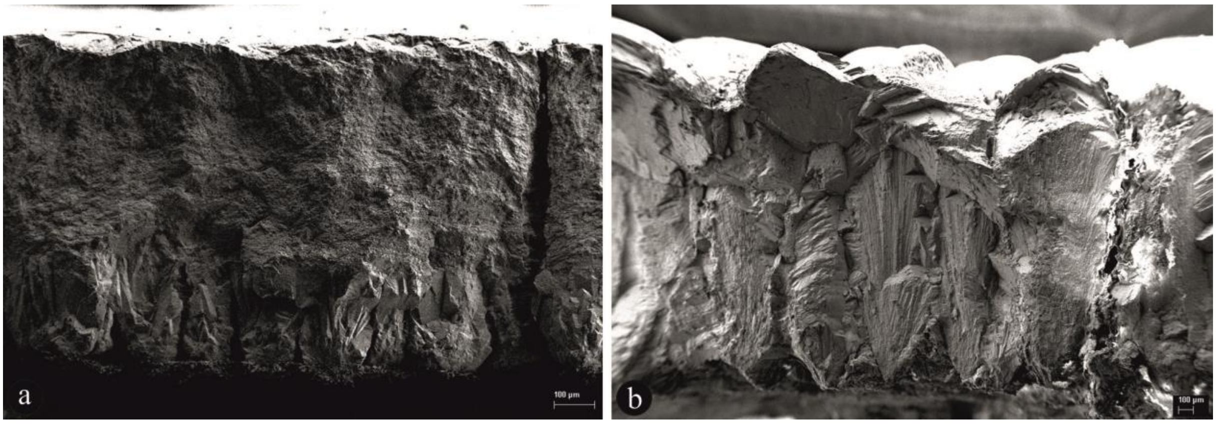

Figure 4. Radial sections in eggshells of: a. ostrich (*Struthio camelus*, CPR 1052), and b. *Megaloolithus siruguei* (MTC 1220132). Note the striking difference among the compact mammilary layer and the palisade layer in ostrich, as in all the birds, while in the *Megaloolithus* eggshell the radial-tabular ultrastructure of the mammillary layer continues up to the top of the medial layer. The outer surface of the *Megaloolithus* eggshell presents closely packed rounded nodes, 0.4-0.7 mm above the surface.

The SEM images in the three main vertical parts of the bird eggshell, from the shell membrane to the top of the eggshell, reveal the succession of different biomineralization processes, which can be interpreted on a comparative basis in the dinosaur eggs.

Fundamentally, eggshell formation consists in the crystal formation within the proteinaceous filament network, a process which in birds starts in the isthmus, where the first calcium crystals are formed, and advances in the uterus, where the external shell membrane (*membrana testacea*) is added. The membrana testacea (MT) is the part of the eggshell where the interaction between the organic and mineral components of the matrix controls the growth of the hard part of the eggshell. From the nucleation centre in the upper part of the MT radiates the wedges of acicular crystals which build the mammillary layer and above this the palisade layer.

Further on we present aspects of biomineralization in birds and megaloolithid eggshells, revealed in SEM images, in the three main layers.

MEMBRANA TESTACEA

The SEM images in the birds examined in this work reveal a two layered MT, the inner layer thinner than the outer one, with a subparallel disposition of the organic fibers, the outer with thicker interlacing fibers. The thicker aspect of the fibers in the outer layer is owed to the more advanced calcification process (Fig. 5a–b). At high magnification the process of crystal formation starting from amorphous carbonate, which grows along the organic (collagen) fibers can be observed (Fig. 5c–e). Disk-shaped ACC particles accumulate on specific organic sites on the eggshell membrane, which are rich in proteins and sulfated proteoglycans, promoting the nucleation and stabilization of the calcite crystals in the mature eggshell (Rodríguez-Navarro *et al*., 2015). The confined mineralization of amorphous calcium carbonate (ACC) within the collagen fibrils was recently explained by the the electrostatic attraction of the negatively charged ACC to the positively charged gap regions of fibrils, followed by the nanocrystals development along the longitudinal axis (Ping *et al*., 2016). The samples analyzed in this study show how the outermost fibers of the MT penetrate the base of the mammillae and generate through fusion small calcite plates (*basal plates*). Apparently, the plates are isolated within the matrix in a preliminary stage, followed by the plate fusion in a later stage to form the base of the mammillae (*basal caps*).

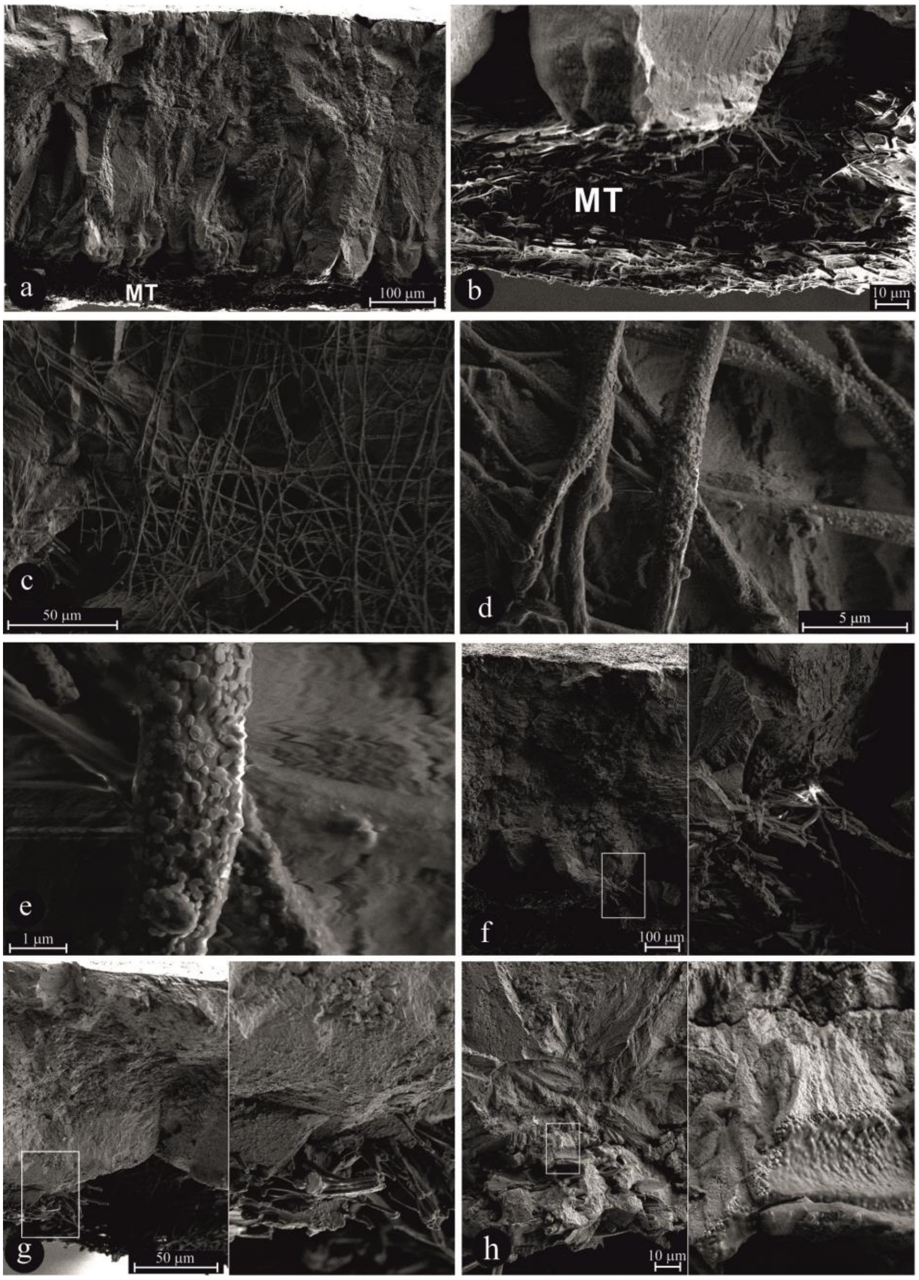

Figure 5. The shell membrane (*membrana testacea*) in birds: a. Membrana testacea (**MT**) in chicken (*Gallus gallus domesticus*, CPR 0721) – disorganized collagen fibers disposed in two discrete superposed layers; b. At greater magnification the two layers are clearly visible (CPR 0728); c–e. The mineralization of the organic fibers at increased high magnification in goose (*Anser anser domesticus*: c.CPR0025; d. CPR0028; e. CPR0027); f–h. Stages in the formation of the *basal plates*: f. Thicker calcified fibers in the outermost **MT** (duck – *Anas platyrhynchos domesticus*: CPR 0786, laterally magnified 6 times); g. Loose calcitic plates within the calcified organic matrix at the base of the mammillary layer (pigeon – *Columba livia domestica*: CPR 0755); h. Fusion of individual plates to form the basal plate (*Anas platyrhynchos domesticus* – CPR 0811, ×1380, laterally-magnified 4 times showing the granular structures on the plate).

The sequential process of fibers binding in small, isolated plates which then fuse into the basal plates is illustrated in Fig. 5f-h based on SEM fracture sections in different bird eggshells. In the mineralization process, a series of granular ultrastructures and spherical voids are formed (Fig. 5h, right).

The development of the hard shell starts above the basal caps, in the *nucleation centers*, which are also known as *organic cores*. The nucleation centers are minute spherical aggregates of calcite crystals in a protein matrix, not always preserved. Following the stages of disorganized development of the calcite crystals in the MT matrix, from these cores start to grow the regular carbonate prismatic crystals, grouped in wedges which form the mammillary layer (Fig. 6).

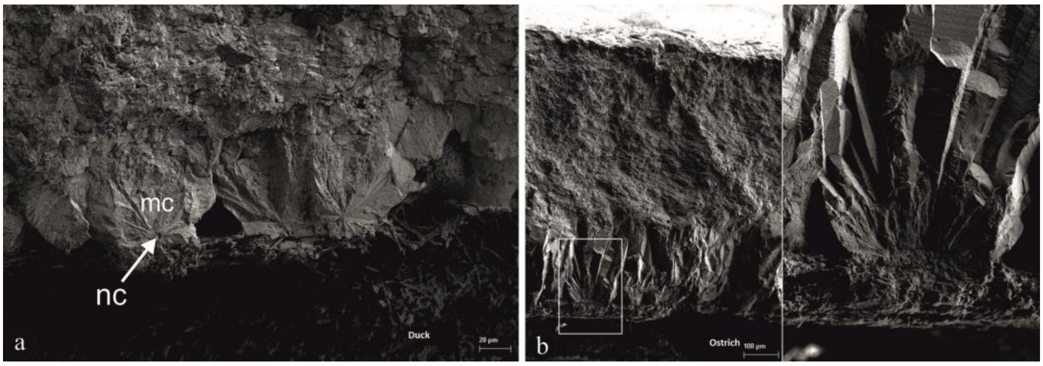

Figure 6. Nucleation centre and the radial structures at the base of the hard shell units: a. Radial section at the base of the mammillary cone (mc) in duck (*Anas platyrhynchos domesticus*) showing the petal-like assemblage (*nc* – nucleation centre), CPR 0813; b. Radial section at the base of the ostrich (*Struthio camelus*) shell unit showing the robust wedges, polygonal in cross section, CPR 1057, magnified 2.5 times on the right.

In the hatched eggs, calcium is absorbed in the process of the skeletal formation of the embryo leaving small depressions ("absorption craters") at the base of the MT, that might be also recognized in the fossil eggs (Hirsch & Quinn, 1990; Jackson *et al*., 2002) (Fig. 7a-b). In the few encountered cases of MT preservation in the megaloolithid eggshells from Tuștea, it forms a compact layer of diagenetically calcified fibers (0.20–0.30 mm thick) which at lower magnification do not reveal clear difference between the two layers, as shown in birds. At high magnification the distinctive thickness and the fibers growth direction amongst the two layers is shown, in spite of the diagenetic changes (Fig. 7d). Basal plates (*eisospherites*) are formed in the outermost part of the MT, most probably following the same stages as shown in birds (Fig. 7c). It is worth to notice that the calcareous bodies at the base of the individual mammillae are radially structured as the calcite wedges, apparently concomitantly with these (Fig. 7d). From the nucleation centers the radially structured calcite crystals wedges develop as in birds (Fig. 7e-f).

MAMMILLARY LAYER

Investigations on the growth of avian eggshells microstructures and ultrastructures focused on the organic-mineral relationships have detailed the internal composition of the mammillary body (*m.b.).* From the base to the top of the *m.b.* different structures were recognized, structures that are closely linked in a sequentially functional assemblage above the outer shell membrane: the *base plate*, the *calcium reserve body* (*CRB*) with a central *CRB sac*, a *CRB cover* and the *CRB crown* (Dennis *et al*., 1996; Chien *et al*., 2008). The three-dimensional crystals growing from the base plate to CRB is shown in Fig. 8. The *base plate* is considered to represent the foundation of the hard eggshell; it incorporates the calcified fibers of the outer shell membrane and transfers the dominant mineral matrix to the *CRB*. The *CRB* represents the region of solubilized calcite used for the embryo skeletal growth

(Dennis *et al*., 1996). The *CRB sac* corresponds to the nucleation centre from which the radial crystals grow at the base of the mammillary layer; it contains spherical granules and it is surrounded by a membrane film. At the boundary between the *CRB sac* and the *CRB crown,* numerous vesicles are present, probably representing remains of the protein that encircled the spherical voids, through which fluid and/or gas circulate (Chien *et al.,* 2008).

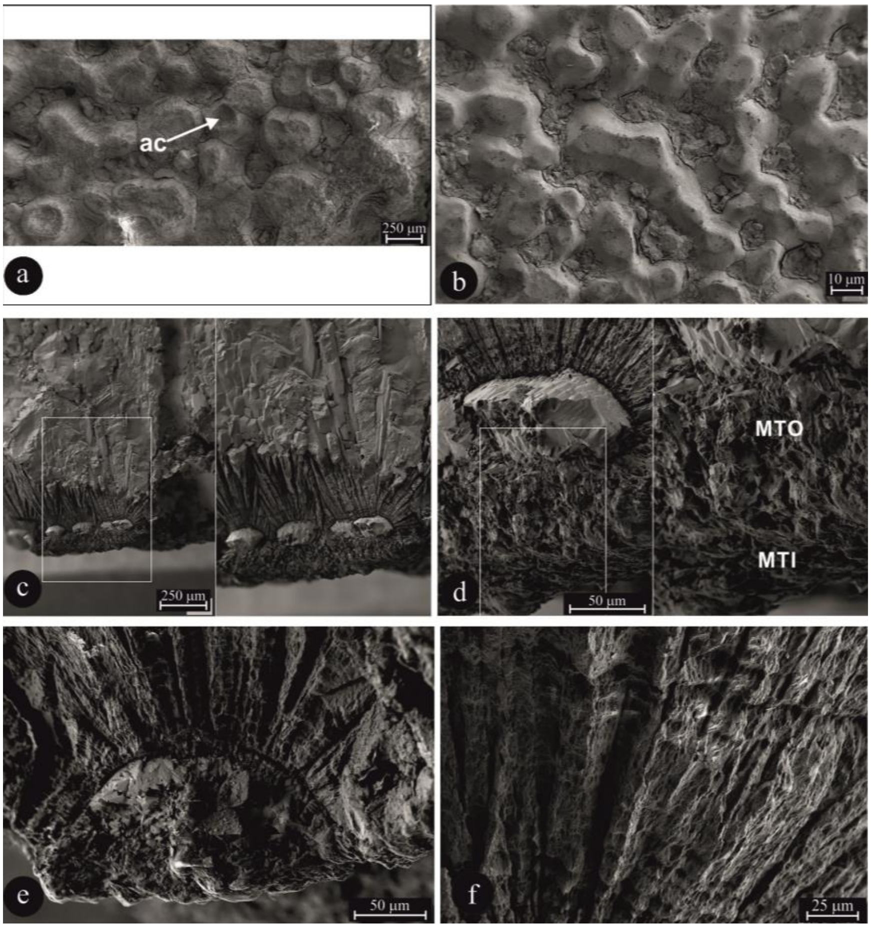

Figure 7. The shell membrane in *Megaloolithus siruguei* from Tuștea: a. The inner surface of the eggshell showing the concave base of the shell units ("calcium absorption craters" – *ac*), MTC C1079; b. The amorphous diagenetically calcified inner layer of the MT wraps the base of the shell units, MTC C1071; c. Basal plates (*eisospherites*) in the outermost part of the MT. The nucleation centres are not preserved, their places being marked by the eisospherites at the base of the shell units, MTC A0145. On the right – details on the radiating calcite wedges as shown in Fig. 6b, in the ostrich base of mammilla; d. The calcareous bodies (*eisospherites*) in the upper most part of the diagenetically calcified MT is radially structured as the calcite wedges of the mammillary layer, MTC.A0150. On the right – detail of the MT ultrastructure – the inner layer (MTI) with amorphous calcified remains of the organic fibers, the outer layer (MTO) with scaly calcite crystals; e. Nucleation centre filled with microgranular calcite crystals, partially recrystalized and reminiscences of calcified fiber and basal plates, MTC 140123; f. Detail of the calcite wedges ultrastructure, MTC.D0001. Note the voids entrapped within the calcite crystals.

The ultrastructural subunits of the mammillary layer in modern birds, described above, especially the *CRB sac* are not clearly evidenced in our SEM sections due to different reasons: the rather small number of analyzed samples, the loosely packed content of the *CRB sac* which favors the displacement during the fracturing in the sample preparation. However, the transition from ACC to crystalline wedges can be noticed (Fig. 9a). It was shown that, despite the different ultrastructural basic types to which the birds and megaloolithid eggshells belong, also of the diagenetic changes in the megaloolithid eggshell, the aspects of the crystal growth displayed by the mammillary layer in the SEM images are very similar. Another aspect which endorses the similarities in building the mammillary layer between birds (chicken) and *M. siruguei* is presented in Fig. 9a–b showing the same pattern of calcite crystals growth from the base of the *CRB* above the basal plate *(BP).* Presumably, the not seen CRB sac (*nucleation center*) is located more internally, at the base of CRB crown. The SEM photographs (Fig. 9a–b) illustrate, at progressively increased magnification, the radial-tabular ultrastructure of the individual mammillae above the nucleation centers.

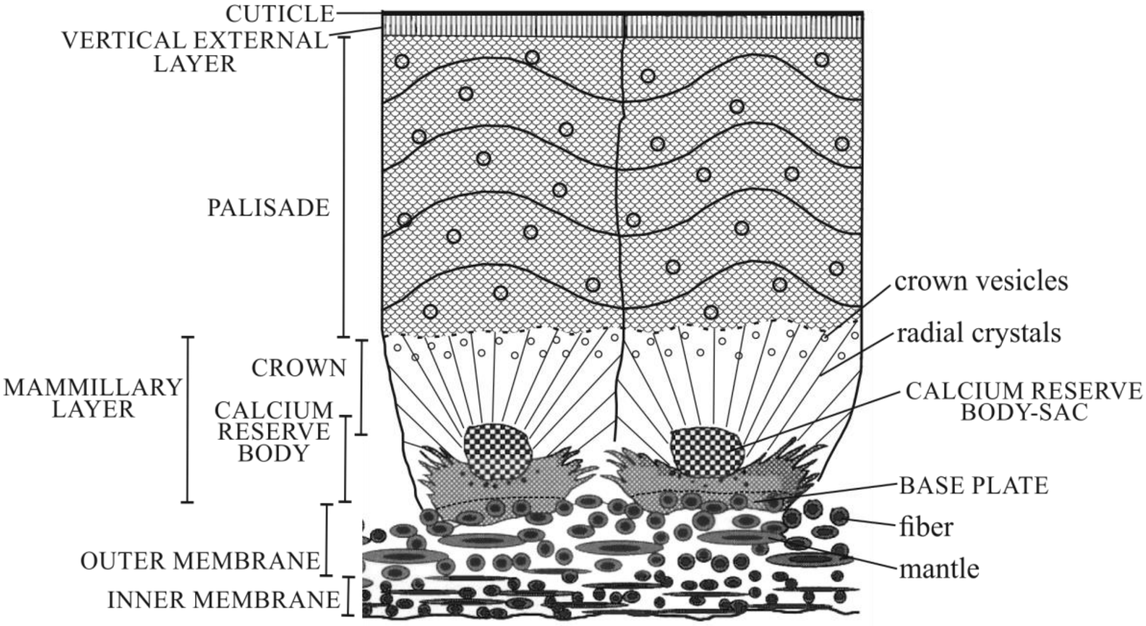

Figure 8. Diagramatic representation of the organic matrix of the chicken eggshell (after Dennis *et al*., 1996).

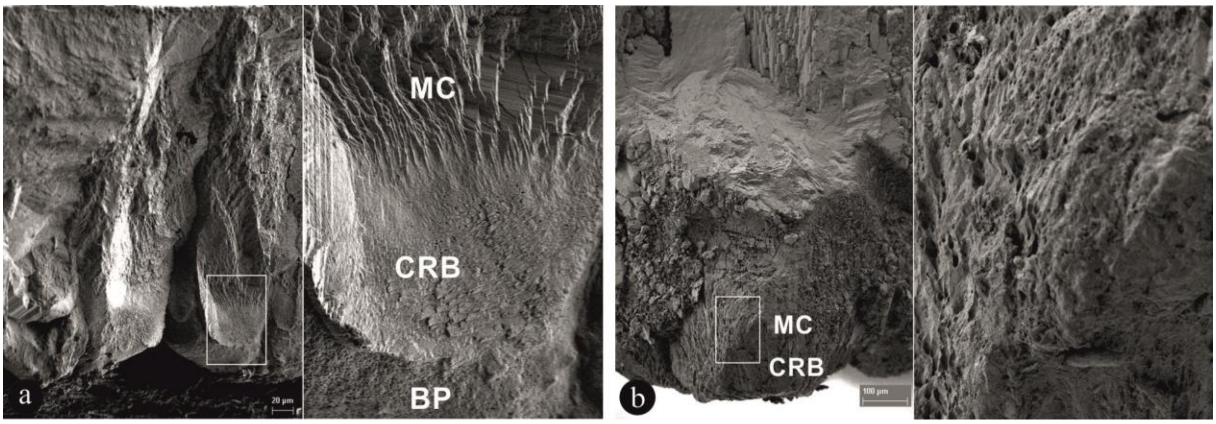

Figure 9. Calcite crystals growth from the base of the ***CRB*** (calcite reserve body) above the basal plate (***BP***) in: a. the chicken eggshell, CPR 0462, x202, magnified 5 times on the right; and b. *Megaloolithus siruguei*, MTC 1920309, magnified 4 times on the right. Note in both cases the compact microgranular texture of the CRB, and the radial-crystalline texture of the mammillary cone (*MC*). Also note the remains of the calcified fibers (*cf)* at the base of the mammilla in *M. siruguei*.

CONTINUOUS LAYER (PALISADE)

In modern avian eggshell the mineral deposition within the organic matrix continues above the mammillary layer to generate the thickest part of the shell. It is composed of tightly packed calcite columns which give a fence or palisade aspect; the columnar structure continues laterally shadowing the distinction among the individual shell units. On these characters the medial layer of the eggshell is denominated *palisade* by ornithologists (e.g. Hinke *et al*., 2012), while the dinosaur oologists prefer to use the term *continuous* layer (e.g. Mikhailov, 1997). In the domestic birds examined in this work, the palisade (PL) thickness vs. the mammillary layer (ML) varies between about 3.5–2.5/1 in chicken, 3.0–2.5/1 in duck and ostrich, 2.5–2.0/1 in turkey, goose, and pigeon (Fig. 10a-c). In birds the palisade columns present a squamatic ultrastructure, composed of cleaved calcite crystals and regular vesicular structures which give a general porous aspect in the SEM sections (Fig. 10d). Characteristic for this layer in birds are the numerous spherical voids and the remains of the organic matrix represented by membrane films with different dimensions and shapes (Fig. 10e). Local interruptions of the regular development of the palisade ultrastructure are sometime encountered (Fig. 10f).

Contrary to birds, which display lateral continuity of the shell units at the palisade level which impede on the recognition of the individual shell units from the base, in the megaloolithid eggshells the distinction of the units is clear from the base to the top of the eggshell with the same radial-tabular ultrastructure continuing from the base of the mammillae to the top of the palisade layer (Fig. 10g). As in birds, in megaloolithid eggshell, the calcite crystals in the continuous layer wedges include numerous entrapped voids, which give a porous aspect to the ultrastructural assemblage (Fig. 10h).

PORES

The pores represent structures developed from the shell membrane during the early stages of biomineralization, which ensure the gas and vapor exchange, essential for the embryo life. Although our comparative study is limited to a relatively small number of samples, belonging to only 6 species of birds, mostly domestic ones, some general aspects regarding the pore system might be concluded. In all the investigated bird eggshells the pore density (no. pores/mm^2) is low and very low: in chicken from 2 pores/47.943 mm^2 (minimal) to 15 pores/0.850 mm^2 (maximal), much lower in pigeon: from 6 pores/1.528 mm^2 to 10 pores/3.68 mm^2. The pores are narrow, with variable diameters (6–55 μm in chicken samples, smaller in the pigeon ones), round to oval in cross section, unevenly distributed, rarely straight from the base to the top of the eggshell, frequently sinuous and branching (Fig. 11a–c). The pore system, common in all the studied bird samples in this work belong to the *angusticanaliculate* type, indicative for a low gas conductance of the eggshell, characteristic for dry terrestrial incubation conditions (Mikhailov *et al*., 1994). The low eggshell porosity in the studied birds differs from the porosity of the megaloolithid eggs from Tuștea (Grigorescu *et al*., 1994; Grigorescu, 2017). Their pore pattern corresponds to the *tubocanaliculate* system, which consists in a complex network of differently shaped canals: straight tubes with funnel-like orifices (Mikhailov, 1997). In tangential sections the pore openings are subcircular, 30 to 70 μm in diameter, and variable along the pore length with bottleneck, Y shapes in cross sections (Fig. 11e–f). Numerous pore openings, up to six, coated on margins with diagenetic sparry calcite surround the closely packed ornamental tubercles (Fig. 11g). In the Tuștea eggshells, the pores cover about 3.7% of the total egg surface, with a pore density of about 100 pores/cm^2 and a calculated average value for shell water vapor conductance of about 2080 mg H_2O day^{-1} $Torr^{-1}$. These values are much higher than those reported for the Argentinian *M. patagonicus* (341 mg H_2O day^{-1}), but about half than those calculated for the *M. siruguei* eggshells from Pinyes, Spain (3979 mg H_2O day^{-1}) (Jackson *et al*., 2008). The eggshell porosity in Tuștea megaloolithids is consistent with a high-humidity, underground, low oxygen incubation environment, supporting the previous inferences of incubation for European megaloolithid eggs (Deeming, 2006).

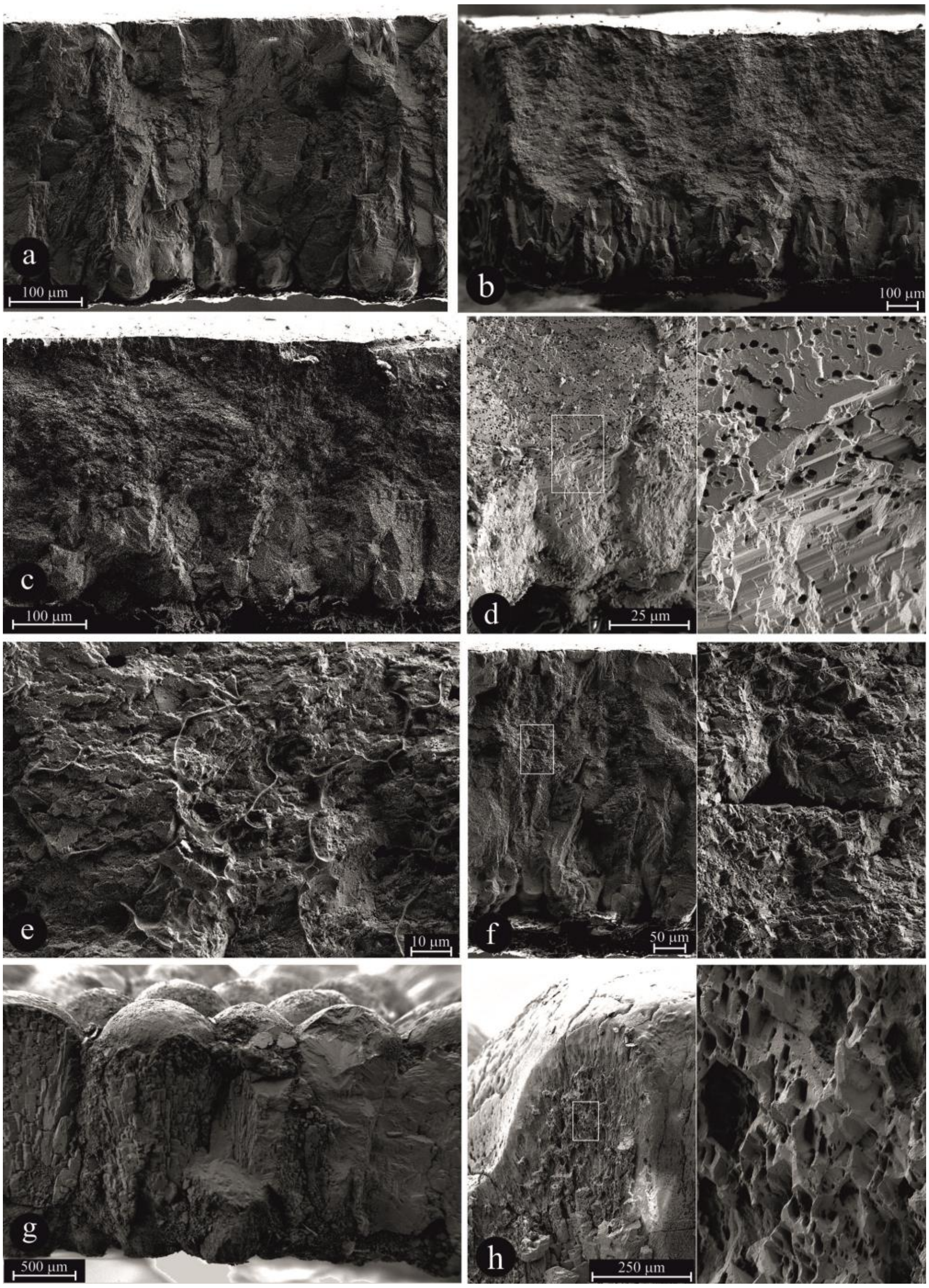

Figure 10. The palisade layer. Radial sections of three domestic bird eggshells showing the different thickness proportion between the mammillary (*ML*) and palisade layer (*PL*) in: a. chicken, CPR 0708; b. ostrich, CPR 1048; c. turkey, CPR 0037. Ultrastructure of the palisade layer in domestic birds: d. Porous nature common for the upper part of the mammillary crown and the palisade, composed of calcite crystals, displaying predominant single orientation of the crystallographic faces and spherical voids in pigeon, CPR 0769, magnified 2.8 times on the right; e. Twisted organic membranes within the squamatic ultrastructure of the palisade in turkey, CPR 0056; f. Dislocation in the chicken palisade ultrastructure, CPR 0722, magnified 12 times on the right. Ultrastructure of the palisade in *Megaloolithus siruguei* from Tuștea: g. The radial-tabular ultrastructure on the entire thickness of the shell units. The ornamental dome-shaped tubercles at the top of the eggshell mark also the distinction of the individual spherolites, MTC D1220132; h. Cleaved calcite crystals and voids at the top of the palisade, MTC C0263, magnified 9 times on the right.

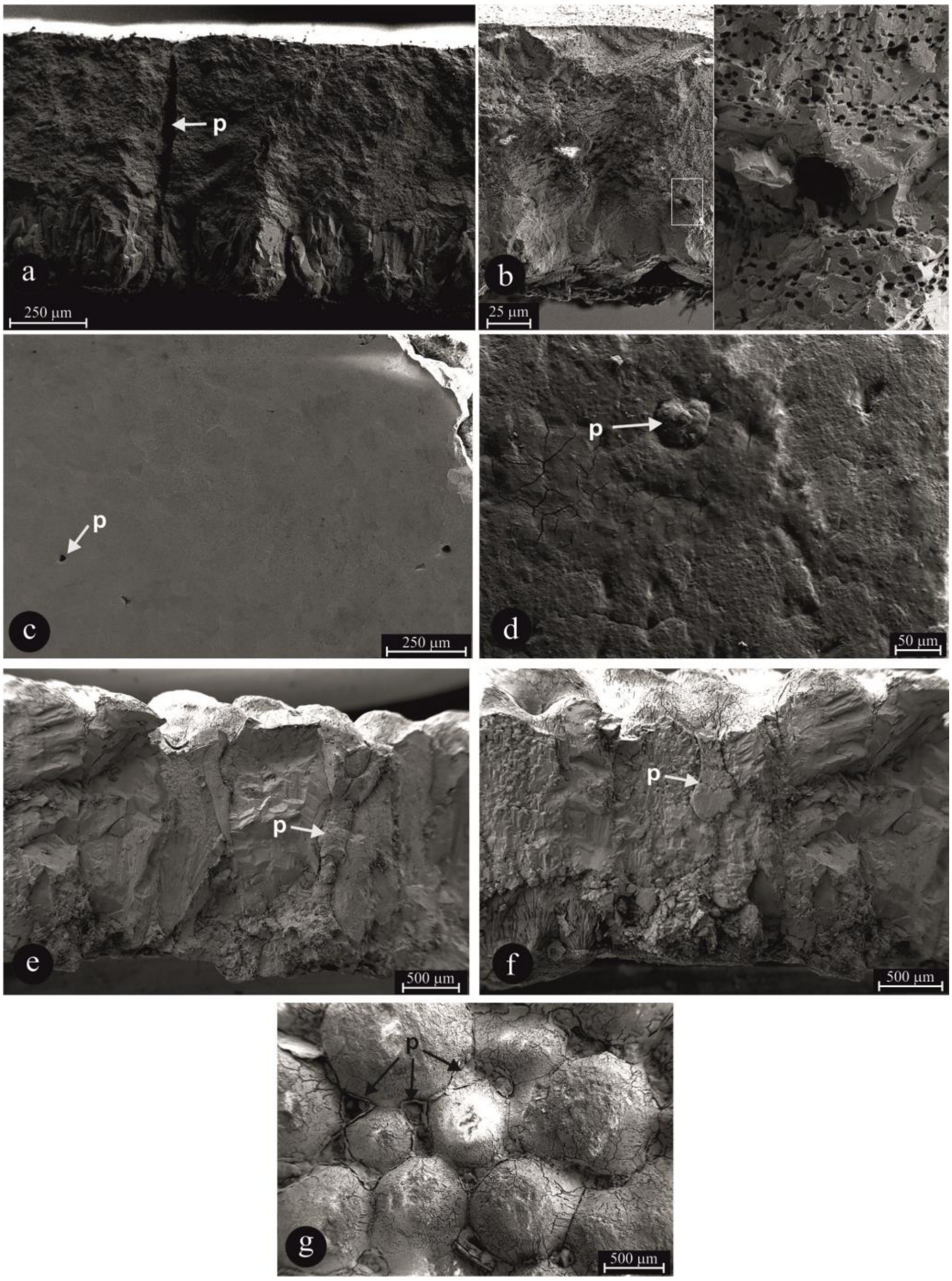

Figure 11. The pore (*p*) characters in birds: a. Radial section in ostrich eggshell showing a straight pore which separates the shell units from the base to the top, CPR 1049; b) Circular profile of a transversal pore (3.35µm in diameter) in a fracture radial section in the pigeon eggshell, CPR 0751, magnified 5.2 times on the right. Note the ultrastructural assemblage made of cleaved calcite crystals and numerous vesicles (c and d). The very low porosity shown on the upper surface of the eggshell in: c. the pigeon (CPR 0780), and d. the chicken (CPR 0697). Note the circular shape of the larger pores openings and the slit-like ones of the smaller ones. Pores in megaloolithid eggshells: e.–f. Radial sections showing the different pore shapes (twisted, Y-shaped, bottle-neck) in the Tuștea eggshells (e. MTC A0134; f. MTC A0135). Note the pore infillings with cemented clastic material and the sparry calcite coatings on the pore margins. g. High density of the pores openings at the top of the Tuștea megaloolithids, five to six subcircular or elliptical openings, isolated or twinned, surrounds the ornamental tubercles (MTC A0478). Note the calcite coatings around the pores.

ABNORMAL SHELL UNITS

Normally the shell units develop continuously from the base of the mammillae up to the top of the eggshell, however abnormalities in the shell units growth were frequently mentioned in both modern and fossil amniotic eggshells: double or multilayered eggshell, shells abnormally thick or thin, secondary shell units which grow above the base of the normal units. A common encountered abnormality is represented by the secondary shell units, consisting in smaller shell units which mimic the true shell units. In a recent study on the secondary shell units in megaloolithid eggshells, Moreno-Azanza *et al*. (2016) recognize three different types of secondary shell units: a) *aborted shell units*, which "grow from the shell membrane but do not reach the outer surface, due to competition with neighboring shell units"; b) *double-layer shell units* which grow above the normal shell units as an additional unit; c) *extra-spherulites*, small radiating shell units developed from the middle of the true shell units. Similar forms to the *a* and *c* types were found also in our study: one in modern birds (chicken) and several in the megaloolithid eggs, exclusively from the Livezi site.

In the chicken case, a tiny secondary shell unit develops just above the shell membrane, similar to the *aborted* type described by Moreno-Azanza *et al*. (2016), but growing slightly above the shell membrane. At an increased magnification it can be noticed the stopping of the radial growing tendency by the pressure of the two neighbor, normally growing, shell units (Fig. 12a).

In the megaloolithid eggshells from Livezi, combinations or special cases of the *a* and *c* types of Moreno-Azanza *et al*. (2016) are recognized, which suggest that the typology of the secondary shell units in the megaloolithid eggshell is more diverse (Fig. 12b–d).

The origin of abnormal shell units in dinosaurs, sometimes mentioned as hypothetical cause of the dinosaurs extinction (Erben *et al*., 1979), was differently interpreted, either due to the primary biological conditions (an imbalance among the hormones, generally involved in the vertebrates fetal development (vasotocin and estrogen), or pathology of the female reproductive system, or stress due to overcrowding, inadequate nutrition, sudden climatic changes (Zelenitsky *et al*., 1997)), or to secondary, diagenetic changes during the taphonomic history (Grellet-Tinner *et al*., 2010). Criteria to be used in distinguishing the primary causes from the secondary ones were discussed by Jackson & Schmitt (2008). The hypothesis that, at least in some cases, the secondary shell units represent taphonomic artifacts, due to diagenetic recrystallization of inorganic calcite around organic relics within the eggshell structure is much documented by the combined study of Moreno-Azanza *et al.* (2016) based on electron backscatter diffraction in combination with SEM and cathodoluminescence analysis.

The state of preservation of the megaloolithid eggshells from Livezi in which most of the primary characters are erased by recrystallization supports the taphonomic origin of the encountered secondary shell units.

DIAGENETIC CHANGES IN MEGALOOLITHID EGGS

Although the eggshells from Tuștea and Livezi which provided the megaloolithid samples studied in this work belong to the same species (*M. siruguei*), the state of the eggshell preservation strongly differs. The ultrastructural aspects displayed by the Tuștea eggshells, seem to preserve much of the original characters, including reminiscences of the soft tissues. The cathodoluminescence analysis revealed that the eggshells were not much affected by diagenesis (Bojar *et al*., 2005). Contrary, the Livezi eggshells are much altered by recrystallization and weathering which impede on the recognition of the primary characters (Fig. 13a–b).

As shown above the pattern of the original radial-tabular and vesicular ultrastructures in the Tuștea eggshell, as well as the pores distribution and size, do not seem to be changed by diagenesis. More eloquent in this regard, also in interpreting the Tuștea taphonomic conditions, are the numerous cases of soft tissue preservation. These include the conservancy of the double layered *membrana testacea* (see Fig 7a–d), the permineralized fibers at the base of the mammillary layer, the compact membrane coverings of the basal plates or the mammillary knobs, the permineralized respiratory channels (Fig. 13c–e).

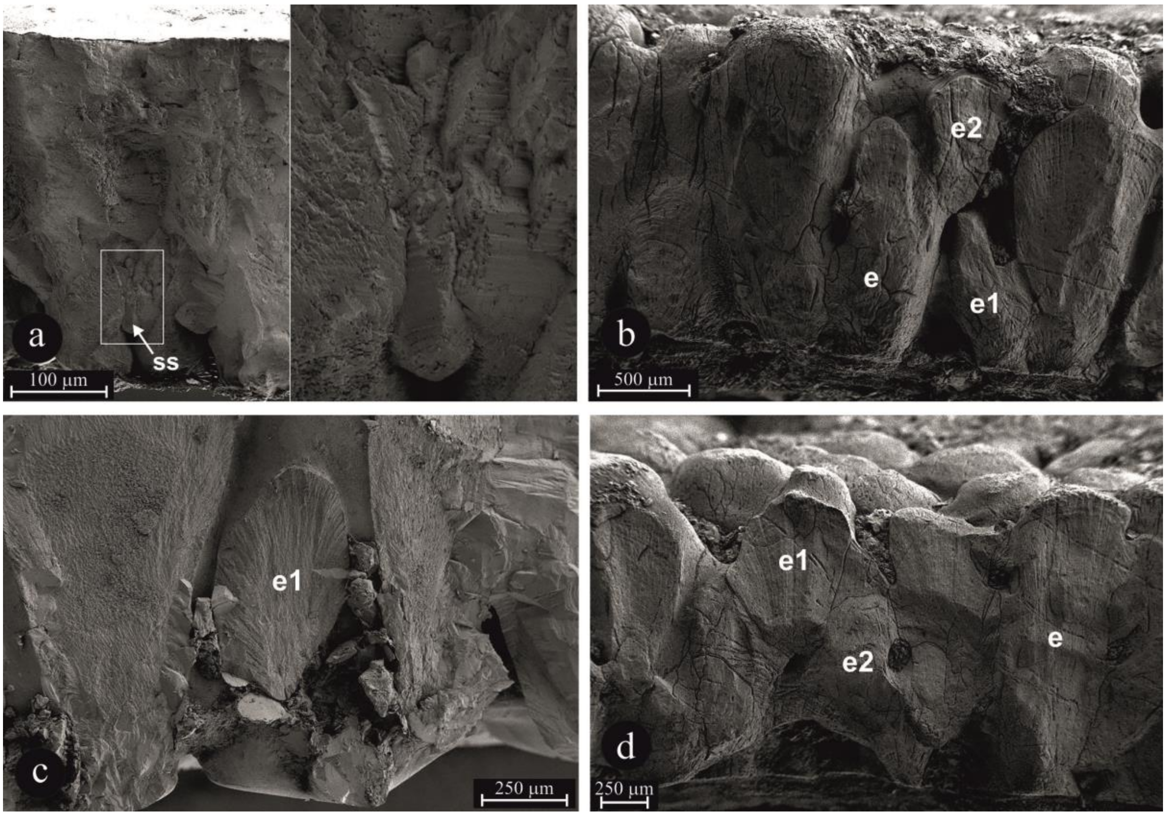

Figure 12. Secondary shell units**:** a. Secondary shell unit (*ss*) developed at the twining base of two units in a chicken eggshell, CPR 0439, magnified 4.5 times on the right. Note the accretion lines in a secondary shell unit continue in the right shell unit. b–d. Secondary shell units in megaloolithid eggshells from Livezi: b. aborted shell unit (e1) stopped in growing by an extraspherulit (e2) grown from un incomplete shell unit (e), MLC 100005; c. aborted shell unit (e1), apparently not influenced by the neighbor shell units, MLC 520010; d. aborted shell unit (e1) and extraspherulit (e2) with similar width to the normal shell unit (e) MLC 10002.

As mentioned by Grellet-Tinner (2005) citing Bottjer *et al*. (2002), the preservation of µm-sized protein strands is rare in the fossil record and therefore must be the result of exceptional taphonomic processes resulting from microbial biomediation. The biomediation can be effective under anoxic conditions, favored by the burial of the eggs during the incubation time or soon after hatchling by a compact mass of fine sediments, like mud, during floodings, which prevents the oxidation. Otherwise, under the air exposure, the soft tissues would be desiccated and finally completely destroyed. The anoxic conditions allow the bacteria to drive the decomposition of the inorganic and organic compounds, preserving the structural arrangements of the crystals and parts of the organic matter.

These were indeed the incubation and taphonomic conditions in Tuștea as recently revised by Grigorescu (2017) and Botfalvai *et al*. (2017). Most probably the incubation of the eggs at Tuștea, took place in a calcic soil, developed during a dry period on the distal part of a relatively low-energy floodplain, sparsely vegetated with low-growing plants (Bojar *et al*., 2005; Therrien, 2005), following the fine sediments deposition in a previous humid season. The females presumably sheltered the eggs from water loss by covering the clutches with fine debris and vegetation. The covered egg clutches hypothesis is sustained by several aspects: the high porosity of the eggshell, the position of pore openings at the base of the external nodes, representing a specialization to facilitate gas and water vapor conductance by preventing obstruction of the openings (Sabath, 1991), also by the identical composition of the infilling and egg-encasing sediments and the reduced quantity of small eggshell fragments within the nests; contrary, under open conditions, the quantity of eggshell fragments resulting from hatching in the nest is large (cf. Mueller–Töwe *et al*., 2002).

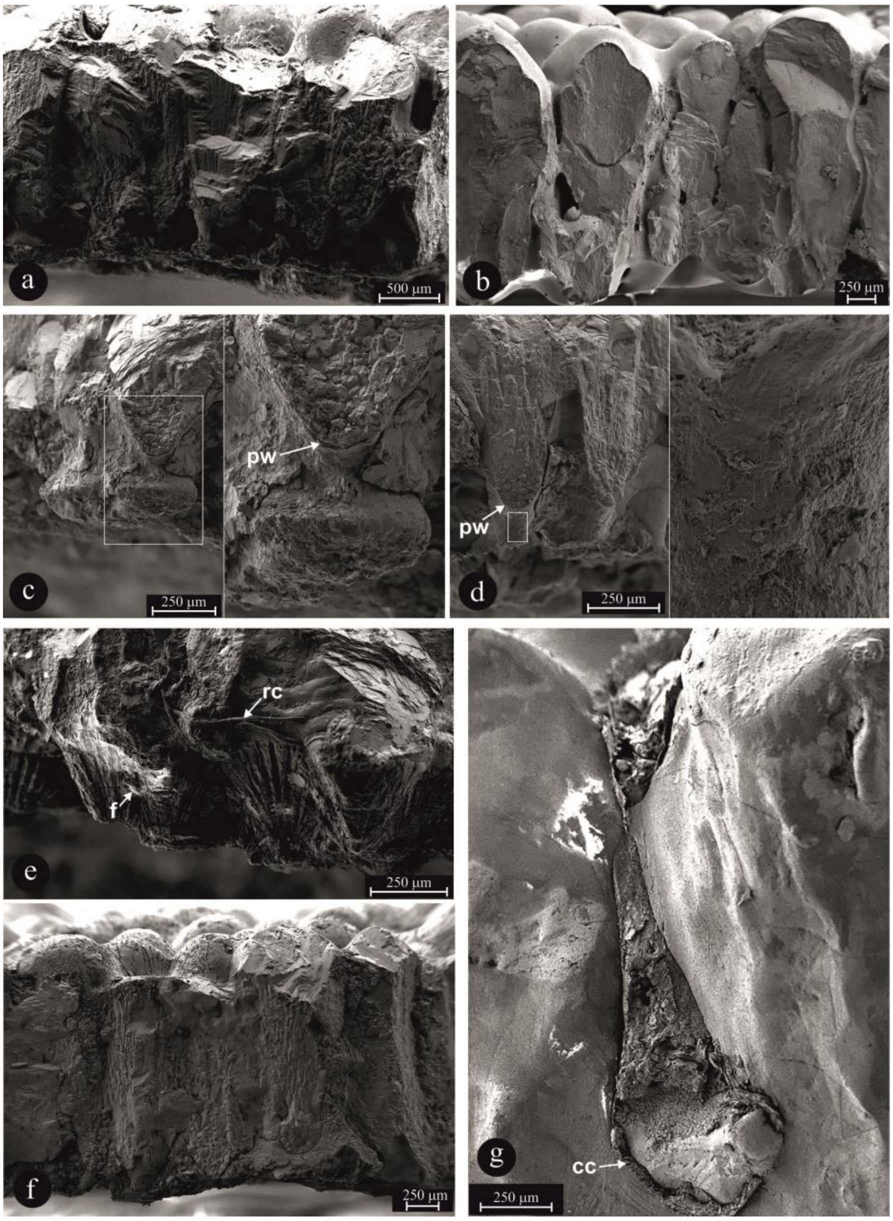

Figure 13. Diagenesis in megaloolithid eggs. Radial thin sections in eggshells from: a. Tuștea, MTC 1450318; and b. Livezi, MLC L520002. Note the well preserved ultrastructures in a, hidden by recrystallization in b. Soft tissue preservation. Upward extensions of the outer *membrana testacea*: c. Permineralized cover (*pw*) of the basal plate (*eisospherite*), MTC 1450332, magnified 1.4 times on the right; d. Permineralized wrapping (*pw*) of the mammilla knob, MTC 1450335, magnified 7 times on the right. Note the amorphous texture of the membranous cover; e. permineralized branching respiratory channel (*rc*) in the mammillary cone, MTC 110120. Note the numerous permineralized membrane fibers, below and above the nucleation center (*f*); f. Radial thin section showing the clear distinction between the underlying clastic cemented material resulted during the eggs burial and early diagenesis, and the preserved radial structure of the shell units, MTC 1920302; g. Sparry calcite coating (*cc*) on the pore margins, MTC 1810220.

The isolation from oxidic condition in Tuștea probably occurred concomitantly with the eggs hatchling by the rapid infilling of the broken eggs by the surrounding sediments which collapsed from the sloping margins of the nests, as indicated by the computed tomographies (Grigorescu, 2017, Fig. 5). It is also possible that the isolation occurred even during the hatching or immediately after that, by a thin flooding mud sheet which covered the nests, inducing the embryo death in all the eggs, or only in those with an underneath position in the nests. Soon after the burial of the egg remains, the dissolution on the eggshell surface started, the resulted voids together with the existing small depression along the uneven surface of the eggshell and with the empty pore canals were filled with fine clastic sediments, subsequently cemented by the calcite precipitated from the percolating solutions (Fig. 13f). Presumably, in a more advanced stage of diagenesis, the calcite crystals in the eggshell structure were replicated in an atom-by-atom process, through the microbial mediation, preserving the original crystallographic characters. During diagenesis, the pore margins and openings were coated by sparry calcite (Fig. 13g).

The precise taphonomic environment of the Livezi eggs is difficult to reconstruct due to the displacement of the samples from the place of incubation. Contrary to Tuștea, where the preserved incubation site was covered by a thick mass of sediments, the section outcropping only after a recent rock fall, in Livezi, the megaloolithid eggshells and egg fragments were for a long period of time exposed to the surface. Although in light microscopy the signs of weathering are not obvious on the eggshell inner and outer surfaces, the SEM sections on fractured eggshells display the high alteration of the primary ultrastructure through recrystallization. Probably recrystallization has been developed in successive phases of diagenesis in oxidic conditions which destroyed the organic matrix and determined the fusion and compaction of the calcite crystals. It is difficult to conclude if the oxidic environment characterized the original condition of the eggs incubation in Livezi, or this was secondarily achieved by the eggshells displacement.

ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS) DATA

Generally, the EDS elemental analysis shows a similar content variation and weight per cent ratios of the most common elements (C, O, Ca) in the two eggshell categories, in both membrana testacea (MT) and hard shell (Fig. 14a–d; Table 1). Close similarities in the three elements distribution were noticed at the interface between the MT and the mammillary layer, at the base of the mammillary knobs, but with many differences at the inner part of the MT. Table 1 shows the **Membrane** row in two columns: *interstices*, meaning spaces between mammillary knobs and *base mammilla*. The elemental contents in the two zones were analyzed by spectra in horizontal plane for the megaloolithid eggshell while for the chicken the spectral data were shown in radial sections. As mentioned above, the C, O, and Ca content and the three ratios: Ca/C, O/C, O/Ca are similar to very similar at the base of the mammillae and, generally, in the hard eggshell (Table 1). The similar contents and ratios in the eggshell parts in which the mineral composition prevail on the organic one confirm the minimal diagenetic alteration of the megaloolithid eggshells, as indicated by the ultrastructural analysis. The differences at the inner part of the MT are most probably due to the diagenetic calcification of the collagen fibers during the early stage of the hatched megaloolithid eggs burial.

The Ca content continues to increase, not-linearly, from the mammillary cone to the palisade layer. Some decreases in the Ca content and variations in O and C which were noticed in the vertical elemental distribution through the shell are probably due to the position of spectra on the pore spaces, voids or defects in the shell structure.

Similar distributions of minor elements (Na, Mg, K), rarely more than 1%, are also seen in the megaloolithid and chicken eggshells.

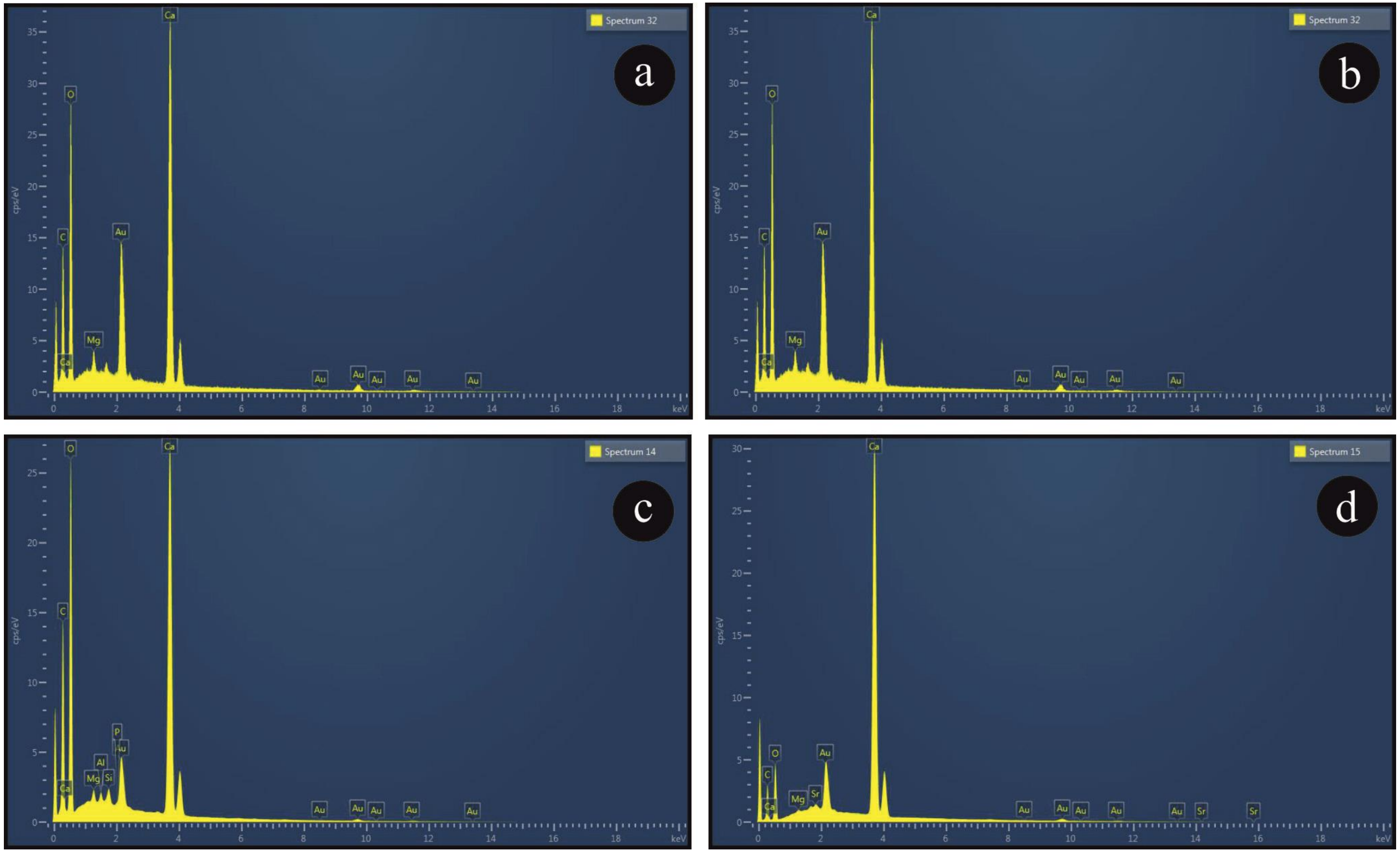

Figure 14. Energy dispersive X-ray spectroscopy (EDS) elemental profiles of *Megaloolithus siruguei* membrane (c) and shell (d) compared to extant chicken membrane (a) and shell (b). The comparison reveals similar content of C, O, and Ca. Mg is the only common trace element, whereas Al, Si, and P are present only in the *M. siruguei* membrane, probably in connection with the taphonomic infilling of the eggshell voids with clastic material.

Table 1.

The content (weight %) of the most common elements (C, O, Ca) in the membrane and shell of *Megaloolithus siruguei* from Tuştea, extant chicken, and ostrich. In the lower part of the table, the relative values of Ca/C, O/C, and O/Ca. Note the differences among the Ca content in the shell unit (*base mammilla*) and the interstices, in both *M. siruguei* and chicken.

Elements	*Megaloolithus* - Tuştea			Chicken			Ostrich	
	Membrane		Shell	Membrane		Shell	Membrane	Shell
	Interstices	Base mammilla		Inner part	Base mammilla			
	Limits of variation							
C	6.84-20.56	13.77-34.01	8.93-24.07	61.20-80.49	21.77-23.54	1.15-22.92	20.08-26.47	11.95-22.69
O	44.43-52.64	35.84-45.20	22.43-55.14	11.32-14.42	39.86-45.29	30.42-65.69	61.44-72.17	47.91-65.26
Ca	2.48-37.92	26.29-49.10	20.13-59.40	1.53-5.23	32.05-37.59	11.07-68.37	0.34-17.94	12.05-39.95
Ca/C	1.23	1.73	2.74	0.04	1.54	2.01	0.37	1.12
O/C	3.77	1.67	2.29	0.17	1.89	3.48	2.85	3.11
O/Ca	3.05	0.96	0.83	4.33	1.22	1.72	7.63	2.77

Different values are shown for Si and Al, the two elements closely associated in the chemical composition of minerals. Both elements are missing in the chicken membrane and shell, with only one exception on an organic fiber in the inner MT which shows relatively high values for Si (11.63) and Al (2.42). Contrary Si and Al are always present in the dinosaur eggshell membrane (0.37–25.78 weight % for Si, respectively 0.28–12.43 for Al) and frequently in the shell (0–30.26 weight % for Si and 0–9.95 for Al). The highest values for both elements are registered in the interstices between the mammillary knobs where Si overpass the Ca value, but not in all the cases Si and Al are present in these zones. The high values of Si and Al in the shell are shown at the base of the mammillary layer, or at different levels, probably corresponding to the pore infillings. We interpret the differences in Si and Al values between the fossil and extant eggshells as a result of the fossil eggs burial when the uneven parts of the eggshell surface and the pores were infilled with the surrounding mudstone material, dominated by clay minerals rich in Si and Al. Some diagenetic substitution of minerals might be also involved, but less probable taking into account the minimal diagenetic alteration indicted by the SEM ultrstructures. To draw a clearer conclusion, more detailed chemical analyses are needed.

The limited number of EDS we did on the ostrich eggshell prevents us to comment on the ostrich closer similarity with sauropod eggshells than to other extant shells which was concluded in a elaborated study by Schweitzer *et al*. (2005).

CONCLUSIONS

Intensively studied in the last two decades, the biomineralization processes in modern birds (e.g. the transition from the organic matrix to the calcite crystals) in the dinosaur eggshell ware rarely investigated.

Recent studies on the matrix-mineral relationship in the avian eggshell growth and the ultrastructure development (Chien *et al*., 2008; Nys & Guyot, 2011; Hincke *et al*., 2012; Rodríguez-Navarro *et al*., 2015) offer an excellent comparative basis in interpreting the biomineralization processes in the dinosaur eggshell formation.

Although the two eggshell categories compared in the present study belong to different basic morphotypes: the birds to the ornithoid morphotype, respectively the megaloolithids to the dinosauroid-spherulitic basic type (Mikhailov, 1997), the main phases of biomineralization, starting from the development on the organic fibers of the shell membrane of disk-shaped amorphous calcium carbonate (ACC), followed by the nucleation and stabilization of ACC into the calcite crystals of the hard shell, are very similar.

The present study was enabled by the lack of major diagenetic changes of the Tuştea eggshells, favored by the taphonomic conditions which allowed the preservation of reminiscences of the original soft tissues. Contrary, the advanced diagenesis of the Livezi eggshells, the other site in the Hațeg Basin which provided megaloolithid remains studied here, has replaced almost totally the primary characters and, probably it is at the origin of the described abnormal shell units. The role of diagenesis in this case and, generally, in the megaloolithid ultrastructures needs further clarifications.

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REFERENCES

Bojar, A.-V., Grigorescu, D., Ottner, F., Csiki, Z., 2005. *Palaeoenvironmental interpretation of dinosaur-and mammal-bearing continental Maastrichtian deposits, Haţeg basin, Romania*. Geological Quarterly, 49(2), 205–222.

Chien, Y.C., Hincke, M.T., Vali, H., McKee, M.D., 2008. *Ultrastructural matrix-mineral relationships in avian eggshell, and effects of osteopontin on calcite growth in vitro*. Journal of Structural Biology, 163(1), 84–99. https://doi.org/10.1016/j.jsb.2008.04.008

Deeming, D.C., 2006. *Ultrastructural and functional morphology of eggshells supports the idea that dinosaur eggs were incubated buried in a substrate*. Palaeontology, 49(1), 171–185. DOI: 10.1111/j.1475-4983.2005.00536.x

Dennis, J.E., Xiao S.-Q., Agarwal, M., Fink, D.J., Heuer, A.H., Caplan A.I., 1996. *Microstructure of matrix and mineral components of eggshells from White Leghorn chickens (Gallus gallus).* Journal of Morphology, 228(3), 287–306. https://doi.org/10.1002/(SICI)1097-4687(199606)228:3<287::AID-JMOR2>3.0.CO;2-#

Erben, H.K., Hoefs, J. & Wedepohl, K.H., 1979. *Paleobiologic and isotopic studies of eggshells from a declining dinosaur species*. Paleobiology, 5, 380–414. https://doi.org/10.1017/S0094837300016900

Gill, F.B., 2007. *Ornithology*. Third edition. W.H. Freeman, 720 p.

Grellet-Tinner, G., 2000. *Phylogenetic interpretation of eggs and eggshells of Palaeognathae*. In: Bravo, A.M. & Reyes, T. (eds.) First International Symposium on Dinosaur Eggs and Babies. Spain, Isona i Conca Della' Catalonia, pp. 61–75.

Grellet-Tinner, G., 2005. *Membrana testacea of titanosaurid dinosaur eggs from Auca Mahuevo (Argentina): Implications for exceptional preservation of soft tissue in Lagerstätten*. Journal of Vertebrate Paleontology, 25(1), 99–106. http://www.jstor.org/stable/4524421.

Grellet-Tinner, G., Corsetti, F. & Buscalioni, A.D., 2010. *The importance of microscopic examinations of eggshells: Discrimination of bioalteration and diagenetic overprints from biological features*. Journal of Iberian Geology, 36(2, 181–192. doi:10.5209/rev_JIGE.2010.v36.n2.6.

Grigorescu, D., 2017. *The 'Tuştea puzzle' revisited: Late Cretaceous (Maastrichtian) Megaloolithus eggs associated with Telmatosaurus hatchlings in the Haţeg Basin*. Historical Biology, 29(5), 627–640. https://doi.org/10.1080/08912963.2016.1227327.

Grigorescu, D., Garcia, G., Csiki, G., Codrea, V., Bojar, A.-V., 2010. *Uppermost Cretaceous megaloolithid eggs from the Haţeg Basin, Romania, associated with hadrosaur hatchlings: Search for explanation*. Palaeogeography, Palaeoclimatology, Palaeoecology, 293, 360–374. https://doi.org/10.1016/j.palaeo.2010.03.031

Grigorescu, D., Weishampel, D., Norman, D., Şeclăman, M., Rusu, M., Baltreş, A., Teodorescu, V., 1994. *Late Maastrichtian dinosaur eggs from the Haţeg Basin (Romania).* In: Carpenter, K., Hirsch, K.F. & Horner, J.R. (eds.) Dinosaur eggs and babies, Cambridge University Press, pp. 75–87.

Hincke, M.T., Nys, Y., Gautron, J., Mann, K., Rodriguez-Navarro, A.B., McKee, M.D., 2012. *The eggshell: structure, composition and mineralization*. Frontiers in Bioscience, 17, 1266–1280.

Hirsch, K.F., Quinn, B., 1990. *Eggs and eggshell fragments from the Upper Cretaceous Two Medicine Formation of Montana.* Journal of Vertebrate Paleontology, 10(4), 491–511. https://doi.org/10.1080/ 02724634.1990.10011832

Jackson, F.D., Schmitt, J.G., 2008. *Recognition of vertebrate egg abnormalities in the Upper Cretaceous fossil record.* Cretaceous Research, 29(1), 27–39. https://doi.org/10.1016/j.cretres.2007.02.004

Jackson, F.D., Schweitzer, M.H., Schmitt, J.G., 2002. *Dinosaur eggshell study using scanning electron microscopy.* Scanning, 24, 217–223. doi: 10.1002/sca.4950240501.

Jackson, F.D., Garrido, A., Schmitt, J.G., Chiappe, L.M., Dingus, L., Loope, D.B., 2004. Abnormal, multilayered titanosaur (Dinosauria: Sauropoda) eggs from in situ clutches at the Auca Mahuevo locality, Neuquen Province, Argentina. Journal of Vertebrate Paleontology, 24(4), 913–922. https://doi.org/10.1671/ 0272-4634(2004)024[0913:AMTDSE]2.0.CO;2

Jackson, F.D., Varicchio, D.J., Jackson, R.A., Vila, B., Chiappe, L.M., 2008. *Comparison of water vapor conductance in a titanosaur egg from the Upper Cretaceous of Argentina and* a *Megaloolithus siruguei egg from Spain*. Paleobiology, 34(2), 229–246. https://doi.org/10.1666/0094-8373(2008)034 [0229:COWVCI]2.0.CO;2

Mikhailov, K.E., Bray, E.S., Hirsch, K.F., 1996. *Parataxonomy of fossil egg remains (Veterovata): principles and applications*. Journal of Vertebrate Paleontology, 16(4), 763–769. https://doi.org/10.1080/ 02724634.1996.10011364.

Mikhailov, K.E., 1997. *Fossil and recent eggshell in amniotic vertebrates: fine structure, comparative morphology and classification*. Special Papers in Palaeontology, 56, 1–80.

Moreno-Azanza, M., Bauluz, B., Canudo, J.I., Gasca, J.M., Fernández-Baldor, F.T., 2016. *Combined use of electron and light microscopy techniques reveals false secondary shell units in Megaloolithidae eggshells*. PLoS ONE 11(5), e0153026. https://doi.org/10.1371/journal.pone.0153026.

Mueller-Töwe, I.J., Sander, P.M., Schüller, H., Thies, D., 2002. *Hatching and infilling of dinosaur eggs as revealed by computed tomography*. Palaeontographica, Abteilung A, 267(1), 119–168.

Nys, Y., Gautron, J., Garcia-Ruiz, J.M., Hincke, M.T., 2004. *Avian eggshell mineralization: biochemical and functional characterization of matrix proteins*. Comptes Rendus Palevol, 3(6–7), 549–562. https://doi.org/ 10.1016/j.crpv.2004.08.002.

Nys,Y., Guyot, N., 2011. *Egg formation and chemistry*. In: Nys, Y., Bain, M. & Van Immerseel, F. (eds.) Improving the Safety and Quality of Eggs and Egg Products, Volume 1: Egg Chemistry, Production and Consumption, Woodhead Publishing, pp. 81–132. doi:10.1533/97808570939 12.2.83

Ping, H., Xie, H., Wan, Y., Zhang, Z., Zhang, J., Xiang, M., Xie, J., Wang, H., Wang, W., Fu, Z., 2016. *Confinement controlled mineralization of calcium carbonate within collagen fibrils*. Journal of Materials Chemistry B, 4, 880–886. http://dx.doi.org/10.1039/C5TB01990G

Rodríguez-Navarro, A.B., Marie, P., Nys, Y., Hincke, M.T., Gautron, J., 2015. *Amorphous calcium carbonate controls avian eggshell mineralization: A new paradigm for understanding rapid eggshell calcification*. Journal of Structural Biology, 190(3), 291–303. doi: 10.1016/j.jsb.2015.04.014

Sabath, K., 1991. *Upper Cretaceous amniotic eggs from the Gobi Desert*. Acta Palaeontologica Polonica, 36(2), 151–191.

Schweitzer, M.H., Chiappe, L., Garrido, A.C., Lowenstein, J.M., Pincus S.H., 2005. *Molecular preservation in Late Cretaceous sauropod dinosaur eggshells*. Proceedings of the Royal Society B: Biological Sciences, 272(1565), 775–784. doi:10.1098/rspb.2004.2876.

Therrien, F., 2005. *Palaeoenvironments of the latest Cretaceous (Maastrichtian) dinosaurs of Romania: insights from fluvial deposits and paleosols of the Transylvanian and Haţeg basins*. Palaeogeography, Palaeoclimatology, Palaeoecology, 218(1–2), 15–56. https://doi.org/10.1016/j.palaeo.2004.12.005.

Zelenitsky, D.K., Hills, L.V., 1997. *Normal and pathological eggshells of Spheroolithus albertensis, oosp. nov., from the Oldman Formation (Judith River Group, late Campanian), Southern Alberta.* Journal of Vertebrate Paleontology, 17(1), 167–171. https://doi.org/10.1080/02724634.1997.10010960.

GEOLOGICAL RESERVES IN ROMANIA

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Preamble

In order to enhance the knowledge on the most important geological sites, ProGEO – the European Association for the Conservation of the Geological Heritage, promotes a more organized presentation by countries and regions of the geological reserves. This is considered a necessary step in a more complex understanding of the nature with two distinct but firmly interconnected components: the *biodiversity* (the animated part of the nature) and the *geodiversity* (the inanimate one), an approach which might sustain a more efficient protection. Romania is a ProGEO member since 1991 when the First International Symposium on the Conservation of our Geological Heritage took place at Digne-les-Bains (France), ended by the "Declaration of the Rights of the Memory of the Earth". Romania is also a founder member of the ProGEO Working Group 1-Balkans and Turkey established in 1995, participating actively in the meetings and joint activities of the Group. A more recent initiative of the ProGEO WG1 is to publish a selection of the most representative geological reserves in Balkans and Turkey. We accomplish here this task, by the presentation of 15 geological reserves in Romania which belong to different categories: paleontological, stratigraphical, mineralogical and petrological, speleological, historical. The articles, written by well-known Romanian palaeontologists, geologists and speleologists, are organized in an informative system in order to provide the data on the location, accessibility, brief description, scientific and touristic information of the sites, references, also illustrated by maps, site views, geological objects. The short articles are addressed not only to geologists, but to other naturalists, also to the general public which should be properly informed on the values of the natural heritage in order to sustain a minimum of geological education, which practically disappeared in the School. We hope the presentation of the outstanding geological reserves will continue in the following issues of the Revue Roumaine de Geologie, tomes 61–62, in its constant endeavor of promoting the values of the Romanian Geology.

Avant-propos

Afin de renforcer les connaissances sur les plus importants sites géologiques, ProGEO, l'Association Européenne pour la Conservation du Patrimoine Géologique, promeut une présentation plus organisée des réserves géologiques, par pays et régions. Cela est considéré comme une étape nécessaire pour avoir une compréhension plus approfondie de la nature, avec ses deux différentes parties, qui sont étroitement interconnectés: la biodiversité (la partie animée de la nature) et la géodiversité (la partie inanimée de la nature). C'est une approche qui pourrait soutenir une protection plus efficace. La Roumanie est membre de ProGEO depuis 1991. C'est l'année où le premier Colloque International sur la Conservation de notre Patrimoine Géologique a eu lieu à Digne-les-Bains (France). Il a été clôturé par la « Déclaration des droits de la mémoire de la Terre ». La Roumanie est aussi membre fondateur du Groupe de travail ProGEO 1 (les Balkans et la Turquie), établi en 1995 – notre pays participe d'une façon active aux réunions et aux activités communes du Groupe. Une initiative plus récente du Groupe de travail ProGEO 1 consiste à publier une sélection des réserves géologiques les plus représentatives qui se trouvent en Balkans et en Turquie. Nous y accomplissons cette tâche, en présentant 15 réserves géologiques de la Roumanie, qui appartiennent à de différentes catégories: la paléontologie, la stratigraphie, la minéralogie et la pétrologie, la spéléologie, l'histoire. Les articles, écrits par des renommés paléontologues, géologues et spéléologues roumains, sont organisés dans un système d'information, afin de fournir : des données sur la localisation, sur l'accessibilité, une brève description, des informations scientifiques et touristiques des sites, des renseignements, des cartes, les panoramas des sites, des objets géologiques. Ces articles courts s'adressent non seulement aux géologues, mais également aux autres naturalistes, ainsi qu'au grand public, qui doit être correctement informé des valeurs du patrimoine naturel. Le but de cette action est de renforcer l'éducation géologique, qui a pratiquement disparu de l'École. Nous espérons que la présentation des réserves géologiques exceptionnelles continuera dans les prochains numéros de la *Revue Roumaine de Géologie,* tomes 61–62, qui fait des efforts constants de promouvoir les valeurs de la géologie roumaine.

PERŞANI QUATERNARY BASALTIC FIELD (BRAŞOV COUNTY)

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Type: Geological natural reserves: Racoșul de Jos (site 1) – 95 ha. Category IV IUCN; Comăna – Piatra cioplită (site 3) – 1 ha. Category III IUCN; Bogata (site2) – not yet declared natural reserve.

Coordinates: Racoşul de Jos (site 1): N 46°1′33.87″/ E 25°25′32.28″
Bogata (site 2): N 45°57′17.48″/ E 25°21′27.42″
near Comăna (site 3): N 45°53′27.95″/ E 25°18′8.19″

Access: Locations described here are three abandoned quarries, each of which displays volcanic stratigraphy as well as transitions to post-volcanic covering units. Site 1 (Racoşul de Jos): proceed north of the village towards the mesa above, which is the old quarry. A clearly marked sign points to the location of the columnar basalts, which require a short, 300 m hike from the parking lot at the end of the road. Site 2 (Bogata area/Barc): the old quarry at Barc is accessible from the main road from Brasov to Târgu Mureş (DN13). A short drive along an unpaved road from location N 45°57′37″/ E 25°21′14″ toward the SW leads to an extensive quarried area called the Old Barc quarry. Immediately to the north, there is an active, "New Barc" quarry. Access to New Barc requires permission from Vectra company, sometimes granted on location. Site 3 (Comăna): At the southern end of the volcanic field, drive to Comăna de Jos along the Hoghiz – Şercaia road (DN15). From there, proceed eastward to Comăna de Sus and onward for about 3 km along the unpaved road of the Comăna Valley until the old quarry becomes visible on the right-hand side. All sites are within 300 m or less from roads accessible by cars or small buses and do not require 4×4 transportation.

Description: The Perşani basaltic field comprises several Quaternary lava flows and pyroclastic deposits located in an extensional basin within and immediately west of the Perşani Mountains in the oroclinal bend area of the East Carpathian Mountains (Downes *et al*., 1995; Harangi *et al*., 2013). The area is well known following a series of high profile studies performed over the past twentysomething years starting with the pioneering papers by Downs *et al*. (1995) on basalts and Vaselli *et al*. (1996) on mantle xenoliths. The area is forested and the best outcrops are found in numerous quarries, some of which are still active and require permission from the owners/operators to be visited. Products of the volcanic field rest on top of Mesozoic basalts, limestone or flysch deposits in the southwest, whereas elsewhere they were erupted onto regionally extensive Miocene silicic tuff whose source is not known and other Miocene terrigenous deposits (Fig. 1, Panaiotu *et al*., 2013). Various undated volcaniclastic and lacustrine deposits represent the cover of the basaltic field. Volcanic products amount to about 5 km^3, making it an average sized continental extensional basaltic field although individual lava flows can be as thick as 20 m, which is somewhat larger than average flows in similar fields. Cinder cones are identifiable in some places (Fig. 2, Racoș cinder cone) and inferred in others, and they represent the most likely source areas for lava flows. Petrographically, almost all rocks are olivine-phyric alkali basalts; many of them are primitive and contain mantle-derived xenoliths (Fig. 3). Basaltic melts were generated at shallow mantle levels (50–60 km) presumably by decompression melting of the asthenosphere (Harangi *et al*., 2013).

Age and origin: Flows and pyroclastic deposits range in age from 1.2 Ma to 0.68 Ma (Panaiotu *et al*., 2013, see Fig. 1) and represent five or possible six individual eruptive events. The Perșani field, while contemporaneously formed with the southernmost parts of the nearby calk-alkaline arc of Călimani –

Gurghiu – Harghita is not genetically related to it. This basaltic field is in some form driven by the poorly understood continental extension in the region and was speculatively connected to the "trap-door" delamination mechanism of the Vrancea slab.

Importance:

a. ***Geologic*:** Two of the three locations (Comăna and Racoş) have been designated as geologic monuments due to the presence of columnar textures in basaltic flows, whereas the third one (the Bogata region and specifically the Old Barc quarry in the Bogata region), while not technically a protected area, contains similar if not better columnar features as well as easily identifiable mantle xenoliths. Columnar basalts form when a lava flow cools and decreases in volume leaving a columnar pattern of fractures that are perpendicular to the cooling surface (Fig. 4). While the Perşani monuments at Racoș and Comana expose some large scale examples of columnar basalts, such features also form at smaller scale throughout the volcanic field. In addition, normal faults typical for this extensional basaltic field are visible in the quarries, as well as in the volcanic stratigraphy. All outcrops reveal a complex volcanic stratigraphy above and below the columnar basalts. Of great significance is the presence of mantle xenoliths in many of these flows (Vaselli *et al*., 1996). Peridotites made of olivine, two pyroxenes and spinel are physical samples form the Earth's lithospheric mantle beneath the Carpathians. Among the peridotites from Perșani, some represent the most isotopically depleted rocks of the continental lithosphere in Europe and perhaps even globally (Vaselli *et al*., 1996), and are probably fragments of Eastern European craton subducted under the Carpathian orogen. The Bogata area is rich in xenoliths, while at Racoş the only xenolith-bearing flow is the one at Mateiaș, south of the village of Racoș, a site not described here. The most abundant xenolith-bearing flow is the one uncovered by the New Barc quarry; this is possibly the most abundant xenolith-bearing flow in Europe. Here, xenoliths are as large as 40 cm in diameter. Complex petrographic and textural features include but are not limited to cross-cutting veins of pyroxenites.

b. Historical: Several quarries from Racoș were in activity since the late 19th century (the main Racoș quarry started rock cutting in 1880). Cubical basalt cuttings from Racoș were used for cobblestones that paved the bulk of many cities in Trasylvania (Sibiu, Brașov, Cluj Napoca, etc.) as well as European capitals and were prominently used in Bucharest, Budapest and Vienna. The main operation was owned in its beginnings by the Glassner Brothers outlet from Budapest. Ownership changed to a Cluj based private company ("Carierele de Piatră de Granit Poieni") after 1918. The company was nationalized by the Romanian Communist Party in 1948. Over time, several generations of skilled workers were trained in the nearby villages. Today quarrying operation and various forms of stone cutting continue at Mateiaș under the ownership of Olhib, a local private company founded in 1999. The Racoș quarries are permanently closed and were turned into a protected geologic site.

REFERENCES

Downes, H., Seghedi, I., Szakács, A., Dobosi, G., James, D.E., Vaselli, O., Rigby, I.J., Ingram, G.A., Rex, D., Pécskay, Z., 1995. *Petrology and geochemistry of the late Tertiary/Quaternary mafic alkaline volcanism in Romania*. Lithos 35: 65–81.

Harangi, S., Sági, T., Seghedi, I., Ntaflos, T., 2013. *A combined whole-rock and mineral-scale investigation to reveal the origin of the basaltic magmas of the Perşani monogenetic volcanic field, Romania, Eastern-Central Europe*. Lithos 180–181: 43–57.

Panaiotu, C.G., Jicha, B.R., Singer, B.S., Ţugui, A., Seghedi, I., Panaiotu, A.G., Necula, C., 2013. *40 Ar/39 Ar chronology and paleomagnetism of Quaternary basaltic lavas from the Perşani Mountains (East Carpathians)*. Physics of the Earth and Planetary Interiors 221: 1–14.

Vaselli, O., Downes, H., Thirlwall, M., Dobosi, G., Coradossi, N., Seghedi, I., Szakacs, A., Vannucci, R., 1995. *Ultramafic xenoliths in Plio-Pleistocene alkali basalts from the Eastern Transylvanian Basin: depleted mantle enriched by vein metasomatism*. Journal of Petrology 36(1): 23–53.

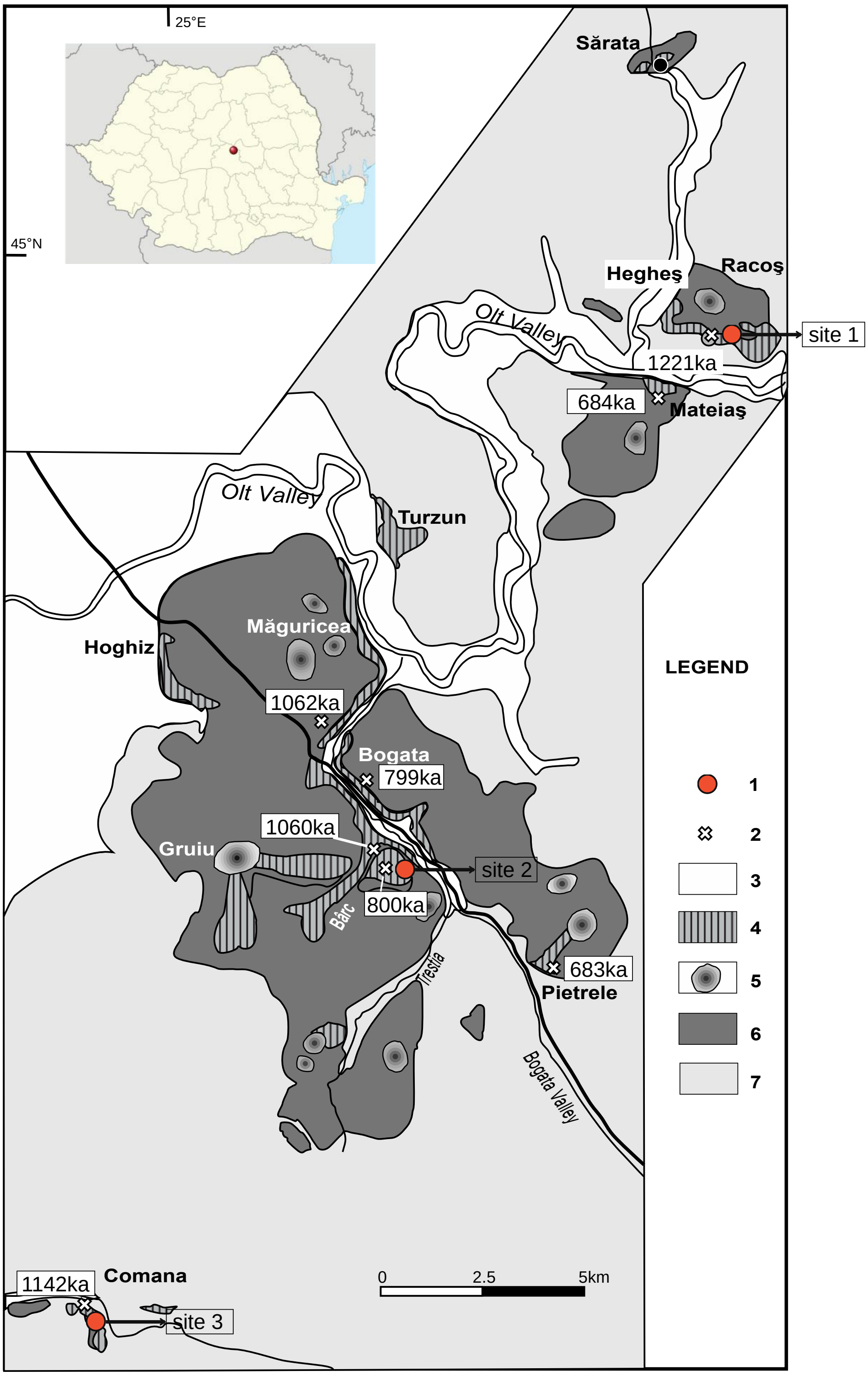

Figure 1. Simplified geologic map of the Racoş region (modified after Panaiotu *et al.*, 2013). Inset shows location of area within Romania. Key: 1 – locations of sites described in text, 2 – Ar/Ar age; 3 – Holocene alluvia; 4 – lava flows; 5 – scoria cones; 6 – pyroclastic rocks (phreatomagmatic deposits); 7 – pre-volcanic basement (Mesozoic and Cenozoic)

Figure 2. Cinder cone representing the main vent at the Racoș locality.
The vent and its intricate structure are well exposed in this abandoned quarry (Photo M. Ducea)

Figure 3. Left panel – peridotite xenolith in volcanic bomb from Mateiaș, right panel – peridotite xenolith in lava flow from Mateiaș. Scale bar for both images is shown in the left photo (Photo S. Harangi).

Figure 4. The main geologic monument at Racos (site 1) displaying well developed columnar basalts. Rocky outcrop is about 20-25 m tall (Photo M. Ducea).

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THE TRACHYANDESITE NECK OF UROI HILL (HUNEDOARA COUNTY)

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Type: Category IV IUCN – Geological nature reserve (since 1979), 10 hectares.

Coordinates: N 45°51′43″/ E 23°02′37″, elevation at the top: 349 m.

Location and access: Shared between Simeria town and Rapoltu Mare commune, Hunedoara County. Located about 2 km north-east from Simeria, on the left (northern) bank of Mureș River, just upstream of the confluence with the Strei River.

Access: County road 700A going north-east from Simeria to Uroi village, and County Road 107A going south-east from Uroi village. Simeria can be reached: from the east, via A1 Highway Sibiu–Orăştie–Deva, or on European road 68 Sebeș–Simeria; from the south, via European road E79 from Hațeg; or from the west, via European road 79 from Deva.

Figure 1. Southern view of Uroi Hill (Picture taken by the author on August 9, 2014)

Description: Uroi Hill (also known as Măgura Uroiului, in Romanian, or Arany Hegy, in Hungarian) is a volcanic neck that tops the surrounding lowlands of the Mureș River terraces (Fig. 1). It represents, alongside the nearby Deva andesites, the southernmost occurrence of the Apuseni Mountains Neogene igneous province, formed in the context of the extensional tectonic that took place in the area during Neogene times. Recent absolute dating of the trachyandesites from Uroi Hill revealed a K–Ar age of 1.6±1 million years (Roșu *et al*., 2001, 2004), which makes it the youngest volcanic body in the Apuseni Mountains.

Petrographically, Uroi Hill consists of trachyandesites, being one of only three occurrences of alkaline igneous rocks in the Apuseni Mountains (Roșu *et al*., 2001, 2004). A large number of thermally altered quartzitic, limestone, and hematite-rich xenoliths are found within the trachyandesites, and host a great variety of minerals, such as augite, fluoro-magnesiohastingsite, fluorine-rich phlogopite, tridymite, feldspar, pseudobrookite, titanite, fluorapatite, enstatite, ilmenite, and fluorite (Bojar and Walter, 2006). Two of these minerals, pseudobrookite (Koch, 1878) and fluoro-magnesiohastingsite (Bojar & Walter, 2006) were first described from this location. Other minerals, found in the trachyandesite, include: andradite, chondrodite, hematite, and magnetite (Koch, 1898; König *et al*., 2001).

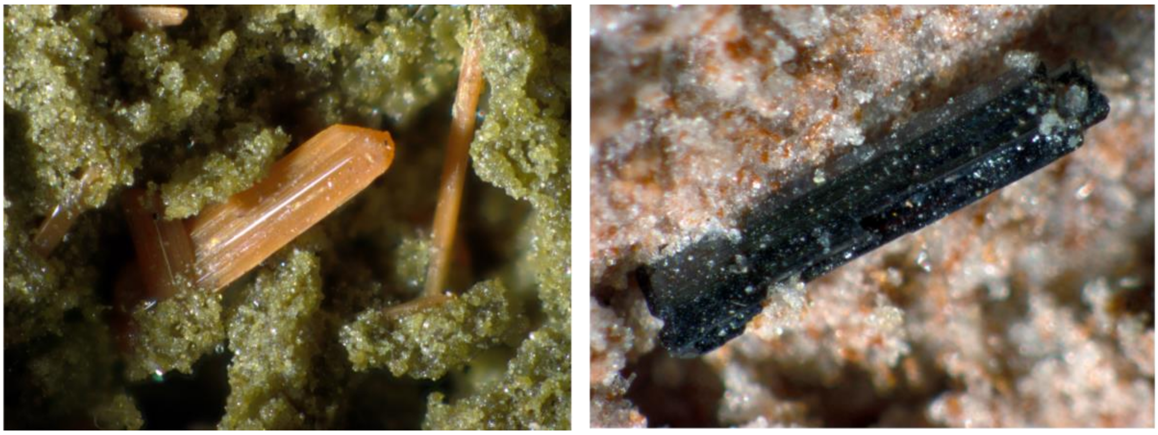

Figure 2. Fluoro-magnesiohastingsite (left) and pseudobrookite (right) crystals from Uroi Hill (Photos courtesy of Hans-Peter Bojar, Graz)

Another peculiar aspect of Uroi Hill is its shape, with a contrasting abrupt southern margin, with several plateaus at the base, and a gentle northern slope. The present shape of the hill is the result of both natural and anthropic factors, archaeological evidence showing that the trachyandesite was quarried at the site during multiple historical ages, starting with the Early Neolithic, and continuing to Iron Age, Roman, and Middle Age times (Barbu and Bărbat, 2017).

Age: Early Pleistocene, 1.6 mil. years.

Importance:

a. Scientific: Being the geologically youngest igneous body from the Apuseni Mountains, and having a unique petrographic composition, Uroi Hill is of great scientific importance in understanding the tectonic evolution of the region. It is also important from a mineralogical viewpoint, not only because of the great variety of minerals occurring in the xenoliths, but especially because it is the *locus typicus* of two minerals: pseudobrookite and fluoro-magnesiohasingsite (Fig. 2). Next to the presence of ancient quarries, several other archaeological findings, such as Neolithic, Bronze Age, Hallstatt and La Tène (Dacian) settlements and earthwork fortifications, a Roman villa, and World War II anti-aircraft entrenchments and training trenches, make Uroi Hill a very important archaeological site.

b. Touristic: The geological and archaeological importance of the site is currently not presented to the public. The unique morphology of the site, with a gentle northern slope and a steep southern edge, as well as its height relative to the surrounding area, make it very attractive for paragliders, who are often seen flying around the hill when weather allows it.

REFERENCES

Barbu, M.G, Bărbat, I.A., 2017. *New archaeological information regarding the exploitation of andesite in Măgura Uroiului (Hunedoara County).* Sargetia. Acta Musei Devensis (S.N.) 8: 71–121.

Bojar, H.-P., Walter, F., 2006. *Fluoro-magnesiohastingsite from Dealul Uroi (Hunedoara county, Romania): mineral data and crystal structure of a new amphibole end-member*. European Journal of Mineralogy 18: 503–508. https://doi.org/10.1127/0935-1221/2006/0018-0503

Koch, A., 1878. XXII. *Neue Minerale aus dem Andesit des Aranyer Berges in Siebenbürgen*. Tschermaks Mineralogische und Petrographische Mitteilungen 1 Neue Folge: 331–361.

König, U., Benea, M., Göske, J., Pöllmann, H., 2001. *Der Berg Magura Uroiului in Rumänien – Locus Typicus des Pseudobrookits.* Der Aufschluss 53: 271–281.

Roşu, E., Szakács, A., Downes, H., Seghedi, I., Pécskay, Z., Panaiotu, C., 2001. *The origin of Neogene calc-alkaline and alkaline magmas in the Apuseni Mountains, Romania; the adakite connection*. Romanian Journal of Mineral Deposits 79 (Suppl. 2): 3–23.

Roşu, E., Seghedi, I., Downes, H., Alderton, D.H.M., Szakács, A., Pécskay, Z., Panaiotu, C., Panaiotu, C.E., Nedelcu, L., 2004. *Extension-related Miocene calk-alkaline magmatism in the Apuseni Mountains, Romania: Origin of magmas*. Schweizerische Mineralogische und Petrographische Mitteilungen 84: 153–172.

THE RED PRECIPICE FROM SEBEȘ-ALBA

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Type: Geological and floral nature reserve (with a surface of 10 ha). Protected area of national interest since 1969, Category III IUCN.

Coordinates: N 45°59′14″/ E 23°35′32.8″; elevation: 285-425 m.

Location and access: The nature reserve is located in the central part of the Alba County, on the administrative territory of Sebeș town, 4 km North, nearby the A1 highway that links the cities of Deva and Sibiu.

Description: The torrential erosion of the latest Cretaceous (Maastrichtian) fluvial-lacustrine deposits, with repetitive interleaving of gritty channel fillings (including pebbles, microconglomerate, sand, weakly cemented, with high weathering tendencies) and over bank deposits (red mudstones) erected a specific relief with rock vertical pyramids and columns resembling organ tubes. The alternation between the more cemented levels and the softer ones, led to differential erosion and prominence of the harder rocks, usually the channel fills. Following on vertical section the evolution of this sedimentation, one can easily observe a fining upward tendency. The rock deposits are dominated by far by bigger clasts in the basal sequences, which become finer upwards. Such a size distribution of the clasts is indicative for the evolution of the ancient fluvial system, very dynamic at beginning, later with slower waters. The most specific feature of these rocks is their color, reddish in dominance. All these features led to a very specific landscape, extremely rare in Romania, very close to the ‘badlands’ well known in other parts of the world, as in North America (e.g. Montana, South Dakota, Wyoming in U.S.). The Cretaceous succession was later eroded during Middle Miocene, when the sea covered the land. The rocks of marine origin can be observed on the easternmost side of the outcrop, forming a short sedimentary sequence between 405-423 m in altitude. A closer look to these deposits worth to be done, because in their basal part one can find rather numerous blocks of Lower Cenozoic (Paleogene) limestones and sandstones. It is an evidence of the former existence of marine Paleogene deposits, once lying on the northern border of the Southern Carpathians, completely eroded and razed by the Miocene transgression. Part of these rocks fell down on the slopes of the Red Ravine and led to confusions about the geological age of the underlying rocks, considered for many years as Paleogene. Last but not least, the sizes of the ravine are impressive: 800 m in length, and highs increasing from west (50 m) to east (125 m).

Lithostratigraphy and Age: Sebeş Formation, Latest Cretaceous – Maastrichtian (72–66 mil. years).

Importance:

a. Scientific: The specific torrential erosion is a case study in Romania, offering a very peculiar, exceptional landscape. The fluvial Cretaceous rocks yielded rare vertebrate remains documenting the insular realm known as the ‘Hațeg Island’ (an island in the former Tethys Ocean), with endemic dinosaurs (*Zalmoxes*, *Telmatosaururs*, *Strutiosaurus*, *Magyarosaurus* etc.), some of them with dwarfing tendencies and other reptiles (like the giant pterosaur *Hatzegopteryx*, turtles as *Kallokibotion* or crocodiles). As the Red Ravine hosts just a restricted part of such deposits, one may expect in future other fossils like fish, birds or mammals, all known from the neighboring areas of this region. Apart fossils, the site hosts some rare plants too, as *Dianthus serotinus* var. *demissorum*, *Salvia nutans*, *S. transsilvanica*, *Quercus pubescens* and other taxa specific to the warm steppe environments.

b. Touristic: This site have to be a destination both for scientists and nature lovers, a 'must to see' place. The unique landscape that offer variable rock colors depending the different hours of each day, or in each season, in rain or in hot sunny time, is already a strong reason for a visit. The extremely rare fossils and the specific plants are attracting professional scientists. In the last decades the number of visitors increased a lot, and it continue.

Figure 1. General view of the site Sebeș Red Ravine (Alba County). Photo Vlad Codrea

REFERENCES

Bleahu, M., Brădescu, V., Marinescu, F., 1976. *Rezervații naturale geologice din România*. Ed. Tehnică, 225 p.

Codrea, V., Murzea-Jipa, C., Venczel, M., 2008. *A Sauropod vertebra at Rapa Rosie (Alba district).* Acta Palaeontologica Romaniae 6: 43–48, Iași.

Codrea, V., Vremir, M., Jipa, C., Godefroit, P., Csiki, Z., Smith, T., Fărcaş, C., 2010. *More than just Nopcsa's Transylvanian dinosaurs: A look outside the Haţeg Basin.* Palaeogeography, Palaeoclimatology, Palaeoecology 293: 391–405. https://doi.org/10.1016/j.palaeo.2009.10.027

Csiki-Sava, Z., Vremir, M., Vasile, S., Brusatte, S.L., Dyke, G., Naish, D., Norell, M.A., Totoianu, R. 2016. *The East Side Story – the Transylvanian latest Cretaceous continental vertebrate record and its implications for understanding Cretaceous-Paleogene boundary events*. Cretaceous Research 57: 662–698. https://doi.org/10.1016/j.cretres.2015.09.003

Solomon, A., Miclea, A., Jipa, C., Feigi, Ș.V., 2010. *Paleogenul remaniat de la Râpa Roșie (jud.Alba): implicații asupra vârstei „Formațiunii de Sebeș”*. (coord. V. Codrea, I.I. Bucur), Geoecologia 10: 83–86.

THE NUMMULITIC LIMESTONE FROM DEALUL PIETREI (*THE STONE HILL*), ALBEŞTI-MUSCEL (ARGEŞ COUNTY)

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Type: Geological and paleontological natural reserve. Category III IUCN, 1.5 ha.

Coordinates: N 45°18′32″/ E 25°00′27″.

Location and access: Center of Albeşti commune, 6 km North-West of Câmpulung-Muscel town, on the County road DJ735.

Description: The outcrop consists of two lithologic banks: a lower calcareous bank (cca. 6 m thick) dominated by calcirudite in the base and biocalcarenite at the upper part, and an upper sandstone bank with sandy-marls interbbedings (Fig. 1). In the geology of the region, the limestone group overlies crystalline schists and Upper Cretaceous marls of marine origin. The lower calcareous bank, especially the biocalcarenites, pale-yellow, or gray- reddish in color, contains a rich assemblage of large foraminifera among which *Nummulites*, *Assilina*, *Operculina*, together with numerous invertebrates: brachiopods, bryozoans, mollusks, crustaceans, crinoids and echinoids, more rarely fish remains, especially shark teeth.

The rich fossil assemblage reveals an eulittoral benthic ecosystem, in a few ten of meters deep environment, normal salinity (cca. 34 mg/l), warm, subtropical waters with a rather high content of suspensions from the continent, which prevented the coral reefs development. The upper sandstone bank, much less fossiliferous, provided rare bone remains of sirenian mammals ("sea-cows").

The limestone has very good technical qualities, being for this very much used in monumental buildings, since the 13^{th} century AD. Among these, the Curtea de Argeş and Cozia monasteries, the Cernavodă bridge over the Danube, the Casino in Constanţa, numerous buildings in Bucharest: the Triumphant Arch, the National Museum of History, the Free Press House and many other. It is worth to mention that nummulitic limestones of the same age are at the origin of other monumental buildings in the world, such as the Pyramids from Giza in Egipt, the Notre Dame cathedral and the Triumphant Arch in Paris, etc.

To avoid the limestone exhaustion, in 1954 the northern part of the Albeşti quarry was declared Natural monument, under the law protection.

Age: Lower–Middle Eocene (Ypressian–Lutetian, aprox. 50–44 mil. years) for the limestone bank; Upper Eocene (Priabonian - ca. 34–38 mil. years) for the sandstone bank.

Importance:

a. Scientific: The main scientific importance of the site is linked with the rich micro- and macrofaunal assemblage in the limestone bank, which allowed an accurate geological dating and the interpretation of the environmental conditions in which the benthic ecosystem has lived. The bone fragments found in the upper, sandstone bank represent the only sirenian mammal remains in Romania, outside Transylvania, where these are rather common in the Eocene deposits.

It should be mentioned that the Albeşti limestone was also the subject of one of the first geological papers in Romanian language, written by the first professor of Geology in the University of Bucharest, Gregoriu Ştefănescu, published in the same year (1864) with the paper of the founder of Geology at the University of Iaşi – Grigore Cobălcescu, the author of the paper on the Repedea limestone.

b. Touristic: The school pupils guided by their teachers are the common visitors of the reserve; here they have the opportunity to see, usually for the first time, fossils in place and to get information on the life in the geological past. However, besides this educational significance, the visits occasion uncontrolled fossil collecting, which may include rare specimens, especially echinoids and shark remains.

Figure 1. The Dealul Pietrii nummulitic limestone – Nature Monument of geological and paleontological type in the center of the Albeşi – Muscel commune

REFERENCES

Bleahu, M., Brădescu, V., Marinescu, F., 1976. *Rezervații naturale geologice din România. Editura Tehnică*, Bucureşti, p. 44–45.

Bombiță, G., 1963. *Contribuții la corelarea Eocenului epicontinental din România*. Editura Academiei R.P.R, Bucureşti, p. 14–25.

Grigorescu, D., 1967. *Asupra prezenţei sirenidelor în Paleogenul de la Albeşti–Muscel*, Analele Univ. Buc., Ser. Geologie-Geografie, XVI, 1, p. 72–78.

MUNTICELU MASSIF AND ȘUGĂU GORGES

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Type: Natural reserve of mixt type: geological, floral and faunal, Category IV IUCN, 90 hectares.

Coordinates: The Munticelu Massif: N 46°50′07. 29″/ E 25°50′45.37″, elevation: 1241–1337 m.
Șugău Gorges**:** N 46°49′28.47″/ E 25°51′00.03″, elevation: 690 m.

Location and access: Bicaz-Chei commune, Neamț County.
Access from the east: National road DN Piatra Neamț–Bicaz-Chei (46 km).
Access from the west: National road DN Gheorghieni–Bicaz-Chei (37 km).

Description:

The **Munticelu Massif** represents a N-S oriented limestone narrow crest, with widths ranging between 100 and 500 m and a length of 3 km, with a maximum altitude of 1337 m. The limestones, white-grey or red in colour, contain a faunal assemblage of corals, brachiopods and pachyodont bivalves, characteristic for the Late Jurassic (Tithonian) – Early Cretaceous (Lower Barremian). The outcropping section reveals that the Tithonian-Barremian limestone formation is in a tectonic position (*Hăşmaş Nappe*), unconformably overlying the younger Barremian–Albian wildflysch (Fig.1). Currently, the wildflysch deposits and the tectonic contact can be examined in the old quarry, known as Stan's cliff, which escaped the intenssive extraction in the past.

Şugău Gorges. Very picturesque, deep gorges were created by the Şugău river which carved a 350 m long gorges, very narrow (2-3 m wide), and forms a row of waterfalls in the southern part of the Munticelu Massif. The gorges cross, on their longest course, the Aptian–Albian wildflysch and conglomerates, but upstream of the confluence with the Bicaz River, they cross the limestone barrier on a NW-SE direction, sculpting along about 350 m the narrowest gorges in the area.

In the Şugău Gorges, the potholes, hanging up to 30 m height, represent not only an exokarstic microrelief, but the evidence for the epigenetic origin of the gorges, too. In the upstream entrance of the Şugău Gorges there is a karstic spring indicating the underground water flow.

Age: Late Jurassic.

Importance:

a. Scientific. The Munticelu Massif, including the Şugău Gorges, represents a key stratigraphical and tectonical place for the geology of the Late Jurassic–Early Cretaceous in the Eastern Carpathians, subject of several scientific publications. The area exhibits interesting forms of exo- and endokarst relief.

Besides the geological significance the Munticelu Massif – Şugău Gorges area host an exceptionally rich botanical association including about 500 species and subspecies. The floral fund is dominated by Eurasian elements (36.75%), followed by European (10.42%), Central-European (12.42%) and circumpolar elements (8.84%). An important role have the alpine (5.23%), Mediterranean, sub-Mediterranean, continental and Pontic elements. The Dacic element is well represented (3.01%), including as main species *Aconitum toxicum*, *Cardamine glandulicera*, *Hepatica transsilvanica*, *Pulmonaria rubra*, *Symphytum cordatum*, *Silene zawadskii*, *Thymus comosus*, etc. There are numerous Carpathian endemic species, favoured by the limy thermophile bedrock. This category is represented by *Larix decidua* ssp. *carpatica*, *Aconitum moldavicum*, *Silene dubia*, *Hieracium pojoratense*, *Campanula carpatica*, *Poa nemoralis*, *Androsacae villosa* ssp. *arachnoidea*, *Primula leucophylla*.

The faunal assemblage is also very rich, characterized by the rarity and or uniqueness of some species. It includes the chamois, lynx, wild cats, bats, birds, reptiles, amphibians, insects (among which the endemic little rock butterfly (*Tichodroma muraria*). Due to the urgent needs for special protection of the endangered species, an area within the Şugău-Munticelu Gorges Nature Reserve was declared *Site of Community Importance* under European legislation, integrated into the international network of protected areas *Natura 2000*.

b. Touristic. The mountainous landscapes with colourful limestone walls in which the rapid streams dug deeply, creating karstic forms, and the alpine vegetation attract many visitors, in all seasons. Their interest in coming increased recently after the setting of an adventure and recreation park which combine the mountain climbing and hiking, accessible to the general public. The park is led by Ticu Lăcătuşu, the first Romanian to climb the Everest.

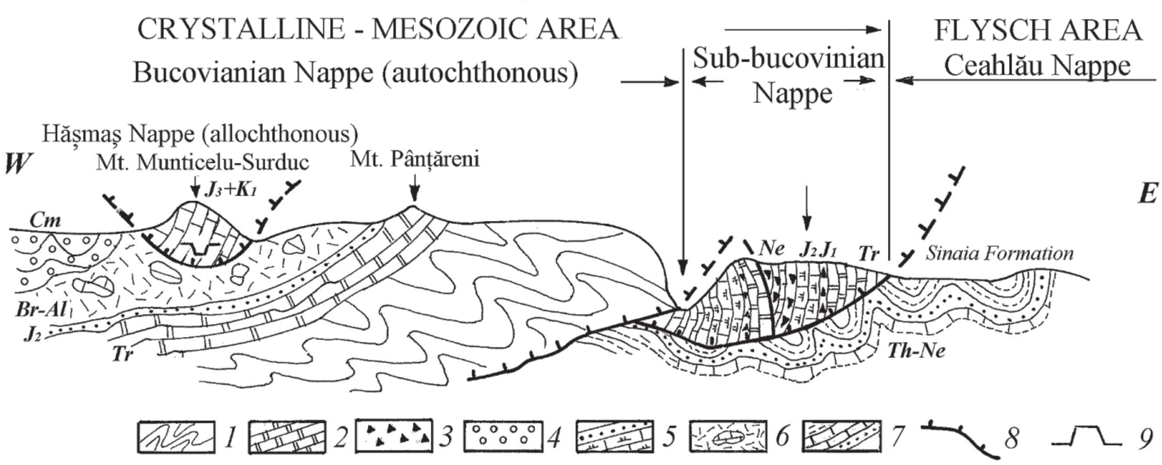

Figure 1. Geological cross-section of the external limb of the Hăşmaş Syncline along the Bicaz River: 1 – low- and middle rank metamorphic rocks; 2 – dolomites; 3 – breccias; 4 – post-tectonic conglomerates; 5 – sandstone and sandy nodular limestones; 6 – wildflysch; 7 – sandstone, limestones, marls, clays (flysch); 8 – nappe; 9 – limestone quarry

REFERENCES

Bleahu, M., Bradescu, V., Marinescu, F., 1976. *Rezervaţii geologice din România*. Editura Tehnică, Bucharest, p. 163–165.

Grasu, C., Brânzilă, M., Miclăuş, C., Baciu, D.S., 2011. *The necessity to widen the Cheile Bicazului-Hăşmaş Naţional Park. Scientific substantiation*. Geo-Eco-Marina 17: 261–275.

Grasu, C., Brânzilă, M., Miclăuş, C., Baciu, D.S., 2011. *Parcul naţional Cheile Bicazului-Hăşmaş. Ghidul siturilor geologice şi fizico-geografice*. Editura Universităţii „Al. I. Cuza”, Iaşi, 95 p.

Photo 1: Munticelu Massif

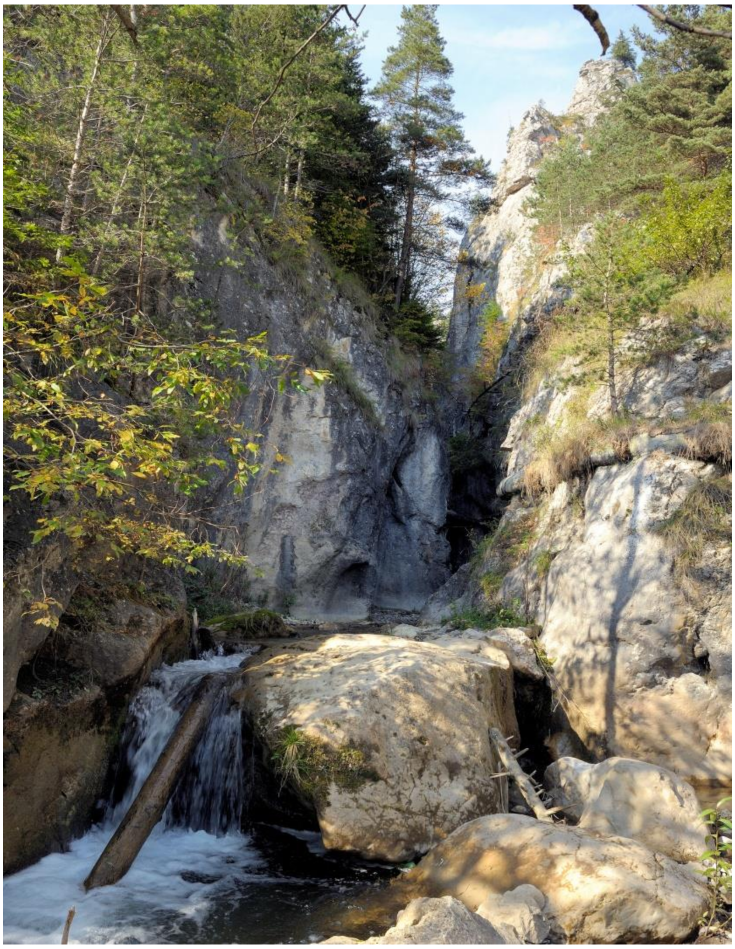

Photo 2: Şugău Gorges

Photo 3: Municelu – Șugău Gorges Reserve

REPEDEA HILL – MIDDLE MIOCENE (SARMATIAN) FOSSILIFEROUS LIMESTONE

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Type: Paleontological, Historical. Natural reserve of paleontological type, 5 hectares. Category IV IUCN.

Coordinates: N 47°05′16.4522″/ E 27°38′43.6103″, elevation: 365 m.

Location: Bârnova commune, Iași County.

Access: DN24 Iași–Bârnova (9 km).

History of the reserve: Grigore Cobălcescu's paper "Calcariul de la Răpidea" (*The Limestone from Repedea*), published in 1862, represents the first scientific geological paper written in Romanian. The Repedea Hill was declared a Nature monument in 1955, in 1973 the protected area being enlarged and separated into a scientific area of 0.058 km² and a transition zone of 0.385 km².

Description: The protected area from Repedea Hill belongs to the Moldavian Central Plateau. It is located in the "Pietrăria" (*Stony*) quarry, also named "Repedea Big quarry" (Fig. 1). In the quarry, the limestone and clastic rocks alternate on 15 m thickness. The limestone rocks, represented by oolitic yellow or grey limestone and biosparites, prevail at the lower and middle part of the quarry, while the sandstone and sands predominate at the upper part of the section.

The fossils are common in all the lithologic types (litons), the most common are the mollusks (bivalves and gastropods with more than 50 species, followed by benthic foraminifera (24 species) and ostracods (3 species). Among the characterstic species are: *Mactra podolica*, *M. naviculata*, *M. vasluiensis*, *M. fabreana*, *Plicatiforma fittoni*, *Tapes vasluiensis*, *Pholas hommairei* (Bivalves), *Gibbula beaumonti*, *Potamides nefaris* (Gastropods), *Quinqueloculina sinzovi*, *Triloculina pseudoinflata*, *T. ukrainica sarmatica* (Foraminifera), *Leptocythere mironovi*, *Aurila kolesnikovi*, *A. sarmatica* (ostracods). Two premolars of the perissodactyl *Aceratherium incisivum* represent the only vertebrate remains in the paleontologic assemblage, obviously transported into the sea from the land where the rhinoceros died.

Paleoenvironment: Sedimentologic studies indicate that the Sarmatian deposits were accumulated in a near-shore environment with physical and chemical characteristics similar to those of the present Black Sea. The high influx of freshwater from the rivers led to the development of a brackish environment (of about 17–18 parts per thousand, salts) to which the faunal assemblage of mollusks and forams adapted.

Lithostratigraphy and Age: Repedea Formation, *Basarabian*, the Middle substage of *Sarmatian*, the regional stage for Middle Miocene in the Paratethys Basin, cca. 11.5–11 mil. years.

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The importance of the site:

a. Scientific: Besides the historical value, as the first scientific geological work in Romanian, the Repedea limestone quarry provides a comprehensive view on the faunal assemblage and the benthic ecosystem in the brackish environment during the Middle Miocene in the *Paratethys* which allows a detailed biostratigraphic zonation of the *Basarabian* substage) in the Moldavian Platform.

b. Touristic: The site attracts especially the scholars and educated people, interested in the history of the Earth and Life sciences in Romania. In connection with this, The Pietrăria quarry outcrop was digitalized in order to preserve it in a digital form, by combining "Structure from motion", Photogrammetry (Fig. 2) and other 3-D modeling techniques with the ability of a game engine, all the data being thus incorporated to create an immersive interactive of the area (Fig. 3). By interacting with the surrounding environment, without any threat on the geological reserve, people will learn more about the area's protection, including the rules and recommendations to follow. Using a game engine as a platform, the virtual environment is accessible not only to adults, but to children as well, teaching them a sense of responsibility towards protected areas.

The 3-D virtual tour has also been made available freely on the internet (http://geology.uaic.ro/3d-geological-modelling/) so it can be found with relative ease and increase the sensibility among different people and organization towards the area, thus safeguarding the future of Repedea's geological reserve.

REFERENCES

Brânzilă, M., 1999. *Geologia părţii sudice a Câmpiei Moldovei.* Editura Corson, Iaşi, 221 pp.

Cobălcescu, G., 1862. *Calcarul de la Răpidea*. Revista Română pentru Ştiinţe, Litere şi Arte 2: 585–699.

Dumitriu, T.C., Brânzilă, M., Baciu D.S., 2015. *Preserving History. „Calcariul de la Răpidea" 3-D Virtual Tour (Iaşi, Romania)*. Analele Ştiinţifice ale Universităţii „Al. I. Cuza" din Iaşi, Seria Geologie 61(1–2): 41–46.

Kalmar, I., 1991. *New data for the sedimentology and the geochemistry of the Repedea oolites*. Lucrările seminarului Geologic „Gr. Cobălcescu" 3: 36–56 (in Romanian).

Ionesi, L., Ionesi, B., Roşca, V., Lungu, A., Ionesi, V., 2005. *Sarmatianul mediu si superior din Platforma Moldoveneasca*. Editura Academiei Romane: 347–349.

Figure 1. Repedea Big quarry outcrop

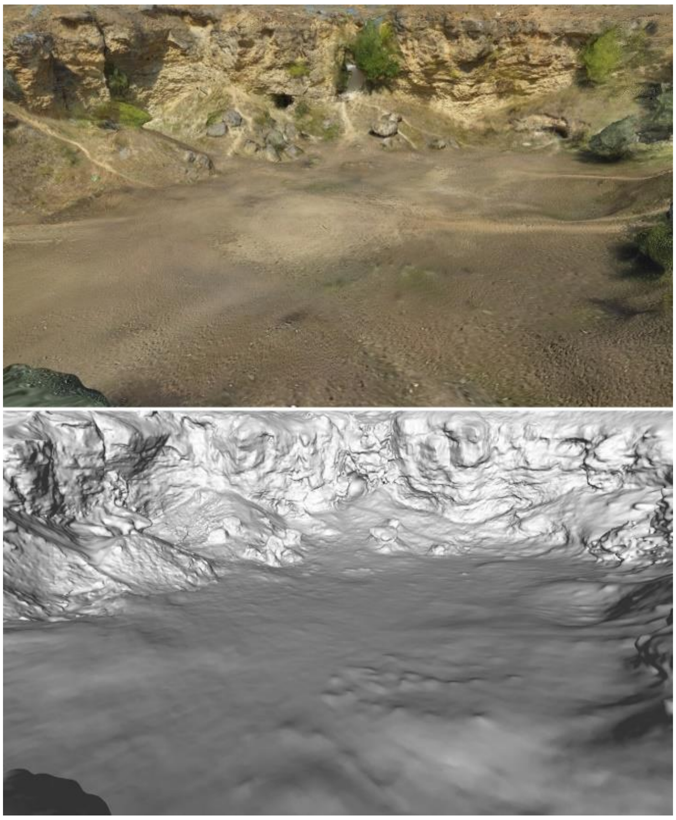

Figure 2. Repedea's Big Quarry Outcrop obtained through "Structure from Motion" Photogrammetry. Up is the 3D outcrop mesh with textures. Bottom is the 3D outcrop mesh without textures

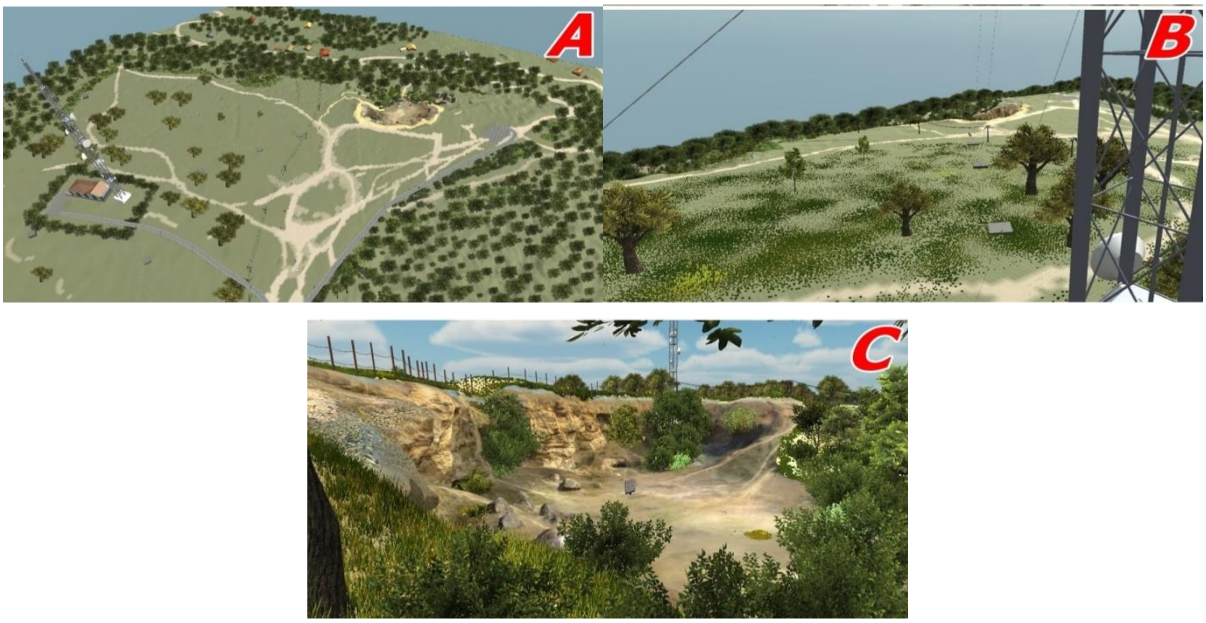

Figure 3. Some parts of the 3D virtual environment during its creation. A – Overview of the area; B – Image from the television tower; C – Image from the north side of Repedea's big quarry outcrop

MUD VOLCANOES FROM PÂCLELE MICI (BERCA)

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Type: Geological, faunal and floral nature reserve (with a surface of 10.20 ha). Protected area of national interest, Category IV IUCN since 2000.

Coordinates: N 45°20'22"/ E 26°42'30.2"

Location and access: The nature reserve is located in the central part of Buzău County (322 m altitude), on the administrative territory of Scorțoasa locality, near the DJ108 county road that links Policiori and Pâclele villages.

Description: The mud volcanoes are created by natural gas that comes from more than 3,000 meters depth, from the Middle Miocene sediments (i.e., the Sarmatian stage of the Eastern Paratethys), passing through a clay soil in combination with the groundwater. Hence, the gases are pushing to the surface water mixed with clay. The mud formed by them reaches the surface and dried in the contact with the air, forming cone-like structures similar with the volcanoes (Fig.1). The soil contains sulfur and salt, improper for the vegetation. However, here are developing some plant species adapted to this type of soil, i.e. *Nitraria schoberi* and *Obione verrucifera*. The protected area contains a natural habitat composed of meadows and brackish pounds, Pannonian and Ponto-Caspian types. A connection between the occurrence of the mud volcanoes from the Berca area, including the intensity of the mud and gas emanations and the seismicity of the region, situated at 50 Km towards S from one of the most seismically active zone in Europe, the Vrancea area, may be assumed. Geologically, the mud volcanoes appear in the Inner Foredeep of the Eastern Carpathians, along the axis of a faulted anticline, striking NS and affected by longitudinal and transverse faults. In the axis of the anticline occur Upper Miocene (Maeotian) deposits, and on the flanks uppermost Miocene-lowermost Pliocene deposits of the Pontian, followed by the Pliocene ones (Dacian and Romanian). Methane emissions of the mud volcanoes from the Pâclele Mici sites were estimated at 7,383 tones/year. The composition of the exhalations recorded in the site is over 95% CH_4 and a very small amount of CO_2.

Importance:

a. Scientific: The mud volcanoes from Berca represent a unique geological site in Romania, and one of a very few known in Europe. Even the mud volcanoes have been known from immemorial times by local people, their geological context was described since the middle part of the 19th Century. It is to mention the large morphological variety, along with the size cones (Fig. 2). Their shape and size is determined by the viscosity of the ejected fluids (water and hydrocarbons), along with gases and detritus (Fig. 2). Because the ejections are coming from Sarmatian deposits (situated at an appreciable depth), frequently macrofossils characterizing this stage, especially bivalves belonging to the *Mactra* and *Cardium* genera, may be found in the expelled rocks.

b. Touristic: This site is a wonderful destination for scientists and nature enthusiasts. The constant gas and mud emissions all seasons have created a spectacular moon-like landscape. For these reasons, thousands of tourists from all over the world are yearly visiting this area.

Figure 1. General view of the site Mud volcanoes from Pâclele Mici (Berca). Photo Andrei Briceag, June 2014

Figure 2. Gas bubble at the Mud volcanoes from Pâclele Mici (Berca). Photo: Adrian Popa, August 2014

REFERENCES

Baciu, C., Caracausi, A., Etiope, G., Italiano, F., 2007. *Mud volcanoes and methane seeps in Romania: main features and gas flux.* Annals of Geophysics 50(4): 501–511.

Brustur, T., Stănescu, I., Macaleţ., R, Melinte-Dobrinescu, M.C., 2015. *The Mud Volcanoes from Berca: a significant geological patrimony site of the Buzău Land Geopark (Romania).* Geo-Eco-Marina 21: 73–96.

Cobălcescu, G., 1883. *Studii geologice şi paleontologice asupra unor terâmuri terţiare din unele părţi ale României*. Memorii Geologice ale Şcolei Militare din Iaşi, 161 pp.

Coquand, H., 1867. *Sur les gîtes de pétrole de la Valachie et de la Moldavie et sur l'âge des terrains qui les contiennent*. Bulletin de la Société Géologique de France 24: 505–570.

Melinte-Dobrinescu, M.C, Brustur, T., Jipa, D., Macaleţ, R., Ion, G., Ion, E., Popa, A., Briceag, A., 2017. *The Geological and Palaeontological Heritage of the Buzău Land Geopark (Carpathians, Romania)*. Geoheritage 9(2): 225–236. https://doi.org/10.1007/s12371-016-0202-3

THE SALT MOUNTAIN AT MÂNZĂLEŞTI

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Type: geological, speleological, botanical and zoological. This site is included in the Meledic Plateau that is a protected area (with a surface of 136 ha) of national interest corresponding to the category IV IUCN.

Coordinates: N 45°29′06.5″/ E 26°36′58.6″

Location and access: The site is located in the Buzău County (the administrative territory of Mânzăleşti locality), on the DJ203K county road, at the southern extremity of the Meledic Plateau, at the left side of Slănicul de Buzău Valley.

Description: The Salt Mountain is represented by massive salt deposits, in which karst features such as sinkholes, ditches, ravines and caves may be observed, along with abrupt slopes (Figs. 1 and 2). Small valleys are formed on the slopes, with reduced lengths and high gradient thalweg; in some places, deep canyons may be observed. The salt breccia deposits occur at the contact between the Subcarpathian Nappe and the inner (western) Tarcău Nappe. At the upper part of the salt breccia, 10-30 m thick beds of grey and green clays and marls have been sedimented. In the salt breccia, different in origin and age clasts include Oligocene bituminous rocks, conglomerates with elements of green schists of outer (eastern) provenance (i.e., the Eastern European and Moesian platforms) and Miocene sediments, all pierced by the salt. Rarely, fragments of corals from Middle Miocene deposits of the eastern platforms are encountered. At the base of the slopes, salt springs, as well as small caves produced by the dissolution of the salt, have been formed.

Importance:

a. Scientific: The occurrence of the lowermost Miocene salt (Aquitanian–Burdigalian in age, around 20 Ma in age) is linked to the diapirism, a geological phenomenon that it was firstly described in Romania, at the beginning of the last century. Due to the penetration of the salt in older rocks and different structures, such as the nappes of the Eastern Carpathians and the platforms (Eastern European and Moesian), a large variety of rocks, many Oligocene and Miocene, brought at the surface, may be seen. The site, as the whole plateau, is important from speleological point of view, as well. Hence, 47 saline endokarsts, including the Europe's biggest salt cave and the second in the world is comprised in the Meledic Plateau. The cave 6S Meledic has 1,257 m in length and 32 m depth, and contains stalactites of diverse colors, i.e. white, yellow, pink, reddish, grey and brown, as well as stalagmites, up to 15–20 cm in height.

b. Touristic: The Salt Mountain, as the whole Meledic Plateau, is a natural reserve of a great touristic potential. The morphological aspects produced by the salt dissolution (such as caves and ravines) have created spectacular landscapes, unique in Europe. In the protected area, there are also lakes with fresh water, not salty as expected. When rain water infiltrates, the salt dissolves only in small cone shapes, as the salt is covered by thin layers of impermeable rocks, such as clays. Besides geological and geomorphological features, a specific faunas and floras (including an endemic scorpion species, turtles and small mammals) may be observed.

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Figure 1. The Salt Mountain at Manzăleşti (Photo Andrei Briceag. August 2015)

Figure 2. Salt micro-ravines at Manzăleşti (Photo Adrian Popa, July 2015)

REFERENCES

Jipa, D.C., Olariu, C., 2012. *Sediment routing in a semi-enclosed epicontinental sea: Dacian Basin, Paratethys domain, Late Neogene, Romania*. Global and Planetary Change 103(1): 193–206. https://doi.org/10.1016/j.gloplacha.2012.06.009

Dumitrescu, I., Săndulescu, M., Bandrabur, T., Săndulescu, J., 1968. *Covasna Sheet, scale 1:200, 000*. Printing House of the Geological Institute of Romania.

Melinte-Dobrinescu, M.C, Brustur, T., Jipa, D., Macaleţ, R., Ion, G., Ion, E., Popa, A., Briceag, A., 2017. *The Geological and Palaeontological Heritage of the Buzău Land Geopark (Carpathians, Romania).* Geoheritage 9(2): 225–236. https://doi.org/10.1007/s12371-016-0202-3

Mrazek, L., 1907. *Despre cute cu sâmbure de străpungere*. Buletinul Societăţii de Ştiinţe din Bucureşti-România, Annuaire 16(1-2).

Stoica, M., Lazăr, I., Krijgsman, W., Vasiliev, I., Jipa, D.C., Floroiu, A., 2012. *Palaeoenvironmental evolution of the East Carpathian foredeep during the late Miocene - early Pliocene (Dacian Basin, Romania).* Global and Planetary Change 103(1): 135–148.
https://doi.org/10.1016/j.gloplacha.2012.04.004

VAMA STRUNGA – BUCEGI NATURE PARK: MIDDLE JURASSIC MARINE FAUNAS

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Type: Paleontological, Nature Reserve, 10 hectares (cf. L 5/2000); administrated by the Bucegi Nature Park. Category III IUCN.

Coordinates: N 45°23′43″; E 25°24′49″, elevation: 1925 m.

Location: The fossiliferous site is located in the alpine zone of the western flank of Bucegi Mountains (the eastern part of the Southern Carpathians), in the area of Strunga Plateau, between Tătaru Peak and Vama Strunga Pass, Brașov County.

Restricted access: The fossiliferous area is included within the integral protection zone of the Bucegi Nature Park.

Description: One the most interesting succession of the Middle Jurassic deposits from the southern Carpathians occurs in the Bucegi Mountains, in the area Vama Strunga Pass – Strunguliţa Pass – Obârşia Văii Tătarului, confined northwards by the Vama Strunga Pass and southwards by the Tătaru Valley. The Jurassic sequence from the Bucegi Mountains belongs to the sedimentary cover of the Getic Domain (Getic Nappe), one of the major geotectonic units of the Carpathians.

The litostratigraphy and biostratigraphy of the Middle–Upper Jurassic deposits that crop out on the western site of Bucegi Mountains have been studied since the middle of the 19th century. An elaborated study on the geology of the Bucegi Mountains is due to Patrulius (1969). Recent contributions were added by Lazăr (2006), Lazăr *et al*., 2013, 2014). The Jurassic sedimentary succession overlay the pre-Hercynian metamorphic rocks of the Leota Formation that represent the basement of the Getic Nappe. The strata of the Bajocian–Kimmeridgian interval are well bedded and dip at 10° to 12° towards the NW. The lower part of the succession (Strunguliţa Member, Lower–Middle Bajocian, almost 23 m thick) is represented by quartzitic conglomerates followed by medium bedded calcarenites, argillaceous silts, biocalcarenites and bioclastic sandstones containing rich fossil assemblages of marine faunas. The next unit is represented by ooidal bioclastic grainstone and ooidal bioclastic grainstone-packstone with thin, discontinuous, quartzitic micro-conglomerate intercalations. These deposits belong to the Tătaru Member (17–25 m thick) and their top is marked by a sharp hardground discontinuity. The next bed (Grohotişul Member) is only 0.65–1 meter thick and is represented by a grey-green to reddish bioclastic ooid packstone-grainstone with cavities and fractures filled with bioclastic wackestone-packstone, respectively oncoidal floatstone and rudstone. This bed has a nodular aspect and contains numerous ferruginous macro-oncoids, ferruginous ooids and a rich fossil assemblage including ammonites, belemnites, and sponges, crinoids, besides rare bivalves, gastropods, brachiopods, echinoids, and rare solitary corals. The top of this bed is represented by a complex hardground surface, strongly mineralized with 1-3 cm thick ferruginous laminated crusts (microstromatolites); these are distributed along the top of the bed, but they also occur within fissures, fractures and small neptunian dykes. The following overlying units represented by 1 meter thick of red, thin stratified marly limestones with rhyncholites and foraminifera (Middle Callovian –

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Oxfordian), covered by 0.5–1 meter thick Middle Oxfordian jasper and radiolarites. The next unit is represented by more than 100 meter-thick white-grey massive limestone that contain (in the lower part) ammonites and brachiopods representative for the Kimmeridgian stage.

Lithostratigraphy and Age: Strunga Formation, Middle Jurassic (Bajocian–Callovian, aprox. 170-163 mil. years). The successions from Vama Strunga belong to the Strunga Formation which is made up of three members: the Strunguliţa Member (Lower–Middle Bajocian), the Tătaru Member (Middle–Upper Bajocian), and the Grohotişul Member (Lower Bathonian–Lower Callovian).

Importance: The Jurassic deposits that crop out along the western flank of the Bucegi Mountains, especially those from the Vama Strunga site, are distinguished by the richness of their fossil fauna. The macrofaunal fossil assemblages from this site are represented by corals, bivalves, gastropods, ammonites, nautiloids, belemnites, serpulids, arthropods, brachiopods, bryozoans, crinoids, echinoids and chondrichthian and holostean teeth. A comprehensive list of over 100 fossils species from these fossil assemblages was given by Patrulius (1969) and the description of over 70 fossils taxa (mollusks, echinoids, arthropods, corals) from this area and taphonomical and paleoecological studies were accomplished by Lazăr (2000-2006). To the paleontological and biostratigraphical importance of the site, the recent studies added a detailed interpretation of the paleoenvironmental and paleoecological conditions in the Middle Jurassic carbonatic platform from the area. It was thus shown that some of the faunal assemblages were developed in open-marine shelf environments, within the deep euphotic zone, characterized by low sedimentation rates, but high rates of shell accumulation and early marine cementation. Intervals of omission / non-deposition, erosion and in-situ reworking produced by bottom currents and/or storm events generated dysoxic/anoxic interfaces were spectacular ferruginous micro-stromatolites-agglutinated worm-tubes assemblages were formed (cf. Lazăr *et al*., 2013; Lazăr & Grădinaru, 2014).

Figure 1. Western flank of the Bucegi Mountains in the Vama Strunga-Grohotișul Mountains sector

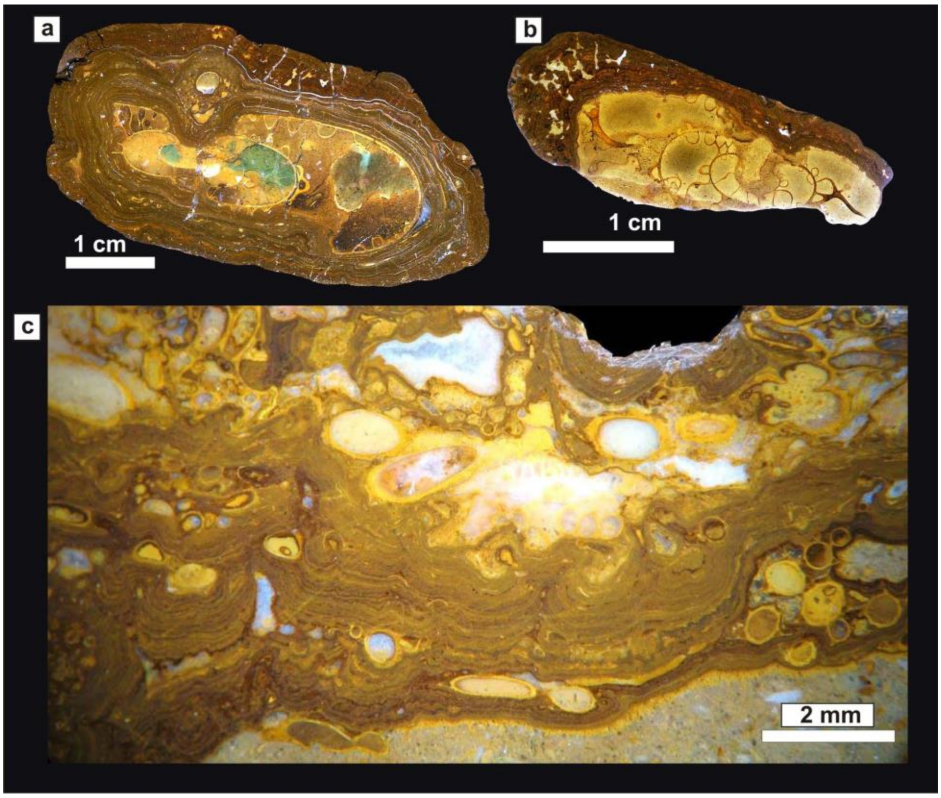

Figure 2. a, b. Ammonites encrusted by ferruginous microstromatolites;
c. Ferruginous microstromatolites-serpulid worm-tubes assemblages
from the Midlle Jurassic condesed strata, Vama Strunga)

REFERENCES

Lazăr, I., 2006. *Jurasicul mediu din Bucegi – versantul vestic – Paleontologie şi paleoecologie*. Editura Ars Docendi, Bucureşti, 185 p.

Lazăr, I., Grădinaru, M., 2014. *Paleoenvironmental context and paleoecological significance of unique agglutinated polychaete worm tube–ferruginous microstromatolite assemblages from the Middle Jurassic of the Southern Carpathians (Romania).* Facies 60: 515–540. https://doi.org/10.1007/s10347-013-0390-0

Lazăr, I., Grădinaru, M., Petrescu, L., 2013. *Ferruginous microstromatolites related to Middle Jurassic condensed sequences and hardgrounds (Bucegi Mountains, Southern Carpathians, Romania).* Facies 59(2): 359–390. https://doi.org/10.1007/s10347-012-0313-5

Patrulius, D., 1969. *Geologia Masivului Bucegi şi a Culoarului Dâmbovicioara*. Editura Academiei Române, Bucuresti, 321 p.

FOSSILIFEROUS SITES WITH DINOSAUR REMAINS FROM SÂNPETRU (HAŢEG BASIN)

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Type: Paleontological natural reserve, 5 hectares. Category IV IUCN.

Coordinates: "*La Scoabă*" site: N 45°32′37.8″/ E 22°54′33.7″, elevation: 430 m
"*La Groapă*" site: N 45°32′40.0″/ E 22°54′54.8″, elevation: 442 m

Location and access: Hunedoara County. Sânpetru village, Sibişel Valley

Access from East: National road DN66 Petroșani–Hațeg up to Sântămăria Orlea, until the intersection with DJ868 up to the communal road 79 Sânpetru–Ohaba Sibişel. Leave the car at the information point and visit the sites by foot on both banks of the river.

Access from West: National road DN68 Caransebeș–Hațeg up to Păclişa, then on the county road DJ686B Păclişa–Sânpetru up to the intersection with DJ686. Follow then the *Dinosaur Valley* touristic route, south of the Sânpetru village.

The outcrops are more accessible on the left side of the river, along the road, while on the right bank the only easy accessible site is number 6 in Fig. 1 – "*La Cărare*", which can be visited after crossing the bridge from the information point; all the other sites are on steep, rather dangerous, slopes. The most visited site is "La *Scoabă*" on the left side of the valley, 300 m from the information point, which includes informative panels and facilities for the visitors.

Description: Series of several fossiliferous sites on both sides of the Sibişel Valley (Fig. 1) each of them consisting of pararhythmic successions of conglomerates, coarse sandstone, grey, blackish, and reddish silty mudstones. The deposits crop out, more or less continuously, on the left side of the valley. They were folded at the end of Cretaceous, showing dips up to 45°, even more (70°) in the southern part on the right side of the river (site 17 in Fig. 1 – "*Sub Târnov*"). The deposits represent a complex fluvial, braided river system, formed and functional during the last four million years of the Cretaceous (approx. 72–68 mil. years), after the uplift of the marine deposits formed during most of the Mesozoic in this Eastern region of the Alpine-Carpathian realm. Sedimentologically, the coarser rocks, conglomerates and coarse sandstones, correspond to sediments accumulated into the channels, whereas the finer rocks, cross-bedded or finely laminated sandstones and siltstones are indicative for the channel margins: levees, bars and crevasse splays. The overbank includes the flood plain environments with humid, swampy zones in which the buried vegetation generated coal lenses, and much drier zones on which reddish soils including carbonate concretions (calcrets) have been formed.

From the Sibişel valley outcrops came the first dinosaur bones in the Haţeg Basin and, generally, in Romania, described by Franz Nopcsa, the renowned paleoherpetologist. The dinosaur remains were found in 1897 by the sister of the scientist, at that time student in Geology in Vienna (the precise location of these bones is not known). Many thousands bones and bone fragments were later found in the valley outcrops, and were studied by Nopcsa who published several articles on them. Nopcsa's historical collection is located in the British Museum Natural History from London. A new collection started to grow after 1977, when the systematic searches on the Sibişel valley were resumed, 60 years after Nopcsa ceased his studies in the region. A few thousands of more or less fragmented bones were found, most of them inventoried in the Paleontological collections of the Universities of Bucharest and Cluj, and also of the Museum of Dacian and Roman Civilization in Deva. The bone remains belong to at least 15 species of dinosaurs, both herbivorous: sauropods (*Magyarosaurus*), ornithopods (*Zalmoxes*, *Telmatosaurus*), ankylosaurs (*Struthiosaurus*), and carnivorous: mostly dromeosaurids, identified upon their characteristic teeth. Remains of turtles and crocodilians are also common.

The fossil remains are generally represented by disarticulated bones and bone fragments, found isolated in different types of rocks or associated in the same place, in so-called "fossiliferous pockets" (*multitaxic bonebeds*). At the origin of the "fossiliferous pockets" are the streams on the hill slopes, more active in the spring time, which transported and accumulated the remains of the dead animals, or, especially catastrophic events (flooding, fire, disease), which caused mass deaths. The remains were transported by streams into the river channel where they were fragmented and abraded, being deposited, mostly in the marginal parts of the river, when the current slowed down. This explains why in a "fossiliferous pocket" tens and even more than a hundred bones belonging to different species and having different ages, (remains of young and old individuals) are found together.

Lithostratigraphy and Age: Sânpetru Formation, Maastrichtian (aprox. 72–68 mil. years).

Importance:

a. Scientific: Besides the historical importance, as the place where the first dinosaur remains in Romania were found, the fossiliferous sites from Sânpetru provided a very large number of dinosaur and other fossil vertebrate bones. The discoveries occasioned tens of papers published in prestigious scientific journals throughout the world, authored and co-authored by outstanding specialists, but also young researchers. The papers refer to new taxa of dinosaurs and turtles. The oldest mammal remains in Romania were also discovered in this region.

The geological section of the Sibişel Valley, south of Sânpetru, also represents the lithostratigraphic stratotype for one of the two uppermost continental units in the Haţeg Basin, namely the Sânpetru Formation. The area is important for sedimentologic studies on fluvial deposits, favored by the continuous outcrops, also for the taphonomic studies, documenting the *multitaxic stratiform bonebed* type of bone accumulation.

b. Touristic: The entire geological Haţeg Basin is included since 2004 in a Geopark ***(Haţeg Country dinosaurs geopark)*** – a new type of protected area in the world, focused on geosite protection within an integrated approach to the protection of the natural and cultural heritage of a region. Several geotrails were created in the Haţeg Geopark, among these a very interesting one was organized along the Sibişel Valley, south of the Sânpetru village – ***The Dinosaurs Valley***, marked by informative panels at the parking lot, but also at some geosites (*La Scoabă* – Fig. 2, *La Cărare*). A small museum, ("*The house of the dwarf dinosaurs*") which includes a reconstruction of a fossiliferous site and dinosaur paintings made children from the village, can be visited in Sânpetru village. Few bone remains might be seen in the Vulc family house (no. 107 in the Sânpetru village), where the visitors can listen to interesting old stories about the dinosaur discoveries in this region, from Mr. Doenel Vulc, a villager who participated at the first excavations in the Sibişel Valley, after Nopcsa's time.

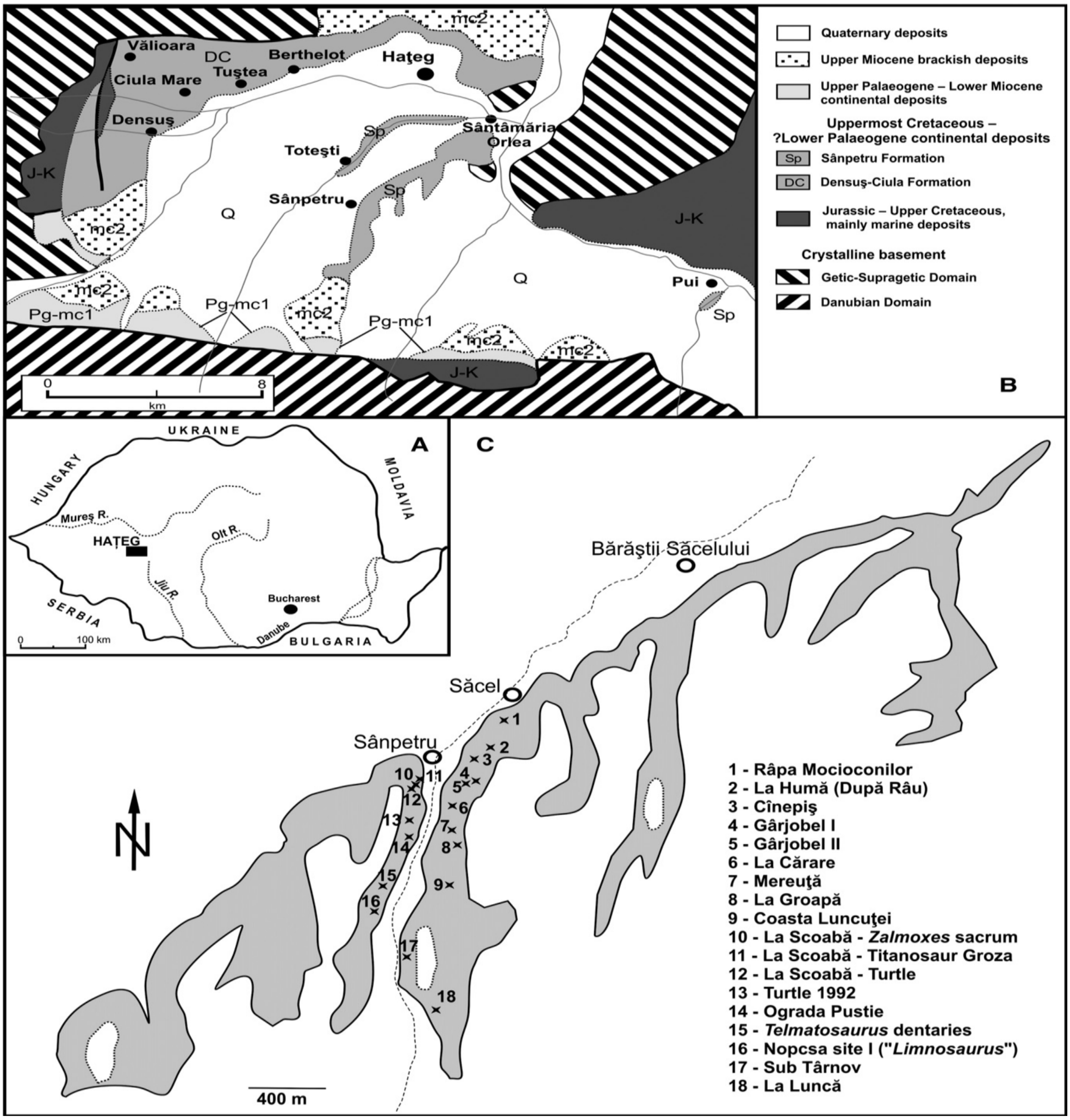

Figure 1. Dinosaur-bearing vertebrate fossil sites from Sânpetru. A. Location of the Haţeg Basin in SW Romania. B. Synthetic geological map of the Haţeg Basin. C. Location of dinosaur-bearing vertebrate fossil sites along Sibişel Valley

Figure 2. General view of “La Scoabă” site, showing the fossil-bearing fluvial deposits of the Sânpetru Formation

REFERENCES

Csiki-Sava, Z., 2014. *Peisaje cu dinosauri*. In: Grigorescu, D., Vasile, Ş., Csiki-Sava, Z. (eds.), Geodiversitatea Ţării Haţegului, Editura Universităţii din Bucureşti, pp.82–85.

Csiki-Sava, Z., Vremir, M., Vasile, Ş., Brusatte, S.L., Dyke, G., Naish, D., Norell, M.A., Totoianu, R., 2016. *The East Side Story – the Transylvanian latest Cretaceous continental vertebrate record and its implications for understanding Cretaceous-Paleogene boundary events*. Cretaceous Research 57: 662–698. http://dx.doi.org/10.1016/j. cretres.2015.09.003

Grigorescu, D., 2010. *The Latest Cretaceous fauna with dinosaurs and mammals from the Haţeg Basin — a historical overview*. Palaeogeography, Palaeoclimatology, Palaeoecology 293: 271–282. http://dx.doi.org/ 10.1016/j.palaeo.2010.01.030.

TUŞTEA – DINOSAUR INCUBATION SITE

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Type: Paleontological. Protected area, 0.5 hectares. Category IV IUCN – Natural reserve of paleontological type.

Coordinates: N 45°36′25.4″/ E 22°50′53.1″, elevation: 540 m.

Location and access: Hunedoara County. General Berthelot commune. Oltoane Hill, ca. 500 m north of the Tuştea village.

Access from East: National road DN66 Petroşani–Haţeg (55 km) up to the intersection with DJ 687C Haţeg–Răchitova until Tuştea (8 km).

Access from West: National road DN68 Caransebeş–Haţeg up to the intersection with the communal road Toteşti–Densuş (6 km), cross the bridge at the entrance in Densuş and continue 2 km until the intersection with the county road DJ 687C Răchitova–Haţeg, turn right and go 2.5 km to Tuştea.

Description: A rock fall along a 10 m high vertical escarpment in the Oltoane Hill, north of the Tuştea village occasioned in 1988, the discovery of few dinosaur eggs, apparently disposed in superposed rows. The real distribution of the eggs was clarified some years later, after the section leveling, which allowed the detailed mapping of the site.

The egg-bearing levels are located in the upper part of a 3 m thick brick-red siltic mudstone with superposed pedogenic levels with carbonate nodules (calcrets), overlied by a 6 m thick packet of matrix-supported conglomerate and cross-bedded coarse sandstones. A scour erosional surface marks the contact between the red mudstone and the conglomerate bed (Fig. 1).

According to the sedimentological studies, coupled with isotope analysis, the conglomerate and the associated coarse sandstone correspond, respectively to channel-lags, point bars and lateral accretion-lags, while the red mudstone beds represent deposition in a well-drained floodplain submitted in a warm, subtropical climate to pedogenetic processes, which lead to the formation of the calcisol in which the eggs were laid.

More than hundred egg remains were found in the two levels of the red mudstone section. The eggs are subspherical, 14-16 cm in diameter with a 2.1–2.8 mm thick eggshell, ornamented by compact semispherical tubercles. The eggs usually preserve only the bottom parts, almost complete eggs were rarely found. The eggs are tightly packed, grouped in clusters of 2 to 14 eggs, either randomly or linearly disposed (Fig. 2). The disposition of the eggs within the clusters seems to preserve much of the original nests setting, affected by the pre-burial erosion and weathering and by the post-burial processes of lithostatic compaction and diagenesis. According to the eggs shape and size, and the eggshell structural characters, the eggs were assigned to *Megaloolithus siruguei*, one of the oospecies of the Megaloolithidae family, the largest one among the dinosaur oofamilies. Traditionally, the *megaloolithid* eggs are assigned to the sauropod-titanosaurid dinosaurs, but in Tuştea, the hatchling remains, including partial skeletons, found near the egg clutches or even within them, belong to the hadrosaurid ("duck-billed dinosaur") *Telmatosaurus transsylvanicus*, a common dinosaur species in the fauna from the Haţeg Basin. Due to this unexpected association of eggs and hatchlings, the case is currently quoted as "the Tuştea puzzle", more debated by specialists in dinosaur oology.

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The red mudstone beds of Tuştea also provided macroscopic and microscopic bone remains of more than 20 taxa of vertebrates, including frogs, lizards, snakes, turtles, crocodiles, ornithopod, sauropod and theropod dinosaurs, pterosaurs and multituberculate mammals.

Lithostratigraphy and Age: Densuş-Ciula Formation, Middle member, Late Cretaceous –Maastrichtian, 70–68 mil. years.

Importance:

a. Scientific: Associations of dinosaur eggs and baby skeletal remains are rarely known in the world, no more than 10 clear cases are known, Tuştea included among these. The fact that hadrosaurid baby remains were found associated to the megaloolithid eggs, and not those of a titanosaurid sauropod, as would have been expected, based on other cases in the world, sustains that the megaloolithid type of eggs were laid by different herbivorous dinosaurs which increases the scientific significance of the site. Tuştea, discovered in 1988, is the first site with dinosaur eggs found in Romania, five new places were added afterwards, all of them in Late Cretaceous deposits, most of them in the Haţeg Basin.

b. Touristic: Tuştea is one of the most attractive place for the visitors of the "Haţeg Country dinosaurs Geopark". A museum of dinosaur eggs and babies is planned to be created in the Tuştea village.

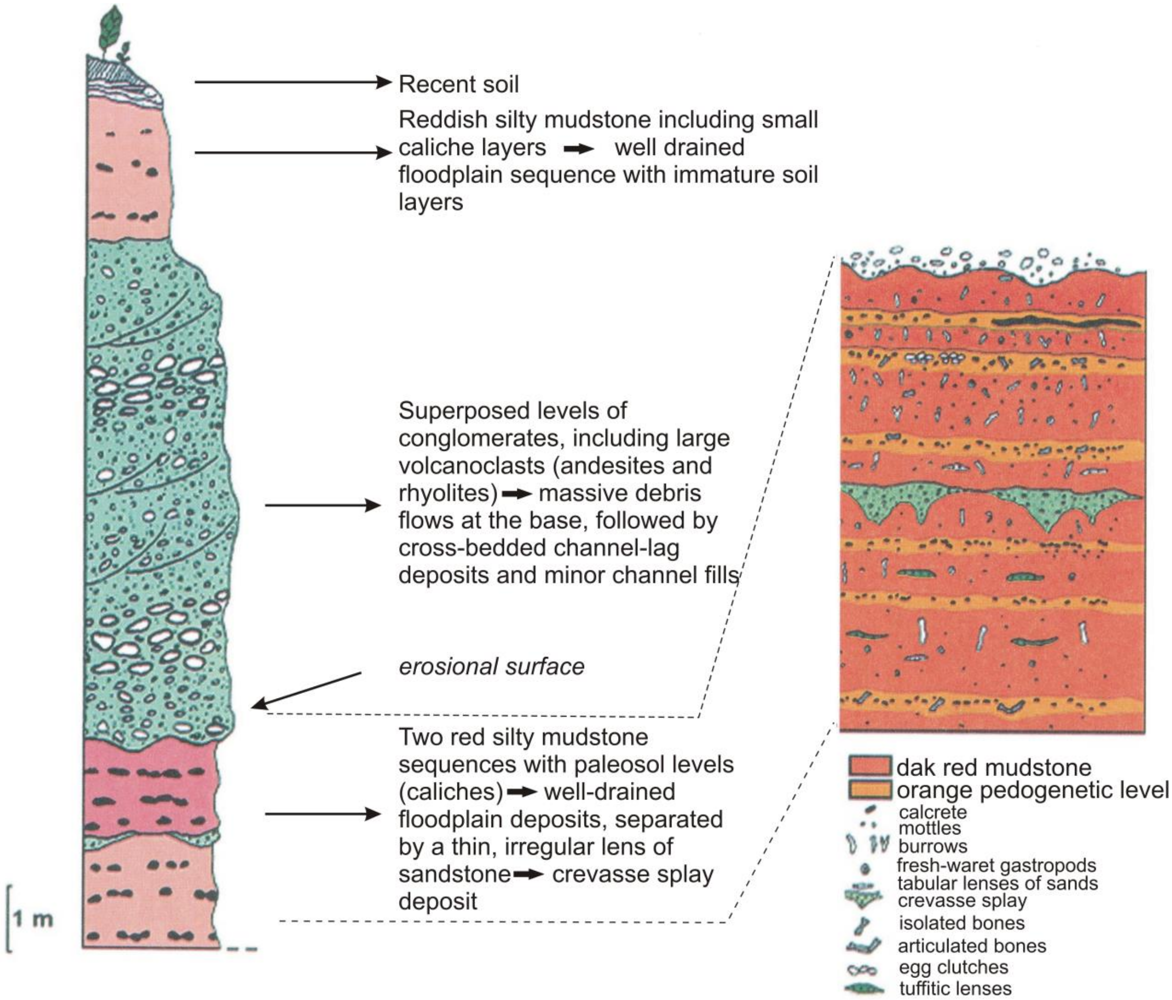

Figure 1. Litostratigraphic column of the sedimentary succession from Tuștea

Figure 2. Cluster with 14 egg remains. It seems the cluster reflects the form and size of the original nest

Figure 3. Partial skeleton of a *Telmatosaurus transsylvanicus* hatchling

REFERENCES

Botfalvai, G., Csiki-Sava, Z., Grigorescu, D., Vasile, Ș., 2017. *Taphonomical and palaeoecological investigation of the Late Cretaceous (Maastrichtian) Tuştea vertebrate assemblage (Romania; Haţeg Basin) - insights into a unique dinosaur nesting locality*. Palaeogeography, Palaeoclimatology, Palaeoecology 293: 271–282. https://doi.org/10.1016/j.palaeo.2016.12.003

Bojar, A.-V., Csiki, Z., Grigorescu., D., 2010. *Stable isotope distribution in Maastrichtian vertebrates and paleosols from the Hațeg Basin, South Carpathians*. Palaeogeography, Palaeoeclimatology, Palaeoecology 293(3-4): 329–342. https://doi.org/10.1016/j.palaeo.2009.08.027

Grigorescu D**.**, Weishampel D., Norman D., Şeclăman, M., Rusu, M., Baltreș, A., Teodorescu V., 1994. *Late Maastrichtian dinosaur eggs from the Hațeg Basin (Romania).* In: Carpenter, K., Hirsch, K.F., Horner, J.R. (eds.), Dinosaur Eggs and Babies, Cambridge University Press, p. 75–87.

Grigorescu, D., 2017. *The 'Tuştea puzzle' revisited: Late Cretaceous (Maastrichtian) Megaloolithus eggs associated with Telmatosaurus hatchlings in the Haţeg Basin*. Historical Biology 29(5-6): 627–640. https://doi.org/10.1080/08912963.2016.1227327

Grigorescu, D., 2014. *Puii de dinosaur*. In: Grigorescu, D., Vasile, Ș., Csiki-Sava, Z. (eds.), Geodiversitatea Ţării Haţegului, Editura Universităţii din Bucureşti, p. 80–81.

OLIGOCENE ICHTHYOLOGICAL SITES FROM THE PIATRA NEAMŢ REGION: COZLA, PIETRICICA, CERNEGURA

IONUŢ GRĂDIANU

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Type: Paleontological reservations. Category IV IUCN (2000).
Reservations surface: Cozla: 0.1 km^2
Pietricica: 3.95 km^2
Cernegura: 1.98 km^2

Coordinates: Cozla: N 46°56′99″/ E 26°21′65″, elevation: 650.6 m
Pietricica: N 46°55′77″/ E 26°22′84″, elevation: 526.9 m
Cernegura: N 46°54′42″/ E 26°21′57″, elevation: 852 m

Location and access: northern/eastern/southern part of the Piatra Neamţ city (Fig. 1).

Description: The hypoxic to anoxic conditions which dominated throughout the Oligocene and part of the Early Miocene in the Paratethys Sea, influenced the sedimentation within the basins and resulted in the formation of various bituminous rocks: menilites, bituminous marls, dysodilic shales. Such sediments were predominant during this period of time and are referred to as "maykopian and menilitic facies" (e.g. Popov *et al*., 2004). Systematically and biogeographically significant Oligocene to Miocene fish faunas have been collected from the bituminous rocks of the Romanian Eastern Carpathians region. In the Piatra Neamţ area, the excavations were made in the outcrops situated on the Pietricica, Cozla, and Cernegura Mountains as well as Agârcia village. Geologically, these mountains are positioned at the contact between the Carpathians and the Subcarpathians. From tectonic point of view, the geological formations of this region pertain to the Bistriţa Half-Window of the Marginal Folds Nappe (Grasu *et al*., 1988). The fish fossils are preserved in the bituminous marls and the dysodilic shales.

Age: Lower to Upper Oligocene (34–23 mil. years)

Importance:

a. Scientific: The presence of the Oligocene fish fossils on the Cozla Mountain was noted for the first time to the end of the 19th century by Leon C. Cosmovici. Later on, M. Ciobanu continues the collecting and the study of the fish fossils from the Oligocene formations from the Piatra Neamț area and based on the remarkable number of the specimens he organized the Natural Sciences Museum of Piatra Neamţ in the late sixties. Presently, most of the type specimens collected from Cozla and Pietricica Mountains (Fig. 1) as well as numerous additional materials from the Romanian Eastern Carpathians were deposited in the paleontological collections of the Natural Sciences Museum Piatra Neamţ (Figs. 2, 3) and at the Department of Geology of "Alexandru Ioan Cuza" University of Iaşi. These fishes are well preserved and the Lower Oligocene collections to date (Cosmovici, 1887; Simionescu, 1904; Ciobanu, 1977; Baciu, 2001, Grădianu, 2010) contain specimens of more than 50 species representing about 20 families, sardines (Clupeidae), bristlemouths (Gonostomatidae), hachetfishes (Sternoptychidae), lightfishes (Photichthyidae), lanternfishes (Myctophidae), codlets (Bregmacerotidae), squirrelfishes (Holocentridae), dories (Zeidae), boarfishes (Caproidae), shrimpfishes (Centriscidae), bigeyes (Priacanthidae), sharksuckers (Echeneidae), jacks and pompanos (Carangidae), pomfrets (Bramidae), snake mackerels (Gempylidae), cutlassfishes (Trichiuridae), mackerels and tunas (Scombridae), driftfishes (Nomeidae), lefteye flunders (Bothidae), triplespines (Triacanthidae). In addition, there are representatives of several extinct fish families (Palaeorhynchidae, Euzaphlegidae, Repropcidae, Digoriidae). The Oligocene ichthyofauna from this part of the Romanian Eastern Carpathians, will improve the understanding of the morphology, taxonomy and phylogenetic relationships of several taxa as well as the evolutionary and paleoegoegraphical framework and traits, concerning the development of the present-day fish fauna of the Atlantic Ocean and the Mediterranean Sea, with implications for that of the Indo-Pacific as well.

b. Educational, Cultural: Oligocene fish fossils collection is emblematic for the Piatra Neamţ Natural Sciences Museum and represents one of the most important and valuable scientific collection of this type from Romania, part of the specimens being included in the national cultural heritage.

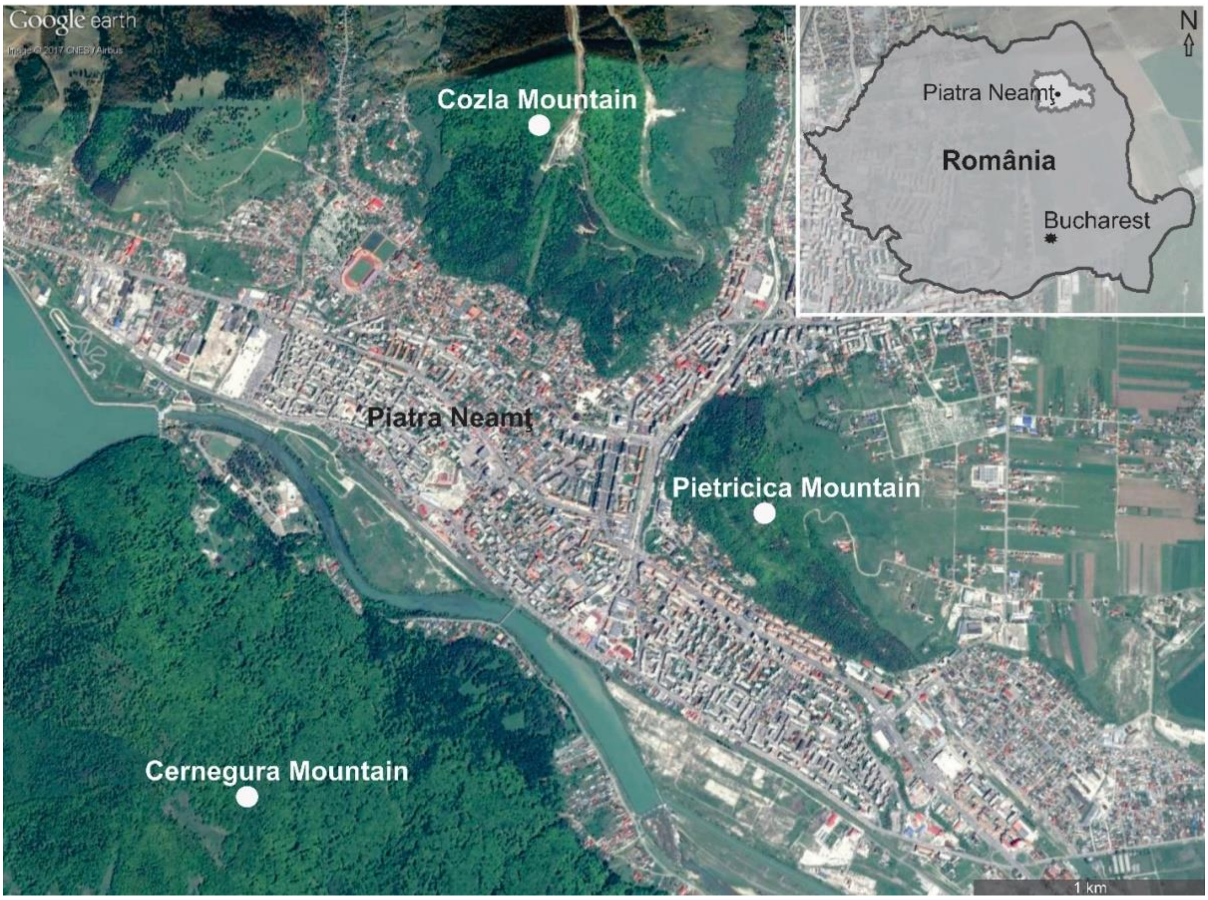

Figure 1. Satellite view of the Piatra Neamț city region and the location of the Oligocene fish fossils sites

Figure 2. *Auxides cernegurae* (Ciobanu, 1970), No. 158, Bituminous Marls, Cernegura Mountain, paleontological collection of the Natural Sciences Museum Piatra Neamţ

Figure 3. *Gymnosarda dysodilica* Ciobanu, 1977, No. 156, Lower Dysodilic Shales, Cozla Mountain, paleontological collection of the Natural Sciences Museum Piatra Neamţ

REFERENCES

Baciu, D.S., 2001. Studiul ihtiofaunei fosile din Oligocenul și Miocenul inferior al Pânzelor de Tarcău și Vrancea-sectorul central și nordic. Ph.D. thesis, “Alexandru Ioan Cuza” University, Iași, Romania, 197 p.

Ciobanu, M., 1977. *Fauna fosilă din Oligocenul de la Piatra Neamț*. Editura Academiei Republicii Socialiste România, București, 159 p.

Cosmovici, L.C., 1887. *Les couches a Poissons des Monts Pietricica et Cozla, District de Neamtz, Ville de Peatra (Roumanie).* Buletinul Societății de Medici și Naturaliști, Iași, 1: 96–105.

Grasu, C., Catană, C., Grinea, D., 1988. *Flișul carpatic. Petrografie şi consideraţii economice*. Editura Tehnică, București, 208 p.

Grădianu, I., 2010. Studiul peştilor fosili din flișul terţiar dintre valea Moldovei și valea Sucevei (Carpații Orientali). Ph.D. thesis, Universitatea „Alexandru Ioan Cuza”, Iași, Romania, 250 pp.

Popov, S.V., Rogl, F., Rozanov, A.Y., Steininger, F.R., Shcherba, I.G., Kovac, M., 2004. *Lithological-Paleogeographic maps of Paratethys (10 Maps Late Eocene to Pliocene).* Courier Forschungsinstitut Senckenberg 250, 1–46.

Simionescu, I., 1904. *Asupra câtorva pesci fosili din terţiarul românesc*. Academia Română, Publicațiunile Fondului Vasile Adamachi, Bucureşti, 6: 205–222.

THE LITTORAL NEAR-SHORE VERTEBRATE FAUNA FROM CREDINŢA (CONSTANŢA COUNTY)

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Type: Paleontological natural reserve – Nature Monument, 9.64 ha. Category III IUCN.

Coordinates: N 43°58′43.05″/ E 28°13′40.63″, elevation: 140 m.

Location and access: Sand quarry in the south-west of Credința village, Chirnogeni Commune, Constanța County. Access: The county road Medgidia-Cobadin (30 km), follow then the comunal road Cobadin- Negrești-Plopeni-Casicea (32 km).

Description: The quarry of poorly cemented quartzose sandstone at the outskirts of the Credința village is known for the rich vertebrate assemblage characteristic for the littoral and the near-shore of the Sarmatian sea. The largest number of isolated bones was provided by pinipeds (seals) – *Phoca pontica*, followed by the perciform-sparid and clupeid fishes. However the largest taxonomic diversity is shown by birds which include several new taxa: a pelecaniform *Sarmatosula dobrogensis* (nov. gen., nov. sp.), a stork *Ciconia sarmatica* nov. sp., a crane (*Grus miocaenicus*), together with species of ducks (*Anas, Aythia*), gooses (*Anser*), gulls (*Larus*), albatroses (*Diomedea*), and limnicol seabirds (charadriiformes). In the faunal assemblage, the seals are the only group represented by a complete ontogenetic series, from very young to adults and old individuals. It's worth mentioning that the ratio between babies and the adult remains suggests a high mortality of the pups at birth or soon after, similar with what happens today within various communities of seal species.

The taphonomic research processed through methods of numeric taxonomy, completed by sedimentological analysis on the origin and transportation of the sands revealed the origin of the animals in three biotopes, more or less distant one to another, their remains being gathered together into the fossil assemblage mostly by the sea currents. The recognized original biotopes are: the rocky littoral - for the seals and birds, the latter inhabiting distinct niches; the arenitic benthic eulittoral for the sparid fishes; the pelagic eulittoral - for the clupeids. A fourth biotope – pelagic-sublittoral was recognized, about 9 km north of Credința, where few remains of cetaceans (dolphins and small whales – cetotheres) were found within the sands interbedded with *Nubecularia* (benthic foraminifera) and *Mactra* (bivalve mollusk) limestones.

Importance:

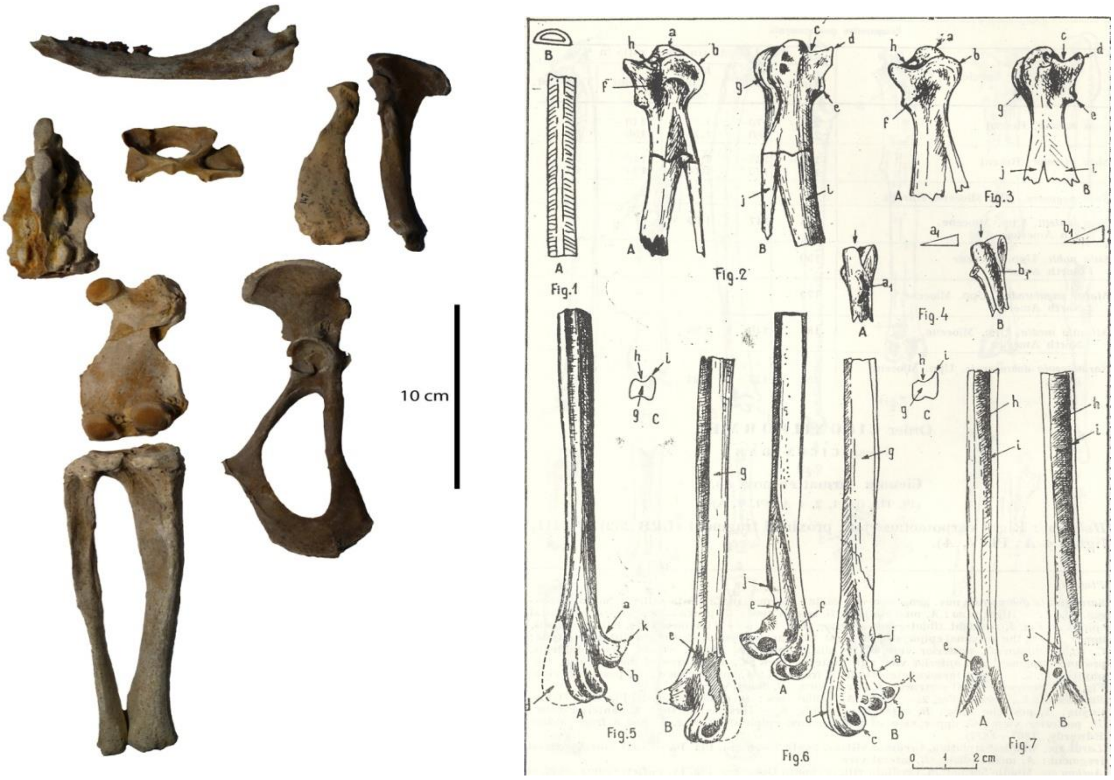
a. Scientific: Besides the interesting fossil vertebrate assemblage which depicts a complex ecosystem interrelating different littoral and near shore biocenoses, the geology of the site indicates, contrary to the previous paleogeographic reconstructions, the uneven relief of the sea bottom in the South Dobrogea sector of the Sarmatian sea, with uplifted islands, inhabited by coastal animals. The fact was confirmed by the geophysical measurements which outlined areas of gravimetric maximum in both Credinţa and Ciobăniţa regions (Airinei *et al*., 1967).

b. Touristic: Presently the flatness and the dry aspect of the region does not attract the visitors. An elaborated touristic planning linking the natural and cultural sites in the Cobadin-Ostrov-Negru Vodă region, including the Tropaeum Traiani monument at Adamclisi, the Ciobănița-Osmancea bird reserve, the Plopeni Lake, together with arrangements in the fossiliferous sites, would definitely improve the situation.

Rev. Roum. Géologie, Tomes **61–62**, p. 111–113, 2017–2018, București

Lithostratigraphy and Age: The sandy facies of the Cotu Văii Formation. Middle Miocene (Middle Sarmatian: Basarabian), 11.0–11.5 mil. years.

Figure 1. Credința quarry. The poorly cemented quartzose sandstone overlied by limestone with *Mactra* shells



A B

Figure 2. Seal (*Phoca pontica*) (A) and bird remains (B): the stork *Ciconia sarmatica* (upper row) and the crane *Grus miocenicus* (bottom row), both new species in the Sarmtian sand from Credinţa

REFERENCES

Airinei, S., Stoenescu, S., Velcescu, G., 1967. *Studiul anomaliilor gravimetrice regionale și locale din Dobrogea şi zonele limitrofe pentru stabilirea structurii geologice de adâncime*. Arhiva Institutului, Geofizică aplicată, Bucharest.

Grigorescu, D**.**, 1978. *Paleoecologia faunei de vertebrate marine din Sarmatianul Dobrogei de Sud*, Anuarul Muzeului de Științe Naturale Piatra Neamț 4: 193–202.

Grigorescu, D**.**, Dinu C., 1978. *Aspecte sedimentologice și paleogeografice relevate de nisipurile cuarțoase Basarabiene din Dobrogea de sud.* Analele Universității din București, Seria Geologie 27: 37–45.

Grigorescu, D**.**, Constantinescu, V., Dragomirescu, L., 1986. *A paleoecologic analysis of the Bassarabian (Middle Sarmatian) vertebrate association from Credința and Ciobănița (Southern Dobrogea) based on the taphonomic characters processed through methods of numerical taxonomy*. Travaux du Museum d'Histoire Naturelle "Grigore Antipa" 28: 257–283.

Grigorescu D**.**, Kessler E., 1988. *New contributions to the knowledge of the Sarmatian birds from Southern Dobrogea in the frame of the Eastern Paratethyan avian fauna*. Revue Roumaine de Géologie 32: 91–97.

ŞOMLEU HILL – BETFIA

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Type: Paleontological, Speleological, Floral and Faunal. Category III IUCN.

Coordinates: N 46°58'94"/ E 22°01'19", elevation: 347 m.

Location and access: Betfia is situated in Bihor County about nine kilometres southwest from Oradea. It is accessible from the route E 79, through Băile 1 Mai and Haieu. In the local limestone quarry, situated on the south-western slope of Şomleu Hill, numerous fossil sites yielding abundant vertebrate remains of early Pleistocene age have been unearthed during the last century. The fossil sites are protected by national law (listed as 2.187 – Şomleu Hill Fossil Point) and integrated within the ROSCI008 Betfia site of Natura 2000 network (1758 ha).

Description: The most important objective in this area is the presence of a partly destroyed endokarst system (local name: Betfia crater), formed in early Cretaceous limestone of Barremian–Aptian age, representing a mostly vertically developed cave with pot-hole like vertical corridors connecting larger cavities (Figs. 1, 2). The so-called Betfia 'pothole' has been discovered by a local miner using explosives to extract limestone. Presently, part of the brecciated cave sediments crop out due to weathering or being unearthed during the mining activities (Fig. 3). The main fossil vertebrate localities are located in the vicinity of Betfia 'pothole' and in the north-eastern part of the new limestone quarry, recently closed. **Betfia 2** (sometimes referred as Püspökfürdő), situated in the vicinity of Betfia 'pothole', is the most famous fossil locality. Kormos (1930) published first the mammalian fauna of Betfia 2 (1–4), which served later as the stratotype of Biharian faunas (Kretzoi, 1941, 1953; Jánossy, 1986). The fossil vertebrate fauna of this locality is representative for the biozone of *Mimomys pusillus – Mimomys savini* (Fejfar *et al*., 1998) with an approximate age of 1.4–1.2 Ma (Matuyama chron). Other vertebrate localities in the close vicinity of Betfia 2 have been numbered as Betfia 1, 3 and 4 by Kormos (1930), whereas the others as Betfia 7 and Betfia 9 by Terzea & Jurcsák (1969), Terzea (1984, 1988, 1994, 1995). The latter locality probably represents the remnant of Betfia 2 (e.g., see Hír & Venczel, 1997) and may be also correlated with the biozone of *Mimomys pusillus – Mimomys savini*. The same is true for the localities Betfia 10–12, located in the north-eastern part of the local limestone quarry. Beside the members of *Mimomys*, *Allophaiomys pliocaenicus* appears as one of the commonest fossil rodent from these localities (Hír & Venczel, 1997), whereas among insectivores the most frequent are: *Sorex* (*Drepanosorex*) *margaritodon, S. minutus, S. runtonensis, Beremendia fissidens*, *Talpa minor* and *T. fossilis* (Rzebik-Kowalska, 2000a, b). Unique extinct taxa described from the above localities are: the palaeobatrachid frog *Palaeobatrachus* (=*Pliobatrachus*) *langhae* (Fejérváry, 1917; Venczel, 2000) and the hynobiid land salamander *Parahynobius betfianus* (Venczel, 1999). Betfia 13, situated approximately 100 m north to the Betfia pothole, is the geologically oldest locality from Şomleu Hill yielding among others: insectivores (e.g., *Blarinoides mariae, S. minutus, S. runtonensis, Petenyia hungarica, Beremendia fissidens, Desmana thermalis* (Rzebik-Kowalska, 2000a, b), rodents (*Prospalax priscus, Trogontherium boisvilletti, Glis minor, Villanyia exilis, Mimomys* gr. *pliocaenicus, Allophaiomys pliocaenicus deucalion, Lagurus arankae*), several rare mammal taxa (*Epimeriones dacicus, Sminthozapus betfianus,* and *Macaca sylvana* cf. *florentina* (Terzea, 1973, 1984, 1991, 1995; Terzea & Jurcsák, 1976) and birds (e.g., *Anas* cf. *crecca*, *A. querquedula*, *Lyrurus* cf. *tetrix*, *Francolinus capeki*) (Kessler, 1975). Based on the presence of *Mimomys pliocaenicus* and *Villanyia exilis* the fauna may be correlated with the *Mimomys pliocaenicus* biozone (Fejfar *et al*., 1998). The youngest fauna from Betfia is represented by that known from the upper layer of Betfia 7 (Betfia 7/4), which may be correlated with the biozone of *Mimomys savini* (Terzea 1994, 1995).

Age: Early Pleistocene (biozones: *Mimomys pliocaenicus*; *Mimomys pusillus – Mimomys savini*).

Importance:

a. Scientific: The Betfia site has an important scientific relevance for several reasons:

– the locality Betfia 2 was designated as the type locality (*stratotype*) of the Biharian land mammal age, very rich in macro- and microvertebrate remains, subject of numerous scientific papers;

– the fossil faunal assemblage is relevant for the climatic changes at the Pliocene/Pleistocene boundary;

– the area presents various forms of exo- and endokarst relief.

Figure 1. Șomleu Hill with distant view of the Betfia pothole

Also, the rich extant floral and faunal associations of Betfia have an outstandind scientific importance:

Floristic: Betfia is listed as a characteristic habitat (no. *6250* within ROSCI008 protected area) for the Pannonic loess steppic grasslands, as part of the Pannonian biogeographical region. Among the rare floral taxa within the ROSCI008 Betfia site there are: *Ruscus aculeatus*, *Galanthus nivalis*, *Erythronium dens-canis*, *Orchis purpurea*, *O. morio*, *Platanthera bifolia*, and *Crocus reticulatus*.

Faunistic: Betfia cave represents an important habitat (8310 Caves – not open to public) to protect the bat populations of *Barbastella barbastellus*, *Miniopterus schreibersii*, *Myotis bechsteinii*, *M. blythii*, *M. myotis*, *M. daubentonii*, *Rhinolophus ferrumequinum* and *R. hipposideros*. Within the site appear a series of European protected species, e.g., gastropods (*Chilostoma banaticum*), insects (*Lucanus cervus*, *Carabus hampei*), amphibians (*Triturus cristatus*, *Bombina variegata*), lizards (*Lacerta viridis*, *L. agilis*), snakes (*Elaphe longissima*, *Coronella austriaca*), birds (*Falco tinnunculus*, *Dryocopus martius*, *Oenanthe oenanthe*, *Lanius collurio*), and mammals (*Mustela nivalis*, *Capreolus capreolus*).

b. Touristic: The main touristic attraction of the area is linked to the karstic forms.

Figure 2. The Betfia slope with the improvements
for the Biharan faunas stratotype

Figure 3. The closed limestone quarry

REFERENCES

Fejfar, O., Heinrich, W.-D., Lindsay, E.H., 1998. *Updating the Neogene rodent biochronology in Europe*. Mededelingen Nederlands Instituut voor Toegepaste Geowetenschappen TNO 60: 533–554.

Kretzoi, M., 1941. *Die unterpleistozäne Säugetierfauna von Betfia bei Nagyvárad*. Fäldtani Közlöny 71: 308–355.

Terzea, E., 1995. *Mammalian events in the Quaternary of Romania and correlations with the climatic chronology of Western Europe*. Acta Zoologica Cracoviensia 38(1): 109–120.

Venczel, M., 1999. *Land salamanders of the family Hynobiidae from the Neogene and Quaternary of Europe*. Amphibia-Reptilia 20(4): 401–412.

THE WOMEN'S CAVE
(PEŞTERA MUIERILOR)

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Type: Archaeological, paleontological, and mineralogical.

Coordinates: N 45°11′13.61″, E- 23°45′22.05″; elevation: 650 m.

Location and access: The Women's Cave is situated in southeastern area of the Parâng Mountains (Southern Carpathians) near the locality of Baia de Fier (Gorj County).

Description: Peștera Muierilor (The Women's Cave) is a tiered karst system (Fig. 1) carved in the Upper Jurassic - Lower Cretaceous limestone (Fig. 2), from the SE Parâng Mountains, on the right side of the Galbenul Gorge, at 650 m a.s.l. The cave network is broadly NNW-SSE trended, matching the main local fracture lines. It has been created by the limestone dissolution by waters infiltrated along a fracture system, simultaneously with the incision of Galbenul stream through the gorge. The cave has functioned as a succession of underground meanders of the Galbenul River and has a total length of about 8 km. The Women's Cave has stirred scientific interest since the 1870s, when several researchers visited the site and noticed the fossil bone accumulation. The excavations in the Women's Cave started in 1929 and continued during the '1950s. Besides the human remains, researchers also found fossils of a MIS (Marine Isotope Stage) 3 fauna consisting mainly of *Ursus spelaeus*, *Panthera spelaea*, and *Crocuta crocuta spelaea*. The excavations extended from the Southern Entrance towards the Mousterian side-passage. At that time, only a small part of the cave's lower level was known, and the researchers assumed that the actual entrance had been used as a shelter and entryway for both humans and large mammals. In 1952 fossil human bones have been discovered in two areas of the cave. Holocene human remains were found in the entrance area, while the Upper Paleolithic human remains were found much deeper in the cave, in the Mousterian Passage (Nicolăescu-Plopșor, 1938; Păunescu *et al*., 1982). The Women's Cave is famous mostly for hosting the remains of one of the earliest modern humans (*Homo sapiens*) in Europe (Photo 1), directly dated to ~35 ka cal BP (Olariu *et al*., 2003; Soficaru *et al*., 2006). In the last decades, new passages have been discovered by "Hades" Caving Club, containing a massive deposit of fossil remains and bioglyphs. The recent documentation of the Hades Passage shed new light on the possible evolution of the cave during the MIS 3 and the cave sector that is more likely to host the largest fossil accumulation. A new paleontological excavation was conducted by an interdisciplinary team of the "Emil Racoviță" Institute of Speleology, revealing outstanding amounts of fossil remains belonging to cave bears, cave lions, wolf and cave hyenas (Photo 2). In addition, fossil remains of herbivores and micromammals contemporaneous with the fossil carnivore remains were found in the same excavation trench. This work is undergoing but preliminary data show that most fossil remains are MIS 3 in age with a high degree of reworking owing to successive phases of flooding of cave passages. The speleothems are relatively well represented in all the cave passages. The most important mineralogical work was done by Diaconu (2008), who studied the presence of peculiar cave minerals as related to guano deposits. Besides common carbonate mineral species such as calcite and aragonite and silicates such as illite, he reported phosphate minerals such as hydroxylapatite [$Ca_5 (PO_4)_3(OH)$] and brushite [$CaH (PO_4)] \cdot 2H_2O$. In 1975, Diaconu reported the presence of carbonate hydroxylapatite in the lower level of the cave, under the name of *dahllite*. Speleothem samples from an upper level of the cave have been dated using the U/Th method and yielded ages between 90 (+/-6) - 120 (+/-5) ka. The archaeological, paleontological and mineralogical findings from the Women's Cave represent unique features that highlight the exceptional importance of this cave as the repository of these "archives" and offers new perspectives in understanding the evolution of the Upper Pleistocene palaeoenvironment in Southern Carpathians.

Age: Upper Jurassic for the limestone; MIS 3 or older for most of cave sediments.

Importance:

a. Scientific. This cave is of particular scientific significance due to its archaeological, paleontological and mineralogical features. These provide important data on the evolution of the cave as well as the evolution of environment, fauna and humans in the southern part of the Parâng Mountains (Southern Carpathians).

b. Touristic. It was the first cave of Romania fitted with electric light (1963) and it typically has more than 100, 000 visitors/year. The touristic passage has a length of 800 m and the main attractions are speleothem formations and fossil remains including a reconstructed cave bear skeleton.

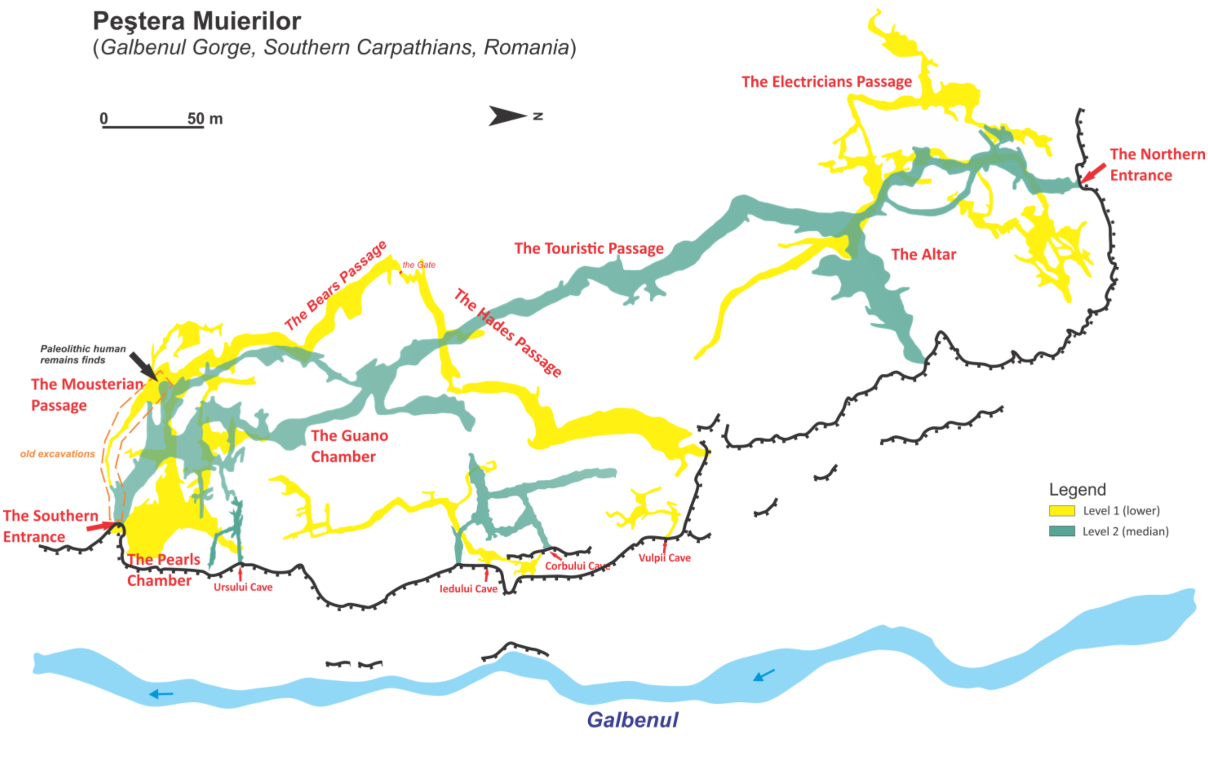

Figure 1. Simplified map of the Women's Cave surveyed by the "Emil Racoviţă" Institute of Speleology and "Hades" Caving Club (Base map courtesy of Grigore Stelian)

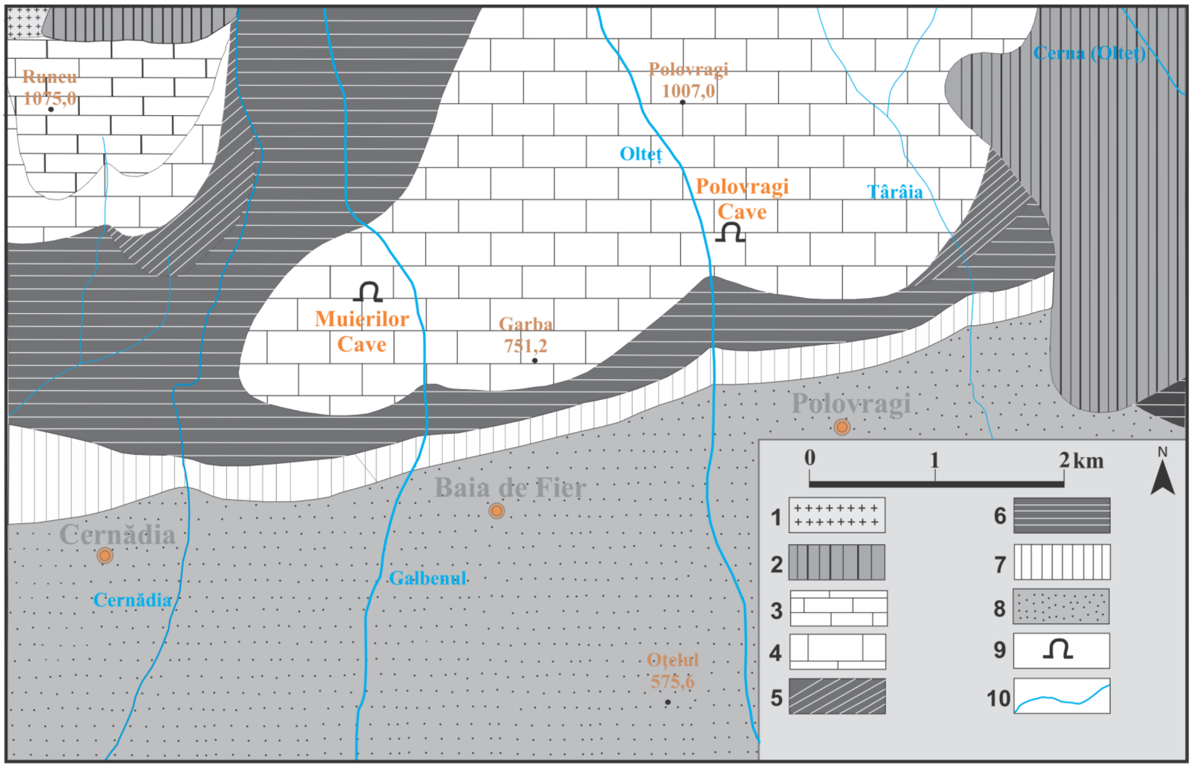

Figure 2. Geological map of the Polovragi - Cernădia area (after Diaconu *et al*., 2008): 1-Parâng Granites; 2-Metamorphic rocks; 3-Early Jurassic (limestone); 4-Late Jurassic (limestone); 5-Late Cretaceous (conglomerates, sandstones and clays); 6-Early Miocene (marly clays); 7-Middle Miocene (sands and clays); 8-Late Miocene (gravels and sands); 9-Caves; 10-Rivers

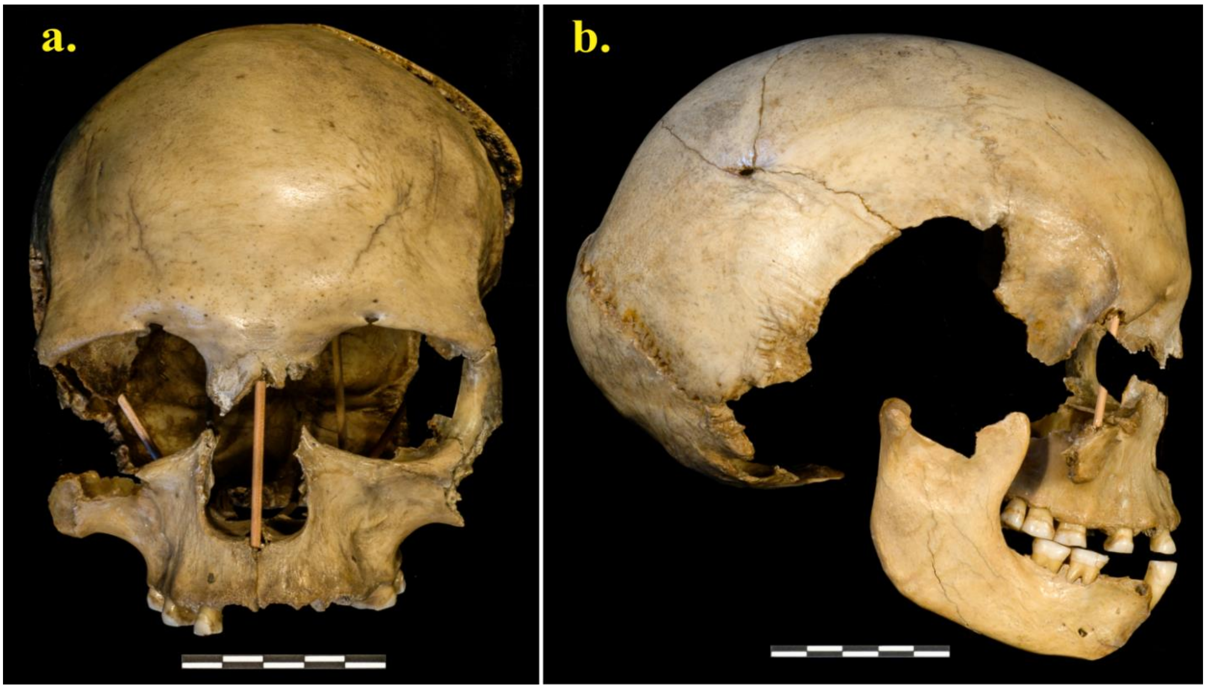

Photo 1: a. The Muierii 1 cranium (anterior view); **b.** The Muierii 1 cranium (right lateral view)
Photos: Museum of Oltenia, through the courtesy of Aurelian Popescu.

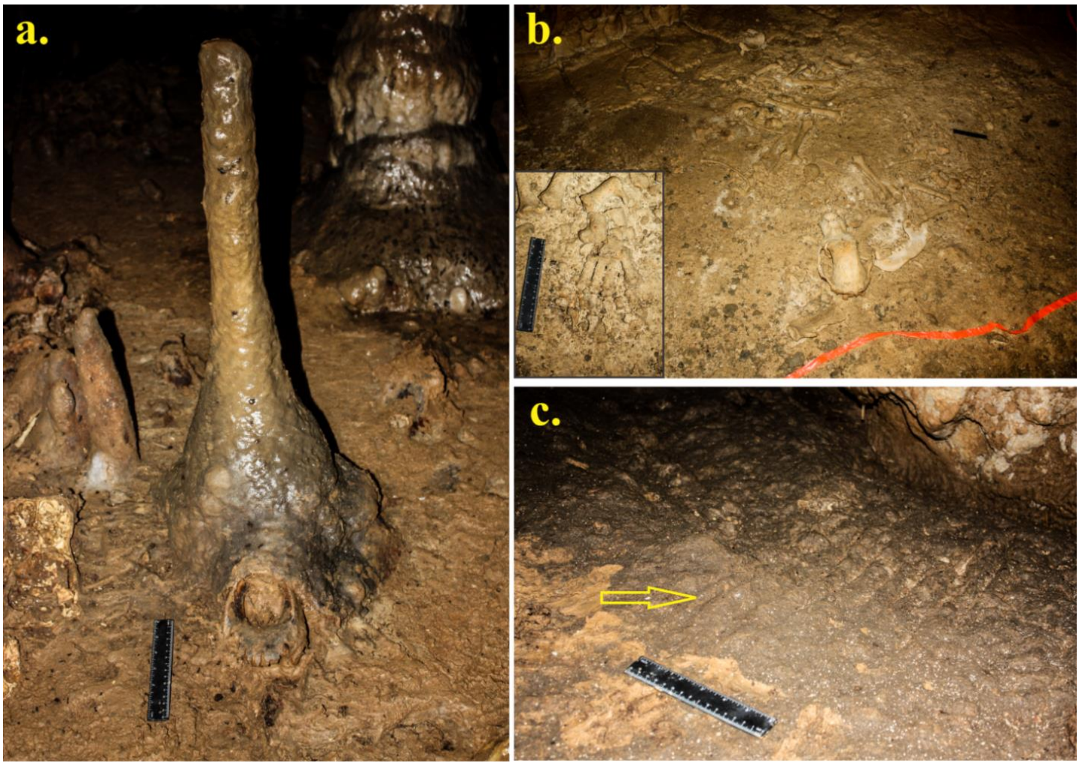

Photo 2: a. A cave bears skull with a stalagmite grown on top (Urșilor Pasage); **b.** *Ursus spelaeus* skeleton in anatomical connection (Hades Passage); **c.** Cave bear scratch marks from Urșilor Passage.

Photo 3: a. Aragonite crystals; **b.** Calcite (gray); **c.** Hydroxylapatite crust (red).

REFERENCES

Diaconu G., Medeşan A., 1975. *Spéléothemèmes de dahllite dans la grotte "Peştera Muierii", Baia de Fier, Roumanie.* Travaux de l'Institut de Spéologie „Émile Racovitza" 14: 149–165.

Diaconu, G., Dumitraş, A., Marincea, Ş., 2008. *Mineralogical analyses in Peştera Polovragi (Olteţului Gorges) and Peştera Muierii (Galbenului Gorges). Gorj County*. Travaux de l'Institut de Spéologie „Émile Racovitza" 47: 89–105.

Doboş, A., Soficaru, A., Trinkaus, E., 2010. *The Prehistory and Paleontology of the Peştera Muierii, Romania.* Études et Recherches Archéologiques de l'Université de Liège 124, 112 pp.

Nicolăescu-Plopşor C.S., 1938. *Le paléolitique en Roumanie*, Dacia 5-6: 1935–1936.

Olariu, A., Alexandrescu, E., Skog, G., Hellborg, R., Stenström, K., Faarinen, M., Persson, P., 2003. *Dating of two paleolithic human fossils from Romania by accelerator mass spectrometry.* In: Oancea M., Schiaua C., Grecu D., Dumitriu M. (eds.), IFIN-HH Scientific Report 2001-2002: "Horia Hulubei" National Institute for Physics and Nuclear Engineering, Bucharest, p. 81.

Păunescu A., Rădulescu C., Samson P., 1982. *Découvertes du paléolithique inférieur en Roumanie*. Travaux de l'Institut de Spéologie „Émile Racovitza" 21: 53–62.

Soficaru A., Doboş A., Trinkaus E., 2006. *Early modern humans from the Peştera Muierii, Baia de Fier, Romania.* Proceedings of the National Academy of Sciences USA 103(46): 17196–17201. https://doi.org/10.1073/pnas.0608443103