POLSKA AKADEMIA NAUK • KOMITET NAUK GEOLOGICZNYCH

PAŃSTWOWE WYDAWNICTWO NAUKOWE • WARSZAWA

acta geologica polonica

Vol. 39, No. 1-4 Warszawa 1989

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The Cretaceous/Tertiary boundary in Central Poland

ABSTRACT: Paleomagnetic stratigraphy coupled with dinocyst biostratigraphy demonstrates in the Nasiłów Quarry (topmost part of the well-known mid- and Upper Cretaceous sequence exposed along the Middle Vistula Valley) in Central Poland the presence of chalk sediments belonging to paleomagnetic periods *30 N* and *29 R*. The latter contains the biostratigraphic Cretaceous/Tertiary boundary. The overlying sediments can be placed in period *29 N*.

Trace element studies show that iridium is present in the lower part of the greensand overlying the chalk, and exposed also in the neighboring locality Bochotnica. Iridium is also recorded in an opoka-like filling in the shell of the Upper Maastrichtian brachiopod *Carneithyris* sp. contained in the greensand.

On the basis of trace elements and ultrastructures it is suggested that dissolution has removed both a glauconitic chalk, the Cretaceous/Tertiary boundary beds, as well as an equivalent of the Danish *Cerithium* Limestone. The iridium-bearing elemental carbon was trapped in the greensand-timed burrows.

INTRODUCTION

Recently, RADWAŃSKI (1985) and MACHALSKI & WALASZCZYK (1987, 1988) have concisely outlined the problems with respect to faunal condensation and mixing at the Cretaceous/Tertiary (K/T) boundary, as recorded in the well-known section of the Middle Vistula Valley, Central Poland, and exposed in the vicinity of Kazimierz-on-Vistula (*see* Text-fig. 1). They suggested a series of events that might have led to the present-day geological situation as well as an assumed hiatus covering a part of the Danian.

During fieldwork in the summer of 1987, sixteen large oriented rock-samples covering the profile exposed in the Nasiłów Quarry were collected (*see* Text-fig. 1*B*). The sampled interval covers 28 meters. The sampling was made with the aim of establishing a magneto-stratigraphy that would possibly allow an estimate of the duration of the hiatus occurring in this area at the K/T transition.

Biostratigraphical studies of dinocysts were made of all the sampled levels from both the Maastrichtian as well as from the overlying Lower Tertiary marine sediments. Material from the greensand deposited on top of the Maastrichtian chalk is also included.

The boundary sediments have been analyzed for iridium and other elements by instrumental neutron activation analysis (*INAA*).

This paper presents the preliminary results of all these diverse investigations.

SECTION AT NASIŁÓW QUARRY

The section exposes (Text-fig. 1*B*) from bottom to top: (i) A series about 15 m thick of "Opoka", which is a local term (in the current context meaning a foundation stone) for a white, siliceous chalk type which contains abundant impressions of siliceous sponge spicules. Only the imprints are left, while the sediment itself shows a high frequency of lepidospheres, which is here interpreted as the precipitation product after dissolved opaline spicules. On the basis of mollusks the age of the Opoka is assigned to the uppermost Maastrichtian (POŻARYSKI 1938, PUTZER 1942, BŁASZKIEWICZ 1980, RADWAŃSKI 1985, ABDEL-GAWAD 1986, WIEDMANN 1988).

According to POŻARYSKA (1965, 1967) and POŻARYSKA & PUGACZEWSKA (1981) the foraminiferal *Pseudotextularia* Zone otherwise characterizing the uppermost Maastrichtian in other parts of Europe is missing in this area.

The Opoka is capped by a hardground with burrows filled with greensand and containing scattered lumps of white limestone (*see* POŻARYSKA 1952, RADWAŃSKI 1985).

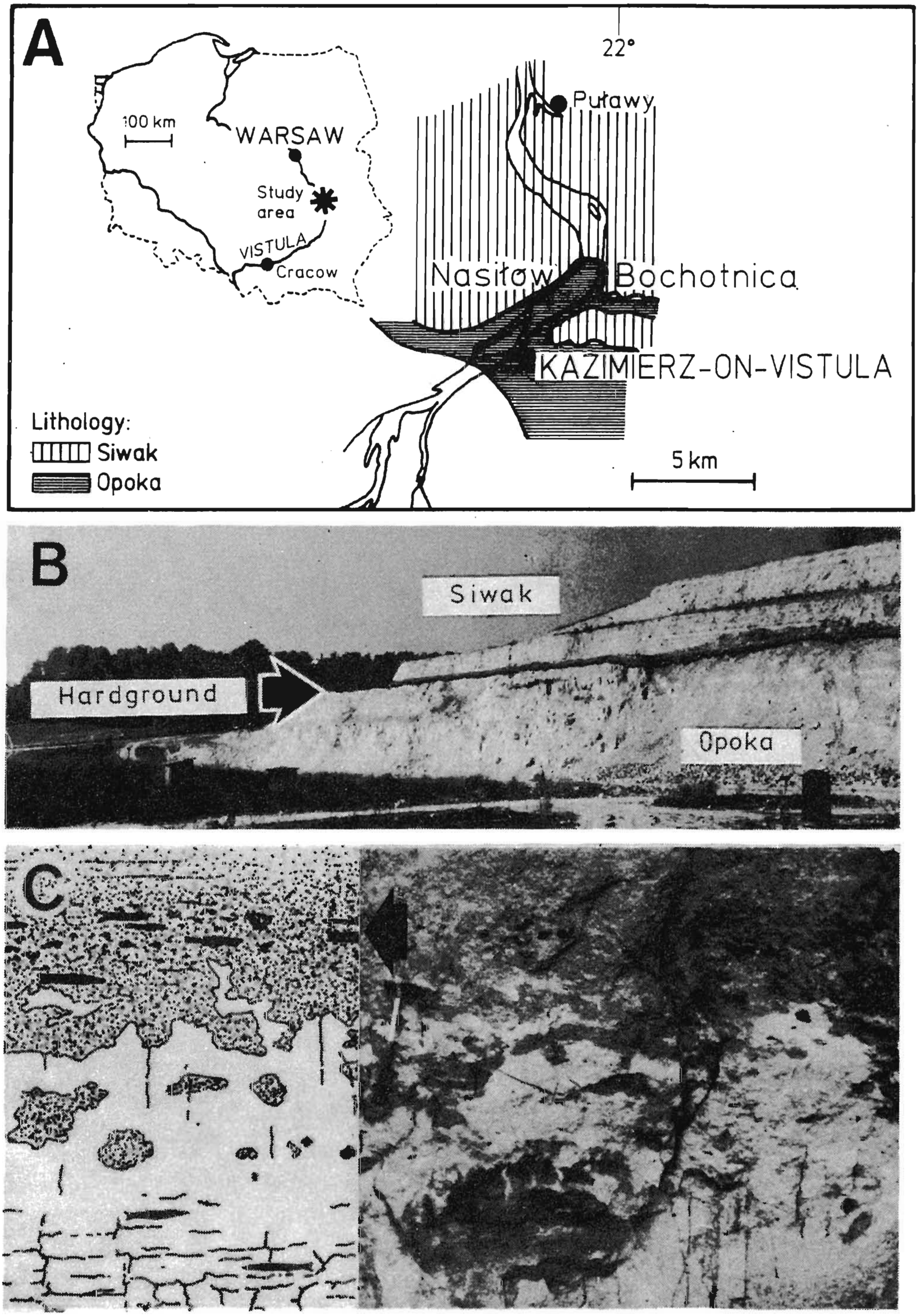
Above the Opoka occurs: (ii) A layer (up to 0.5 m thick) of greensand containing numerous macrofossils, and overlain by: (iii) A set (about 12 m thick) of "Siwak" (which is a local term for gray marly gaizes; in Polish language, the word "*siwak*" means grayish and is used as a term describing solely this very rock-type in the region).

Fig. 1

A — General sketch-maps, to show location of the study area in Poland and the investigated sections in the vicinity of Kazimierz-on-Vistula

B — General view of the Nasiłów Quarry, to show the sedimentary sequence yielding the Cretaceous/Tertiary boundary (the same photo as used by ABDEL-GAWAD 1986, Fig. 9*B*)

C — Close-up of the Cretaceous/Tertiary boundary sequence exposed at Bochotnica (the same photo as used by ABDEL-GAWAD 1986, Fig. 10*B*; sketch-drawing taken from RADWAŃSKI 1985, Fig. 47); arrowed is the residual lag


A
22°
100 km
WARSAW
Study area
VISTULA
Cracow
Puławy
Nasiłow
Bochotnica
KAZIMIERZ-ON-VISTULA
Lithology:
Siwak
Opoka
5 km
B
Siwak
Hardground
Opoka
C

The underlying Opoka is still used as a local building stone while the Siwak is much more loosely cemented and locally shows bedding and some cleavage, making the rock unsuitable for building purposes.

The Siwak has recently been regarded as an equivalent of Upper Danian age (RADWAŃSKI 1985, MACHALSKI & WALASZCZYK 1987). On the basis of published evidence it seems as if the Greensand between the two carbonate-dominated sediment series represents a hiatus covering the lower (and maybe the middle part of the Danian).

The hardground surface seems rather incomplete, and the present study was in part made to see if it was possible to find reversely magnetized rocks close to the K/T boundary, or if erosion had gone so deep as to remove any trace of sediments of the reversed magneto-zone 29. In other regions of the world the reversed period 29 contains the K/T boundary, and has been estimated to have a duration of 470.000 years (LABRECQUE & *al.* 1977) or 600.000 years (BERGGREN & *al.* 1985).

This might also throw light on the extinction time of the mosasaurs found at the base of the Greensand (RADWAŃSKI 1985, HANSEN 1988).

SECTION AT BOCHOTNICA

The section exposed at Bochotnica (*see* Text-fig. 1*C*) does not differ strongly from the one at Nasiłów. The exposures are, however, poorer and the rocks are more strongly lithified. Heavy vegetation makes the access more difficult. The burrows at the Cretaceous/Tertiary boundary penetrate deeper and are in general easier to study at this locality than at Nasiłów.

PALEOMAGNETIC MEASUREMENTS

In each oriented block two to six 1-inch diameter plugs were drilled in the laboratory. The samples were measured on a United Scientific *SCT-A100 SQUID*-magnetometer. After NRM measurements, the samples were demagnetized in an AC-field. During AC-demagnetization the samples were randomly tumbled. The ambient DC-field was reduced to below 50 nT during the AC-demagnetization. The AC-field washings were performed at 100, 200, 300, 400 and 800 Oersted. A treatment of 100 Oe seemed to be appropriate (Text-fig. 2), as this left on average 50% of the original NMR intensity. The resulting inclinations after 100 Oe demagnetization are well readable (Text-fig. 3).

DINOCYST BIOSTRATIGRAPHY

Material of all blocks used for paleomagnetic measurements were processed by standard palynological preparation methods. The acid residues were studied with respect to their content of dinocysts.

All Opoka samples (*i.e.* No. 1 to 9) contained *Palynodinium grallator* and can thereby safely be placed in the uppermost Maastrichtian *Palynodinium*

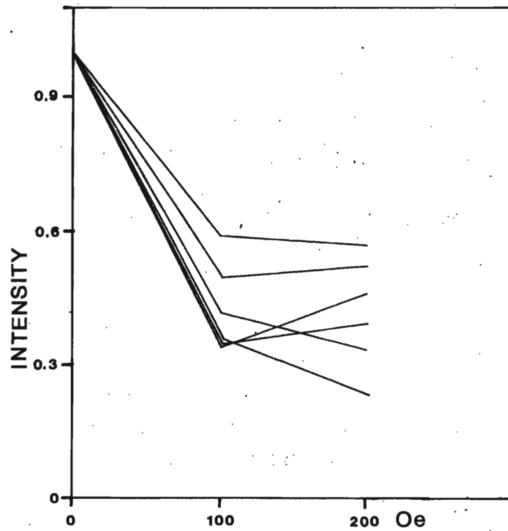


Fig. 2. Intensity of residual magnetism in samples No. 1 to No. 6 from Nasiłów depicted as intensity versus demagnetization field

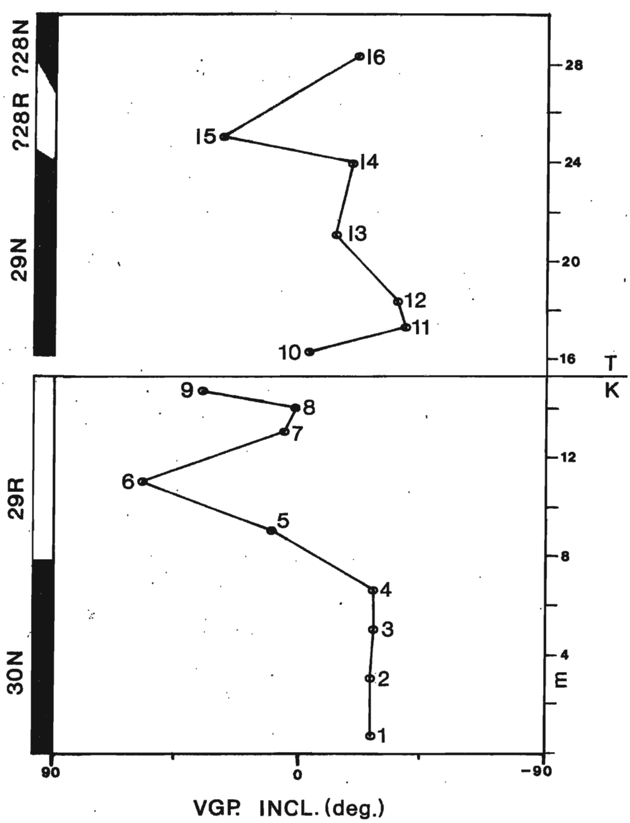


Fig. 3. Stratigraphic section of the deposits exposed at Nasiłów, with the interpreted paleomagnetic stratigraphy

grallator Zone as defined by J. M. HANSEN (1977). In the Danish area it has been noted, that the uppermost part of the Maastrichtian chalk also contains *Thalassipora pelagica*, but this species was not found in the uppermost Opoka sample from Nasiłów (*i.e.* No. 9) possibly indicating, that the very highest level of the Maastrichtian chalk (*i.e.* some decimeters) is missing in Central Poland.

The Siwak series overlying the Maastrichtian opoka and the greensand (*i.e.* samples No. 10 – 16) also yielded dinocysts. The samples No. 10 – 15 all contained *Chiropteridium inornatum* which is the lowermost Danian dinocyst biozonal marker (J. M. HANSEN 1977).

The uppermost sample in the Nasiłów Quarry did not contain any biozonal marker-species of dinocysts. The assemblage is dominated by representatives of the genus *Spongodinium* with a few specimens of the genus *Cyclonephelium*. In the "Dania" Quarry in central eastern Jutland in Denmark, the genus *Spongodinium* is absolutely dominating in the Danian deposits from 10 meters above the K/T boundary. This may be entirely ecological and may not have any biostratigraphical importance at all. However, it is herein suggested that there may be time equivalence between the dominance of the form in question in view of the fact that both localities are situated within the Danish-Polish basin at the time of deposition.

Since the samples No. 10 to 14 all belong to the *Chiropteridium inornatum* Zone, it can safely be concluded, that the normal magneto-zone encompassing the samples No. 10 – 14 can be identified as belonging to period *29 N* with a duration of 560.000 years (LABRECQUE & *al.* 1977). The sample No. 15, which still belongs to the same Zone, is magnetically reversed but represents an interval of maximum 4.5 meters. If a reversed polarity is accepted in this interval, it would mean that the interval covering up to 4.5 meters would represent *28 R* with a duration of 310.000 years while the top sample No. 16 would represent the lowermost part of the magneto-zone *28 N*.

If one assumes that the interval *29 N* is almost complete, the accumulation rate would be 1.42 cm/1000 y. If one further assumes a thickness of *28 R* of. 4.5 m it leads to an accumulation rate of 1.45 cm/1000 y.

THE PHOSPHATIC NODULES

In the Greensand, approximately 30 cm above the hardground in the Nasiłów Quarry a series of phosphatic nodules were collected (residual lag of RADWAŃSKI 1985; *see also* MACHALSKI & WALASZCZYK 1987, 1988). They were cut, and from some of their interiors small plugs were drilled, which later were subjected to palynological preparation. It was found that they contain no identifiable dinocysts. This is quite surprising, in view of the fact, that a well-preserved prasinophyte alga and wood with preserved tracheid structures were observed. Thus, if the dinocysts were destroyed, it is difficult to understand that the prasinophytes and wood were not destroyed at the same time. Thus it can not be excluded that the investigated clasts belong to the now dissolved Żyrzyn Beds, once possibly present in the Nasiłów sequence when its deposition took place (*see* discussion below).

OBSERVATIONS ON THE GREENSAND FOSSILS

In addition to the phosphatized clasts, a series of fossils were collected from the residual lag in the Greensand (*see* Text-fig. 1*C*). Many of these fossils (brachiopods, bivalves and a small belemnite) contained fillings of a white material, reminiscent of un-hardened Opoka.

When studied in the scanning electron microscope, the material in the brachiopod was found to be a coccolith-rich carbonate rock, identical with the Opoka but less diagenetized (Text-fig. 4). By contrast, the material filling the alveole in the belemnite had quite a different texture (Text-fig. 5) strongly reminiscent of the texture of the *Cerithium* Limestone of the Stevns Klint region and its equivalent in other parts of Denmark, *i.e.* the so-called "dead layer".

Among the phosphatized elements siliceous sponges are dominating. The majority of fossils in the lag horizon show no signs of transport and they are unsorted, *i.e.* larger and smaller fossils are present among each other without signs of wear.

One peculiar fact regarding the belemnites from the Greensand is that they commonly show an absolutely smooth surface lacking the normal impression of bloodvessels seen on other specimens collected from the Greensand and on those from the underlying Opoka. This indicates that the belemnite rostra have often been subjected to dissolution, but never to mechanical transport (*see* Text -fig. 6).

GEOCHEMISTRY

Samples were analyzed by neutron activation involving irradiation at the Risø National Laboratory in the heavy water reactor *DR 3* with a neutron flux of 3×10^{13} n/cm^2/sec for periods of 4 hours. The resulting gamma spectra were measured on a *PGT Ge(Li)* detector with a 14% efficiency.

HANSEN & *al.* (1987) demonstrated that it is possible to obtain erichment of Ir from Cretaceous/Tertiary boundary sediments using various chemical treatments in order to concentrate the carbon fraction. This results in enrichments in the order of 10 times or more over whole rock concentrations.

This technique was applied to sediments from Nasiłów and Bochotnica. At Nasiłów one sample consisting of the uppermost Opoka was dissolved and the carbon fraction subjected to *INAA*. The detection limit for Ir was 1.65 ppb in this experiment. No iridium was detected above this level, which, keeping the

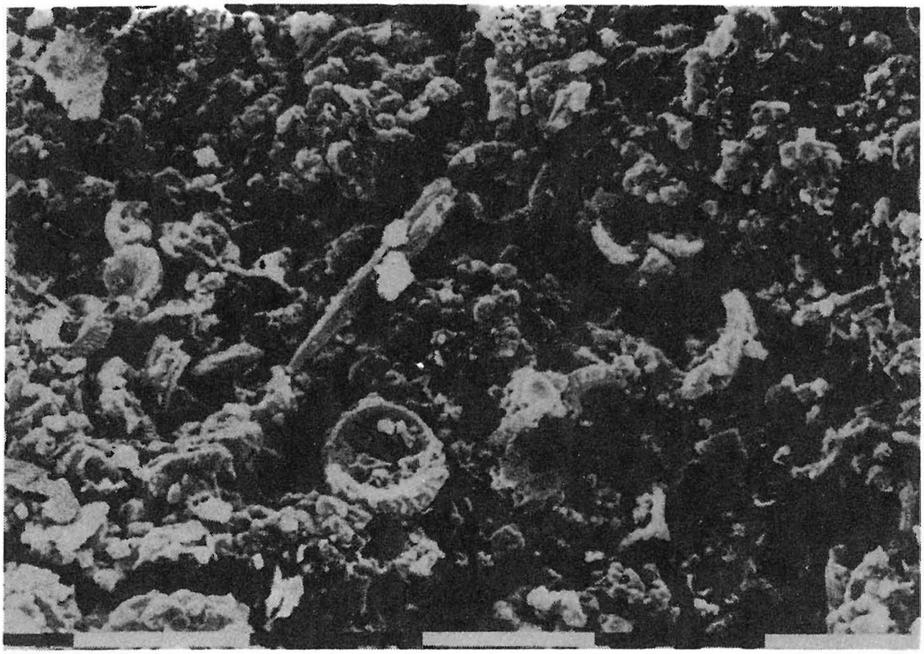


Fig. 4. Scanning electron micrograph of infill of the brachiopod *Carneithyris* sp. from the Greensand of Bochotnica; each scalebar = 10 microns

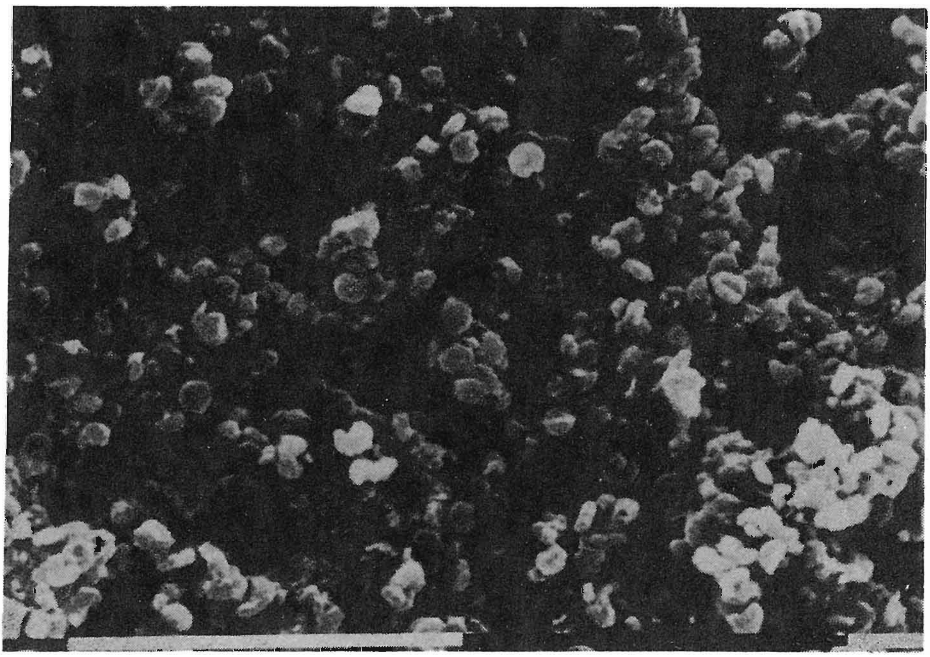
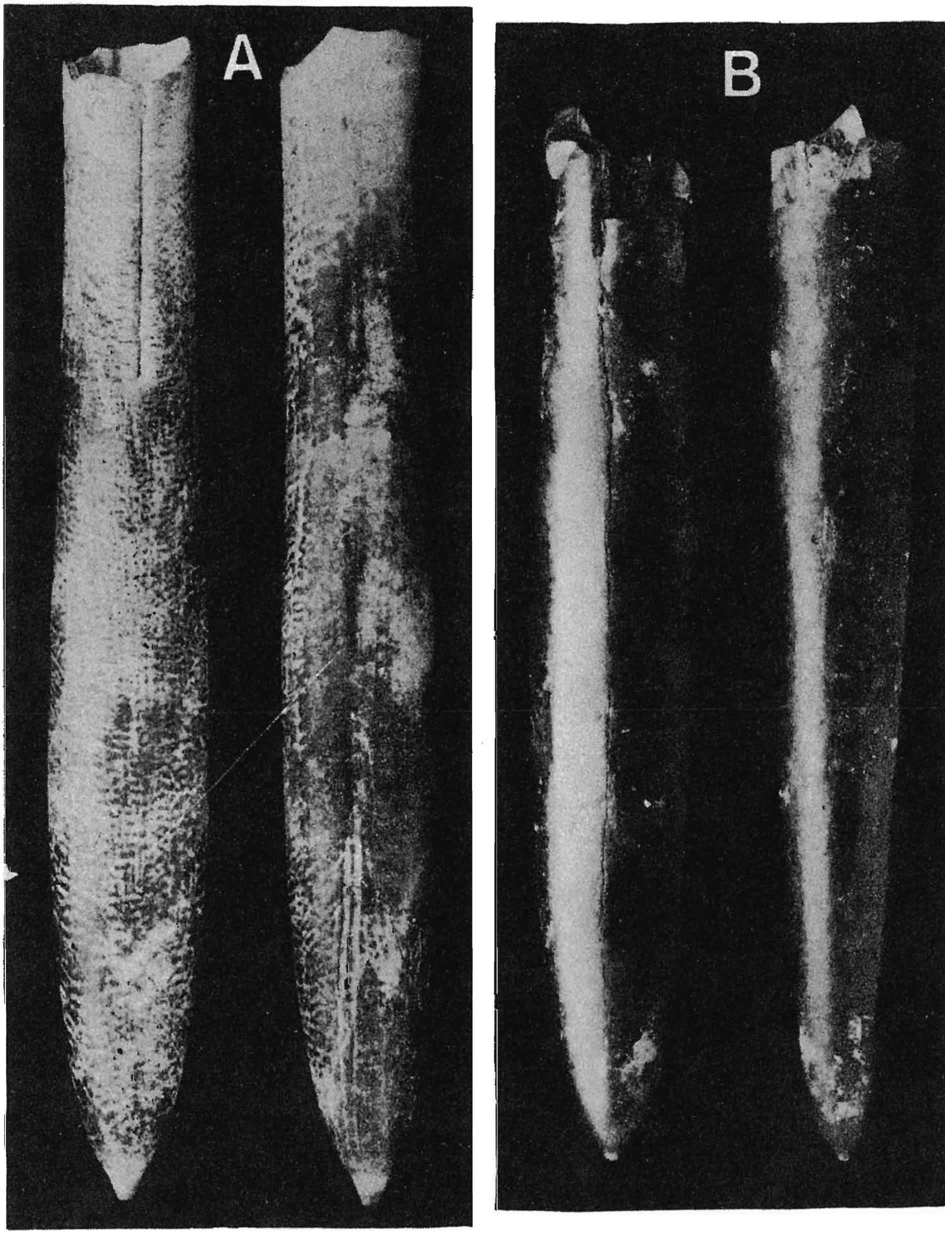


Fig. 5. Scanning electron micrograph of infill of a belemnite alveole of *Belemnella kazimiroviensis* (SKOŁOZDRÓWNA) from the Greensand of Nasiłów; each scalebar = 10 microns



Belemnite guards of *Belemnella kazimiroviensis* (SKOŁOZDRÓWNA) from the Greensand of Nasiłów: **A** – Specimen with well-preserved imprints of bloodvessels, ventral and left-side view; **B** – Specimen with smooth surface and bloodvessel-imprints dissolved, ventral and right-side view

Both specimens are × 1.5; taken by S. ULATOWSKI possible chemical enrichment factor of 10 in mind, means that the whole-rock iridium value was less than 0.16 ppb.

Since the uppermost Maastrichtian is capped by a hardground it was speculated, that the hardground topography could have acted as a trap for iridium-bearing elemental carbon at the Cretaceous/Tertiary boundary. Accordingly, samples from the lower and upper part of the Greensand at Bochotnica were analyzed for Ir, again on the basis of carbon concentrates.

In both samples Ir was detected. The carbon sample from the lowermost Greensand showed 16 ppb Ir and also a high content of Au (244 ppm). The carbon concentrate from a sample from the upper part of the Greensand at Bochotnica contained much less Ir, namely 3.9 ppb and only 1.67 ppm Au.

Three bulk samples of the Opoka from the levels 6.6 m, 14.0 m and 14.7 m at Nasiłów were also analyzed (Table 1). The latter sample is from the top part of the opoka right below the Greensand. It is quite evident that there is a tendency towards higher trace element values in the two stratigraphically younger samples as compared to the older one; most elements show almost doubling from the older to the younger part of the section.

Table 1

Selected elements from *INAA* of Opoka samples from Nasiłów and of Greensand fossils; all values in ppm unless otherwise indicated

Bra. — brachiopod infill from Bochotnica, **Bel.** — belemnite infill from Nasiłów

Element	Sample levels of Opoka 6.6 m	14.0 m	14.7 m	Greensand fossils Bra.	Bel.
Ca	26.6%	24.6%	26.1%	17.1%	28.5%
Sc	0.83	2.28	2.30	3.1	4.5
Cr	13.2	44.1	39.3	52.1	63.0
Fe	0.44%	1.70%	1.07%	1.3%	2.4%
Co	0.54	1.28	1.05	1.16	2.21
Zn	8.34	15.3	17.9	7.6	40.7
Ga	0.82	3.92	2.91	–	–
As	–	–	–	4.2	34.0
Se	20ppb	95	57	0.11	14.1
Br	0.84	1.02	0.92	0.93	–
Rb	11.1	34.3	32.7	34.8	32.8
Sr	715	844	942	1150	2220
Sb	80ppb	129	137	218	1140
Cs	0.56	1.62	1.65	1.97	1.79
Ba	?	69.5	76.2	139	22
La	2.9	6.4	6.6	22.8	80.1
Ce	6.0	14.0	14.2	30.6	251.0
Nd	3.2	8.8	7.9	17.4	196.0
Sm	0.6	1.2	1.3	2.37	6.32
Eu	0.11	0.25	0.25	0.50	3.25
Tb	0.10	0.17	0.17	0.34	2.04
Yb	0.29	0.55	0.57	0.65	3.73
Lu	39ppb	83 –	94 –	0.13 –	0.51 –
Hf	0.63	1.92	1.50	1.65	1.74
Ta	95ppb	280 –	252 –	294 –	321 –
Ir	–	–	–	1.53ppb	–
Au	2.9ppb	52.8 –	1.9 –	–	–
Th	0.91	2.39	2.37	3.56	3.31
Ce/La	2	2	2	1.3	3

Table 2

Comparison between trace element concentrations on a non-carbonate basis from Opoka (6.6 m level), Greensand from the hardground (Na 2), Greensand from the surface of a phosphatized clast (Na 2GS), all from Nasiłów; opoka-like infilling from a brachiopod from the Greensand at Bochotnica (Bra.), and the alveolar infilling from a belemnite from the Greensand at Nasiłów (Bel.)

The barium value marked with (*) is from Na8 (level 14.0m)

Element	Opoka sample 6.6 m	Greensand samples		Greensand fossils	
		Na2	Na2GS	Bra.	Bel.
Ca	–	–	–	–	–
Sc	1.26	3.80	1.35	4.1	7.1
Cr	20.2	198	39.4	69.8	98.9
Fe	0.67%	5.73%	4.99%	1.7%	3.8%
Co	0.83	4.40	6.83	1.55	3.46
Zn	12.76	42.9	63.4	10.2	63.9
As	–	20	22.8	5.6	53.4
Se	30ppb	212	600	0.15	22.1
Br	1.28	0.39	0.72	1.25	–
Rb	16.9	104.8	94.3	46.6	51.5
Sr	1094	351	610	1541	3485
Sb	122ppb	593	606	292	1789
Cs	0.86	2.53	2.69	2.64	2.81
Ba	104*	207.0	202.0	186	22
La	4.4	12.8	15.1	30.5	125.7
Ce	9.2	26.5	32.6	41.0	394.0
Nd	4.6	16.2	18.3	23.3	307.0
Sm	0.9	2.9	3.1	3.18	9.92
Eu	0.16	0.52	0.59	0.67	5.10
Tb	0.15	0.38	0.45	0.45	3.20
Yb	0.44	1.60	1.02	0.87	8.99
Lu	59ppb	230 –	227 –	147 –	800 –
Hf	0.96	12.8	13.3	2.21	2.73
Ta	145ppb	466 –	544 –	394 –	503 –
Ir	–	–	–	2.0ppb	–
Au	4.4ppb	–	–	–	–
Th	1.39	4.58	4.35	4.77	5.20

When compared on a carbonate-free basis a rather clear difference between the Greensand and the underlying Opoka is observed (Table 2). The Fe-content is much higher in the Greensand than in the Opoka, and so are the rare earth elements (REE). This is true of both the light and the heavy REE. The Sr-content is distinctly lower in the Greensand than in the Opoka, while Ba is reversely distributed.

Both Sr and Ba are usually minor elements in chalk, where Sr is dominating in biogenic aragonite while Ba is more common in biogenic calcite (where Mg forms the dominant minor element).

It is, however, noteworthy that the infill in the brachiopod shell (*Carneithyris* sp.) appears under the light microscope as very "diluted" greensand, or in other words as "white chalk" with scattered glauconite grains. This infill differs in this respect from the underlying opoka where such grains were more rare. The discussed brachiopod infill is within the same range of minor and trace element concentrations recorded both in the Opoka and in the Greensand, though there appear some enrichment in REE. The Sr- and Ba-contents point in direction of a biogenic limestone which is in accordance with the structure observed in the scanning electron microscope (*see* Text-fig. 4).

The belemnite infill is geochemically quite different. It has a very high Sr-content, which may well be connected to its placement in the former aragonitic phragmocone of the belemnite. This phragmocone during recrystallization might well have supplied its Sr to the carbonate infill. By contrast, the Ba-content is below the detection limit. This indicates a non-biogenic origin of the infilling carbonate. The REE show strong enrichment. This is herein interpreted as indicative of the presence of phosphate grains which are known to scavenge REE. The enrichment in elements such as Zn would appear to be connected with the higher Fe content and is in some ways reminiscent of what is seen in the two Greensand samples. It would thus seem that the belemnite infill chemically differs from the brachiopod infill by the presence in the belemnite of both glauconite and phosphatic grains, while the brachiopod infill consists of dominating glauconite grains in addition to the carbonate.

The difference is very clearly seen in the scanning electron microscope, where the belemnite infill was found to be composed of equidimensional, loose (*i.e.* non-cemented) small carbonate grains (*see* Text-fig. 5). There is a complete lack of coccoliths or fragments thereof. In the infills of both the brachiopod and the belemnite are found numerous tubular cavities left after dissolution of opaline sponge spicules. This phenomenon is common also in the underlying chalk.

A bulk sample of the infill of the brachiopod shell from the Greensand showed a significant iridium concentration of 1.5 ppb.

DISCUSSION AND CONCLUSIONS

Recently, MACHALSKI & WALASZCZYK (1987) suggested as one possibility for explanation of the faunal condensation and mixing of Danian and Maastrichtian forms in the Greensand overlying the Maastrichtian chalk, that a limestone, no longer preserved, had been deposited and had later been removed.

The obtained results of the trace element and scanning electron microscope studies are apparently a support for such suggestion. The sediment which was deposited prior to the Greensand, but after the deposition of the top of the now preserved Maastrichtian chalk, was a coccolith-rich but slightly glauconitic white chalk-type represented by the brachiopod infill which also carried a slight Ir-enrichment. The time of deposition was very close to, but still prior to deposition of Cretaceous/Tertiary boundary beds which have subsequently been eroded. At Stevns Klint in Denmark, it has been demonstrated that the Ir-enrichment takes place before the onset of the boundary clay sedimentation (ROCCHIA & *al.* 1987, HANSEN & *al.* 1987), *i.e.* in the uppermost part of the Maastrichtian white chalk.

After the deposition of the slightly glauconite-bearing chalk followed the deposition of a boundary clay with Ir-carrying elemental carbon.

After the time with deposition of glauconitic chalk and boundary beds a period with deposition of chemically precipitated carbonate appeared, being an equivalent of the *Cerithium* Limestone of Stevns Klint or the "dead layer" in the other parts of Denmark. This sediment is now observed as the infill of the belemnite at Nasiłów with its complete lack of coccoliths or fragments of coccoliths and low Ba-content.

After the deposition of the *Cerithium*-Limestone-equivalent a similar dissolution process, which at Stevns Klint led to the formation of the truncated surface of the *Cerithium* Limestone and the truncation of the white chalk banks, took place in the Middle Vistula sequence. This caused dissolution of already deposited chalk with glauconite and the chemically precipitated layer. At this time the phosphatization process progressed leading first of all to the phosphatic impregnation of the siliceous sponges and of the various fragments, *i.a.* those of limestones which are coated with silica from dissolved opaline sponge spicules. It is a well-known laboratory phenomenon, that chalks with disseminated silica from recrystallized or dissolved opaline spicules show rather strong resistance towards dissolution even in strong acids like HCl. Phosphatized ammonites and other fossils of Maastrichtian age redeposited into the *Cerithium* Limestone at Stevns Klint in Denmark were reported by BIRKELUND (1979).

The time of formation of the burrows in both Nasiłów and Bochotnica sequence must be fixed to "Greensand time". At Bochotnica, the burrows penetrate to at least 80 cm below the chalk surface. The chalk must have been soft or only very slightly lithified at that time, and no borings could develop. Also, the material in the burrows consists exclusively of greensand and in some places the same burrow has been re-burrowed. The material of the first and the second generation of burrows is, however, not much different.

This situation parallels that at the *Cerithium* Limestone hardground surface at Stevns Klint in Denmark, where the burrows penetrating into the *Cerithium* Limestone and into the uppermost Maastrichtian white chalk exclusively contain material deposited in bryozoan limestone time (i.e. *Globigerina danica* time).

The paleomagnetic stratigraphy coupled with the biostratigraphy indicates that the uppermost 7 meters of opoka in Central Poland belong to the reversed interval 29 underlain by 7 meters of sediments with normal magnetization which we interpret as normal period 30. The overlying marls of the Siwak-type can, according to the dinoflagellates, be ascribed to normal period 29. The authors have not measured the paleomagnetic signal of the Greensand due to its heavy bioturbation. Accordingly, one can not know if it was deposited in period *29 R* or in *29 N*.

The overlying Siwak was deposited in *29 N*. The single reversed sample level 15 could possibly represent *28 R*, but this is not certain. There are no sedimentological indications as to a much slower accumulation rate at this level in comparison with the under- and overlying sediments.

In consequence of the above observations it can be concluded, that the Cretaceous/Tertiary transition in Central Poland is slightly less complete than the corresponding transition in Denmark. However, it seems as if only some decimeters of chalk have been removed by dissolution, corresponding to the iridium-bearing uppermost Maastrichtian gray chalk at Stevns Klint. The suggested hiatus in Central Poland then appears to cover a much shorter interval than previously estimated. It encompasses at least a period of time corresponding to some decimeters of white chalk, the boundary clay, as well as the equivalent of the *"dead layer"* in Denmark, but not a major part of the Lower Danian.

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