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The weathering-modified iridium record of a new Cretaceous–Palaeogene site at Lechówka near Chełm, SE Poland, and its palaeobiologic implications

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In the light of integrated biostratigraphic and geochemical data, a complete shallow-marine succession across the Cretaceous–Palaeogene (K–Pg) boundary, with the critical boundary clay coupled with a burrowed siliceous chalk (“opoka” in Polish geological literature), possibly equivalent of the basal Danian *Cerithium* Limestone in Denmark, has been discovered at Lechówka near Chełm, SE Poland. An extraterrestrial signature marking the K–Pg boundary is confirmed by anomalously high amounts of iridium (up to 9.8 ppb) and other siderophile elements (especially Au and Ni), as well as by an elevated Ir/Au ratio consistent with a chondrite meteoritic composition. The major positive iridium spike surprisingly occurs in Maastrichtian marls, 10 cm below the boundary clay interval, which can be explained by diagenetic mobilisation and re-concentration of the impact-derived components. Thus, intensively infiltrating, humic acid-rich ground waters during the long-lasting Palaeogene weathering in tropical humid regimes were probably responsible not only for the large-scale decalcification of the Lechówka section, but also for both downward displaced position of the iridium enrichment, a dispersed profile of this anomaly and its significantly lessened value, but still approaching an increase by a factor of 100. This modified record of the K–Pg boundary event points to a careful reconsideration of the iridium anomaly as a trustworthy marker for studying the extinction patterns across the K–Pg boundary, as supported by the recent data from New Jersey, USA.

Key words: Iridium anomaly, lithology, biostratigraphy, extinctions, geochemistry, Cretaceous–Palaeogene boundary SE Poland.

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Introduction

Decades of multidisciplinary research have clearly linked the Cretaceous–Palaeogene (K–Pg, formerly K–T) mass extinction to the catastrophic meteorite impact into carbonate- and evaporite-rich target rocks that formed the ~200-km-diameter Chicxulub crater in Yucatan, Mexico. Thirty years ago, the discovery by Alvarez et al. (1980) of an anomalous iridium concentration in the K–Pg boundary clay at Gubbio, Italy, was a starting point to the attractive hypothesis that an asteroid ~10 km in diameter collided with Earth 65 million years ago. This spectacular scenario has been confirmed worldwide with multiple lines of evidence, including high resolution iridium data and a diversity of other proxies (such as shocked minerals,

spherules, Ni-rich spinels, Os isotopes, diamonds, amino acids, among others); it is widely agreed that the unique geochemical signature originated from global settle-out of extraterrestrial matter, derived from a carbonaceous chondrite-type body (see summary in Alvarez 2003; Koeberl 2007; French and Koeberl 2010; Schulte et al. 2010).

The K–Pg boundary is formally defined in the global stratotype section near El Kef, Tunisia, at the base of the boundary clay (= impact ejecta), and therefore is determined precisely by the instant of an extraterrestrial body impact (Molina et al. 2009), resulting in a devastating stress on the global biosphere (see, e.g., reviews in Toon et al. 1997; Robertson et al. 2004; and Kring 2007). More than 350 K–Pg boundary localities are presently known, and these impact

ejecta reveal a spectacular distribution pattern controlled worldwide by distance from the Chicxulub crater (Claeys et al. 2002; Schulte et al. 2010).

As a natural stratigraphic boundary (cf. Walliser 1984), it is generally easy to identify the K–Pg boundary in distal marine successions, because it represents a sudden collapse of carbonate production, characterised by a thin ejecta-rich dark clay horizon (up to 10 cm thick; e.g., Smit 1999; Claeys et al. 2002; Molina et al. 2009; Schulte et al. 2010). The stratigraphic continuity of many K–Pg successions is questionable (e.g., MacLeod 1995), and, therefore, correlation by impact evidence offers a specific chronostratigraphic tool (see Molina et al. 2009). The preserved sedimentary record of a geologically instantaneous event, corresponding to the synchronous fallout of impact-related material that persisted at most several months for the finest, sub-micrometre iridium-rich stratospheric dust (Toon et al. 1997; see also Kring 2007), is the best available proof of continuous record and eliminates the frequent ambiguity of biostratigraphic dating. However, the completeness is either unknown or a significant hiatus is evident at almost 60% of the localities in KTbase of Claeys et al. (2002). This fundamental limitation was clear for the shallow-water, inner neritic sections at Nasiłów and Bochotnica in the reference Middle Vistula Valley section (central Poland; Fig. 1A), where the K–Pg boundary is marked by a burrowed erosional surface overlain by a greensand horizon with residual lag composed of mixed late Maastrichtian and early Danian fossils (e.g., Machalski and Walaszczyk 1987; Machalski 1998). However, a relic of geochemical impact tracers is still preserved in this interrupted depositional record (Hansen et al. 1989).

In this preliminary paper, we report the first Polish continuous succession across the K–Pg boundary, distinguished by an undoubted iridium anomaly even if distinctly overprinted by the Palaeogene weathering processes. The exposure studied is an abandoned quarry at Lechówka near Chełm (Popiel 1977; Harasimiuk and Rutkowski 1984), which is located 110 km east of the Vistula valley (Fig. 1), in the area where a more complete depositional pattern across the system boundary was predicted by Machalski (2005a), based on facies and biostratigraphic analysis. Biostratigraphic and geochemical aspects are highlighted herein, whilst regional consequences of the discovery will be broadly discussed elsewhere.

Other abbreviations.—INAA, instrumental neutron activation analysis; K–Pg (formerly K–T), Cretaceous–Palaeogene; PGE, platinum group elements; XRF, x-ray fluorescence.

Geological setting

The Lechówka locality is situated in the eastern part of the area of the K–Pg boundary outcrops in central and eastern Poland, ranging from Kazimierz Dolny in the Middle Vistula Valley to the town of Chełm near the Polish–Ukrainian border (Pozaryska 1965; Popiel 1977; Harasimiuk and Rutkow-

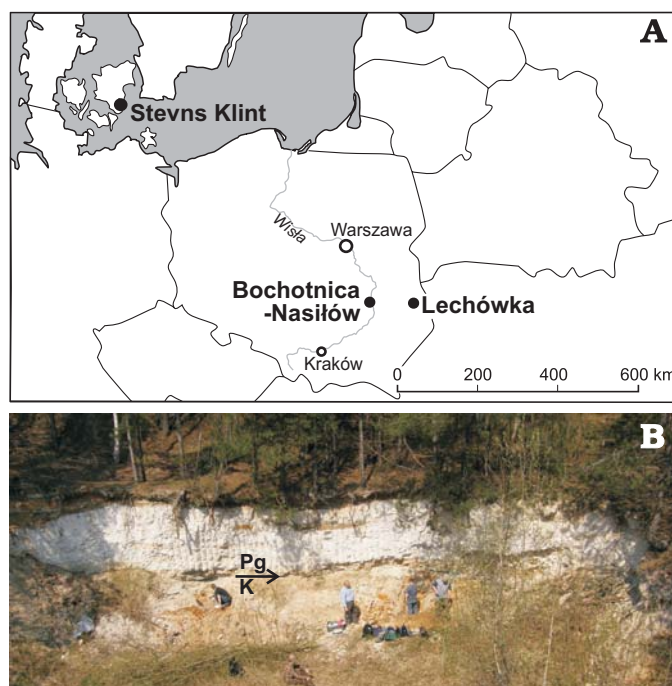


Fig. 1. Location of the Lechówka section in Poland (A), and general view of this outcrop (B). K, Cretaceous; Pg, Palaeogene.

ski 1984; Hansen et al. 1989; Gazda et al. 1992; Machalski 2005a). Palaeogeographically, this site corresponds to the eastern part (in terms of erosional range) of the Danish–Polish basin (Ziegler 1990).

The section studied at Lechówka is over 4 m thick, and eight lithological units can be distinguished (Fig. 2). These are in ascending order:

A, siliceous chalk (known as opoka in the regional lithostratigraphic framework; see Pozaryska 1952), 10 cm thick, representing probably the topmost part of the “calcified opoka” unit, ca. 2 m thick, exposed earlier at Lechówka (Popiel 1977);

B, a tectonic or karstic breccia, ca. 70 cm thick, composed of irregular soft opoka pieces set in a marly matrix;

C, opoka layer, ca. 100 cm thick, with a sharp lower boundary and diffuse, undulating top and a decalcified cover continuously passing into the overlying sediments;

D, marl layer, ca. 30(?) cm thick, with distinct bioturbations at the top 10 cm;

E, clay unit, ca. 10 cm thick, with a rusty layer at the base. Some spots of clay are visible between the burrows protruding from the base of the overlying unit, so the original top of the argillaceous unit was higher than today.

F, white burrowed unit, ca. 10–15 cm thick, with irregular lower and upper boundaries, composed of bright decalcified opoka with numerous decapod burrows (“sponge pseudomorphoses” of Popiel 1977) at the bottom. The burrows often bifurcate, but never cut each other, are filled with overlying glauconitite and surrounded by white opoka aureoles (Fig. 2), probably of eogenetic nature (compare Kaźmierczak 1974; Baird and Fürsich 1975).

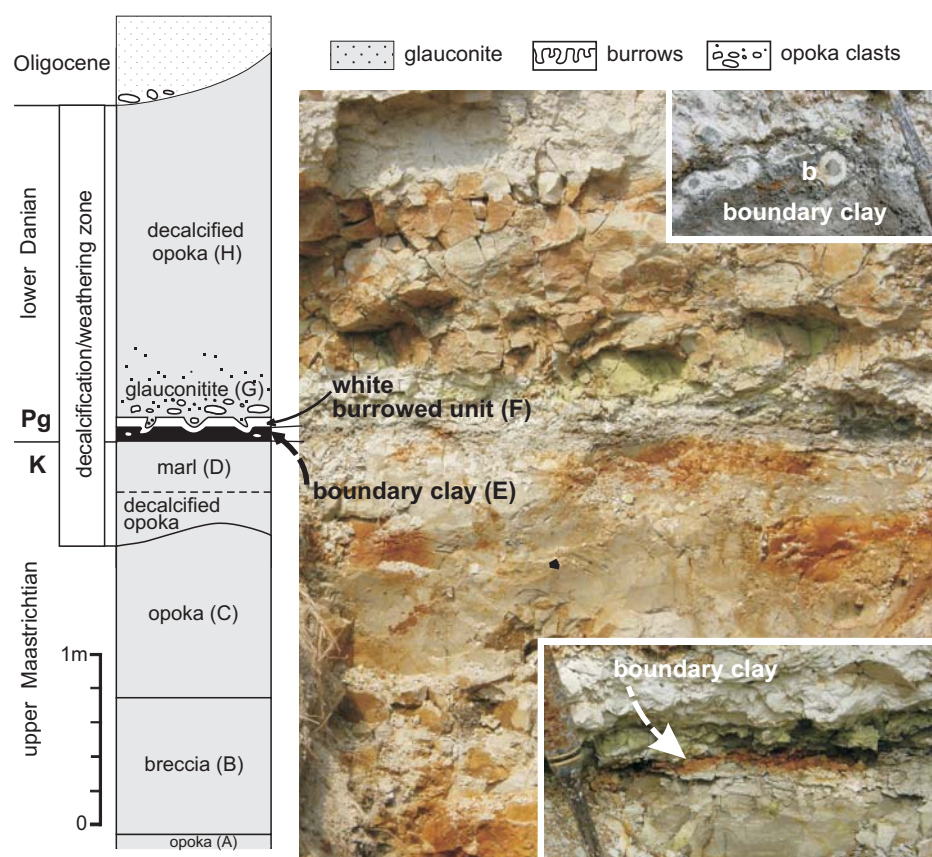


Fig. 2. Lithologic column, field photo and two close-ups of the K–Pg passage at Lechówka. Note a local abundance of burrows (b) and Fe oxy-hydroxides, especially in the boundary clay.

G, glauconitite layer, ca. 40 cm thick, with spotty concentrations of glauconite grains due to mottling of the sediment by bioturbators and irregular clasts of white opoka at the base.

H, decalcified opoka, ca. 150 cm thick, with faint remnants of original limestone intercalations analogous to those occurring in the so called Siwak succession (sandy glauconitic marls with hard limestone intercalations) as exposed in Middle Vistula sections (Pożaryska 1952; Hansen et al. 1989).

The top of the K–Pg succession at Lechówka is locally truncated by glauconite sands with gravel, assigned conventionally to Oligocene (Krzowski 2000; see also Pożaryski 1951). Porous decalcified opoka represents the highly weathered carbonate substratum after regression in the Palaeogene karstification phase (Pożaryski 1951), and was exploited in the quarry as a chemical resource.

Biostratigraphy

The sedimentary succession of the Lechówka section was studied for its macrofossil content. Fragments of the ammonites *Baculites* sp. and *Hoploscaphites constrictus* subsp. indet. (compare Machalski 2005a, b), were found in loose blocks of opoka (units A and C) at the quarry bottom. Sponge fragments, the bivalve *Entolium membranaceum*, and the ammonite *Baculites* sp. occur in the unit C. A well preserved steinkern of “*Nautilus*” *intrasiphonatus* was found around

the middle of the unit C. Unit D yielded sponge fragments and the bivalves *Spondylus dutempleanus*, *Oxytoma danica*, and *Pycnodonte vesicularis*, the latter with a xenomorphic replica preserving part of the *Hoploscaphites constrictus* subsp. indet.

This is a typical Late Cretaceous fauna, composed mostly of stratigraphically long ranging forms. The only exception is *Oxytoma danica* which is restricted to the upper part of the lower Maastrichtian and to the upper Maastrichtian (Abdel-Gawad 1986) and *Hoploscaphites constrictus*, which occurs throughout Maastrichtian and in the lowermost Danian (Machalski 2005b; Machalski and Heinberg 2005). All taxa identified at Lechówka occur in the upper Maastrichtian deposits of the Middle Vistula Valley section (cf. Łopuski 1911; Abdel-Gawad 1986; Machalski 2005a). This macrofaunal dating is supported by planktic foraminiferal assemblage in units A and C, typical of the upper part of Maastrichtian *Guembelitra cretacea* Zone sensu Peryt (1980), easily recognisable due to co-occurrence of abundant specimens of *Heterohelix* and *Guembelitra*; furthermore, numerous moulds of the distinctive Cretaceous genus *Heterohelix* have also been found in marly unit D (Danuta Peryt and Zofia Dubicka, personal communications 2010).

No macrofossils were identified in units E and F. A sparse fauna in mould preservation occurs in unit G. It is represented by minute caryophyllid corals, the bivalve *Nucula* sp., and the gastropods *Ampullospira austriaca*, *Arrhoges gracilis*, *Columbarium herberti*, *Levifusus* sp., and *Metaceri-*

thium sp. Taxa identified to species level are relatively long ranging Palaeocene forms which occur, e.g., in the lower Danian Siwak of the Middle Vistula River succession (Krach 1981; see Hansen et al. 1989 for stratigraphic position of Siwak, based on dinoflagellates).

In summary, a late Maastrichtian age may be postulated for strata below the clay layer and an early Danian age for strata above it, partly by analogy with the Middle Vistula Valley and sections near Lublin (see review in Abdel-Gawad 1986; Hansen et al. 1989; Machalski 2005a), while the clay unit E seems to equate to the K–Pg boundary.

Geochemical anomalies and K–Pg boundary clay

Methods.—Abundances of iridium and up to 36 other major and trace elements were determined in chemostratigraphic context of possible meteoritic contamination in twenty four whole-rock samples, taken from the 4.2 m thick interval in two sets in December 2008 (4 pilot samples) and March 2010 (20 samples), by instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF) analysis at the University of Vienna. Major and selected trace element (i.e., Rb, Sr, Y, Nb, Co, Ni, Cu, Zn, V, Cr, Ba) contents were determined on the ten sandstone samples by XRF spectrometry using standard techniques. All other trace and rare earth elements were determined using INAA. Instrumentation, sam-

ple preparation, data reduction techniques, and standards, precision and accuracy of both methods are described in Mader and Koeberl (2009).

Results.—The results for eight selected elements are presented in Table 1 and Fig. 3, and the major chemical composition refines the field observations of an extensive decalcification/oxidisation front at Lechówka. CaO content is over 42 wt% in the upper Maastrichtian siliceous chalk in the non-weathered lithology (“hard” opoka), but is abruptly reduced in the topmost Maastrichtian marls to less than 3 wt%, and less than 0.6 wt% CaO in the Danian opoka. The K–Pg boundary horizon only is distinguished by heightened Al_2O_3 values compared with the underlying opoka (12.5 vs. 1.8 wt%, respectively). Thus, the clayey fraction admixture increases by a factor of 7 in this distinctive lithological variety.

Separation of terrestrial from extraterrestrial sources in the samples from Lechówka is based on the iridium abundances, representative of the crucial platinum group elements (PGEs; see summary in Kramar et al. 2001 and Palme 2008). This diagnostic element is supplemented by other moderately siderophile elements, also strongly enhanced in cosmogenic material and considered as supplementary impact tracers: Ni, Co, Cr, and especially Au (e.g., Muñoz-Espadas et al. 2003; Koeberl 2007; French and Koeberl 2010; Fig. 3 and Table 2).

As expected, the chemostratigraphic iridium profile shows significant enrichment in the clayey K–Pg level (slightly less than 2 ppb), but a dramatic peak in abundance up to 9.8 ppb is observed in the marl 10 cm below the boundary clay. The

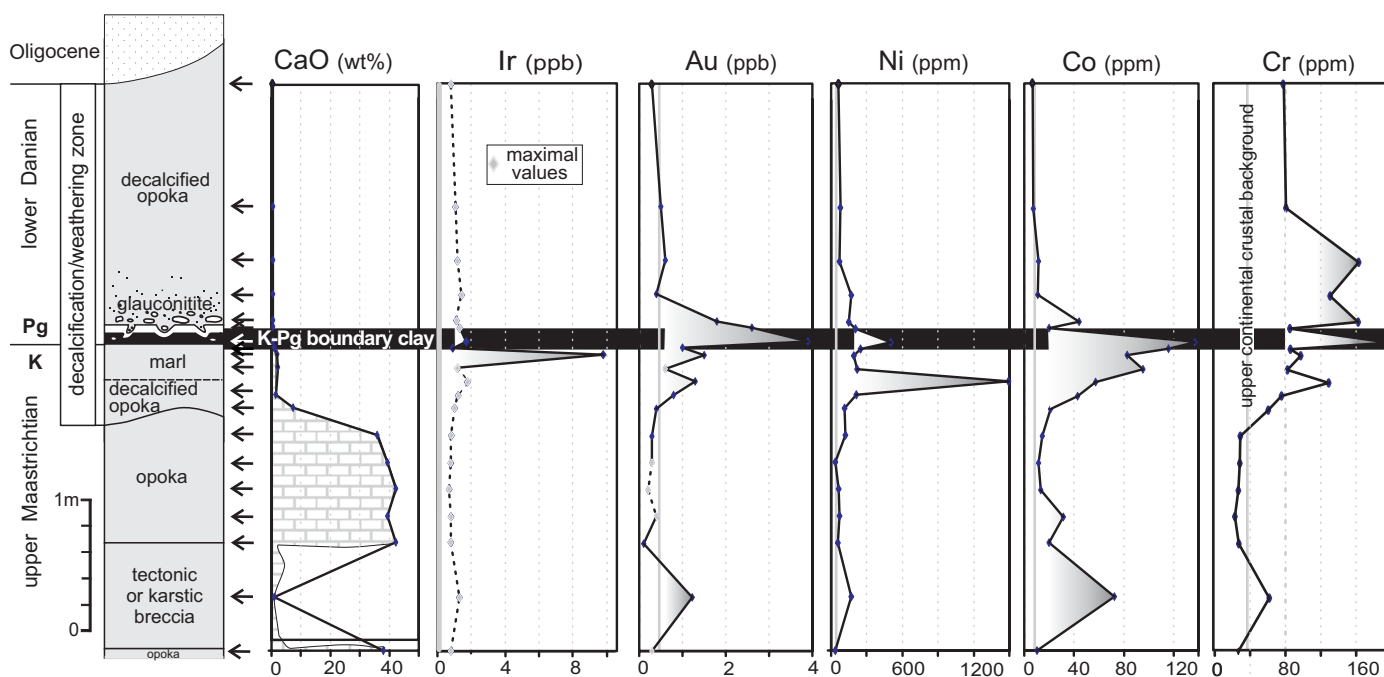


Fig. 3. Concentration of Ca and the siderophiles plotted with the lithological succession at the K–Pg boundary at Lechówka (see Table 1 for a broader set of chemical data); positions of samples analysed are indicated, as well relative enrichment patterns vs. normal crustal content levels (only maximal values are given for the boundary clay samples; see Table 2). Dotted lines cover the values that represent the maximum concentration in the samples allowed by the analyses, i.e., at detection limits.

Table 1. Concentration of selected major and trace element in samples spanning the Cretaceous–Palaeogene transition at Lechówka (Fig. 3).

Sample	Height above the base (cm)	Lithology	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	CaO (wt%)	Cr (ppm)	Co (ppm)	Ni (ppm)	Au (ppb)	Ir (ppb)
KT-230	0	hard opoka	21.98	1.92	37.98	26.7	10.2	36	<0.4	<0.9
KT-190	40	clayey soft breccia	69.54	5.21	0.99	61.9	72.4	169	1.2	<1.4
KT-150	80	hard opoka	15.81	1.57	42.21	27	20.1	55	0.1	<0.9
KT-130	100	hard opoka	16.6	1.59	39.29	22.8	31.7	68	<0.5	<0.9
KT-110	120	hard opoka	15.87	1.82	42.29	26.9	13.1	66	<0.3	<0.8
KT-90	140	hard opoka	19.32	2.03	39.37	28.2	11.6	35	<0.4	<0.9
KT-70	160	hard opoka	22.32	1.95	35.84	29.1	14.4	123	<0.4	<0.9
KT-50	180	hard to decalcified opoka	70.98	5.32	7.32	60.7	21.3	114	0.4	<1.1
KT-40	190	?decalcified opoka	76.95	6.59	1.43	75.6	43	211	0.8	<1.3
KT-30	200	?marl	n.d.	n.d.	n.d.	129	57.2	1495	1.3	<1.9
KT-20	210	marl	74.72	6.63	2.14	82.5	95.4	220	<0.7	<1.3
KT-10	220	marl	74.81	7.50	1.85	97	82.6	189	1.5	9.8
L-1*	226	marl	n.d.	n.d.	n.d.	84.2	112	249	1.1	0.9
L-4*	226	marl	n.d.	n.d.	n.d.	85.5	116	248	0.9	0.8
L-2*	230	boundary clay	n.d.	n.d.	n.d.	186	112	457	3.6	1.6
L-3*	230	boundary clay	n.d.	n.d.	n.d.	196	137	499	3.6	<1.8
KT-0	230	boundary clay	65.64	12.51	0.95	177	37.1	202	1	<1.6
KT-Clay	230	burrowed boundary clay	63.97	11.56	3.01	142	96.5	311	3.9	<1.9
KT+10	240	white burrowed unit	70.46	6.67	0.55	85.1	19.8	145	2.6	<1.4
KT+15	245	glauconitic decalc. opoka	65.82	9.87	0.49	162	44.3	168	1.8	<1.2
KT+35	265	glauconitic decalc. opoka	81.98	6.81	0.48	131	10.8	71.4	0.4	<1.5
KT+60	290	glauconitic decalc. opoka	63.04	5.69	0.38	163	11.5	78	0.6	<1.3
KT+100	330	decalcified opoka	76.78	7.18	0.5	80.4	7.2	60	0.5	<1.2
KT+190	420	decalcified opoka	77.41	6.54	0.4	78.2	6.1	46	0.3	<0.9

* Pilot samples analysed in December 2008; n.d., not determined.

Table 2. Generalised concentrations of Ir, Au, and guide siderophile elements in the Cretaceous–Palaeogene transition at Lechówka (Table 1), as compared with chondrite-type meteorites, the continental crust, and the K–Pg reference sections, in the context of a possible distal ejecta geochemical signature.

Selected terrestrial and extraterrestrial materials	Ir (ppb)	Au (ppb)	Ir/Au	Co (ppm)	Cr (ppm)	Ni (ppm)
Lechówka hard opoka (background) ¹	<0.8 (<0.16 ² ; ?0.044 ³)	?0.2	?	17	27	64
Lechówka boundary clay (max. values from 4 samples)	1.6 (to ?1.8)	3.9	0.41	137	196	499
Lechówka - max. enrichment values (stratigraphical level ⁴)	9.8 (-10)	3.9 (0)	6.53 (-10)	137 (0)	196 (0)	1495 (-30)
Lechówka - minimal K–Pg enrichment vs. regional background (Al-normalised*)	? >100 (?>25*)	?>20 (?>3*)	?	8 (1*)	7 (1*)	23 (6*)
Stevns Klint - Fish Clay ⁵	1.65-87	0.55-47	0.8-11.5	95	146	832
Caravaca - K–Pg boundary	47–56.9 ⁵	13–43 ⁵	1.3–3.6 ⁵	305 ⁶	675 ⁶	1100 ⁶
Continental crust	0.022 ⁷	1.8 ⁷ (0.4 ⁸)	0.01 ⁷ (0.06 ⁸)	8 ⁸	37 ⁸	45 ⁸
Orgueil CI chondrites	490 ⁷	140 ⁷	3.5 ⁷	760 ⁷	3975 ⁷	16500 ⁷
Carbonaceous CK chondrites	772 ⁹	121 ⁹	6.4 ⁹	647 ⁹	3627 ⁹	12218 ⁹

¹ Average from samples KT-230 and KT-150 to KT-70; ²at nearby Nasiłów locality (Fig. 1), after Hansen et al. (1989); ³ K–Pg background for carbonates after Crockett et al. (1988); ⁴ in cm below (-) the K–Pg boundary (see Fig. 3); ⁵ after Tredoux et al. (1989: table 1) and sources compiled by Bruns et al. (1997: table 2); maximal values are presented for Cr, Co and Ni; ⁶ Maximal values from Vannucci et al. (1990: table 5); ⁷ after sources compiled by Koeberl (2007: table 1); ⁸ after sources compiled by Muñoz-Espadas et al. (2003: table 1); ⁹ after sources compiled by Tagle and Berlin (2008: table 1). *Al-normalised contents refers to trace element concentrations divided by the content of immobile element Al.

Maastrichtian opoka exhibits iridium values that are below 0.8 ppb, and this analytical detection limit concerns also Au values. However, the highest Au abundances are placed exactly at the boundary horizon (3.6–3.9 ppb), and this extends also to other siderophile elements (Table 2). A noteworthy Ni spike (1495 ppm) is only found 40 cm below the boundary clay, but there are mostly three more or less distinct siderophile maxima in the K–Pg transition. In fact, this distinct enrichment is clearly not confined to the boundary clay but elevated values tail upward at least 20 cm (260 cm for Cr) into the Danian and certainly 50 cm downward into the Maastrichtian, and there is a slight shifting of stratigraphic peak position for particular elements (Fig. 3). Notably, the breccia in the lowermost part of Lechówka section also reveals a several-fold increase of siderophile elements, as is especially clear in the extended Co enhancement.

Discussion

By analogy with the classical Stevns Klint section, Denmark, Unit E of the Lechówka Section probably corresponds to the boundary clay, locally referred to as Fish Clay of Stevns Klint which marks the K–Pg boundary there; consequently, the strongly burrowed unit F at Lechówka may be interpreted as an equivalent to the heavily burrowed *Cerithium* Limestone at Stevns Klint, Denmark (see Surlyk et al. 2006). The overlying glauconite and decalcified opoka (units G and H) are clearly correlatable with the greensand and Siwak of the Middle Vistula Valley, respectively (Krach 1981; Machalski and Walaszczyk 1987; Machalski 1998).

Geochemical aspects.—A lithological contact of the upper Maastrichtian and lower Danian strata along the clay horizon at Lechówka is supported by the biostratigraphic data quoted above, also in light of the occurrence of the possible equivalent of the burrowed *Cerithium* Limestone (see Fig. 2). Nevertheless, the occurrence of a sedimentary hiatus in the decalcified succession cannot be excluded on basis of biostratigraphic analysis only. Thus, a refined dinoflagellate study, planned in future in co-operation with Henk Brinkhuis, Utrecht, would probably offer a plausible resolution of the K–Pg boundary question at Lechówka.

However, the geochemical data at hand conclusively confirm a complete depositional record across the K–Pg boundary in this locality. Siderophile elements (Ir, Au) exhibit anomalously high values, recording a cosmogenic admixture at the predicted interval, which match the distribution and abundances in other boundary sections (Fig. 4). On the other hand, these variations cannot be exactly evaluated because of the above mentioned analytical detection limits. The non-boundary carbonate lithologies, typical of the K–Pg transition, and deficient in signs of polymetallic mineralisation, certainly reflect the “normal” (background) iridium concentration, as indicated by values given by Hansen et al. (1989) for correlative strata from the Middle Vistula Valley succession. At

Nasiłów, the whole-rock iridium concentration in opoka is below 0.16 ppb. This upper abundance limit corresponds well with “normal” continental crust content (less than 0.1 ppb, Koeberl 2007: fig. 8), as well as with the background carbonate levels in the K–Pg interval, exemplified by similar Danish chalk deposits (as low as 0.004 ppb at Nye Kløv, Schmitz and Asaro 1996) and in the classical Gubbio succession (0.044 ppb; Crocket et al. 1988; 0.008 ppb, Rocchia et al. 1990). Thus, it can be convincingly demonstrated that iridium amounts increase by a factor of about 100 in the broad K–Pg interval (Table 2), and, as confirmed by Al normalisation, this excess value is not correlated with a sudden collapse of carbonate production. Conversely, there is more or less effective incorporation of other siderophile elements into the aluminosilicates (correlations with Al range from 0.47 for Co to 0.88 for Cr), and, therefore, only Ni is undoubtedly concentrated by 6 times in the secondary anomaly horizon (Table 2). Variable chemostratigraphic interelement differentiation of siderophiles has been reported from many K–Pg localities (e.g., Alvarez et al. 1980; Kyte et al. 1985; Crocket et al. 1988; Schmitz 1988; Tredoux et al. 1989; Vannucci et al. 1990; Chai et al. 1995; Ebihara and Miura 1996; MacLeod et al. 2007).

The regional-scale decalcification phenomenon, and other effects of meteoric leaching, were certainly coeval with dramatic increase in the intensity of the hydrological cycle and karstification (see Pożaryski 1951). Enhanced continental weathering/runoff and chemical weathering rates were sustained for a long time in the broadly-defined Palaeocene–Eocene Thermal Maximum (5 My, King 2006: fig. 16.8) in the extremely humid tropical climate. The supergreenhouse conditions were obviously paired with various re-distributions of the potential meteoritic components under study (see Figs. 3, 4). In particular, Ni and Co were easily released during oxidation of metal-rich sulfides. The process should theoretically be less substantial for iridium due to its well-known overall insolubility and diagenetic stability.

However, the large-scale iridium spike is rather unexpectedly discovered 10 cm below the K–Pg boundary clay, conversely to the Au, Cr, and Co maxima. The frequent occurrence of normal-sized representatives of the foraminifera genus *Heterohelix* in this sample confirms its Maastrichtian age, even if the genus belongs to possible “Cretaceous survivors” that crossed the fatal K/Pg boundary (Gallala et al. 2009). The finding of shocked minerals and other impact tracers in the assumed boundary clay would further substantiate this chronostratigraphic pattern, but a pilot mineralogical study remained unsuccessful (Maria Racka, personal communication 2010).

In general, the iridium distribution is not affected by post-depositional processes (e.g., Muñoz-Espadas et al. 2003). However, under specific conditions it can be mobile as well (see review in Sawlowicz 1993 and Evans and Chai 1997), especially in terrestrial settings (Martín-Peinado and Rodríguez-Tovar 2010). A number of studies have revealed that the iridium enhancement is frequently spread out over different intervals, and a diffuse, multi-peaked chemostrati-

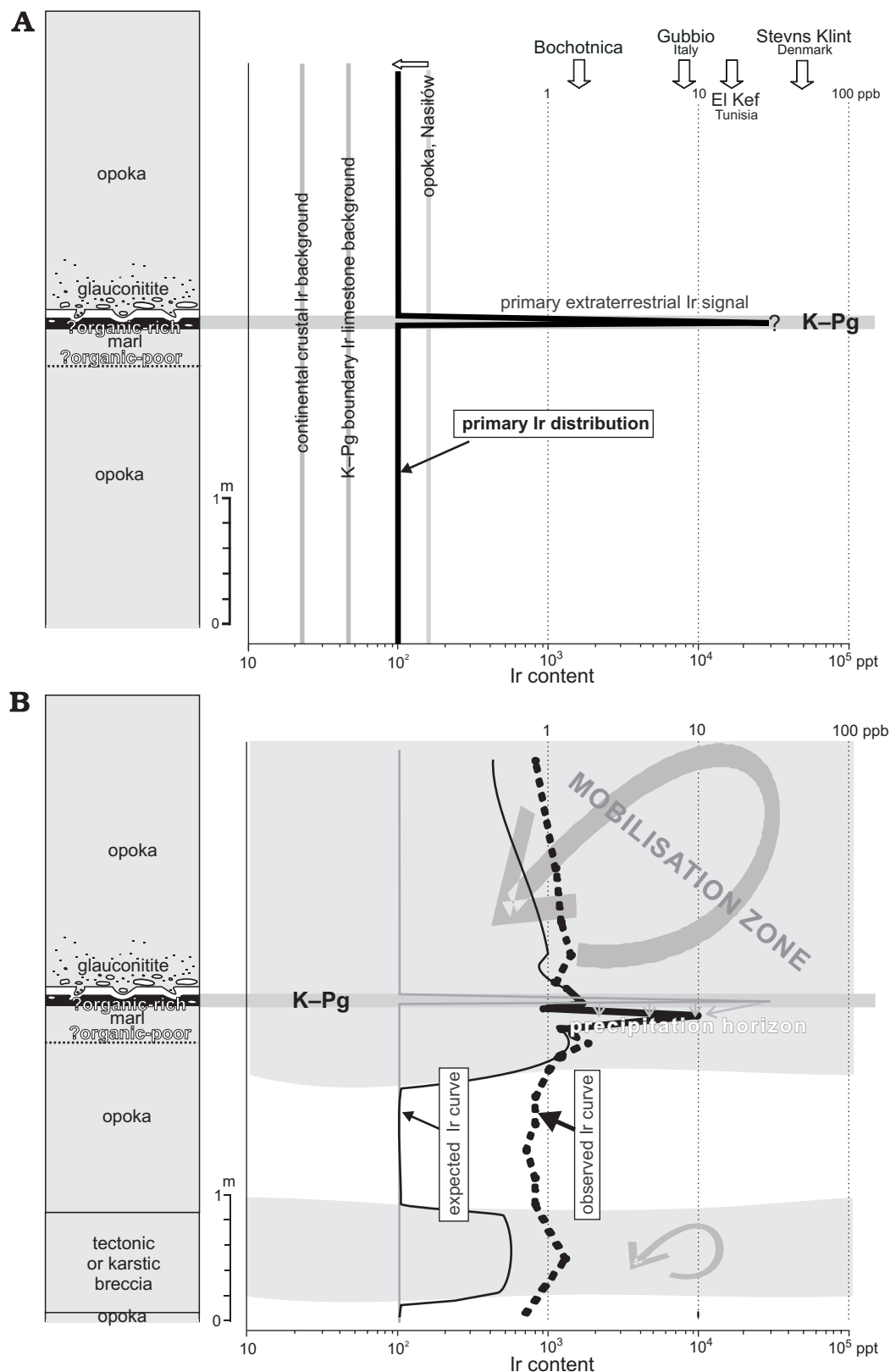


Fig. 4. Two-step interpretation of weathering-modified iridium anomaly in the K-Pg succession at Lechówka (see Fig. 3), showing a significant original iridium anomaly (A) altered by secondary redistribution/participation processes (B), resulting in a substantial extension of the iridium enrichment and a lower position of the diminished iridium spike relative to the K-Pg boundary clay, perhaps controlled by a precipitation front at an assumed redox barrier (cf. Sawłowicz 1993; Gawrilov 2010). Observed and expected weathering-controlled iridium chemostratigraphic profiles are shown (the iridium baseline is carefully taken as 0.1 ppb; see Table 2), as well as the comparative placement of the recognised iridium enrichment against a diversity of K-Pg reference levels and key localities (compiled from Crocket et al. 1988, Hansen et al. 1989, Koeberl et al. 2007, and Schulte et al. 2010).

graphic profile is frequently reported (e.g., Huber et al. 2001), in particular an extensive basal Danian “tail” from the major iridium spike at the K–Pg boundary (e.g., Kyte et al. 1985; Rocchia et al. 1987, 1990; Crocket et al. 1988; Hansen et al. 1989; Tredoux et al. 1989; Ebihara and Miura 1996; Officer and Page 1996; Schmitz and Asaro 1996; Kramar et al. 2001; MacLeod et al. 2007; Premović 2009; Gavrilov 2010); conjectural explanations include a long-term volcanic activity signature, bioturbation reworking, dissolution of carbonates, compactional squeezing of interstitial waters and/or chemical diffusion of metalloorganic compounds.

Nanophase iron grains were suggested by some workers as the original iridium carrier in the K–Pg sites (e.g., Wdowiak et al. 2001), although this interpretation is not universally accepted (see e.g., Schuraytz et al. 1997; Gabrielli et al. 2004). The mechanism of PGE leaching from decomposed extraterrestrial matter and transport in low-temperature aqueous media, especially PGE host phases, has been insufficiently known (Schmitz et al. 1988; Chai et al. 1995). Iridium, which, in some rare circumstances might also behave as a chalcophile element, may be bound at the surface of growing sulfide crystals and polycrystalline aggregates (see Gavrilov 2010), and the release of iridium was recently found at a pyrite-dominated mine tailing due to oxidative weathering in the soil profile (Martín-Peinado and Rodríguez-Tovar 2010). On the other hand, the connection of iridium with organic matter was highlighted by Schmitz et al. (1988), and effective sorption on humic acids is well proved (Varshal et al. 2000). In fact, up to 65% of the initial iridium budget is evidently lost during surficial weathering of labile organic matter in black shales (Peucker-Ehrenbrink and Hannigan 2000). In the K–Pg boundary strata at Stevns Klint, iridium is mostly associated with humic kerogen (Premović 2009), but this link is doubtful for the majority of coeval sites (see also Chai et al. 1995). Secondary iridium re-concentration in neighbouring deposits may occur during mobilisation and re-precipitation due to decomposition of metalloorganic compounds at the trapping boundary, probably between reduced and oxidised sediments (Schmitz 1985; Crocket et al. 1988; Tredoux et al. 1989; Wallace et al. 1990; Sawlowicz 1993; Colodner et al. 1992; Evans and Chai 1997; Martinez-Ruiz et al. 1999; Varshal et al. 2000; Gavrilov 2010). Other factors may also be important, and e.g., Martín-Peinado and Rodríguez-Tovar (2010) demonstrated the dominant control of the clay fraction texture on the iridium redistribution in the soil matrix. However, as noted by Premović (2009: 6): “the association of iridium with this kerogen is not necessary chemical and it could be just physical because micron-size iridium-bearing grains are associated with an acid-insoluble residue, which mainly consists of kerogen”.

As guided by other K–Pg successions, it is tentatively assumed herein that the boundary clay and underlying marly level (cf. the transition layer of Schmitz 1988) were originally dark-coloured, organic-, and pyrite-enriched, as demonstrated by abundant Fe oxy-hydroxides (whole-rock Fe contents above 5%; Fig. 2). A progressive oxidation front

probably penetrated downward these reducing sediments, leading to an appreciable iridium redistribution and a final precipitation near a presently obscured change in lithology and/or redox conditions in the marly unit (Fig. 4). Following the worldwide chemostratigraphic pattern, it therefore seems far more reasonable that the original iridium anomaly was post-depositionally altered and displaced downward (cf. Martín-Peinado and Rodríguez-Tovar 2010; see below). However, the specific explanation of the dispersal of the siderophile elements will be the subject of future research.

In summary, the most likely multiphase decalcification at Lechówka was caused by descending ground waters enriched in humic acids, concurrently with the iridium re-concentration away from the mm-thick ejecta level (Smit 1999; Schulte et al. 2010) into even 1.5 m thick rock column, and also into fault/karst zones (see similar case in Wallace et al. 1990; Fig. 4). This likely redox-controlled dispersal resulted finally in a significant weakening of original extraterrestrial signal (Martín-Peinado and Rodríguez-Tovar 2010). As indicated by other siderophile chemostratigraphic patterns (Table 2), a doubling of the primary iridium signal, at least to anomaly level known from the stratotype El Kef section (18 ppb), seems to be reasonable (Fig. 4). Note also that when compared with the average terrestrial upper-crustal iridium content (0.022 ppb; Table 2), the negatively modified anomaly at Lechówka still exhibits an over 400-fold increase. In addition, the determination of such a cosmogenic component can be proved by the interelement ratios of critical siderophile elements (see review in Koeberl 2007). Despite the evident post-depositional fractionation/ mobilisation through the sediment profile, the Ir/Au ratios still mostly preserve the values observed in chondritic meteorites in the key interval (between 0.4 and 6.5; Table 2), relative to a terrestrial one (at least an order of magnitude lower). By analogy to values from other K–Pg sites (see Table 2 in Bruns et al. 1997), this supports an occurrence of altered impact fallout matter at the distal Lechówka section.

Ir anomaly and the palaeobiology of the K–Pg mass extinction.—At Lechówka, the major iridium anomaly occurs in Maastrichtian marls, 10 cm below the K–Pg boundary clay, and a similar divergence is described in the Manasquan River Basin, New Jersey, where the position of the iridium anomaly is inconsistent with the biostratigraphic data (Landman et al. 2007, 2010).

A fairly rich and well preserved ammonite assemblage, comprising scaphitid clusters reflecting gregarious habit of these cephalopods, occurs in the *Pinna* Bed which is situated above the iridium anomaly. Only late Maastrichtian microfossils are present in the ammonite-bearing horizon. Two alternative scenarios were put forward by Landman et al. (2007) for explanation of this inconsistency. First, that the ammonite assemblage from the *Pinna* Bed actually postdates the iridium anomaly, thus represents remnants of a community living after the Chicxulub impact. Another alternative is that the iridium anomaly at the base of the *Pinna* Bed is postdepo-

sitionally repositioned by percolating water to its present position and originally was present at the top of the ammonite-rich horizon. Neither scenario was favoured by Landman et al. (2007) who left the problem for a future research, but our data clearly support the second hypothesis. Whatever scenario might be true, however, caution is needed in respect to the iridium anomaly as a chronostratigraphic marker of the K-Pg event (see Claeys et al. 2002) when studying the mass extinction patterns across the system boundary.

Conclusions

- In the light of presented biostratigraphic and geochemical data, the re-visited section at Lechówka near Chełm represents the most complete marine section of the K-Pg transition in Poland, with the critical boundary clay preserved together with the burrowed opoka, being a possible equivalent of basalmost Danian *Cerithium* limestone at Denmark. This confirms previous regional correlations leading to the supposition that iridium-enriched deposits were primarily deposited but subsequently eroded in the Middle Vistula Valley succession (Hansen et al. 1989; Machalski 1998). A refined comparative analysis of the primary K-Pg successions is unclear because Hansen et al. (1989) found an iridium enhancement only in ex-situ remnants of the glauconite-bearing opoka in the Vistula Valley.
- An unequivocal extraterrestrial signature, determining the K-Pg boundary at Lechówka, is proved by anomalously high amounts of iridium (up to 9.8 ppb), along with mainly or partly meteoritic siderophile elements (especially Au and Ni; Table 2), as well as by an Ir/Au ratio consistent with a chondritic composition.
- The major iridium anomaly spike occurs 10 cm below the boundary clay interval, requiring an explanation by the poorly-known mechanisms of post-depositional PGE mobilisation and redistribution out of the ejecta horizon. This suggests a decisive role for intensively circulating, humic acid-rich ground waters during the long-lasting Palaeogene weathering in humid regimes, responsible for the pronounced decalcification. This surficial alteration is tentatively accepted as a cause for the downward displaced placement of the major iridium enrichment, a variably dispersed profile of the siderophile enhancement, and also its significantly weakened value, as stressed by Martín-Peinado and Rodríguez-Tovar (2010). All these data undoubtedly corroborate the outstandingly high fossilisation potential of the distal Chicxulub ejecta (cf. Alvarez 2003), as well as call to a careful interpretation of iridium anomalies as trustworthy chronostratigraphic markers of the K-Pg boundary.
- Further micro-chemostratigraphic studies should focus on more precise and extended PGEs analysis, paired with mineralogical search for impact markers across the critical K-Pg boundary level. The main puzzle is why other siderophile elements, such as Au, Cr, and Co, which are much more mobile than iridium, are less reworked. Thus, verti-

cal and lateral variation should be explored, and proper understanding of the enrichment mechanisms and sorption-desorption behaviour of extraterrestrial contamination in the dynamic ground water-carbonate sediment system are the most intriguing questions for the iridium-enriched decalcified succession.

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Note added in proof

In the most recent study of the Cretaceous–Paleogene boundary in subsurface sections of New Jersey, Miller et al. (2010: 867) supported our supposition about post-depositional Ir mobility as they concluded: “We attribute the anomaly at Freehold to the downward movement of Ir and reaffirm the link between impacta and mass extinction”.

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