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Palaeotemperatures of the Palaeogene sea basins in the Lublin area on the basis of oxygen and carbon stable isotopes

Oxygen and carbon stable isotopes entering into fossils' composition are utilized to determine palaeotemperatures of sea basins. Using the isotopes one can also determine the character of sea basins, i.e., estimate whether they were open or inland seas. The paper presents the results of oxygen and carbon isotopic composition studies of some fossils species (foraminifers, molluscs and sea urchin spines). The samples of fossils have been collected in the Nasiłów, Bochotnica and Góra Piotrkowska sediments of the Palaeocene and in Siemień sediments of the Upper Eocene age. The results of isotopic studies confirm the minimum Palaeocene temperature (16.8, 17.4 and 18.8°C) and the optimum Eocene temperature (23.8°C) of the Tertiary basin of the central-east part of Poland. Because the Palaeocene fauna could be redeposited from Upper Cretaceous sediments, only palaeotemperatures of the Upper Eocene sea basin can be treated as authoritative results of the study of the Palaeocene sea area. The determination of isotopic proportion in the fossils indicates the open sea character of the Palaeocene basin.

INTRODUCTION

The isotope analyses of ^{13}C and ^{18}O of well preserved fossils can be used as an indicator of sea basins' character (open sea, inland sea) and their palaeotemperatures.

There are three stable oxygen isotopes known in natural habitats. Their frequency of occurrence in nature is: ^{16}O — 99.763%, ^{17}O — 0.0375% and ^{18}O — 0.1995%. There are also two stable carbon isotopes: ^{12}C and ^{13}C, whose frequency of occurrence is respectively as follows: 99.763 and 0.0375%.

While carrying out isotopic studies, we are most often interested in the relative diversification of the isotope concentration ratio of $^{18}O/^{16}O$ or $^{13}C/^{12}C$. According to Ch. W. Holmes (1983) the ratios of $^{18}O/^{16}O$ in marine carbonates can change as a consequence of the following factors:

— temperature changes that might have been caused by climate fluctuations,
— changes in the isotopic composition of sea water or its circulation,
— changes in the isotopic composition of carbonates caused by diagenetic factors.

Carbonates and feldspars are most pliant to the exchange of oxygen isotopes and water solutions both in natural conditions and in experimental studies (J. R. O'Neil, 1987). The older limestones and other sea sediments are, the less ^{18}O they contain. Likewise the ratio of oxygen isotopes in ocean waters changes noticeably with time (N. J. Shackleton, M. A. Hall., 1984; J. R. O'Neil, 1987; F. Woodruff, S. M. Savin, 1989).

The most appropriate material for study of oxygen isotopes are foraminifers, as well as calcareous nannoplankton, numerous groups of multicellular organisms and a wide range of sedimentary, metamorphic and magmatic rocks (T. J. M. Schopf, 1987).

METHOD OF STUDY

The oxygen and carbon isotope composition is measured with a mass spectrometer and expressed by means of δ value, which is defined as a relative result of the isotope ratio in the sample and in the standard (in promilles). Thus the mass spectrometer measurements are relative. The δ value defines how far the isotope composition of the tested sample departs from the conventional standard. Negative values of δ correspond to lower concentration of a given isotope in the sample than in the standard. Positive values of δ represent the contrary case.

The results of oxygen and carbon isotope analysis are given with reference to international standards. The most often used standards are: SMOW (Standard Mean Ocean Water) and PDB (Belemnite from the Cretaceous Pee Dee Formation, South Carolina, USA). The presently used international standard NBS-19 (National Bureau of Standards, USA) is characterized by the following values: $\delta^{13}C = 1.95‰$ and $\delta^{18}O = -2.20‰$ on the PDB scale. In practice the laboratory equivalent of the SMOW standard, V-SMOW (Vienna SMOW) is used. The V-SMOW has been prepared and preserved in the IAEA (International Atomic Energy Agency) in Vienna. This is a kind of water with the isotopic composition of average ocean water.

According to J. Friedman and J. R. O'Neil (1977) the relationship between the $\delta^{18}O$ values in PDB and SMOW scales are the following:

$$(\delta^{18}O)_{SMOW} = 1.03086(\delta^{18}O)_{PDB} + 30.86$$

$$(\delta^{18}O)_{PDB} = 0.97006(\delta^{18}O)_{SMOW} - 29.94.$$

THE PROBLEM OF PALAEOTEMPERATURES AND DETERMINATION OF SEA BASIN CHARACTER

The values of $\delta^{18}O$ can be used to determine mainly surface water palaeotemperatures, however the $\delta^{13}C$ values seems to reflect the depths at which planktonic and benthic

foraminifers once lived (S. V. Margolis *et al.*, 1975). The ^{16}O and ^{18}O oxygen isotopes and ^{13}C and ^{12}C carbon isotopes are incorporated into the composition of fossils shells and skeletons. The ratio of these isotopes ($\delta^{18}O$), which depends, among other things, on the interdependence of the sea water temperature and the isotopic composition of carbonate shells of organisms (molluscs particularly), up to now has been a unique, reliable method applied to determine the real temperatures of ancient sea reservoirs (B. Burchardt, 1978). The most exact determinations of palaeotemperatures on the basis of oxygen isotopes concern Pleistocene and Tertiary planktonic species, foraminifers especially. Determining temperatures of carbonates older than Cretaceous goes beyond the power of the isotope method. This if because of diagenetic effects (T. J. M. Schopf, 1987). J. R. O'Neil (1987) does not advise utilising the palaeotemperatures studies of material older than Tertiary because of the possibility of isotopes exchange with isotopically light underground waters.

To estimate palaeotemperatures we use the effect of temperature on stable isotope separation according the following reaction:

$$H_2{}^{18}O + 1/3C^{16}O_3^{2-} \rightleftharpoons H_2{}^{16}O + 1/3C^{18}O_3^{2-}.$$

Along with temperature increase, the preferential incorporation of the lighter isotope (^{16}O) into the carbonate takes place.

The empirical equation of the isotope temperature scale in carbonates for temperatures 0 to 30°C according to N. J. Shackleton (1984) is:

$$t(^{\circ}C) = 16.9 - 4.38(\delta_c - \delta_w) + 0.10(\delta_c - \delta_w)^2,$$

where: t (°C) is the temperature of calcium carbonate crystallization expressed in degrees centigrade, δ_c indicates the oxygen isotope composition in carbonate expressed in the PDB scale and δ_w indicates the oxygen isotope composition in sea water expressed in the SMOW scale. The value of δ_w in the sea water of the Palaeocene and Eocene has been established as 0.28‰.

The accuracy of the mass spectrometry method is about ±0.1‰, which corresponds to a temperature change slightly less then by ±0.5°C.

The $^{13}C/^{12}C$ average ratio of CO_2 also changes with time. This variability in the ocean reflects mainly the gradual ageing of deep water masses as a result of gradual depletion of O_2 distributed in them (due to the oxidation of organic substances) (N. J. Shackleton, M. A. Hall, 1984; F. Woodruff, S. M. Savin, 1989). The distributed CO_2 becomes isotopically lighter, increasing content of light carbon isotopes as a result. The variation of $\delta^{13}C$ values can be additionally caused by mixing waters from different surface sources. This is why the isotope gradient of the ocean water carbon is an important indicator of their circulation.

The palaeotemperatures of the Tertiary period of NW Europe on the basis of oxygen isotope studies were interpreted for first time by B. Burchardt in 1978. The oxygen isotope studies of carbonate mollusc shells found in the Tertiary sediments of south England, Holland, Germany, Denmark and south Sweden allowed him to calculate the minimum temperatures in the Palaeocene, the Middle Oligocene and the Upper Miocene in the southern part of the Tertiary North Sea. Warmer climatic conditions prevailed in the Pliocene, at the beginning of the Middle Miocene and in the Eocene. The value of ^{18}O

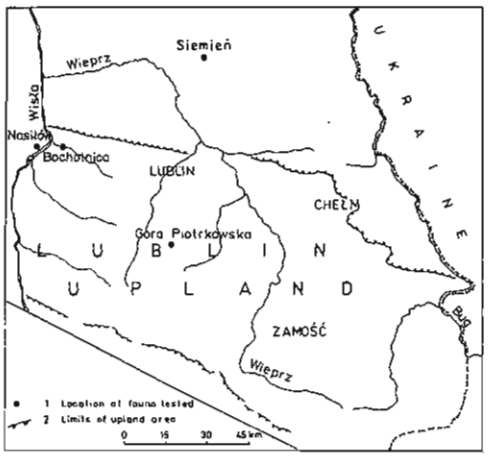

Fig. 1. Location map of the tested fauna
Mapa lokalizacji badanej fauny
1 — lokalizacja badanej fauny, 2 — granice obszaru wyżynnego

decreases at the beginning of the Lower Miocene which indicates warming up the bottom ocean reservoir waters and/or melting the polar ice (F. Woodruff, S. M. Savin, 1989).

M. L. Keith and J. N. Weber (1964), examining the C and O isotope composition of some 500 limestone samples of different age and origin, elaborated the isotope criterion which allows description of a given habitat as either an open or inland sea. The above authors' research indicates that limestones deposited in inland sea basins give evidence of higher values of ^{12}C and ^{16}O light isotopes than open marine limestones. Additionally, the latter demonstrate that lower variations of carbon contained in limestones were practically stable in different geological periods. On the other hand, the average oxygen isotope composition demonstrates a tendency for ^{16}O content growth along with increase in geological age. According to the latest estimations carried out by J. Veizer and J. Hoefs (1976), the average carbon isotope composition also shows an analogous tendency, although to a considerably lower degree.

M. L. Keith and J. N. Weber (1964), taking into account $\delta^{13}C$ and $\delta^{18}O$ values, put forward a criterion allowing distinction between sea- and fresh-water limestones on the basis of the Z parameter. The value of the Z parameter is calculated according to the following formula:

$$Z = 2.048(\delta^{13}C + 50) + 0.498(\delta^{18}O + 50)\,.$$

If the Z parameter >120, the examined material is of sea origin and if the Z parameter <120, the material comes from a fresh-water environment.

RESULTS

For the study of O and C isotope composition we used some fossils from Palaeogene sediments of the Lublin Upland, i.e. Palaeocene from Nasiłów, Bochotnica (Danian) and

Table 1

The O and C isotope composition of some Tertiary species from the Lublin Upland with reference to palaeotemperatures and Palaeocene basin character

Location	Fauna	Age	Mineral composition of fauna	$CaCO_3$ [%]	$\delta^{13}C$ PDB [‰]	$\delta^{18}O$ PDB [‰]	Z	Palaeo-tempera-ture [°C]
Nasiłów	molluscs: *Pecten* sp., *Lima* sp.	Palaeocene (Danian)	calcite	78.4	1.18	–0.25	129.6	16.8
Bochotnica	molluscs: *Pecten* sp., *Lima elongata* Sowerby		calcite, zeolite, quartz, dolomite	82.0	2.37	–0.41	132.9	17.4
Góra Piotrkowska	sea urchin spines: *Acrocidaris* ?	Palaeocene (Montian)	calcite, quartz	92.7	2.37	–0.70	131.8	18.8
Siemień	molluscs: *Pecten* sp., *Lima* sp.	Upper Eocene (Bartonian)	calcite	97.0	1.24	–1.92	128.8	23.8

Góra Piotrkowska (Montian) localities and Eocene from Siemień (Fig. 1). The geological age of the above sediments has been accepted in accordance with their palaeontological dating.

The subjects of the oxygen and carbon isotope studies have been three species of benthic fauna, i.e. foraminifers from Nasiłów (Pl. I, Fig. 3), molluscs from Bochotnica and Siemień (Pl. I, Figs. 4, 6) and sea urchin spines from Góra Piotrkowska (Pl. I, Fig. 5). The fauna comes from the weakly consolidated quartzose-glauconitic sandstones located over a hard-ground in Nasiłów, from calcareous gaizes in Bochotnica, from glauconitic gaizes in Góra Piotrkowska and from dusty quartzose-glauconitic sand in Siemień.

The mineral composition of fossils was determined by means of X-ray diffraction (XRD) using a *HZG-4* diffractometer and $CaCO_3$ content by means of differential thermal analysis (DTA) where a *Paulik-Paulik Erdey* (MOM, Budapest) type instrument was used. The oxygen and carbon isotope composition of the fauna was examined with a modified *M1-1305* mass spectrometer in the Mass Spectrometry Laboratory of the Institute of Physics, Maria Curie-Skłodowska University, Lublin. The accuracy of the measurements was ±0.1‰. In the measurements, the laboratory reference standard of oxygen isotope composition was the laboratory Lublin Water of absolute value relative to SMOW: $\delta^{18}O = -10.6$‰ and in the determination of carbon isotope composition it was NBS-19 standard of calcium carbonate.

On the basis of the results of study using N. J. Shackleton's as well as M. L. Keith's and J. N. Weber's formulas the palaeotemperatures and character of sea basins have been determined (Tab. 1).

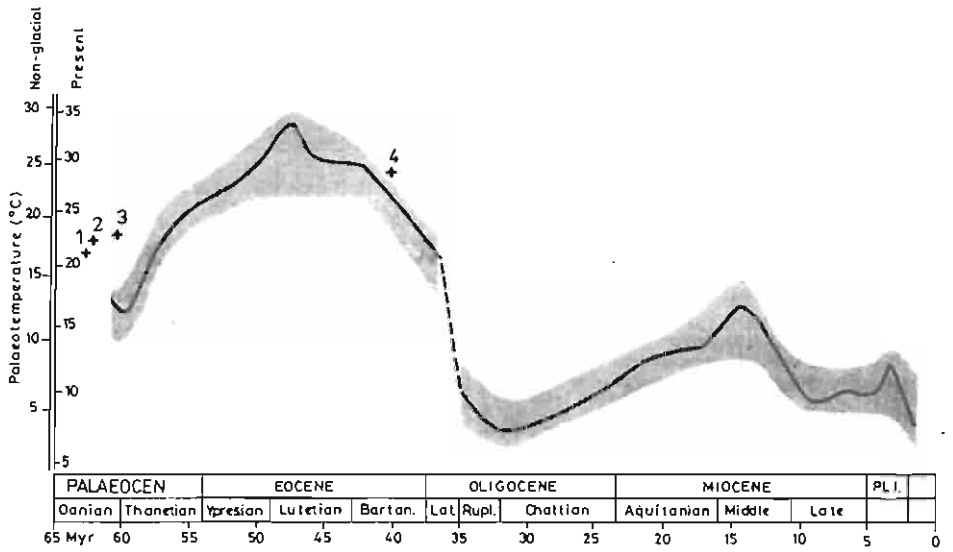

Fig. 2. Palaeotemperature curve of Tertiary North Sea waters determined on the basis of the faunal oxygen isotope composition after B. Burchardt (1978)

The shaded area represents limits of uncertainly due to local variations in the oxygen isotope composition of Tertiary North Sea water; true Tertiary waters temperatures are believed to be within the shaded area; the difference between the non-glacial and the present temperature scales is caused by the shift in average oxygen isotope composition of ocean water, owing to the accumulation of glacial ice on Antarctica; the crosses signify the palaeotemperatures of Palaeogene basin in the area of the Lublin Upland; localities: 1 — Nasiłów, 2 — Bochotnica, 3 — Góra Piotrkowska, 4 — Siemień

Krzywa paleotemperatur wód trzeciorzędowego Morza Północnego określonych na podstawie składu izotopowego tlenu fauny według B. Burchardta (1978)

Zaciemniony obszar przedstawia granice niepewności na skutek lokalnej zmienności w składzie izotopowym tlenu wód trzeciorzędowego Morza Północnego; należy przypuszczać, że prawdziwe temperatury wód trzeciorzędowych mieszczą się w obszarze zaciemnionym; różnica między skalami, bez glacjału i obecną, spowodowana jest przesunięciem w średnim składzie izotopowym tlenu wody oceanicznej na skutek akumulacji lodu glacjalnego na Antarktydzie; krzyżyki oznaczają paleotemperatury basenu paleogeńskiego w rejonie Wyżyny Lubelskiej; lokalizacja — patrz tekst angielski

DISCUSSION OF RESULTS

The temperatures obtained: 16.8°C (Nasiłów locality), 17.4°C (Bochotnica locality) and 18.8°C (Góra Piotrkowska locality) for the Palaeocene basin and 23.8°C (Siemień locality) for the Upper Eocene basin confirm the minimum temperature of the Palaeocene and the maximum temperature at the Eocene announced by B. Burchardt (1978) for the Tertiary basin of NW Europe (Fig. 2) (if the fauna of the Palaeocene was not redeposited from Upper Cretaceous deposits).

Many authors believe that Cretaceous fauna occurs as a secondary deposit in glauconitic sandstones of the Danian near Nasiłów, Kazimierz Dolny, Bochotnica and Puławy localities. E. Ciuk (1974) says that in the layer of glauconitic sandstones in the Nasiłów locality, among the numerous accumulated macrofauna, there occur secondarily accumu-

lated molluscs, sea urchins and brachiopods. The above mentioned foraminifers indicate an age as late as the Montian. On the basis of microfloral studies (spores and pollens) W. Krach (1974) ascertained the absence of the Danian near Kazimierz Dolny, Bochotnica, Nasiłów and Puławy localities. At the same time he included the basal glauconitic sandstones as well as all the *siwak* rocks to the Montian. M. Machalski and J. Walaszczyk (1987) treat the glauconitic sandstones from Bochotnica and Nasiłów partly as Upper Maastrichtian. They explain the occurrence of the Maastrichtian and Danian fauna in the glauconitic sandstones in Nasiłów by the condensation and mixing processes of infaunal organisms (crustaceans, molluscs). In their opinion both processes took place in the Danian. In the light of opinions presented about the Palaeocene (Danian) fauna's character, the results of isotope studies of the fauna from Nasiłów and Bochotnica and probably from Góra Piotrkowska cannot be grounds for estimating palaeotemperatures of the Palaeocene basin waters. However, they may reflect the temperature of Upper Cretaceous sea waters. On the other hand, as reliable results, one can recognize the palaeotemperature of the Eocene basin determined on the basis of the fauna derived from Siemień which confirms the existence of the Eocene climatic optimum on the area of Poland (S. Dyjor, A. Sadowska, 1986).

The isotope studies of heterogeneous fauna derived from lithologically different deposits — from four localities and from two stratigraphic horizons of the Lublin Upland do not aspire to determine the exact palaeotemperatures of the Palaeogene sea basin. They only suggest verification of the investigation method and a presentation of the preliminary palaeoenvironmental results of the study. The elucidation of water palaeotemperatures of the Tertiary sea basin of the Lublin region will demand rich and homogenous research material with respect to the species.

All determinations on the basis of the Z parameter indicate an open sea character ($Z > 120$) for the Palaeogene basin. The earlier O and C isotope studies of Tortonian limestones from the Lublin Palatinate (Kazimierz Dolny, Chełm) and from Roztocze (Zdziechowice) carried out by S. Hałas *et al.* (1979) have also pointed to the open character of the sedimentological basin ($Z = 125$) during this period.

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Zdzisław KRZOWSKI

PALEOTEMPERATURY PALEOGEŃSKICH ZBIORNIKÓW MORSKICH WYŻYNY LUBELSKIEJ NA PODSTAWIE IZOTOPÓW TRWAŁYCH TLENU I WĘGLA

Streszczenie

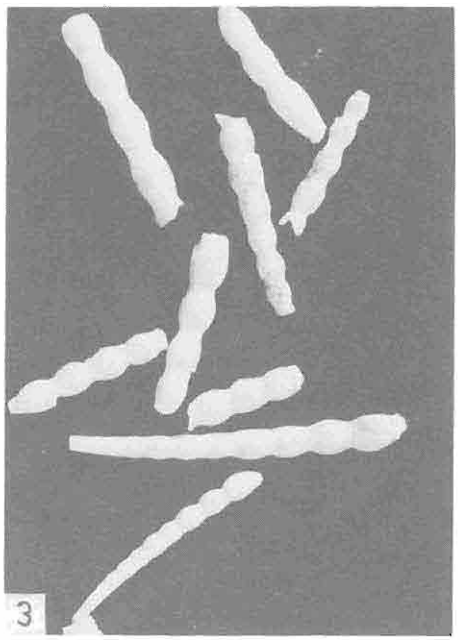
Izotopy trwałe tlenu i węgla, wchodzące w skład szkieletów i skorupek fauny, wykorzystywane są do oznaczania paleotemperatur i charakteru zbiorników morskich — pełnomorskich lub śródlądowych. W artykule zamieszczono wyniki badań składu izotopowego tlenu i węgla niektórych gatunków fauny (otwornice, małże i kolce jeżowców) z paleoceńskich piasków kwarcowo-glaukonitowych oraz gez wapnistych i glaukonitowych z Nasiłowa, Bochotnicy i Góry Piotrkowskiej oraz z górnoeoceńskich piasków kwarcowo-glaukonitowych z Siemienia koło Parczewa. Wyniki przedstawiono jako paleotemperatury paleogeńskich zbiorników regionu lubelskiego. Potwierdzają one temperaturowe minimum paleoceńskie (16,8, 17,4 i 18,8°C) oraz optimum eoceńskie (23,8°C) trzeciorzędowego zbiornika Polski środkowo-wschodniej. Ponieważ istnieje pogląd, że fauna paleoceńska mogła być redeponowana z osadów górnokredowych, dlatego za miarodajne wyniki badań z akwenu

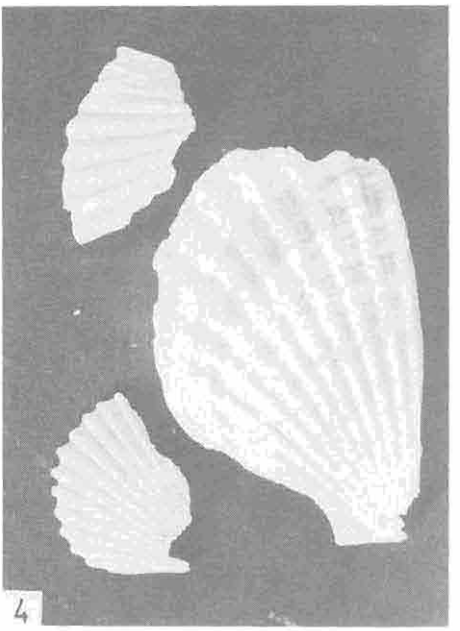
paleogeńskiego można uznać jedynie paleotemperatury zbiornika górnoeoceńskiego. Wszystkie oznaczenia masowo-spektrometryczne skamieniałości fauny wykazały pełnomorski charakter zbiornika paleogeńskiego.

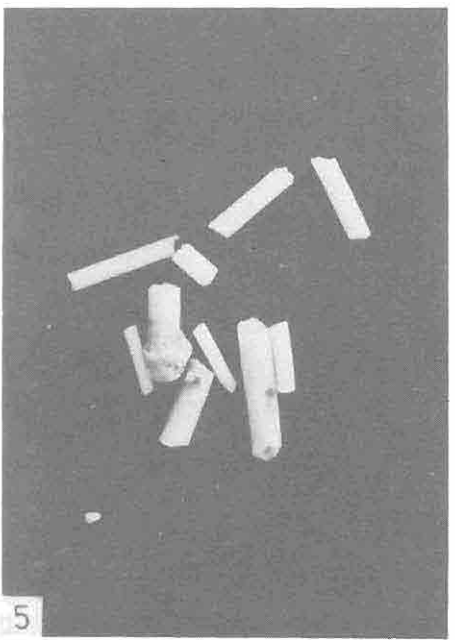
Badania izotopowe fauny różnorodnej gatunkowo i pochodzącej z różnych litologicznie osadów — z czterech stanowisk i dwóch pięter stratygraficznych Wyżyny Lubelskiej — nie pretendują do określenia ścisłych paleotemperatur paleogeńskiego zbiornika wodnego. Stawiały sobie za cel jedynie sprawdzenie metody badawczej oraz zasygnalizowanie wstępnych wyników badań paleośrodowiskowych. Wyjaśnienie paleotemperatur wód zbiorników trzeciorzędowych regionu lubelskiego będzie wymagało dalszych, szczegółowych badań izotopowych, uwzględniających bogaty i jednorodny gatunkowo materiał badawczy.

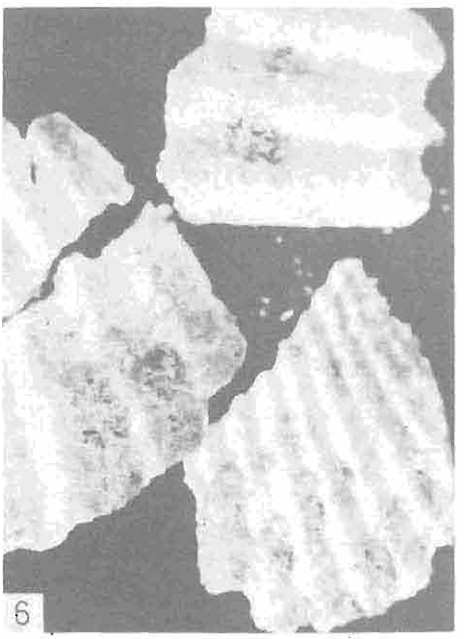
PLATE I

Fig. 3. Foraminifers: *Nodosaria affines* Reuss and *N. limbata* d'Orbigny from glauconitic sands in the Nasiłów quarry; magn. about x 5.5; Palaeocene (Danian)
Otwornice: *Nodosaria affines* Reuss i *N. limbata* d'Orbigny z piasków glaukonitowych z Nasiłowa; pow. ok. 5,5 x; paleocen (dan)
Fig. 4. Molluscs: *Pecten* sp. and *Lima elongata* Sowerby from calcareous gaizes in the Bochotnica outcrop; full size; Palaeocene (Danian)
Mięczaki: *Pecten* sp. i *Limo elongata* Sowerby z gezy wapnistej z Bochotniey; wielkość naturalna; paleocen (dan)
Fig. 5. Sea urchin spines *Acrocidaris* (?) from glauconitic gaizes in the core of the Góra Piotrkowska test well; magn. about x 5.5; Palaeocene (Montian)
Kolce jeżowców *Acrocidaris* (?) z gezy glaukonitowej z Góry Piotrkowskiej; pow. ok. 5,5 x; paleocen (mont)
Fig. 6. Molluscs: *Pecten* sp. and *Lima* sp. from glaueonitic sands in the Siemień well; full size; Upper Eocene (Bartonian)
Mięczaki: *Pecten* sp. i *Lima* sp. z piasków glaukonitowyeh z Siemienia; wielkość naturalna; eocen górny (barton)









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