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**K-Ar Dating of Glauconite According to Its Density:
A First Attempt of Dating of Paleontologically Silent Tertiary
Formation of Lublin Upland**

Datowanie glaukonitu według jego gęstości metodą K-Ar:
pierwsza próba datowania niemych paleontologicznie trzeciorzędowych utworów
Wyżyny Lubelskiej

Abstract. The paper reports on the radiometric dating methodology made on glauconite density fractions from Tertiary glauconitic sand. The sample was collected from Czulczyce sand pit situated in Lublin Upland. Laboratory testing of K-Ar ages of the glauconite fractions were done in the Geochronological Laboratory at the University of Heidelberg, Germany. This kind of geochronological study of Tertiary glauconite from Lublin Palatinate was performed for the first time in Poland. The work contains the results of X-ray diffraction (XRD), scanning electron microscope (SEM) and differential thermal analysis (DTA) of glauconite. Chemical analysis including rare elements was done too. Reported ages of different density fractions of glauconite show that only medium, the most abundant fractions yield reliable results. This has a connection with their mineralogical and chemical composition. The reported radiometric ages suggest the Upper Eocene age of glauconite from sandy deposits of Czulczyce.

INTRODUCTION

The purpose of this paper is two-fold: 1) mineralogical study of Tertiary glauconite from Lublin Upland, 2) age determination of glauconite in its

different density fractions based on K-Ar method and estimation which density fraction of glauconite is the most adequate to radiometric dating. This kind of mineralogical and geochronological study of Tertiary glauconite have not been performed so far in the Lublin Palatinate. The authors of this work made the first step to the stratigraphic assesment of Tertiary sediments in Lublin Upland using the radiometric dating of glauconite. The subject of this study is glauconite from a sand deposit located in the northern part of Lublin Upland near Czulczyce village (Fig. 1). This sand deposit fill up the caving in the Cretaceous bedrock in the Lublin Upland that type of sandy deposits occur usually at places forming the upper parts of so-called island hills (Harasimiuk, Rutkowski, [9]). The sands are of marine origin. There are quartzose, well sorted, fine and medium grained sands, composed chiefly of quartz (92%) and glauconite (6%). In minor amounts a feldspar, muscovite, iron oxides and heavy minerals are also present.

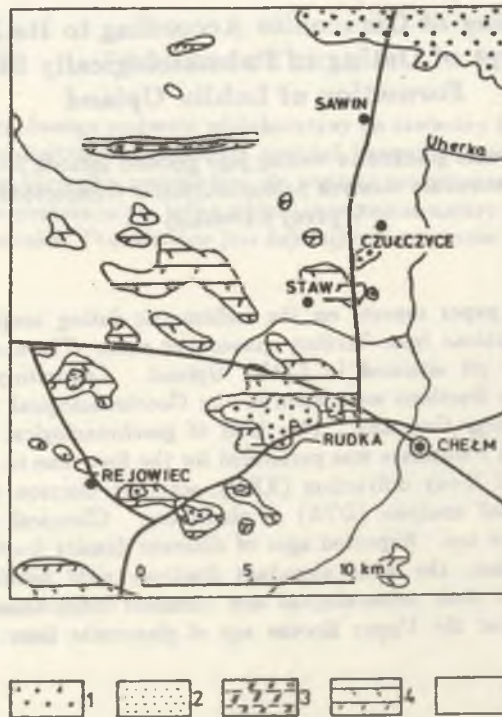


Fig. 1. Geological sketch-map of study area. 1 — Miocene (sands), 2 — Upper Eocene-Oligocene? (glauconitic sands), 3 — Paleocene gaizes, 4 — Maastrichtian (opokas), 5 — Upper Maastrichtian (marls and chalk)

Until now these Tertiary sands are regarded as Lower Sarmatian age (J. Kowalewski [12]; M. Turnau-Morawska [17]; M. Prószyński [15]; J. Morawski [13]; M. Harasimiuk and J. Rutkowski [9]; A. Henkiel [10]) but for the reason of fossils lack it is not possible to date them paleontologically. Hitherto the stratigraphic position of this sand deposit is based on the mineralogical, petrographic, lithologic and sedimentological likenesses in general to adjacent formations. So, until now the correct stratigraphic position of the sand deposits at Czulczyce outcrop has not been resolved. The Sarmatian age of this sand deposit is doubtful. Some geologists suggested its Upper Eocene age (Z. Górecka [8]; A. Henkiel [10]). Now we have the opportunity to date the Tertiary sandy sediments using included in them glauconite as stratigraphic tool with the aid of radiometric K-Ar method.

The glauconite pellets are variable in color, morphology and grain-size. The color is light green, olive and black. The morphology of the glauconite pellets are as follows: mammillated, spheroidal, ovoidal, tabular and discoidal. The ovoidal and spheroidal types prevail. The grain-size of glauconite ranges from 250 to 71 μm in diameter. Three fractions of grain-size: 100 μm (47.5%), 160 μm (25.3%) and 71 μm (20.3%) prevail.

The origin of glauconite is allogenic. The grains of glauconite could be transported as detrital grains from rather short distance from weathering of adjacent Eocene deposits.

SAMPLE PREPARATION

Before dating the glauconite pellets were separated from the sand sample electromagnetically using Frantz electromagnetic separator and were further purified, when necessary, by hand-picking under binocular microscope and next were divided on density fractions in heavy liquid (bromoform). The sample was divided on six density fractions: 2.4–2.3 g/cm^3 (9.0%), 2.5–2.4 g/cm^3 (30.8%), 2.6–2.5 g/cm^3 (33.0%), 2.7–2.6 g/cm^3 (17.3%), 2.8–2.7 g/cm^3 (1.2%) and above 2.8 g/cm^3 (8.4%). Radiometrically there were investigated four first fractions. Last two density fractions were not investigated for which there was insufficient amount of material not permitted to perform chemical analysis.

In order to determine the mineralogy of the glauconite the following investigations were made: X-ray diffraction (XRD), differential thermal analysis (DTA), scanning electron micrographs (SEM), and chemical analysis. Samples of purified grains for X-ray diffraction analysis were subjected to

ultrasonic vibration in an ultrasonic disintegrator until all the glauconite grains had been broken down to clay size (below $2 \mu\text{m}$).

LABORATORY TESTINGS

X-ray diffraction analysis (XRD)

X-ray diffraction determinations were performed on powder and oriented specimens of untreated and glycol-solvated. The oriented preparations were made by pipetting clay suspension on glass slides (10 mg/cm^2) and were glycolated by storing in glycol vapor overnight at temperature of 60° .

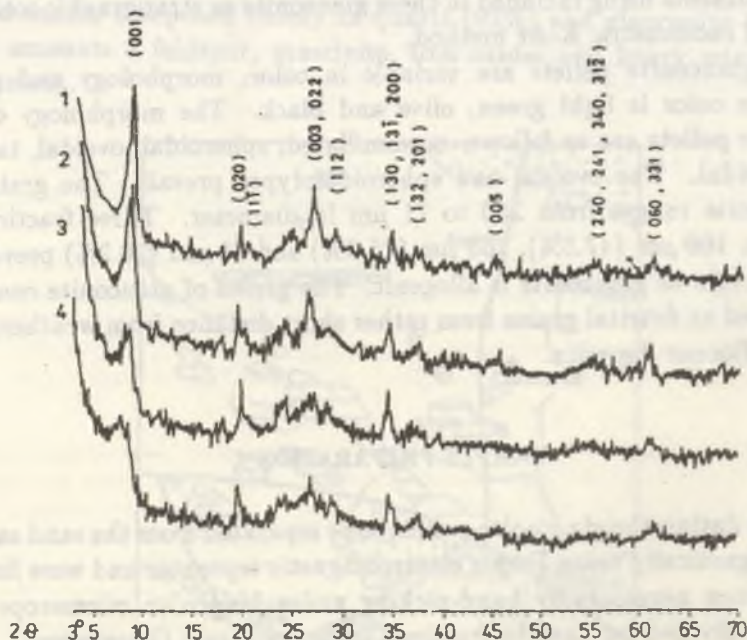


Fig. 2. X-ray diffractograms of glauconite density fractions (non oriented preparations)
1 — 2.7–2.6; 2 — 2.6–2.5; 3 — 2.5–2.4; 4 — 2.4–2.3 (g/cm^2)

The glauconite was examined by X-ray diffraction using $\text{Cu-K}\alpha$ radiation, HZG-4 diffractometer and a goniometer scan speed of $1^\circ 2\theta/\text{min}$. Diffractograms for the glauconite are presented in Figures 2 and 3. All investigated glauconite density fractions are characterized by the interlayering of the expanding layers determined by X-ray diffraction analysis of the oriented, ethylene glycol solvated specimens. In general the differences in density of glauconite pellets have an effect in the expanding layer content and in

chemical composition. The increase of the expanding layers content in the structure of glauconite is accompanied by the decrease of the K_2O and Fe_2O_3 contents.

Tab. 1. X-ray diffraction data of glauconite density fraction

Density of glauconite (g/cm^3)	Colour	Type of illitic material	Percent Smectite	Type of ordering
2.7-2.6	dark green, green, light green	ISII	6	ordered
2.6-2.5	more grain of light green	ISII	6	ordered
2.5-2.4	light green prevail	ISII	6	ordered
2.4-2.3	green, light green, olive	IIS	17-18	mixture

In three density fraction of glauconite pellets (2.7-2.6; 2.6-2.5; 2.5-2.4) there are no distinct structural differences (see Table 1). The fraction 2.4-2.3 g/cm^3 is structurally different. It contains more smectite and is one mineral mixture. X-ray diffractograms of glauconite density fractions are shown in Fig. 2 for nonoriented preparations and Fig. 3 for oriented preparations.

Differential thermal analysis (DTA)

The differential thermal analysis of glauconite in its different density fractions was made on Paulik-Paulik type instrument. The glauconites, similarly as another micas, contain two different kinds of water: molecular and hydroxyl. On the differential thermal curves both kinds of these waters are distinguished by independent endothermic effects. Molecular water goes away in temperature from 20 to 200°C, and hydroxyl water goes away in temperature between 360 and 720°C in general.

DTA confirms the mineralogical composition of glauconite. With the increase of content the expandable layers (2.3-2.4 g/cm^3) increases loss on mass during dehydroxylation process. The relations between dehydration, loss on mass, and density fraction of glauconite one can see in Fig. 4.

Scanning electron microscopy (SEM)

Selected glauconitic grains in different density fractions were studied by scanning electron microscopy using JSM-35 JEOL instrument. Investigations of glauconitic grains with the SEM at high magnification from 2000×

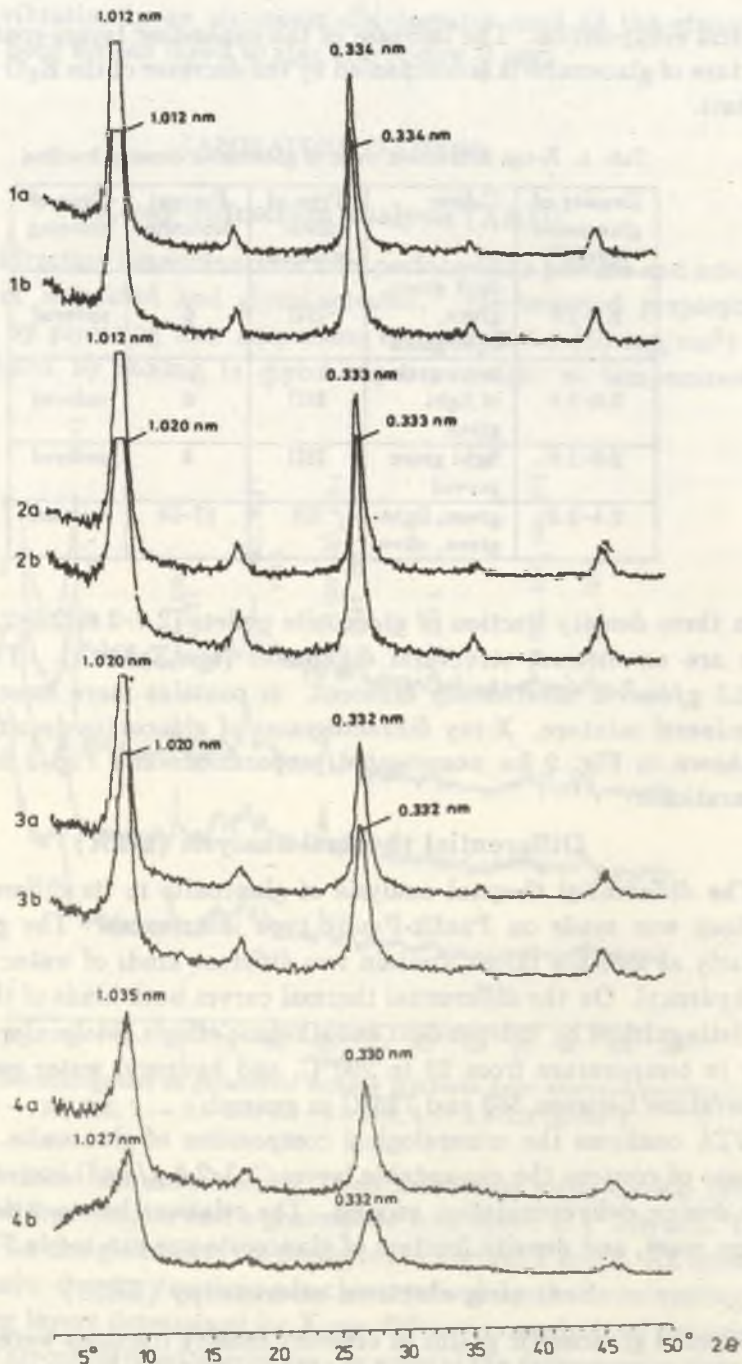


Fig. 3. X-ray diffractograms of glauconite density fractions (oriented preparations), a — untreated preparation, b — ethylene glycol-solvated preparation, numbers 1–4 as Fig. 2

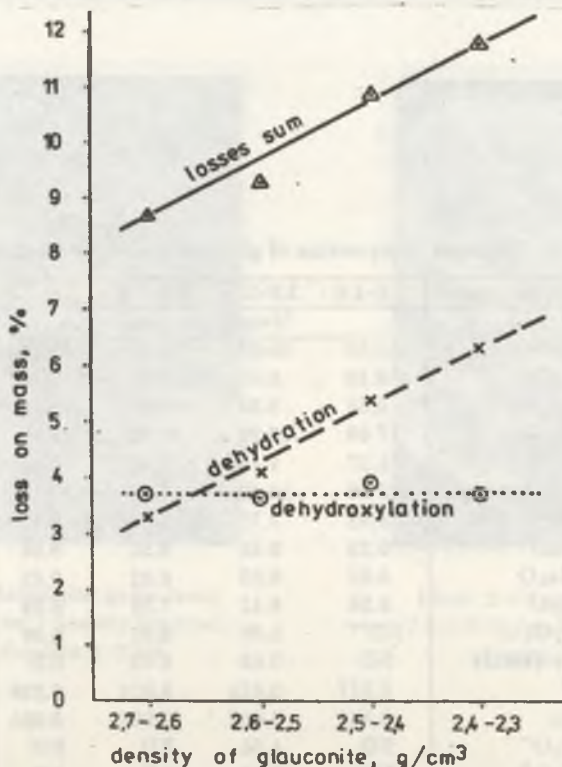


Fig. 4. Relationship between density of glauconite and loss on mass (DTA)

to 4000 \times reveal that thiny glaucony crystals may take on different habits. The changes in internal texture which accompany the external morphological change is related to density fraction of glauconite which we can see in Photos 1-5.

Chemical analysis

All determinations were done for the samples dried in the temperature of 105°C. The moisture determination (H_2O^-) was performed additionally. The samples were digested by HF, HNO_3 , HClO_4 acids. The ASA flame method has been applied. The type of the flame: air—acetylene and nitrogen suboxide—acetylene has been adopted. Each sample has been homogenized by the means of rubbing in ethylene alcohol. Loss on ignition (LOI), S, SiO_2 were determined by weight, TiO_2 with the DAM reagent and FeO with ofenantroline. Remaining constituents were determined by the flame method using the SP-9 spectrometer (Pye Unicam production).

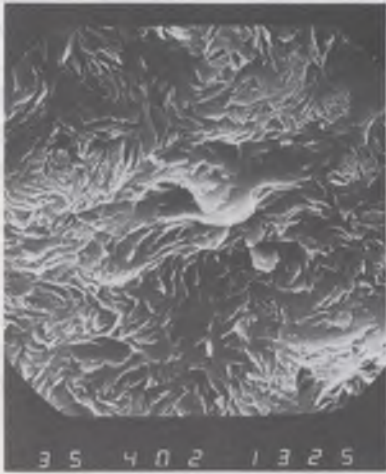
The full chemical analysis of glauconite density fractions are reported in

Tab. 2. Chemical composition of glauconite density fractions*

Components	2.7-2.6	2.6-2.5	2.5-2.4	2.4-2.3
	Weight per cent			
SiO ₂	51.30	50.05	50.35	49.10
TiO ₂	0.10	0.08	0.09	0.13
Al ₂ O ₃	8.58	9.58	11.20	12.60
Fe ₂ O ₃	17.60	18.20	16.30	15.80
FeO	1.27	1.15	0.86	0.53
Fe ₂ O ₃ total	19.00	19.40	17.30	16.40
MgO	3.92	3.77	6.65	3.47
CaO	0.35	0.45	0.50	0.66
Na ₂ O	0.02	0.02	0.02	0.02
K ₂ O	8.96	8.41	7.14	6.99
P ₂ O ₅	ND**	0.09	0.07	0.08
S _T (total)	ND	0.03	0.03	ND
V	0.017	0.021	0.026	0.026
Ba	0.003	0.002	0.002	0.005
H ₂ O ⁻	ND	4.56	ND	ND
H ₂ O ⁺	ND	6.42	ND	ND
LOI 600°C	5.99	6.97	7.77	8.12
LOI 1000°C	7.32	8.12	9.67	10.05
	Weight in g/t			
MnO	105.	118.	120.	124.
Zn	144.	154.	158.	177.
Cu	50.	6.	6.	8.
Ni	32.	41.	47.	56.
Co	11.	14.	20.	21.
Rb	230.	250.	224.	210.
Sr	287.	278.	460.	437.
Cr	64.	88.	101.	127.
Sum	99.34	99.97	99.91	99.46

* Chemical analysis were performed by Ewa Górecka, M.Sc., State Geological Institute in Warsaw.

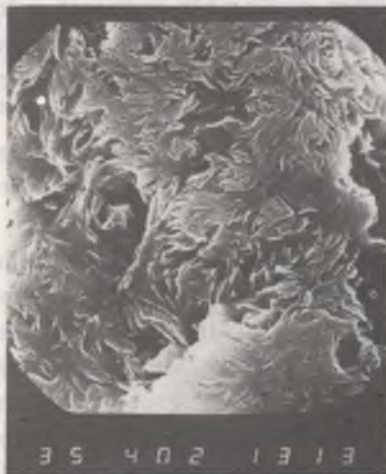
** Not determined



Phot. 1. Glauconite grain from 2.8-2.7 (g/cm³) density fraction, magnification x 2500



Phot. 2. Glauconite grain from 2.7-2.6 (g/cm³) density fraction, magnification x 1200



Phot. 3. Glauconite grain from 2.6-2.5 (g/cm³) density fraction, magnification x 2500



Phot. 4. Glauconite grain from 2.5-2.4 (g/cm³) density fraction, magnification x 1900



Phot. 5. Glauconite grain from 2.4-2.3 (g/cm³) density fraction, magnification x 2500

Element	Weight %			
	1	2	3	4
V	0.07	0.02	0.06	0.04
Fe	0.00	0.02	0.02	0.00
Na ⁺	12	0.00	0.00	0.00
Ca ²⁺	0.00	0.00	0.00	0.00
Li ⁺ (wt%)	0.00	0.00	0.00	0.00
Li ⁺ (at%)	0.00	0.00	0.00	0.00
Weight % O ₂				
MnO	10	10	10	10
Zn	10	10	10	10
Co	10	10	10	10
Si	10	10	10	10
Cr	10	10	10	10
Al	10	10	10	10
O	10	10	10	10
Total	10.0	10.0	10.0	10.0



* Chemical analysis was performed by Geochem. Workers
 ** Geochem. Workers

with using electron microprobe
 analysis (EDS) and
 XRF analysis

Table 2. Chemical composition of glauconite pellets differ according to their density fractions. From heavy fraction (2.7–2.6 g/cm³) to light fraction (2.4–2.3 g/cm³) Al₂O₃, CaO and MnO content increase while SiO₂, Fe₂O₃ FeO, MgO and K₂O content decrease. These changes in chemical composition of glauconite density fractions have their reflecting in mineralogical structure (see Tab. 1) and radiometric K-Ar dating (see Tab. 3).

K-Ar Dating

K-Ar age determinations were made on the glauconite sample divided on four density fractions. The age of individual separate was calculated from the following formula (G. B. Dalrymple and M. A. Lanphere [4], J. Burchart [2,3]):

$$t = -\frac{1}{\lambda} \ln\left(1 + \frac{\lambda}{\lambda_e} \frac{{}^{40}\text{Ar}^*}{{}^{40}\text{K}}\right),$$

where ⁴⁰Ar* is the concentration of radiogenic argon, i.e. the quantity of argon generated in gram of the mineral by the potassium decay (the mineral is considered to be a closed system from its formation to present), ⁴⁰K is the quantity of radioactive potassium in gram of the sample (which was estimated from potassium concentration determined by the ASA flame method and from its natural abundance = 0.0167%), $\lambda = 5.543 \times 10^{-10} \text{y}^{-1}$ and $\lambda_e = \lambda/9.540$ are decay constants of ⁴⁰K (R. H. Steiger and E. Jäger [16]).

⁴⁰Ar* was determined mass-spectrometrically by the isotope dilution technique in which unknown amount of ⁴⁰Ar was mixed with known amount of radioactive ³⁹Ar (T_{1/2} = 269 y.) and resultant isotope ratio ⁴⁰Ar/³⁹Ar was measured. Both argon species were released simultaneously from solid materials: sample and spike (a granulate of quarternary biotite in which ³⁹Ar has been formed by neutron irradiation in a nuclear reactor). One gram of this spike yields 1.972 ± 0.005 nl of ⁴⁰Ar at STP with very low ratio of ⁴⁰Ar/³⁹Ar (U. Furhman [7]).

A portion of glauconite fraction of 50–100 mg was wrapped in aluminium foil. In similar manner a portion of 5–10 mg of the spike was prepared and wrapped together in common Al-foil. The set of samples was put into a glass extraction line which was connected to the mass spectrometer. Argon was released from each sample by a radiofrequency oven. The argon gas extracted was purified in the usual way and analyzed mass-spectrometrically (G. B. Dalrymple and M. A. Lanphere [4]). MAT GD-150 mass spectrometer with 180° ma-

Tab. 3. Radiometric age of glauconite density fractions

Density (g/cm ³)	Fraction (% weight)	K ₂ O content (%)	Radiometric age* (m.y.)
above 2.8	9.6	ND	ND
2.7-2.6	17.3	8.96	31.0 ± 1.0
2.6-2.5	33.0	8.41	37.3 ± 1.1
2.5-2.4	30.8	7.14	36.9 ± 1.31
2.4-2.3	9.0	6.99	22.6 ± 2.0

* Weighted average: 33.6' or 34.5 m.y., see text.

gnet sector, 5 cm curvature and 0.51 T magnet was used in static vacuum mode.

The total amount of ⁴⁰Ar extracted was calculated from the following formula:

$$^{40}\text{Ar} = ^{39}\text{Ar} \frac{1-f}{f} \left[\left(\frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{\text{mixture}} - \left(\frac{^{40}\text{Ar}}{^{39}\text{Ar}} \right)_{\text{spike}} \right],$$

where f is the weight fraction of sample, whereas $1 - f$ is that of spike, and ³⁹Ar is the amount of the radioactive argon determined from the weight of spike, the isotope ratio ⁴⁰Ar/³⁹Ar of mixture was determined mass spectrometrically. In our case this ratio ranged from about 10 to 100 while that ratio for spike was nearly zero, a value of 0.0645 ± 0.077 was assumed on the basis of previous calibration. Note that ⁴⁰Ar calculated from the above formula required correction for atmospheric argon by taking into account the peak of ³⁶Ar which appeared in the mass spectra. The radiogenic component of ⁴⁰Ar is

$$^{40}\text{Ar}^* = (^{40}\text{Ar})_{\text{measured}} - 295.5(^{36}\text{Ar})_{\text{measured}},$$

where 295.5 is ⁴⁰Ar/³⁶Ar ratio for atmospheric argon. Finally, from total radiogenic argon a little fraction of this isotope which came from spike has been subtracted.

The standard error of age was estimated from the error propagation formula assuming relative error of 1% for potassium determination and from estimated variance of ⁴⁰Ar* on the basis of five repetitive argon spectra.

DISCUSSION

Previous works (J. Everndnen, G.H. Curtis, J. Obradovich and R. Kistler [5], J. Valenton and A. Abdul-Raazak [18];

G. S. O d i n [14]; H. F i s c h e r [6]) have shown that glauconitic material is a very good K-Ar clock and that the K-Ar technique can be used to date the glauconitic deposits containing green pellets.

The results of present study show that not all density fractions of glauconite yield a reliable radiometric age. The light density fraction (2.4–2.3 g/cm³) yields too low age. Similarly, but in lesser extent, behave heavier fractions (see Tab. 3). The low age of lighter density fraction has a relationship with chemical composition of glauconite (see Tab. 2). It should be noted that weighted average age of the glauconite sample is 34.5 or 33.6 m.y. depending on assumed weight. In the first case simply the weight fraction was assumed whereas in the second case the product the weight fraction and potassium content was assumed. Therefore one may suppose that a considerable rejuvenation would be possible if bulk glauconite sample (i.e. without density fractionation) is dated.

On the reliability of K-Ar dates can also influence the environmental temperature. According to S. W. Aprub and L. K. Levskij [1] a considerable argon loss may appear at above 25°C. In our opinion in the geological history of Czulczyce deposit such elevated temperatures never existed.

On the basis of the obtained age data one can ascertain the Upper Eocene age of the glauconite from Czulczyce sandy deposit. This result significantly differs, from estimated ages Sarmatian or Upper Eocene, which appeared in the literature. To solve the stratigraphic problems of Tertiary sediments in Lublin Palatinate more detailed work is needed. The authors made the first step in the solution of geochronology problems of glauconitic Lublin Upland sediments.

Extended geochronological investigations of sandy glauconitic deposits from Lublin Upland which cannot be dated paleontologically will be made in Mass Spectrometry Laboratory at Maria Curie-Skłodowska University, Lublin.

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STRESZCZENIE

Celem niniejszej pracy jest: 1) przedstawienie wyników badań mineralogicznych glaukonitu trzeciorzędowego z Wyżyny Lubelskiej 2) określenie wieku bezwzględnego glaukonitu w jego różnych frakcjach gęstościowych za pomocą metody K-Ar. Badania tego typu, tj. mineralogiczne i geochronologiczne glaukonitów trzeciorzędowych Lubelszczyzny nie były dotychczas wykonywane. Przedmiotem badań był glaukonit z piasków glaukonitowych z Czulczyc, na północ od Chełma. Pozycja stratygraficzna tych piasków nie jest dotychczas pewna. Ich wiek górnosarmacki, przyjęty na podstawie podobieństwa litologicznego do innych tego typu osadów, jest wątpliwy. Trudność ustalenia właściwej pozycji stratygraficznej tych osadów wynika z braku dobrze zachowanej fauny.

Autorzy tej pracy podjęli próbę reinterpretacji stratygraficznej niemych paleontologicznie, trzeciorzędowych osadów glaukonitowych na Lubelszczyźnie, stosując datowanie radiometryczne. Przed wykonaniem datowania glaukonitu, minerał ten poddano badaniom mineralogicznym i chemicznym poprzedzonym rutynowymi pracami laboratoryjnymi zmierzającymi do wyizolowania czystego glaukonitu z próby piasku. Frakcje gęstościowe glaukonitu wydzielono używając cieczy ciężkiej (bromoform). Aby ustalić jego strukturę wewnętrzną i skład mineralny wykonano badania rentgenowskie, termiczną analizę różnicową i badania scanningowe. Skład chemiczny glaukonitu określono na podstawie pełnej analizy chemicznej z pierwiastkami rzadkimi włącznie. Badania wieku glaukonitu metodą K-Ar wykonano w Laboratorium Geochronologii Uniwersytetu w Heidelbergu. W artykule opisano metodologię określania wieku radiometrycznego glaukonitu.

Otrzymane daty glaukonitu (około 37 mln lat) pochodzącego z górnioceńskich (sarmackich) piasków glaukonitowych z Czulczyc, sugerują jego wiek górnioceński. Wyniki badań wieku radiometrycznego glaukonitu w jego różnych frakcjach gęstościowych wykazały, że najodpowiedniejszymi frakcjami gęstościowymi do datowania glaukonitu są najobficiej reprezentowane frakcje średnie ($2.4-2.6 \text{ g/cm}^3$) — ich wiek nie różni się znacznie między sobą. Nie nadają się natomiast do datowania frakcje lekkie (poniżej 2.4 g/cm^3). Ich daty są znacznie zanizone.

