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Eocene in Mielnik on the Bug River

Zdzisław KRZOWSKI

Katedra Geotechniki, Politechnika Lubelska, 20-618 Lublin, ul. Nadbystrzycka 40

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Until now in Mielnik on the Bug River residual clays deposited on the chalky limestone of the Upper Cretaceous period have been included in the Eocene. However, lying on top of them quartz-glauconitic sands containing phosphorites belong to the Oligocene. Radiometric dating of glauconite from sandy-glauconitic series showed its Eocene age (41.7±0.4 Ma) which indicates that the Eocene deposit boundary reaches higher than previously thought and that it also comprises of the quartz sands containing glauconite and phosphorites. Dated glauconite has been investigated with respect to its physical, mineralogical and chemical features using X-ray diffraction, thermal and chemical analysis. These studies indicate that the tasted glauconite exhibits a mature nature with a high potassium content and an ordered and well developed structure. All these factors qualify this glauconite for farther geochronological studies.

The mineral composition and petrographic features of the Upper Cretaceous rocks exposed in Mielnik have been determined by microscopic and X-ray diffraction studies.

INTRODUCTION

Until quite recently, in the Lublin region, only two localities have been known with the Upper Eocene deposits containing faunistical documentation. These are: Siemień near Parczew (Z. Wójcik, 1959; E. Woźny, 1966*a, b*, 1967) and Luszawa near Lubartów (J. E. Mojski *et al.*, 1966). Some years later E. Ciuk (1974) announced that Eocene deposits were palaeontologically documented by E. Woźny in other areas of the Lublin region namely, Zawadówka, Dziewicza Góra near Chełm, Góra Puławska and Parchatka near Puławy.

Geological studies performed in the western part of the Lublin Upland showed numerous sites of Eocene deposits also. They appear to be well preserved in the Radawiec Graben (A. Henkiel, 1988*a*) as well as on the residual hills near Piotrków (A. Henkiel, 1988*b*), Białowoda (S. Marszałek *et al.*, 1991) and Wola Studziańska (S. Cieśliński *fide* J. Buraczyński, Z. Krzowski, 1994).

Dating of Tertiary deposits from Polish territory based on K-Ar dating of glauconite was initiated in the 1970's. K-Ar dating of glauconite by H. Kreutzer in the Geochronological Laboratory of Hannover University, Germany, determined that glauconitic deposits in the Szczecin IG 1 borehole (E. Odrzywolska-Bieńkowa, K. Pożaryska, 1978) were from the Middle Eocene age and that glauconitic sands from Boryszew (K. Pożaryska, H. Kreutzer, 1978) were from the Lower Palaeocene age.

In 1991 an Argon Line was installed in the Mass Spectrometry Laboratory of the Physics Institute at the Maria Curie-Skłodowska University in Lublin. This enabled considerable quantities of glauconite samples, originating from the Lublin Upland and the Roztocze Area, to be dated and identified as belonging to Eocene deposits. These deposits were sampled in the following places: Sporniak Palikijski (41.4±3.0 Ma), Janów (41.4±4.0 Ma), Lechówka (50.9±2.9 Ma), Łaszczówka (38.1±4.0 Ma) and Piekiełko (36.3±3.6 Ma) (J. Buraczyński, Z. Krzowski, 1994; Z. Krzowski, 1993, 1995). Moreover K-Ar dating has shown that allogenic glauconite of Eocene age occurs in younger deposits (Mio-Pliocene, Miocene) in Radawiec (54.0±5.0 Ma) and in Czułczyce (37.3±1.0 Ma). Furthermore glauconite of Eocene age has also been shown in Mielnik on the Bug River which is the subject of this paper (Fig. 1).

GEOLOGICAL SETTING

In the area of Mielnik Tertiary deposits which contain the phosphorites are preserved in residual form on the elevated Cretaceous basement.

Fig. 1. Study area on the background of Poland map
LU — Lublin Upland, M — Mielnik

Obszar badań na tle mapy Polski
LU — Wyżyna Lubelska, M — Mielnik

The Upper Cretaceous formations exposed in Mielnik on the Bug River similarly as in the areas around Białystok and Kornica near Biała Podlaska are composed of glaciotectonic floes of terminal moraine of glaciosubstage of Warta (Riss II) (S. W. Alexandrowicz, D. Radwan, 1983; A. Henkiel, personal communication). S. Cieśliński and K. Wyrwicka (1973) include the position of the glacial floe in Mielnik amongst the glaciotectonically translocated floes. However, at the same time the above mentioned authors, expressed doubts as to whether this phenomenon represents a detached glacial block or, whether it is directly connected with Quaternary bedrock since the exact geological position of this Upper Cretaceous outcrop formation has not been determined.

According to the maps of S. Zwierz (1959) and E. Rühle (1955) the Tertiary in the vicinity of Mielnik represents only small island. From this reason Z. Wójcik (1959) proposed that the Upper Cretaceous, Tertiary and Quaternary beds exposed in the Mielnik quarry be recognized as a Natural History Monument due to their classical geological formation (fossil karst, phosphorite-bearing series) and thus be subject to protection. At the bottom of this exposure (Fig. 2) can be seen weakly cemented chalky limestone of the Upper Cretaceous (Campanian, Maastrichtian). These Z. Wójcik (1959) distinguishes as two levels of calcareous rock, that is: a level of *Belemnitella lanceolata* chalk above hard-ground and a level of *Belemnitella mucronata* chalk below the hard-ground. Above the Maastrichtian beds the Tertiary beds overlie transgressively. Lowest of the Tertiary beds, lying on top of the Cretaceous beds, are Eocene brown residual clays. These clays fill numerous karst hollows in the limestone. According to E. Rühle (1947) these clays are probably the equivalent of Toruń clays. Above these residual clays which have witnessed intensive karst processes that occurred between the uppermost Cretaceous and the Eocene lies a phosphoritic series at the base of which lie quartz-glauconitic sands. Just above these sands lie compact sandy concretion series of phosphoritic cement. Where the formation is complete its thickness in places is up to 1.5 m (M. Lazarek, 1957). The quartz-glau-

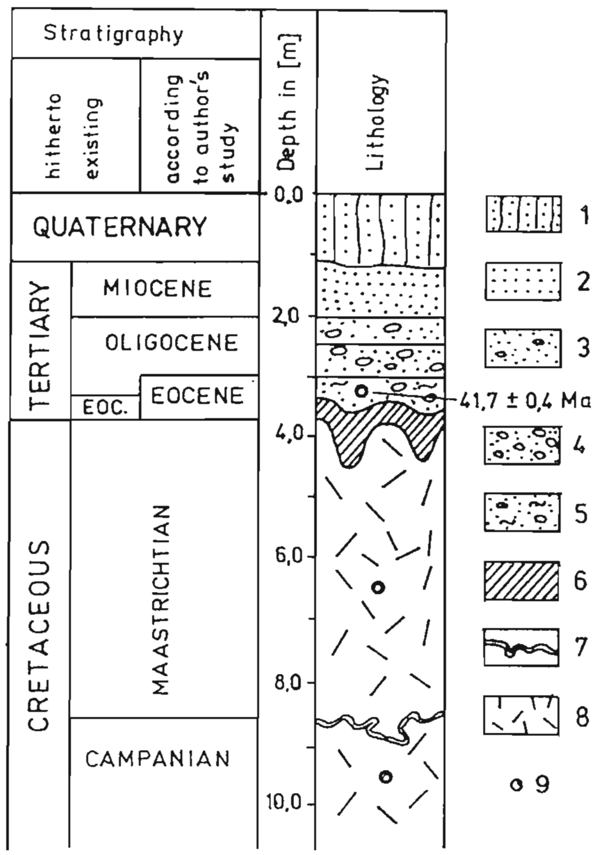

Fig. 2. Schematic geological section of the Upper Cretaceous and the Cainozoic deposits exposed in Mielnik on the Bug River according to Z. Wójcik (1959)

1 — sandy moraine till, 2 — quartz sand, 3 — quartz sand with phosphorites, 4 — sandy concretions of phosphoritic cement, 5 — quartz-glauconitic sand with phosphoritic concretions, 6 — residual clay, 7 — hard-ground, 8 — chalky limestone; 9 — sample location

Schematyczny przekrój geologiczny utworów kredy górnej i kenozoiku odsłoniętych w Mielniku nad Bugiem według Z. Wójcika (1959)

1 — piaszczysta glina morenowa, 2 — piasek kwarcowy, 3 — piasek kwarcowy z fosforytami, 4 — konkrecje piaszczyste o lepiszczu fosforanowym, 5 — piasek kwarcowo-glaukonitowy z konkrecjami fosforytowymi, 6 — ił rezydualny, 7 — twarde dno, 8 — wapień kredopodobny; 9 — miejsce pobrania próbek

conitic sands and phosphoritic series are included in the Oligocene (E. Rühle, 1947; W. Pożaryski, 1960). Above the phosphoritic series lie light yellow sands, which E. Rühle (1947) includes in the Miocene as the equivalent of brown coal series. Then above the Miocene sands lies sandy moraine till. In some places in the quarry the Quaternary lies directly on the Cretaceous.

East Palatinate area and south Podlasie represent the peripheric part of Precambrian East-European Platform. Within this platform the maximum of transgression fall on the Upper Eocene (K. Pożaryska, E. Odrzywolska-Bieńkowa, 1978). In the Upper Eocene all area of Polish Lowland was assumed by large marine transgression which presence in this part of Poland persisted up to the Upper Oligocene (E. Odrzywolska-Bieńkowa *et al.*, 1979).

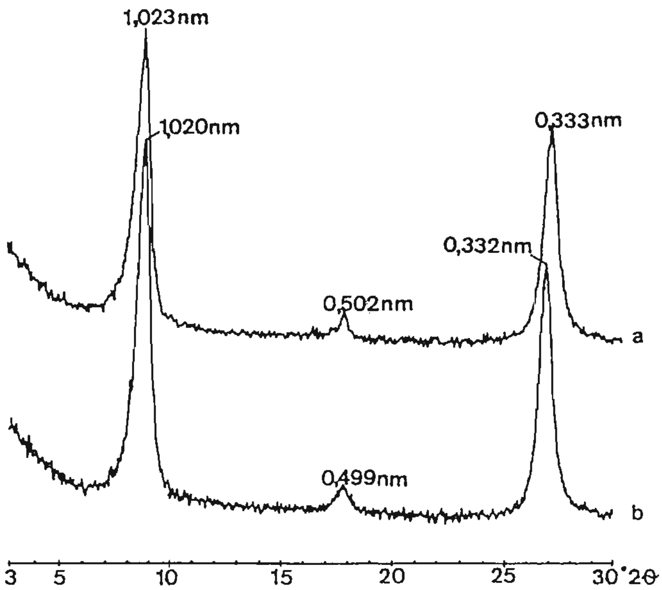

Fig. 3. X-ray diffractograms of oriented preparations of glauconite
a — untreated preparation, **b** — ethylene glycol-solvated preparation

Dyfraktogramy rentgenowskie preparatów zorientowanych glaukonitu
a — preparat nieglikolowany, **b** — preparat nasycony glikolem etylowym

The Eocene deposits were formed in the epicontinental European sea consisting of western and eastern basins (M. Piwocki, I. Olkowicz-Paprocka, 1987; A. Vinlken, 1988; B. Kosmowska-Ceranowicz *et al.*, 1990; M. Piwocki, J. R. Kasiński, 1995).

East-European Basin in the Upper Eocene occupied broad Kiev sea which on the territory of eastern Poland entered also. Fauna set (corals, oysters) ascertained by J. E. Mojski *et al.* (1966) in the borehole Luszawa 6 indicates the shallow-water character of the Upper Eocene basin. Geographical propagation of fauna species indicates the broad connections of this basin with seas of NW Europe, S Europe and Asia.

Marine deposits of this period are known in Poland from many positions — on the east as well as on the west and north (K. Pożaryska, 1976; J. Uberna, E. Odrzywolska-Bieńkowa, 1977). On the Palatinate the Upper Eocene transgression leaved the deposits in form of layers from Siemień formed as quartz-glauconitic sands with phosphoritic concretions containing rich fauna, molluscs, foraminifers and ostracods principally.

Originally continuity of the Eocene cover presently is segmented by erosion and denudation processes chiefly of the Quaternary in age. A. Henkiel (1983) the period from the Palaeocene regression to first Pleistocene continental glacier transgression named the white card in geological history of Palatinate. From this period decalcification processes of the Palaeocene gaizes and Maastrichtian opokas associate after their previously erosional exposure. On the Upper Eocene the sedimentation of marine clays fall also.

Most correct opinion about palaeogeography of Tertiary deposits on the Palatinate A. Henkiel (1983) expressed considering that most probably the beginning of glauconiferous sands sedimentation on all area of the Palatinate was in the Upper Eocene and its continuity up to Lower Oligocene inclusively. That opinion confirm the author's study concerning the glauconite in Mielnik on the Bug River.

METHODS AND RESULTS OF STUDY

The subject of this study was glauconite from the Oligocene quartz-glauconitic sands containing phosphorites as well as the Upper Cretaceous limestone.

The glauconite was characterized according to its physical, mineralogical and chemical features and also its absolute age was determined. Limestones were characterized according to their mineralogical composition and structural features.

A binocular microscope was used to determine the physical features of glauconite (colour and grain morphology). Its density was measured using a solution of bromoform with ethyl alcohol. Mineralogical and chemical features of glauconite were determined by means of X-ray diffraction, thermal and chemical analysis. Mineralogical-structural features of the limestone were assigned on the basis of microscopic studies of thin sections.

The content of glauconite in quartz-glauconitic sands was found to be 6% on average. Glauconite occurs in four grain fractions: 0.25–0.20 mm (16.8%), 0.20–0.16 mm (27.5%), 0.16–0.10 mm (37.5%) and 0.10–0.071 mm (16.4%). The grain size of quartz-glauconitic sands is different. This sand occurs in two essential grain fractions: 1.0–0.5 mm (25.8%) and 0.5–0.25 mm (60.1%). The remain grain fractions (0.25–0.071mm) represent 14% of the sample volume. The different

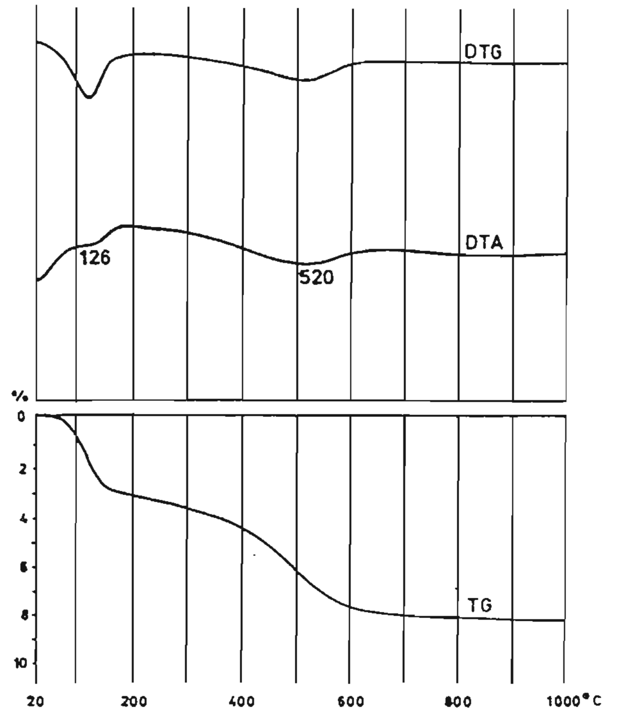

Fig. 4. Differential thermal analysis curves of glauconite

Krzywe termicznej analizy różnicowej glaukonitu

grain distribution of quartz-glauconitic sand and of glauconite is one of the proofs that the glauconite is of authigenic origin.

Table 1

Chemical composition of glauconite

Component	Weight percentage	Cations number per glauconite molecule
SiO_2	46.30	Si 3.561
Al_2O_3	7.32	Al^4 0.439 Al^6 0.269
Fe_2O_3 tot.	22.60	
Fe_2O_3	21.10	Fe^{3+} 1.210
FeO	1.35	Fe^{2+} 0.087
MgO	4.55	Mg 0.495
K_2O	8.21	K 0.797
Na_2O	0.64	Na 0.094
CaO	0.64	Ca 0.074
H_2O^-	4.24	
H_2O^+	7.79	
TiO_2	0.08	
P_2O_5	0.09	
S_T	0.10	
V	0.017	
Ba	0.031	
L01 (600°C)	8.14	
L01 (1000°C)	9.30	
Sum	99.89	
Sum of thetrahedral cations		4.000
Sum of octahedral cations		2.061
Sum of interlayer cations		0.965

Glauconite is characterized by different colours, namely: light green, green, dark green and beige (weathered glauconite). The morphology of glauconite grain is varied. The shape of the grains can be spheroidal, ovoidal, tabular, descoidal and cup-shaped. Generally the structure of glauconite grains is massive.

In heavy liquids (such as bromoform) glauconite separates into three density fractions: 2.4–2.5 g/cm^3 (5.8%), 2.5–2.6 g/cm^3 (91.3%) and 2.6–2.7 g/cm^3 (1.8%).

Following X-ray diffraction of oriented preparations under air-dried conditions as well as saturation with glycol (Fig. 3) it was ascertained that this glauconite has an ordered, monomineral (illite) structure, without expanding layers which represents a polymorphous type 1M.

Under thermal analysis glauconite exhibits two endothermal effects (Fig. 4). The first weak thermal effect occurs at a temperature of 126°C. The second distinct effect occurs at a temperature of 520°C. The total mass loss from the heated sample is 8.2%.

The chemical composition of this glauconite does not vary from the chemical composition of typical glauconites (Tab. 1). Characteristic is the high content of K_2O (8.21%), testifying to the high maturity and good structural order of this glauconite. Chemical analysis, using the Hendrick's and Ross'es methods, allowed the calculation of crystallographic formulae of glauconite which are as follows:

$$(K_{0.797}Na_{0.094}Ca_{0.074})(Fe^{3+}_{1.120}Fe^{2+}_{0.087}Mg_{0.495}Al^{VI}_{0.269})$$
$$[Si_{3.609}Al^{VI}_{0.439}O_{1.0}(OH)_2]$$

and

$$(K, Na, Ca)_{0.935}(Fe^{3+}, Fe^{2+}, Mg, Al^6)_{2.061}$$
$$[Si_{3.609}Al_{0.439}O_{1.0}(OH)_2]$$

Dating of glauconite was performed by the K-Ar method with the application of isotopic dilution technique in the Mass Spectrometry Laboratory of the Physics Institute of Maria Curie-Skłodowska University in Lublin. This glauconite was showed to have an age of 41.7±0.4 Ma which according to W. B. Harland's *et al.* (1989) geochronological time scale corresponds with the Upper Eocene (Bartonian).

On the basis of microscopic studies, apart from phosphorites and glauconite, grains of quartz, single muscovite

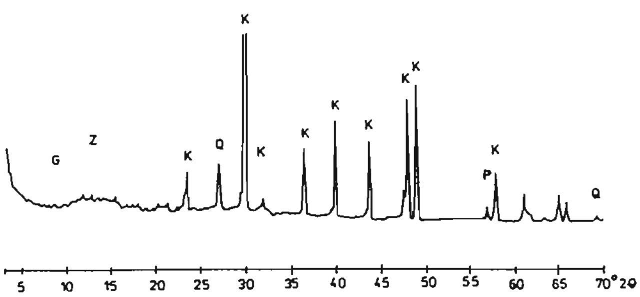

Fig. 5. Powder diffractogram of chalky limestone lying above a hard-ground (Maastrichtian)

K — calcite, Q — quartz, G — glauconite, P — pyrite, Z — zeolite

Dyfraktogram proszkowy wapienia kredowego zalegającego powyżej twardego dna (mastrycht)

K — kalcyt, Q — kwarc, G — glaukonit, P — piryt, Z — zeolit

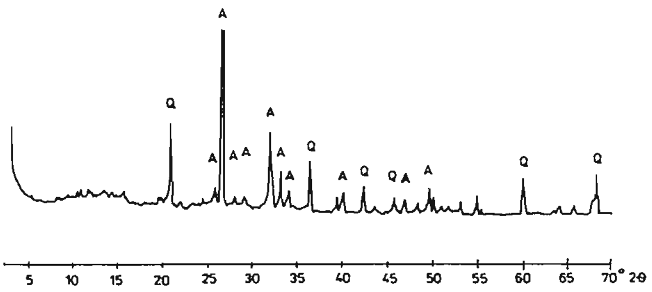

Fig. 6. Powder diffractogram of phosphorites occurring inside of chalky limestone (Maastrichtian)

A — apatite, Q — quartz

Dyfraktogram proszkowy fosforytów występujących wśród wapieni kredopodobnych mastrychtu

A — apatyt, Q — kwarc

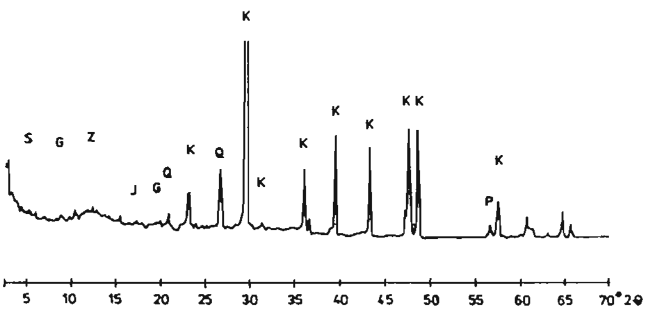

Fig. 7. Powder diffractogram of chalky limestone lying below hard-ground (Campanian)

S — smectite, I — illite; other explanations as in Fig. 5

Dyfraktogram proszkowy wapienia kredowego zalegającego poniżej twardego dna (kampan)

S — smektyt, I — illit; pozostałe objaśnienia jak na fig. 5

plates and grains of feldspars can be distinguished in the chalky limestone of the Maastrichtian lying beneath the residual clays but above the hard-ground. The mineral composition of this limestone determined by means of X-ray diffraction (Fig. 5) is as follows: calcite, quartz, zeolites, glauconite and pyrite. The quantity of $CaCO_3$ in the rocks, determined by thermal analysis amounts to 75%. Moreover, minor quantities of organic matter and goethite occur. Quartz grains of diameter up to 0.3 mm are superficially corroded.

In the rock a foraminifers fauna with calcareous valves occur and its colmatage is siliceous and pyritaceous. Phosphorites of up to 4 cm diameter show a concentric structure. The degree of phosphoritization is higher on the surface and lower inside. Small quartz, plates of muscovite and pyrite occur inside the phosphorite. On the surface of the phosphorites a distinct, stronger phosphoritized bark of about 0.5–0.6 mm thickness occurs. Organic forms preserved within the phosphorites are much more altered than in limestone. Generally, in phosphorites there is a lack of glauconite (Fig. 6).

A light green clay mineral (illite?) which occurs on the surface of the phosphorites has not been identified. Glauconite grains containing pyrite occur and weathered grains change into Fe oxides. The content of glauconite in this rock is 7–8%. The shape of glauconite grains is isometric and elongated. Generally, the grains are rounded. Probably the glauconite formed with sediment and its alterations have an epigenetic character.

Chalky limestone beneath the hard-ground (Campanian) possesses the biogenic structure of skeleton elements mainly of foraminifers and remains of macrofauna (pelecypods, gastropods). The fabric of rock is laminated. The laminae have a biogenic character and also biogenic-detrital character. In the latter laminae glauconite occurs together with quartz. Detrital laminae are less carbonate and more clayey. The presence of two kinds of laminae in limestone manifest the variability of sedimentation environment. Phosphorites concentrate in the laminae together with glauconite. Moreover, the plates of muscovite and fine-grained quartz occur in the amount of 1–2% what can testifies on volcanic episode.

Glauconite grains are pale and light green in colour. Their shape is rounded but irregular. They create the intergrowths on different optic orientation. Pyrite occurring in the forms of botryoidal aggregation fills the empty spaces in the rock. However, the zeolites and pyrite fill the exterior casts of foraminifers.

The content of glauconite in the rock yields less than 1% (~ 0.5%). The grain size of glauconite hesitates within the diameter from 0.1 to 0.2 mm. Mineral composition of limestone determined on the basis of X-ray diffraction (Fig. 7) chiefly constitutes calcite and in minor amounts occur: quartz, glauconite, clay minerals (illite, smectite), zeolites and pyrite. The quantity of $CaCO_3$ determined by means of thermal analysis yields 70%. The magnesian calcite in limestone is present also.

The minor contents of phosphorites, glauconite and quartz in the chalky limestone occurring below hard-ground than in the same limestone occurring above the hard-ground, differ them.

CONCLUSIONS

1. Tested glauconite from Mielnik can be adopted to geochronological studies. This is mature, well crystallized glauconite containing high potassium content.

2. K-Ar data of glauconite suggests the Upper Eocene age of sandy series containing phosphorites overlying on the

residual clays but not the Oligocene as it was accepted until now.

3. New stand of the Upper Eocene on Podlasie region testifies the more extensive range of the Upper Eocene transgression on the east area of Poland.

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EOCEN W MIELNIKU NAD BUGIEM

Streszczenie

Do niedawna w regionie lubelskim znane były tylko dwa stanowiska udokumentowanych faunistycznie osadów górnoeoceńskich, tj. w Siemieniu koło Parczewa i w Luszawie koło Lubartowa. W latach późniejszych następne stanowiska tych utworów zostały stwierdzone we wschodniej części Wyżyny Lubelskiej: w Zawadówce, na Dziewiczej Górze koło Chełma, na Górze Puławskiej i w Parchatce koło Puław. W części zachodniej Wyżyny Lubelskiej osady eoceńskie zachowały się w rowie Radawca oraz w okolicach Piotrkowa, Białowody i Woli Studziańskiej.

Datowanie osadów trzeciorzędowych z terenu Polski na podstawie dat K-Ar glaukonitu rozpoczęto w latach 70-tych. Wówczas to na podstawie datowania radiometrycznego glaukonitu określono wiek środkowoeoceński osadów glaukonitowych w NW części Niżu Polskiego w otworze Szczecin IG 1 i wiek dolnopaleoceński piasków glaukonitowych w otworze Boryszew (centralna Polska). Datowanie glaukonitu wykonano za granicą. Badania te przeprowadził H. Kreutzer w Laboratorium Geochronologicznym Uniwersytetu w Hannowerze.

Znaczną liczbę próbek glaukonitu z utworów glaukonitowych Wyżyny Lubelskiej wydatowano dopiero w 1991 r., po uruchomieniu linii argonowej do datowania K-Ar w Pracowni Spektrometrii Mas Instytutu Fizyki UMCS w Lublinie pod kierunkiem S. Hałasa. W wyniku wykonanych datowań glaukonitu osady eoceńskie stwierdzono również w Sporniaku Palikijskim, Żukowie, Chełmie, Janowie, Lechówce, Piekiełku i Łaszczówce. Wiek górnoeoceński glaukonitu (41.7±0.4 Ma) z serii piaszczystej z fosforytami stwierdzono także na Nizinie Podlaskiej w Mielniku nad Bugiem.

W Mielniku nad Bugiem, wśród utworów kry glacitektonicznej, do eocenu zaliczano dotychczas iły rezydualne zalegające na wapieniu kredopodobnym kredy górnej, natomiast spoczywające na nich piaski kwarcowo-glaukonitowe w fosforytami — do oligocenu. Data K-Ar glaukonitu, pochodzącego z tych piasków, świadczy, iż granica osadów eoceńskich sięga wyżej i obejmuje również piaski kwarcowo-glaukonitowe z fosforytami.

Datowany glaukonit został zbadany pod względem cech fizycznych (barwa, morfologia ziarn, gęstość właściwa) i mineralogiczno-chemicznych (skład mineralny, stopień uporządkowania struktury, politypy, skład chemiczny i wzory krystalochemiczne). Do określenia tych cech glaukonitu zastosowano analizę rentgenowską, termiczną i chemiczną. Badania wykazały, iż jest to glaukonit dojrzały, dobrze rozwinięty, o strukturze uporządkowanej i wysokiej zawartości potasu, co kwalifikuje go do badań geochronologicznych.

Nowe stanowisko eocenu górnego (bartonu) w Mielniku na Podlasiu świadczy o dużo szerszym zasięgu transgresji górnoeoceńskiej niż dotychczas przypuszczano.

Na podstawie badań mikroskopowych i rentgenowskich określono również skład mineralny i cechy strukturalne skał kredy górnej odsłoniętych w Mielniku.