Mineralogical and Geochemical Study of Silto-lutitic Petrofacies of Upper Ypresian/Lower Lutetian Age

Paleoenvironmental significance

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Research on Paleogene deposits of Eastern Carpathian foreland basin revealed the existence of relative geotectonic stability alternating with episodes of increased instability, the change in paleoclimates context, meaning the accentuated cooling at the end of Eocene/ the beginning of Oligocene, the change of source areas/sedimentation basin geomorphological relations and sediment production in exondate land. Significant modifications have been identified in alpine foreland basins within Ypresian (Yp)/Lutetian (Lu) limit interval. In this paper we aimed to follow the „imprints" of these events which are stored in silto-lutitic deposits from Eastern Carpathian foreland basin from Bucovina (Eastern Carpathians), within the Yp/Lu interval. For the documentation of the paleoevents of source areas - paleoclimate - depositional areas system we used geochemical markers. Based on mineralogical and geochemical data, our described paleoevents have been correlated with geotectonic and paleoclimatic data for Eastern Carpathian foreland basin and other alpine basins (Pamplona and Basc from Western Pyrenees).

Keywords: petrofacies, geochemical markers, source areas, paleoenvironment significations

The main purpose of this paper is the study of some paleoevents from Yp/Lu boundary interval, which are mineralogical, petrographical and geochemical stored in Paleogene foreland basin deposits in Bucovina (Eastern Carpathians) [1]. In geologic and structural terms, our studied deposits belong to East Carpathian moldavides, namely, from Eastern Tarcãu Nappe (fig. 1).

The structural genesis of Eastern Carpathian Orogeny took place in connection with cretaceous (dacidic: austric and laramic) and Miocene (moldavidic: stiric and moldavic) tectogenesis [1, 2]. Mesocretaceous dacides edified in austric tectogenesis consist of bucovinic (median dacides), transilvanic (transilvane dacides) overthrust nappes system and the most internal blanket nappes, black and Baraolt (external dacides) flysch nappes. The most external dacides, such as Ceahlãu and Bobu nappes are added to the laramic tectogenesis (Cretaceous-Paleogene). Laramic movements led to peripheral Eastern Carpathian foreland basin setting. Foreland deposits supports the moldavidic structogenesis (stiric and moldavic tectogenesis) with Teleajen, Audia and Tarcãu nappes, marginal and sub-Carpathian creases. Sedimentary environments and source areas of Eastern Carpathian area underwent various changes induced by increased tectonic instability in the interval from the last dacidic (laramic) tectogenesis to the moldavic and miocene tectogenesis [3-6].

Paleoclimate evolution initiated a series of events that caused major effects on ecosystems and sedimentary environments. On a global scale, the paleoclimate evolved from the arid tropical Paleocene (Paleocene-Eocene thermal maximum, PETM), to a gradual cooling (with a thermal optimum in Ypresian, EECO) and to the installation of the glacial phase at the end of Eocene [2, 7]. Relatively deep marine environments have a high degree of inertia and the thermal gradient has low values and decreases with depth. Under these conditions, mineralogical and chemical imbalances that occur are recorded as mineralogical and geochemical markers in the mineral fraction of the sediment. In the particular case of sandstones petrofacies, the paleoclimate imprints are preserved only under relatively small distance sediment transportation and a high rate of sedimentation, these conditions ensuring a rapid and deep enough burial that preserves the chemical and mineralogical sediment composition [8, 9].

Geological data

Pietroasa is our reference section and it opens deposits of Moldavidian Domain, sub-Carpathian Nappe, Vrancea Nappe and Eastern part of Tarcãu Nappe, evolved in Doamna Lithofacies [10]. Tarcãu Nappe consists in a succession of northern-eastern scales vergency, evolved toward the stiric and moldavic overthrust belt. On the Pietroasa's creek, a left tributary of the Voitinel creek outcrop Senonian-Oligocene scales deposits.

In Pietroasa section, cretaceous-oligocene flysch deposits are opened and evolved in Doamna Lithofacies [10]. Lithostratigraphical succesion of Rãu Hill – Cociniº scale begins with Hangu Formation (sandstone-limestone-

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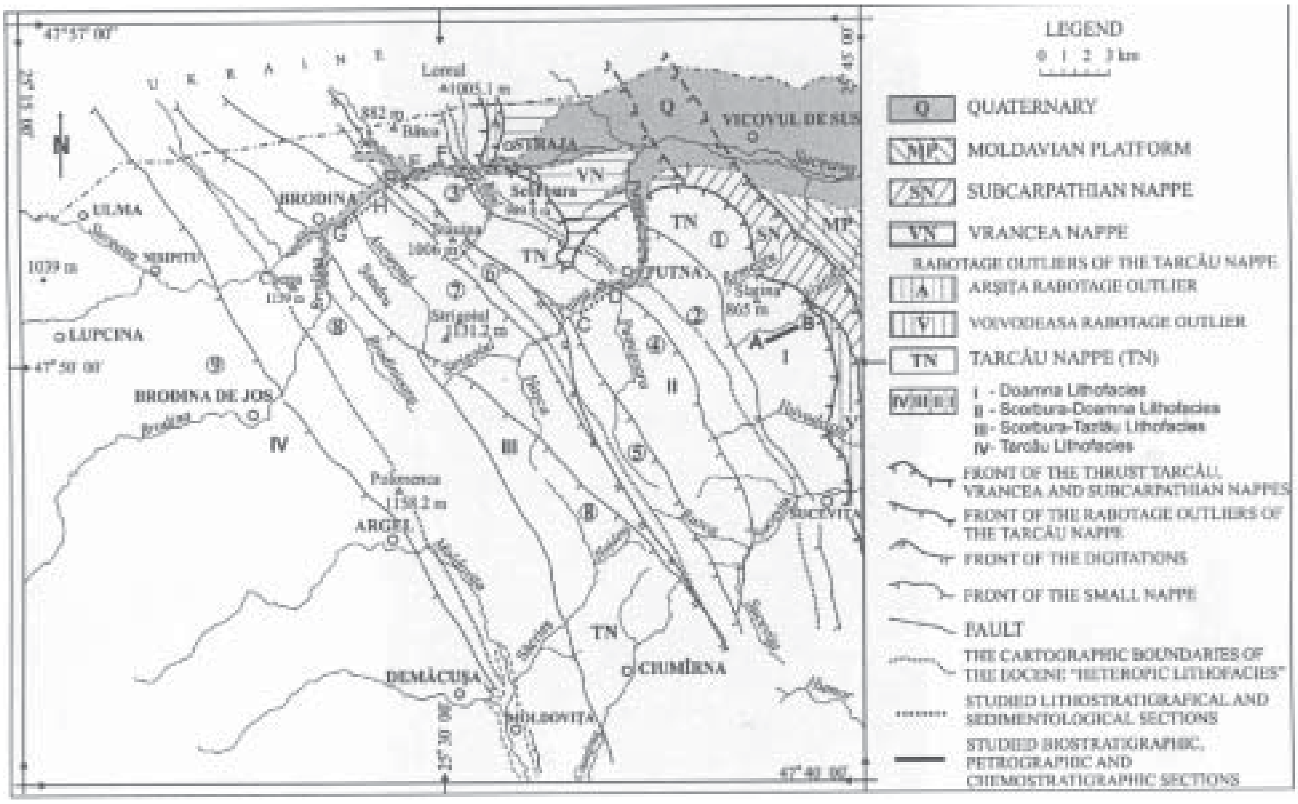

Fig. 1. Simplified geological map of the Outer Moldavides from the Suceava basin (Bucovina, Eastern Carpathians). Area with location of the studied logs [2]. *The subunits of the Tarcãu Nappe*: *Outer digitation*: 1 – The Dealul Rãu - Cocini° Small Nappe; 2 – The Lomul-Scorbura-Suceviþa Small Nappe; 3 – The Straja Small Nappe; 4 – The Bâtca-Glodul-Bercheza Small Nappe; 5 – The Poiana Crucii Small Nappe; *Inner digitation*: 6 – The Stauina-Sihãstria Small Nappe; 7 – The Obcina Mare-Hojdeni Small Nappe; 8 – The Solovanu-Polonenca Small Nappe; 9 – The Ulma-Demãcu°a Syncline.

marl petrofacies, Maastrichtian), on which are arranged eocene deposits of Izvor Formation (sandstone-limestone turbidite; Danian – lower Ypresian), Surcele Formation (sandy debrite; lower Ypresian), Straja Formation (heterolitic petrofacies; Ypresian), Suceviþa Formation (sandstone/sandstone-silt-lutite/heterolitic petrofacies; upper Ypresian – Lutetian), Doamna Formation (calcareous petrofacies , Bartonian), Viþeu Formation (sandstone-silt petrofacies; lower Priabonian), Strujinoasa-Plopu (lutit petrofacies, silt-lutit-sandstone petrofacies; lower Priabonian – upper Priabonian) and „marl with globigerine and Lucãce°ti sandstone" (sandstone-marl petrofacies, upper Priabonian). The column is closed by oligocene deposits evolved on euxinic facies, such as „lower menilite", followed by "bituminous marl" and Kliwa Formation (fig. 1).

Rãu Hill – Cocini° Yp/Lu boundary interval has been separated based on the limestone nannoflora and agglutinated foraminifera assemblages. Suceviþa Formation includes first turbiditic event deposits, sedimentologicaly separated in the sedimentary suite of Suceviþa Formation. The deposits have a 6.5 m stratigraphic thickness [1]. The samples have been taken from Tde sequences of Bouma turbiditic rhythms and they were biostratigraphicaly, mineralogicaly and geochemically analyzed (figs. 1 and 2).

Experimental part

Materials and methods

Based on the calcareous nannoflora, the Yp/Lu limit has been biostratigraphicaly determined in the first turbiditic interval from the base of Sucevita Formation [13-15]. The geographical coordinates of the analyzed profile are: x = 47.84552° N, y = 25.69055° E, z = 591.00 m. The studied interval (18 m thickness) belongs to Sucevia Formation (fig. 1).

The capability to determine isotope abundances is a main feature of mass spectrometry. Inductively coupled plasma mass spectrometry (ICP-MS) provides excellent sensitivity, precision and good accuracy for isotope ratio measurements with practically no restriction with respect to the ionization potential of the element investigated [2, 16].

In order to determine the chemical composition, the samples were crushed by grinding the samples in an agate mill and then were disaggregated by treatment with concentrated nitric acid and concentrated perchloric acid. The total content of silica (SiO_2) was determined by gravimetric and other elements were determined in solution by flame atomic absorption spectrometry [17-20]. Total carbon content was determined by Scheibler volumetric method with a Bernard calcimeter and the electrical conductivity was determined through the conductometric method in aqueous extract (1:5) [17-20]. The pH and redox potential were determined by direct potentiometric method, the suspension method in bidistilled water. (10 g sample / 25 mL solution, the sample particle size <0.1 mm; contact between phases: 30 min) [21].

Results and discussions

Petrographic data

Lithofacial characteristic of upper Ypresian/lower Lutetian limit from Pietroasa section is imprinted by the alternation debritic flow (Lowe sequences) and turbiditic flow (Bouma sequences). Yp/Lu limit interval overlaps with the first turbiditic event, which is separated in the base of Sucevita Formation (fig. 2). Based on Herron diagram [22], the geochemical analysis of siltolutites from Tde sequences indicates a significant variation of petrographic

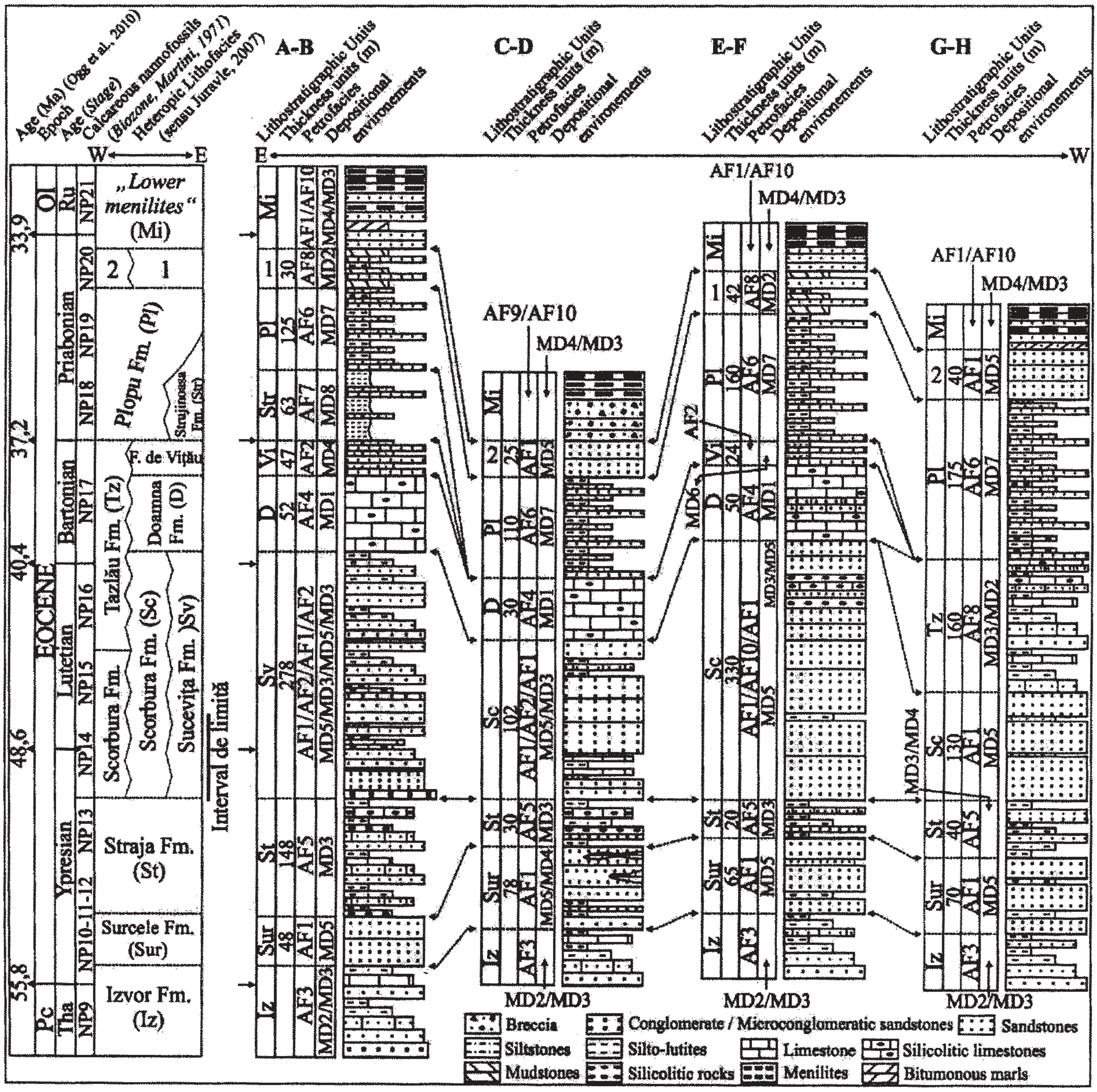

Fig. 2. Lithofacial variation of the Eocene deposits from the northern portion of the Moldavidian Domain, across the Tarcău Nappe (Bucovina, Eastern Carpathians) [2]. Pc - Paleocen, Tha - Thanetian, Ol - Oligocen, Ru – Rupellian; Heteropic Lithofacies (described from East to West [9]): A-B. *Section Pietroasa*- Doamna Lithofacies, C-D ºi E-F. *Sections Putna* and *Caraula*- Scorbura-Doamna Lithofacies, G-H. *Section Frasin* - Scorbura-Tazlău Lithofacies; Lithostratigraphic Units: Vi - Viþãu Formation, Str – Strujinoasa Formation, 1 –„*Globigerina marls and Lucãceºti sandstone*" Formation, 2 - „*Lucãceºti sandstone*" Formation; Petrofacies [11]: AF1 – sandstones petrofacies, AF2 – lutitic-sandstones petrofacies, AF3 – calcareous-sandstones petrofacies, AF4 – limestones petrofacies; AF5 – heterolitic petrofacies;AF6 – sandstones-lutit petrofacies; AF7 – claystones petrofacies; AF8 – calcareous-claystones petrofacies with sandstone intercalations, AF9 – sandstone petrofacies with heterolitic intraclastes, AF10 – silicolitic petrofacies; Depositional environments [3, 4, 12]: MD1 – platform/ramp carbonates, MD2 – oxic shelf, MD3 – upper continental slope, MD4 – lower continental slope, MD5 – proximal sand rich submarine fan, MD6 – proximal/mid submarin fan; MD7 – fringe fan/basinal plain, MD8 – basinal plain.

types Clay and subordinate with ferruginous clay are dominant, followed by sandy siltolutites and sporadic wache (fig. 3). Lithofacial variations are determined by the paleoevironmental and geotectonic context which cause changes in sedimentological characteristic features and depositional environment.

Source area and geotectonic regime

Paleogeomorphological relations between source areas and the sedimentation basin suffer major changes after the tectogenetic laramic movements (Senonian-Danian) [23]. The oceanic crust of external dacides basin it is consumed during the laramic movements, in the subduction process, and, the external dacidic nappe (sedimentation areas) are adjoined to the crystalline areas during the collision between the median crystalline dacides with the East-European craton areas. The peripheral foreland basin which is overlaid on East European continental margins it is configured in vorland. According to the geotectonic model, the area's primary source for Paleogene foreland basin siliciclastic material is the recycled orogeny (crystalline and sedimentary areas), submerged cordilleras (crystalline) and eastern platforms [23, 24]. Because the samples were projected in the continental lands section, the Adeigbe & Jimoh diagram (2013) [25] confirms the siliciclastic Yp/Lu sedimentation system, (fig. 4, and table 1).

High levels of isotope 39K, 27Al, 24Mg, 44Ca and 238U (table 1) indicated a higher contribution of continental sediments. Sudden changes in the abundances of mentioned isotopes at limit Yp/Lu indicates a process of

Table 1

ISOTOPIC ABUNDANCES AND PHYSICAL-CHEMICAL PARAMETERS OF OUR SAMPLES

No. sample	Isotopic abundances [μg/g]									$CaCO_3$ [g/kg]	pH	E_h [Vollts]	EC [μS/cm]	TCSS [mg/100g]
	^{44}Ca	^{85}Rb	^{88}Sr	^{138}Ba	^{238}U	^{23}Na	^{24}Mg	^{27}Al	^{39}K					
1 / 13	11987.10	549.40	76.10	118.90	0.80	171.70	5846.80	36372.80	2210.10	13.65	8.32	0.237	170.2	109.10
2 / 15	12880.70	552.40	75.50	96.20	0.70	127.30	4828.70	33361.60	2363.50	11.83	7.94	0.235	88.0	56.41
3 / 16	18049.20	535.90	71.60	95.50	0.80	158.70	5790.70	37761.00	2234.70	31.86	5.73	0.225	37.0	23.72
4 / 17	10232.20	578.40	62.60	103.90	0.50	143.90	5623.40	37725.80	2514.00	13.05	6.68	0.251	83.2	53.33
5 / 18	13222.90	578.50	82.80	112.40	0.60	172.50	5035.60	36552.10	2388.00	5.16	8.11	0.252	37.8	24.23
6 / 20	14502.30	211.90	79.10	90.10	0.60	176.60	4808.40	31725.60	2085.40	8.80	6.08	0.262	78.8	50.51
7 / 21	10911.00	545.80	63.20	100.00	0.50	179.60	4853.00	34338.70	2283.30	1.52	8.29	0.278	83.6	53.59
8 / 22	11277.50	667.60	93.20	156.40	0.50	250.20	4160.10	39231.40	3252.00	1.82	8.05	0.283	77.2	49.48
9 / 24	19607.90	580.60	101.20	117.30	1.00	147.70	3503.40	29230.20	2761.60	30.04	5.59	0.303	81.8	52.44
10 / 25	9858.60	596.00	59.70	164.90	0.90	136.20	3776.00	31702.30	2679.60	0.30	5.77	0.312	78.0	50.00
11 / 28	17730.30	470.40	78.10	121.40	0.70	85.60	2546.40	23006.60	2311.20	37.92	6.24	0.344	231.0	148.01
12 / 29	22574.80	187.10	116.40	149.20	0.80	110.00	2255.70	18594.90	2017.70	29.43	8.20	0.349	145.1	93.01

E_h – redox potential. EC – electrical conductivity. TCSS - the total content of soluble salts.

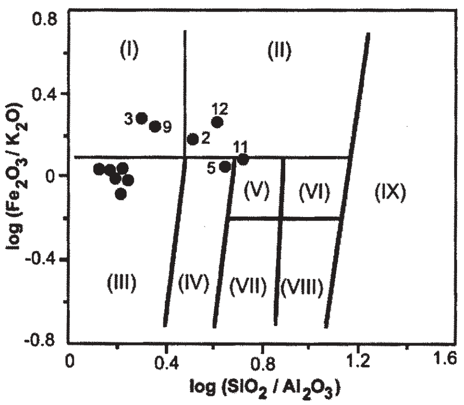

Fig. 3. Siliciclastic rock geochemical classification from Pietroasa section [22]: I. Fe-Shale; II. Fe-Sand; III. Shale; IV. Wache; V. Litharenite; VI. Sublitharenite; VII. Arkose; VIII. Subarkose; IX. Quartz arenite

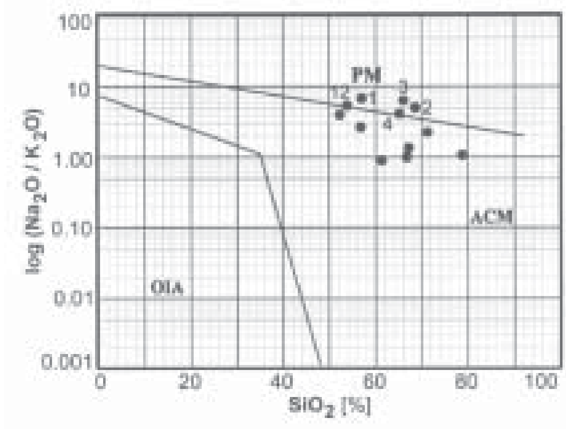

Fig. 5. Geochemical diagram concerning the geotectonic of the source area for silto-lutites from Pietroasa section [26]: PM – Passive Margin, ACM – Active Continental margin, OAI – Oceanic Island Arc

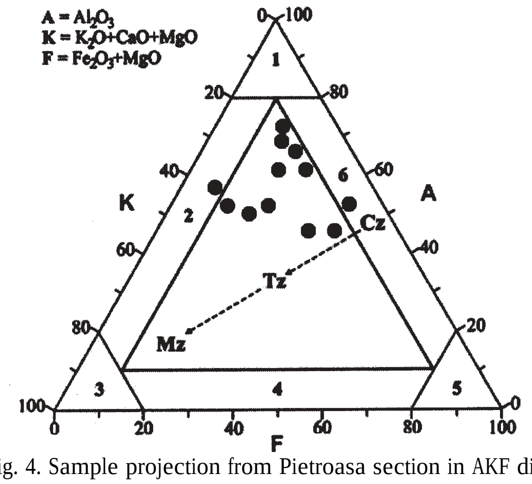

Fig. 4. Sample projection from Pietroasa section in AKF diagram [25]: Cz - continental area, Tz – transitional area, Mz – marine area; 1- Clay Facies, 2 - Clay-limestone Facies, 3 – Limestone Facies, 4 – Ferilitic carbonate Facies, 5 – Ferruginous Facies, 6 – Ferruginous-clay Facies

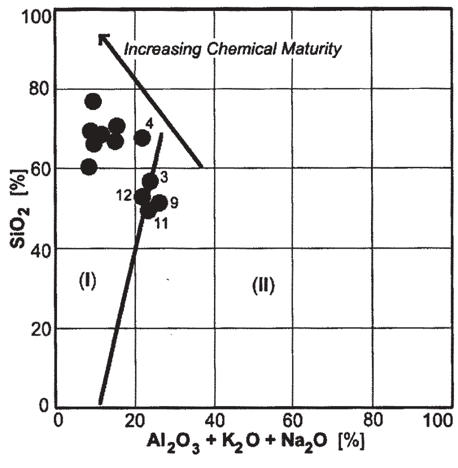

Fig. 6. Pietroasa Section sample projection in paleoclimatic diagram [9]: I - Semi-Humid Paleoclimate, II – Semi-Arid Paleoclimate

quick burial at high depths relatively of the siliclastic sediments, a process accompanied by changes sudden variations and high amplitude of the physico-chemical conditions from sedimentation basin (*p*H, redox potential, salinity) (table 1).

According to the obtained geochemical results, the sedimentation basin is partly placed on active continental margins (transition crust) and partially on passive continental margins (continental crust). The diagram does not describe the configured basin type, but the geotectonic characteristics of the base on which it is installed (stable/ unstable). Because the East European margin is loaded with the dacidic orogenic prism, which is overthrusted to the North-East during the laramic tectogenesis [1], the foreland basins are postcollisional and evolve in a convergence and flexural regime [23]. The sample projection in the 5th diagram confirms the constitution of the basin's base (thinned crust by transition and Eastern Europe continental crust). At the same time, it indicates the described tectonic instability moments in the Yp/Lu limit of East-Carpathian foreland Paleogene [1, 2] and Pyrenees foreland [24] (fig. 5 and table 1).

Paleoenvironment

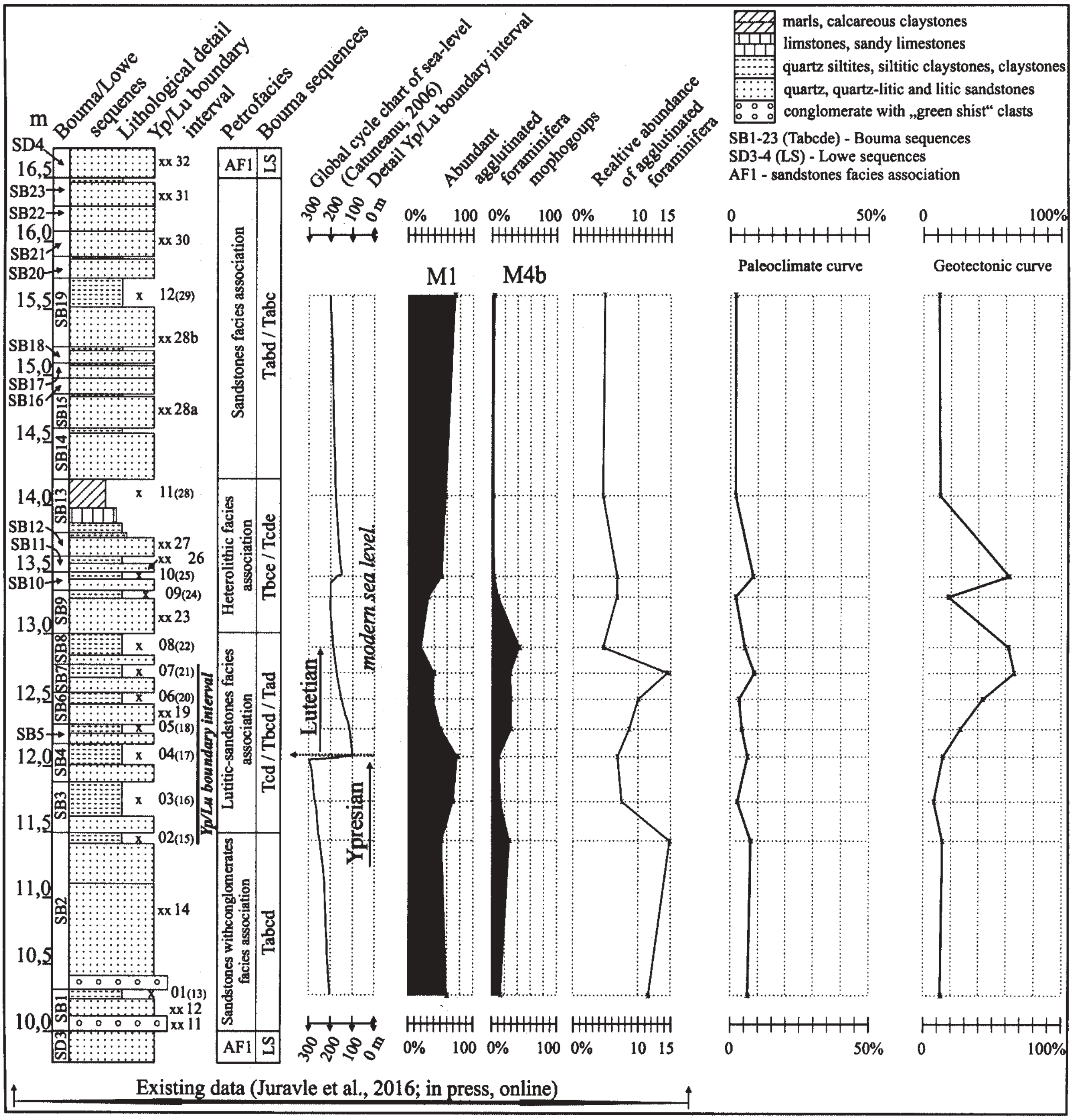

Fig. 7. Paleoevironmental significance of biostratigraphical, lithofacial and geochemical data

The postcretaceous paleoenvirnomental evolutions suffers radical transformations. The transition from an excessive arid climate (thermal maximum in Paleocene, PETM) to the thermal optimum in lower Eocene (EECO) and finally to a glaciation in lower Oligocene, takes place during the Paleocene-Eocene-Oligocene interval. This climate change has a global character and affects the depositional environments and the siliciclastic sediment production in continental areas. Our obtained geochemical results capture climatic changes from Yp/Lu interval that have affected the elevated continental lands and the foreland basin from the Eastern area of Carpathian Orogeny. Climate oscillations transiting to the cold climate of late Eocene are indicated by the sample projection in Suttner and Dutta diagram (1986) [9]. The samples were placed mainly in the field of semi-wet paleoclimate and subordinate in the semi-arid field (figs. 6, 7 and table 1). Our captured climate oscillations have been described in the Paleogene foreland basin of the Pyrenees [24], subarctic lands [7], or in the global paleoclimate trends [27, 28].

The total carbonates content, abundances of the isotopes 85Rb, 88Sr, 138Ba and 23Na and the values of pH, redox potential and salinity (Table 1) marks the paleoclimatic events from the range Yp/Lu (Fig. 7) by sudden changes and with relatively high amplitudes. Consistent with paleoclimatic oscillations and transition to a cold paleoclimate occurred and relatively rapid change (reported on the geological time scale) of physico-chemical conditions to sedimentation. Between Yp/Lu, most likely, the sedimentation basin has functioned in weak acid - weak oxidant, with low salinity.

Conclusions

Using geochemical methods, we proceeded, in this paper, to the analysis of paleoclimatic and geotectonic events held within upper Ypresian/lower Lutetian limit interval.The results were compared with the bio-stratigraphic, sedimentological and a series of geochemical markers in Pietroasa section and on others Paleogene foreland basins. The Yp/Lu limit interval was bio-stratigraphic established using nannoplankton associations and agglutinated foraminifers.

Based on geochemical data presented in this paper and previous research, the obtained results allow the following conclusions:

- the Paleogene foreland basin is installed on the Eastern European margin (proximal on the active transition margin and distal on the passive margin). The source area is predominantly continental (recycled orogeny) and subsidiary submerged cordilleras;

- as shown by the B.P. Roser and R.J. Korsch, in 1986 [26], and O.C. Adeigbe and Y.A. Jimoj, in 2013 [25] used of the diagrams and the shape of geotectonic curve. The depositional environments of the basin are affected by tectonic instability episode installed within the Yp/Lu limit;

- the paleoclimatic curve describes a series of oscillations from semiarid to semi-humid with a general cooling trend;

- the geotectonic and paleoclimatic curves are very well correlated with the dominance of morphogroups and the frequency curve of agglutinated foraminifers to the detriment of limestone and sedimentological characteristics of deposits.

References

1. SÃNDULESCU, M., Geotectonics of Romania, Technical Press, Bucharest, 1984, 450 p.
2. JURAVLE, D.T., CHIRA, C.M., MARE, S., IONESI, V., BULGARIU, D., BREABÃN, I.G., JURAVLE, A., Carpathian Journal of Earth and Environmental Sciences, **11**, no 1, 2016, p. 131.
3. GUERRERA, F., MARTIN MARTIN, M., MARTIN-PÉREZ, A.J., MARTIN-ROJAS, I., MICLÃUS, C., SERANO, F., Geologica Carpathica, **63**, no. 6, 2012, p 463.
4. MICLÃUS, C., LOIACONO, F., PUGLISI, D., BACIU, S., Geologica Carpathica, **60**, no. 5, p. 397.
5. GRASU, C., CATANÃ, C., MICLÃUS, C., BOBOS, I., The molasse of the Eastern Carpathians. Petrography and sedimentogenesis. Technical Press, Bucharest, 199, 227 p.
6. ROMANESCU, G., CURCA, R.G., SANDU, I.G., International Journal of Conservation Science, 6, no. 3, 2015, p. 261.
7. PEKAR, S.F., HUCKS, A., FULLER, M., LI, S., Geol. Soc. Amer. Bull., **117**, 2005, p. 1081.
8. SUTTNER, L.J., BASU, A., MACK, G.H., Journal of Sedimentary Petrology, **51**, 1981, p. 1235.
9. SUTTNER, L.J., DUTTA, P.K., Journal of Sedimentary Petrology, **56**, no. 3, 1986, p. 329.
10. JURAVLE, D-T., Geology of the area between Suceava and Putna Valleys (Eastern Carpathians). (Geologia regiunii dintre Valea Sucevei ºi Valea Putnei (Carpaþii Orientali), Editorial House Demiurg, Iasi, 2007, 319 p.
11. ANASTASIU, N., POPA, M., ROBAN, D.-R., Depositional systems, Romanian Academy Press, 2007, 606 p.
12. JURAVLE, D-T., MICLAUS, C., CHIRA, C.M., GRASU, C., JURAVLE, V., Studia Universitatis Babeº-Bolyai, Geologia, 2009, Special Issue, MAEGS – 16, Cluj-Napoca, p. 193.
13. MARTINI, E., Standard Tertiary and Quaternary calcareous nannoplankton zonation, In: Farinacchi (Ed.): Proceedings II Planktonic Conference, Technoscienza, Roma, 1971, p. 739.
14. OKADA, H., BUKRY, D., Marine Micropaleontology, **5**, 1980, p. 321.
15. KAMINSKI, M.A., GRADSTEIN, F.M. (eds.), Atlas Of Paleogene Cosmopolitan Deep-Water Agglutinated Foraminifera, Grzybowski Foundation Special Publication, 10, 2005, 547 p.
16. BECKER, S.J., J. Anal. At. Spectrom. 17, 2002, p. 172.
17. DEAN, J.A., Analytical Chemistry Handbook, McGraw Hill, Inc., 1995, New York.
18. ROMANESCU, G., TIRNOVAN, A., SANDU, I., COJOC, G.M., BREABAN, I.G., MIHU-PINTILIE, A. Rev. Chim. (Bucharest), **66**, no.10, 2015, p. 1700
19. ROMANESCU, G., PAUN, E., SANDU, I., JORA, I., PANAITESCU, E., MACHIDON, O., STOLERIU, C., Rev. Chim. (Bucharest), **65**, no. 4, 2014, p.401.
20. VASILACHE, V., CRETU, M.A., PASCU, F., RISCA, M., CIORNEA, E., MAXIM, C., SANDU, I.G., CIOBANU, C.I., International Journal of Conservation Science, 6, no. 1, 12015, p. 93.
21. BULGARIU, D., RUSU, C., BULGARIU, L., Analele ªtiinþifice ale Universitãþii din Oradea – fascicula Chimie, **XII**, 2005, p. 37.
22. HERRON, M.M., Journal of Sedimentary Petrology, **58**, 1988, no. 5, p. 820.
23. DINU, C., MAÞENCO, L., DIACONESCU, V., MUNTEANU, I.., Analiza bazinelor de sedimentare, Editura Vergiliu, Bucureºti, 2007, 377 p.
24. PAYROS, A., ORUE-ETXEBARRIA, X., PUJALTE, V., Palaeogeography, Palaeoclimatology, Palaeoecology, **234**, 2006, p. 258.
25. ROSER, B.P., KORSCH, R.J., Journal of Geology, **V. 94**, 1986, p. 635.
26. ADEIGBE, O.C., JIMOH, Y.A., Journal of Environment and Earth Science, **3**, 2013, no. 10, p. 115.
27. ZACHOS, J., PAGANI, M., SLOAN, L., THOMAS, E., BILLUPS, K., Science, **292**, 2001, p. 686.
28. MOLINA, E., GONZALVO, C., MANCHEÑO, M.A., ORTIZ, S., SCHMITZ, B., THOMAS, E., VON SALIS, K., Newsletters on Stratigraphy, **42**, 2006, no. 1, p. 381.

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