The mineralogical record of the Early Toarcian stepwise climate changes and other environmental variations (Ciechocinek Formation, Polish Basin)

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Key words: clay minerals, bulk rock data, warming event, palaeoclimate, Ciechocinek Formation, Early Toarcian, Polish Basin.

Abstract. After the cooling episode of the Late Pliensbachian, a major oceanic anoxic event occurred during the prominent warming event of the Early Toarcian (183 Myr; Early Jurassic). In this paper, new mineralogical and geochemical data (XRD, XRF, SEM, and TOC) measured on four cores from the Polish Basin are presented in order to document the regional impacts of these disturbances at a high sampling resolution. The results show that the clay mineral assemblages (<2 μm fraction) and vertical variations in kaolinite content are generally similar basin-wide and were controlled by the intensity of chemical weathering and climate changes. However, sea-level changes and variations in terrigenous supply are reflected in the bulk rock data. The spatial variability in clay mineral proportions may also be influenced by the distance from shoreline and the lithology of source areas. Generally, the clay minerals from the Polish Basin confirm the stepped nature of the Early Toarcian warming event. After a predominance of illite in the lower part of the Ciechocinek Fm., which suggests a temperate climate in the early *tenuicostatum* Zone, rises in kaolinite in the middle part of the Ciechocinek Fm. indicate a stronger weathering rate and high rainfall due to the onset of the warming event in the late *tenuicostatum* Zone. Importantly, the initial phase of climate change recorded by clay minerals seems to slightly precede the first step of the negative carbon isotope excursion ascribed to massive greenhouse gas releases.

INTRODUCTION

It is generally suspected that warm to temperate climates prevailed in mid-latitudes during the Early Jurassic. Nevertheless, profound climatic changes related to perturbations in the global carbon cycle linked to both the Pangean breakup and the volcanic activity in the Karoo-Ferrar large igneous province have been documented at the Pliensbachian–Toarcian transition (Pálfy, Smith, 2000; McElwain *et al*., 2005) (Fig. 1). The Early Toarcian is considered a time of rapid global warming that followed a possible glaciation in the Late Pliensbachian (Price, 1999; Morard *et al*., 2003; Pieńkowski, 2004; Pieńkowski, Waksmundzka, 2009; Suan *et al*., 2008, 2010) and triggered so-called Toarcian Oceanic Anoxic Event (T-OAE) (Jenkyns, 1988). Widespread organic matter accumulations have been reported in numerous basins spanning the late *tenuicostatum* – early *falciferum* biochronozonal transition. Moreover this Toarcian OAE was accompanied by a marine transgression (Hallam, 1997, 2001; Hesselbo, Jenkyns, 1997) and a second-order biotic crisis mostly affecting marine invertebrates and biocalcifying microorganisms (*e.g*. Little, Benton, 1995; Pálfy, Smith, 2000; Wignall, 2001, 2005; Mattioli *et al*., 2004, 2009; Tremolada *et al*., 2005; Caswell *et al*., 2009). The characteristic record of the carbon cycle disturbances is a broad positive shift in $\delta^{13}C$ reflecting organic matter burial; this positive shift is interrupted by a sharp and pronounced negative $\delta^{13}C$ excursion (CIE) with an amplitude up to 7‰, both in marine settings

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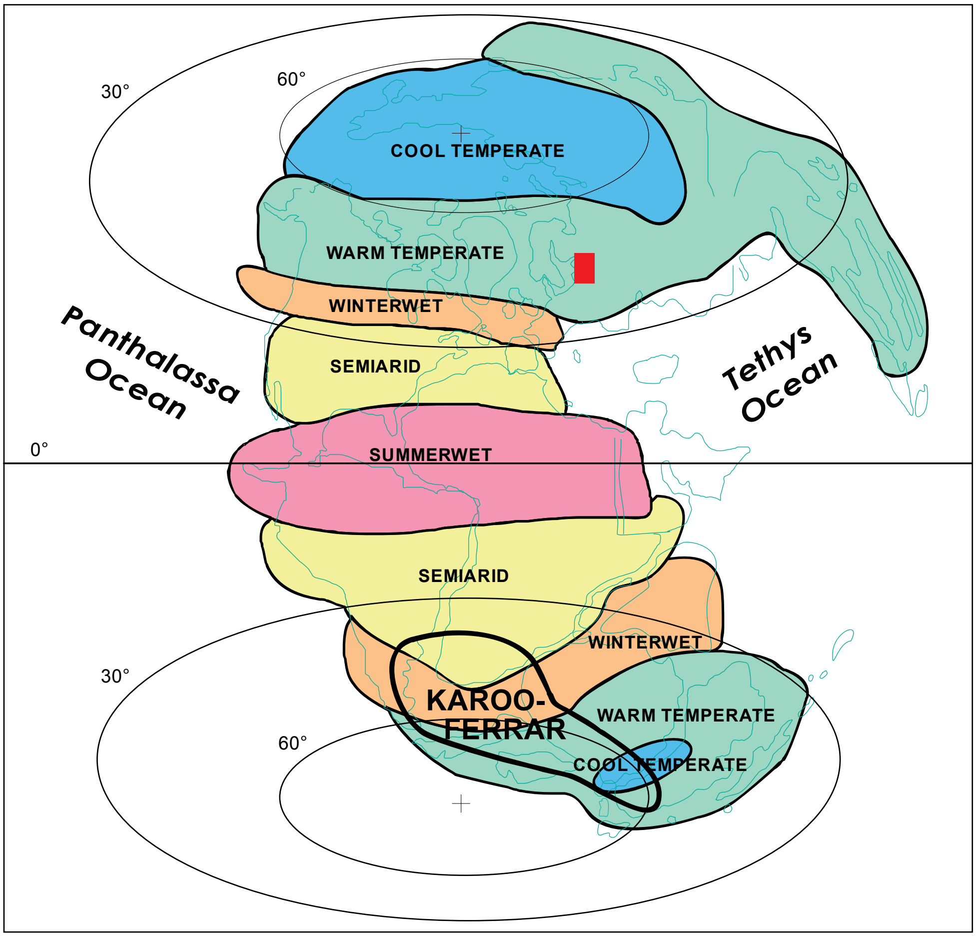

Fig. 1. Palaeoclimatic belts during the Early Jurassic (from Dera *et al.*, 2009a modified) and the approximate extent of the Karoo-Ferrar magmatic province (after Riley, Knight, 2001)

Red rectangle marks the location of the Polish Basin

(*e.g*. Küspert, 1982; Schouten *et al*., 2000; Röhl *et al*., 2001; Hesselbo *et al*., 2000, 2007; Jenkyns *et al*., 2001; Cohen *et al*., 2004; Kemp *et al*., 2005; Hermoso *et al*., 2009, 2012) and in the atmospheric system (Hesselbo, Pieńkowski, 2011) (Fig. 2). This negative CIE (one of the largest of the Phanerozoic) has been described from marine organic matter, marine carbonate as well as terrestrial plant material (Hesselbo *et al*., 2000, 2007; Hesselbo, Pieńkowski, 2011). The global warming event was expressed by a rise in Tethyan seawater palaeotemperatures (McArthur *et al*., 2000; Bailey *et al*., 2003; Rosales *et al*., 2004; van de Schootbrugge *et al*., 2005; Suan *et al*., 2008), as well as huge increases in silicate weathering rates reflected by rises in $^{87}Sr/^{86}Sr$ and $^{187}Os/^{188}Os$ values and major clay mineral changes (Cohen *et al*., 2004, 2007; Waltham, Gröcke, 2006; Cohen, Coe, 2007; Hesselbo *et al*., 2007; Dera *et al*., 2009a). In agreement, the recent GCM modelling of Dera and Donnadieu (2012) validated these observations by showing stronger rainfalls toward the high latitudes.

The negative CIE records the injection of isotopically light carbon into the ocean–atmosphere system during the interval of increased organic-matter burial, most probably as a result of methane hydrate dissociation (Hesselbo *et al*., 2000, 2007; Beerling *et al*., 2002; Cohen *et al*., 2007). High-resolution studies have shown that the shifts toward light carbon isotope values occur as a series of successive abrupt steps, which were astronomically paced (Jenkyns *et al*., 2001; Kemp *et al*., 2005, 2011; Cohen *et al*., 2007; Hermoso *et al*., 2009, 2012; Hesselbo, Pienkowski, 2011, Caruthers *et al*., 2011) (Fig. 2). Alternative hypotheses consider volcanogenic degassing in the Karoo-Ferrar province (Pálfy, Smith, 2000; Erba, 2004; Suan *et al*., 2008) or thermogenic methane

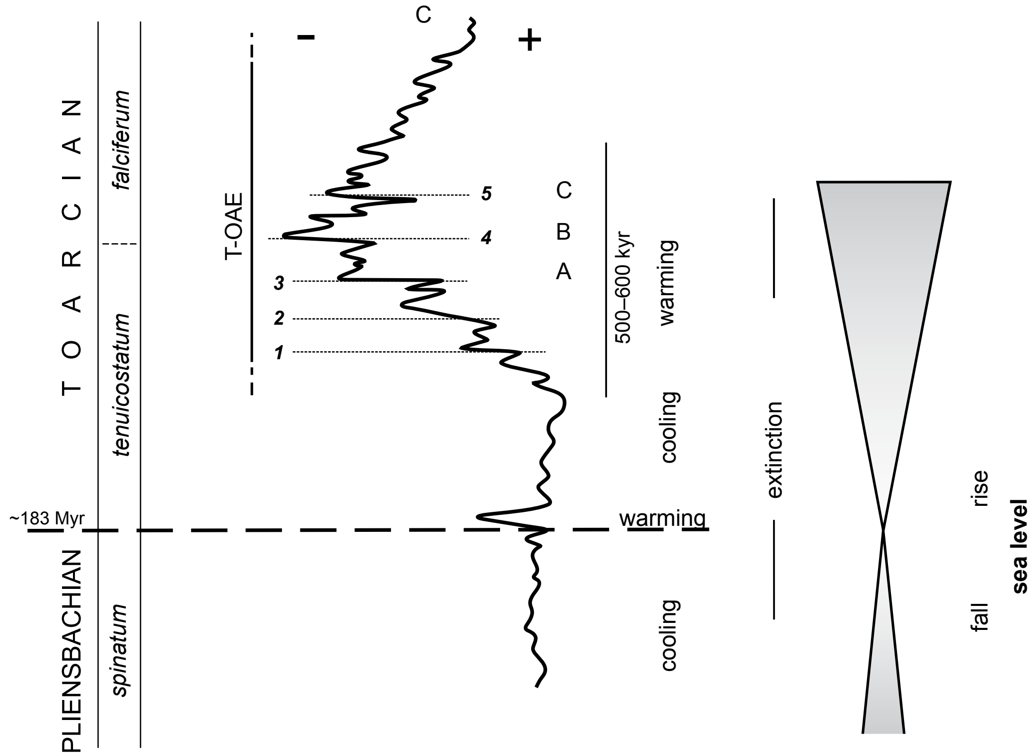

Fig. 2. Cartoon summarising the stratigraphy of the Pliensbachian-Toarcian boundary interval adopted in this paper (compiled by the author)

Generalised carbon-isotope curve (negative CIE), palaeoclimatic changes and approximate duration of global warming after Kemp *et al.* (2005), Hesselbo *et al.* (2007), Cohen *et al.* (2007), McArthur *et al.* (2008), Suan *et al.* (2008), Hesselbo and Pieńkowski (2011) and Hermoso *et al.* (2012) (not to scale). Symbols of CIE steps in the carbon-isotope curve are from Kemp *et al.* (2005) (A–C) and Hesselbo, Pieńkowski (2011) (1–5)

releases related to the intrusion of magma into organic-rich Gondwanan basins (McElwain *et al*., 2005; Svensen *et al*., 2007; Aarnes *et al*., 2011). Nevertheless, this latter mechanism has been challenged by Gröcke *et al*. (2009). Some authors presented the negative CIE and the contemporaneous anoxic event as regional mostly diachronous phenomena, linked to particular oceanographic conditions across European shelves (McArthur *et al*., 2000, 2008; Bailey *et al*., 2003; van de Schootbrugge *et al*., 2005; Wignall *et al*., 2005; Gómez *et al*., 2008; Gómez, Goy, 2011). However, this negative excursion was recently reported on a global scale in Panthalassan Toarcian successions from South-America (Al-Suwaidi *et al*., 2010; Mazzini *et al*., 2010), Canada (Caruthers *et al*., 2011), Japan (Gröcke *et al*., 2011; Isumi *et al*., 2011) and also Arctic regions (Suan *et al*., 2011). Moreover, this anomaly was observed in terrestrial organic matter, which records the atmospheric signal (Hesselbo *et al*., 2000, 2007; Hesselbo, Pieńkowski, 2011) and indicates the global nature of these carbon cycle disturbances.

Current paleoclimatic reconstructions for the Jurassic are mainly based on geochemical data (mostly oxygen isotope measurements) from belemnites (*e.g*. McArthur *et al*., 2000; Rosales *et al*., 2004; van de Schootbrugge *et al*., 2005; Gómez *et al*., 2008; Dera *et al*., 2009b), brachiopod shells (Suan *et al*., 2008), fish teeth (Dera *et al*., 2009b) and also on palynolological data (Pieńkowski, Waksmundzka, 2009), while clay mineral assemblages are less used to recognise the climatic conditions. Nevertheless, clay deposits in marine basins represent the final product of continental weathering processes and they may reveal climatic fluctuations on the continents. Clay mineralogy has been successfully used in Mesozoic palaeoclimate reconstructions (*e.g*. Singer, 1984; Chamley, 1989; Duarte *et al*., 1998; Thiry, 2000; Adatte *et al*., 2002; Ruffell *et al*., 2002; Ahlberg *et al*., 2003; Deconinck *et al*., 2003; Fursich *et al*., 2005; Schnyder *et al*., 2006; Raucsik, Varga, 2008; Hesselbo *et al*., 2009; Brański, 2009, 2010, 2011; Rostasi *et al*., 2011; Duchamp-Alphonse *et al*., 2011). Above all, variations in the detrital kaolinite content of the clay fraction are considered as a reliable proxy for humidity. For example, published and unpublished clay mineral data from European and Mediterranean basins have been recently gathered by Dera *et al*. (2009a) for the Pliensbachian–Toarcian period, and interpreted in this way. Previous mineralogical analyses of Lower Toarcian claystones and mudstones from the Polish Basin (performed on bulk rock samples only from southern Poland) are scarce (Dera *et al*., 2009a) and show in general predominance of illite over kaolinite (Kozydra, 1968; Maliszewska, 1968; Leonowicz, 2005; Brański, 2007). The aim of the present research was to recognize the effects of the rapid climatic changes in the hinterland of the Polish Basin on the clay mineral composition, and to compare these data with the results of carbon isotope analyses published so far. The new data presented in this paper are based on a relatively continuous marine record that is well calibrated in terms of sequence stratigraphy and sedimentological setting. It has a high sampling resolution, which allows a better timing of patterns highlighted by Dera *et al*. (2009a) at the Tethyan scale.

GEOLOGICAL SETTING

During the Early Jurassic, the Polish Basin was a marginal part of the extensive epicontinental sea – the Central European Basin System (Pieńkowski, Schudack, 2008), and was surrounded by landmasses to the north, east and south (Fig. 3). The Lower Toarcian is represented by Ciechocinek Formation, which ranges in thickness from 15–45 metres in the marginal parts to over 100 metres in the Mid-Polish Trough depocenters. This formation is composed of poorly consolidated greenish-grey or grey mudstones, claystones and heteroliths ("verdine facies") with intercalations of siltstones and fine-grained sandstones (Pieńkowski, 2004; Leonowicz, 2005, 2011). Deposits often contain layers and lenses of siderite mudstones and siltstones, as well as siderite and locally pyrite concretions (Pieńkowski, 2004; Leonowicz, 2007). Plant remains are common (Pieńkowski, Waksmundzka, 2009), and horizons with numerous trace fossils also occur (Pieńkowski, 2004; Leonowicz, 2009).

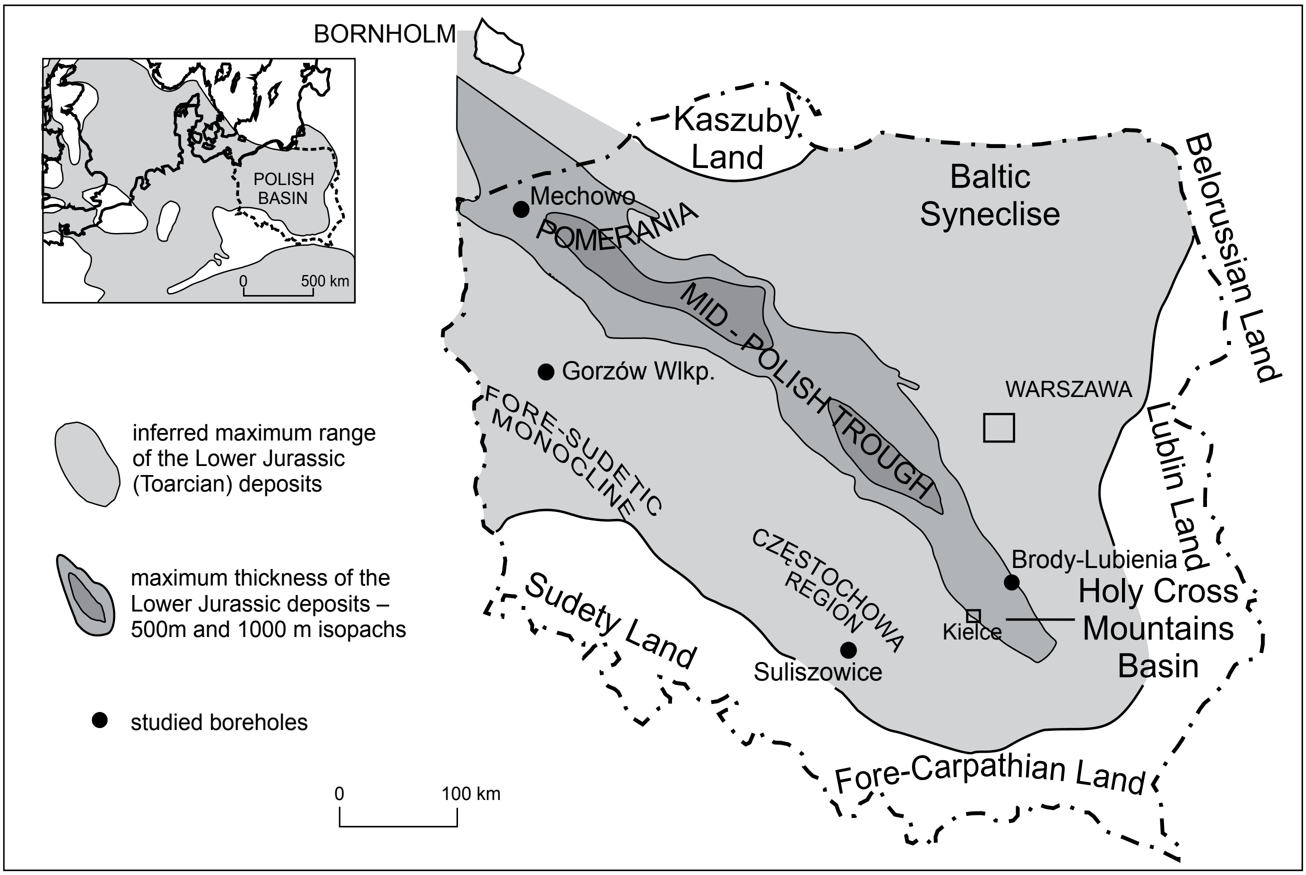

Fig. 3. Palaeographic map for the Early Jurassic epicontinental basin in Poland with locations of profiles sampled (modified from Hesselbo and Pieńkowski, 2011)

Table 1

Stratigraphy of the Upper Pliensbachian and Lower Toarcian in the epicontinental Polish Basin
Ages and ammonite zones are from Gradstein *et al.* (2004) and Ogg *et al.* (2008); lithostratigraphy and sequence stratigraphy is given after Pieńkowski (2004) with modifications from Hesselbo, Pieńkowski (2011)

Age [Ma]	Stage	Ammonite zones	Epicontinental Polish Basin	
			Parasequences	Formation
~ 181	LOWER TOARCIAN	*falciferum*	hiatus	hiatus
			VIII (e)f	CIECHOCINEK FORMATION
~ 183		*tenuicostatum*	VIII (a) bcd(e)	
	UPPER PLIENSBA-CHIAN	*spinatum*	VIII(a)	DRZEWICA–KOMOROWO–BLANOWICE FORMATIONS
		spinatum / *margaritatus*	VII	
~ 187		*margaritatus*	VI	

The Ciechocinek Formation mainly represents a large but shallow brackish embayment. Its lower part was deposited in a restricted offshore environment, including deeper, nearly fully-marine environment in the Pomeranian region (Pieńkowski, 2004). In the upper part and marginal areas of the basin, shallower facies of small deltas, lagoons and marshes predominate (Pieńkowski, *op. cit.*).

The Ciechocinek Formation belongs to the unconformity-bounded depositional sequence, numbered VIII in the Jurassic succession, which has been subdivided into six parasequences, VIIIa–VIIIf (Pieńkowski, 2004; Hesselbo, Pieńkowski, 2011) (Tab. 1). A number of local lithostratigraphic units (Komorowo Fm., Drzewica Fm., Blanowice Fm., and Olsztyn Fm.) were assigned to the oldest alluvial and deltaic deposits of the previous sequence, of latest Pliensbachian age (Pieńkowski, 2004). The Ciechocinek Formation has the widest distribution of all Early Jurassic sedimentary strata in the Polish Basin, which is consistent with the Early Toarcian sea-level rise (Pieńkowski, 2004; Hesselbo, Pieńkowski, 2011). The base of the succession is a transgressive surface of regional extent and the top is marked by an erosional surface that constitutes the lower boundary of the next depositional sequence IX corresponding to the alluvial sandy deposits of the Borucice Formation (Pieńkowski, 2004). A Toarcian age was earlier confirmed by abundant megaspore assemblages (Marcinkiewicz, 1971), miospores (Pieńkowski, Waksmundzka, 2009) and rare dinoflagellate cysts (Barski, Leonowicz, 2002). More accurately, recent works based on sequence stratigraphy (Pieńkowski, 2004; Pieńkowski, Schudack, 2008) and high-resolution carbon isotope chemostratigraphy (Hesselbo, Pieńkowski, 2011) allowed the recognition of the *tenuicostatum* and *falciferum* biochronozones (Tab. 1), suggesting a lower Toarcian age for the Ciechocinek Formation.

MATERIALS AND METHODS

In order to infer the Early Toarcian palaeoclimatic and palaeoenvironmental changes, a set of 83 samples was taken from the four borehole cores (Mechowo IG 1, Gorzów Wlkp. IG 1, Suliszowice BN 38 and Brody-Lubienia BL 1) to analyse the bulk rock mineralogy, clay mineralogy and major element geochemistry. Almost all collected samples represent claystones and mudstones from the Ciechocinek Formation in various parts of the epicontinental Polish Basin: Pomerania region, Fore-Sudetic Monocline, Częstochowa region, and Holy Cross Mountains region (Fig. 3).

All samples were studied at the Polish Geological Institute – National Research Institute laboratories. Bulk rock compositions and clay minerals in the largely impermeable sedimentary rock (claystones and mudstones) samples were identified by X-ray diffraction (XRD) using a Phillips PW 3020 X'Pert diffractometer with CuKα radiation. Each rock sample was coarsely crushed in Fritsch crusher, dried at a temperature of 110°C, and ground to obtain a fine, homogeneous powder of the bulk rock with particles <63 µm. The bulk-rock mineralogy was determined on XRD patterns of powder samples compared with the external standards to quantify each mineral phase. The following X-ray diffraction peaks were used: quartz ~3.34 Å, feldspar 3,19–3,23 Å, siderite ~2,79 Å, hematite ~2,69 Å, calcite ~3,03 Å, dolomite ~2,88 Å, gypsum ~7,54 Å and pyrite ~2,63 Å. It should be noticed that calcite, dolomite, gypsum and pyrite were observed only in single samples. Clay minerals were identified by XRD on oriented mounts of non-calcareous clay-sized (<2 μm) particles. The clay fraction was separated from the suspension by differential settling according to Stoke's Law. Oriented specimens were prepared by smearing a paste of the <2 μm fraction onto a glass slide. For each sample, three X-ray analyses were performed: after air-drying, ethylene-glycol solvation, and heating at 550ºC. The individual clay minerals were identified and semi-quantitatively evaluated on the position of the (001) series of basal reflections on the three X-ray diagrams (Moore, Reynolds, 1997; Środoń, 2006). Kaolinite was identified using the reflection ~7 Å, illite ~10 Å and chlorite ~14 Å (on the basis of X-ray diagrams of air-dried and heated specimens) (Fig. 4). Rarely and locally observed smectite and illite-smectite mixed-layers (mostly with >90% illite content) were here determined on ~15 Å peak and 11 Å – 13 Å peaks (Fig. 4B), respectively. Semi-quantitative estimations of the clay mineral content were based on the peak areas of its basal reflections and summed to 100% (taking TOC content into consideration). Illite-smectite mixed-layers were included in illite.

The SEM observations of selected samples were also performed using a LEO 1430 scanning electron microscope with an energy dispersive spectrometer (EDS Oxford Instrument).

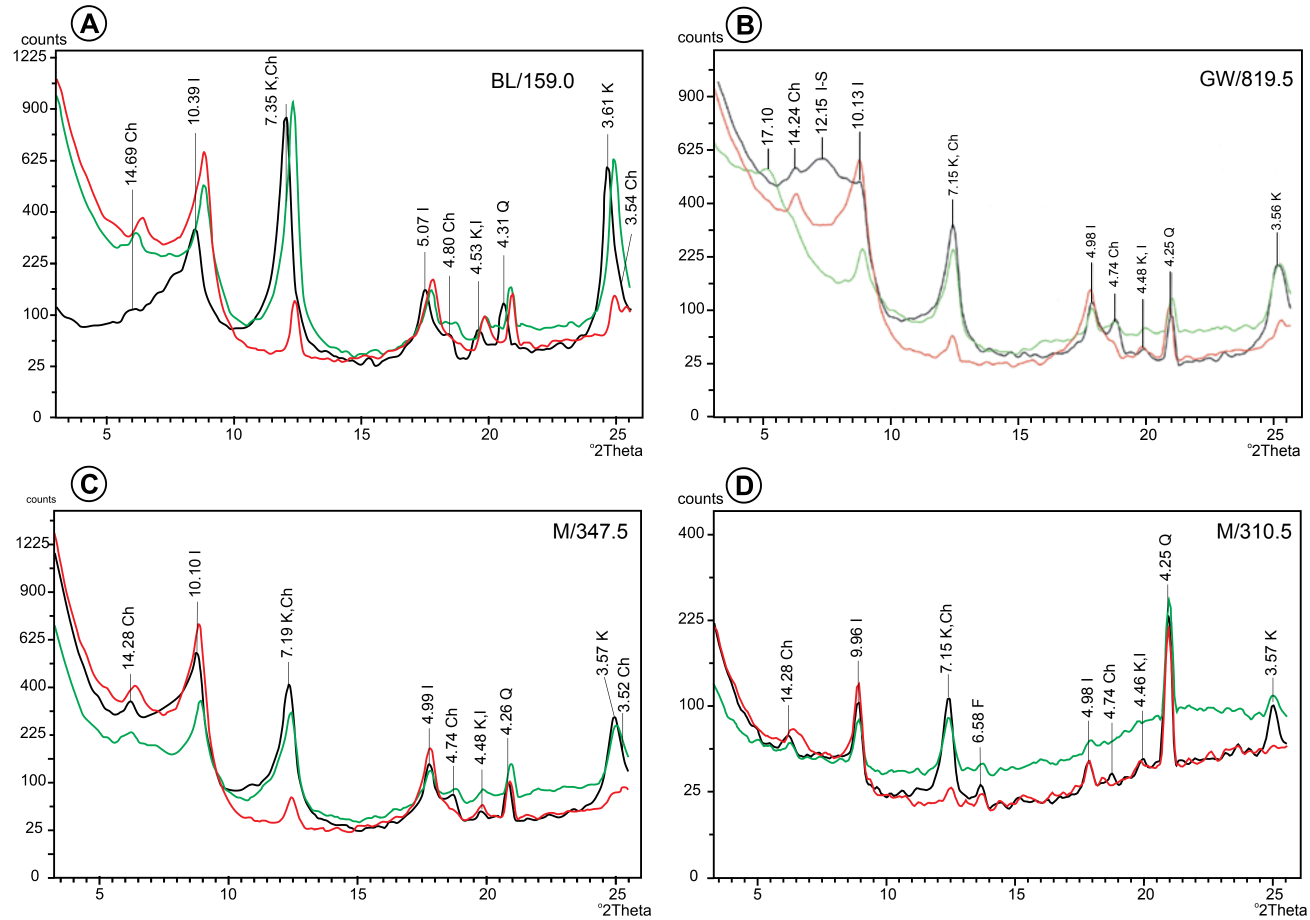

Fig. 4. Selected X-ray diagrams of Lower Toarcian samples (<2 μm fraction) (accomplished by W. Narkiewicz)

A – kaolinite-dominated claystone with subordinate illite and trace amount of chlorite (Brody-Lubienia borehole, depth 159.0 m); **B** – mixture of kaolinite, illite and random illite-smectite mixed-layers with small quantities of chlorite in claystone (Gorzów Wlkp. borehole, depth 819.5 m), this type of XRD is uncommon in the Ciechocinek Fm.; **C** – kaolinite-dominated claystone with minor amount of illite and subordinate chlorite (Mechowo borehole, depth 347.5 m); **D** – illite-dominated mudstone with minor amount of kaolinite and very subordinate chlorite (Mechowo borehole, depth 310,5 m)

Black line – air-dried sample, green line – glycolated sample, red line – heated sample (550ºC); K – kaolinite, I – illite, Ch – chlorite, I-S – illite-smectite mixed-layers, Q – quartz, F – feldspar. Clay mineral content was determined on the peak areas of characteristic basal reflections (kaolinite ~7 Å, illite ~10 Å, chlorite ~14 Å, illite-smectite mixed-layers 11–13 Å)

Geochemical analyses of major elements and organic matter were performed on bulk rock samples. Major elements were measured by X-ray fluorescence using a Phillips PW 2400 spectrometer. Total organic carbon (TOC) content was established by the coulometric method.

For each bulk rock sample, a "clay index" (CI) was calculated on X-ray diffraction percentage results, using the formula: clay index (CI) = clay minerals (CM)/ [quartz (Q) + feldspar (F)]. Moreover, were calculated two indices reflecting the mineralogical weathering by using the clay mineral composition of the samples. The kaolinite/illite (K/I) and kaolinite/illite+ chlorite (K/I+ Ch) indices are expressed by ratios of the main diffraction peak intensity of these minerals. Additional chemical weathering indices were determined using major element concentrations: chemical index of alteration CIA (Nesbitt, Young, 1982) or CIA* (Goldberg, Humayun, 2010), and Al/K ratio. For calculation of all chemical indices, raw abundances of individual elements were converted into moles by dividing the weight percent by the molecular weight (Retallack, 2001; Sheldon, Tabor, 2009). Finally, all new mineralogical and geochemical data were plotted along with the lithology, facies succession, sequence stratigraphy (after Pieńkowski, 2004) and carbon isotope data (after Pieńkowski, Hesselbo, 2011) for the all studied sections (Figs 5–8).

RESULTS

All the most important bulk rock data (general mineralogical composition, clay index, TOC content, proportion of P_2O_5, CIA and Al/K values) as well as clay fraction data (clay minerals composition, K/I and K/I+ Ch values) are presented in Table 2 and graphically on Figures 5–8. An average bulk rock mineralogy and average clay mineral composition (<2 µm fraction) have been estimated for each core (Tab. 2). Selected X-ray diagrams are presented on Figure 4. The examples of SEM images were showed in the earlier paper (fig. 8 in Brański, 2010) which contains the preliminary results of this study.

MECHOWO IG 1

A total of 35 claystone and mudstone samples were collected from the Mechowo borehole core in the Pomeranian region of the Polish Basin (Fig. 3). The Mechowo section represents the most distal (offshore) environment compared to other boreholes (*cf.* Pieńkowski, 2004). This profile is also the most expanded one (*op. cit.*). The bulk rock samples are mainly composed of phyllosilicates (25–88%, average of

Table 2

Bulk rock and <2 µm fraction data from the Ciechocinek Fm. in sampled boreholes

	Mechowo IG 1	Gorzów Wlkp. IG 1	Suliszowice 38 BN	Brody-Lubienia BL 1
Clay minerals CM [%]	25–88 (**68**)	54–84 (**72**)	56–82 (**68**)	55–73 (**67**)
Quartz + feldspar Q+F [%]	10–73 (**28**)	8–39 (**24**)	17–43 (**29**)	17–46 (**28**)
Siderite [%]	0–21 (**3**)	0–16 (**3**)	0–8 (**2**)	0–18 (**3**)
Others [%]	(**<1**)	(**<1**)	(**<1**)	(**<2**)
CI=CM/Q+F	0.32–8.80 (**3.44**)	1.20–9.38 (**3.63**)	1.30–4.82 (**2.82**)	1.09–3.89 (**2.56**)
TOC [%]	0.20–3.56 (**1.17**)	–	–	0.10–1.63 (**0.74**)
P_20_5 [%]	0.037–0.201 (**0.102**)	0.092–0.677 (**0.166**)	0.032– 0.350 (**0.133**)	0.038– 0.177 (**0.094**)
CIA*	1.04–4.10 (**3.37**)	2.13–3.71 (**3.05**)	3.31–4.47 (**3.93**)	3.46–5.42 (**4.46**)
Al/K	2.30–5.77 (**4,63**)	4.13–6.06 (**5,34**)	4.42–6.33 (**5.36**)	4.30–6.60 (**5.73**)
Kaolinite K [%]	18–61 (**30**)	28–55 (**44**)	16–54 (**35**)	38–82 (**52**)
Illite I [%]	26–70 (**50**)	30–55 (**43**)	33–50 (**40**)	14–60 (**35**)
Chlorite Ch [%]	0–33 (**20**)	4–21 (**13**)	13–44 (**25**)	0–29 (**13**)
K/I	0.33–2.35 (**0.66**)	0.51–1.63 (**1.08**)	0.40–1.64 (**0.91**)	0.67–6.00 (**1.83**)
K/I+ Ch	0.22–1.56 (**0,47**)	0.39–1.22 (**0.83**)	0.19–1.17 (**0.57**)	0.67–4.62 (**1.32**)

CIA* – chemical index of alternation after Goldberg, Humayun (2010); The average values were given in parentheses (bold font)

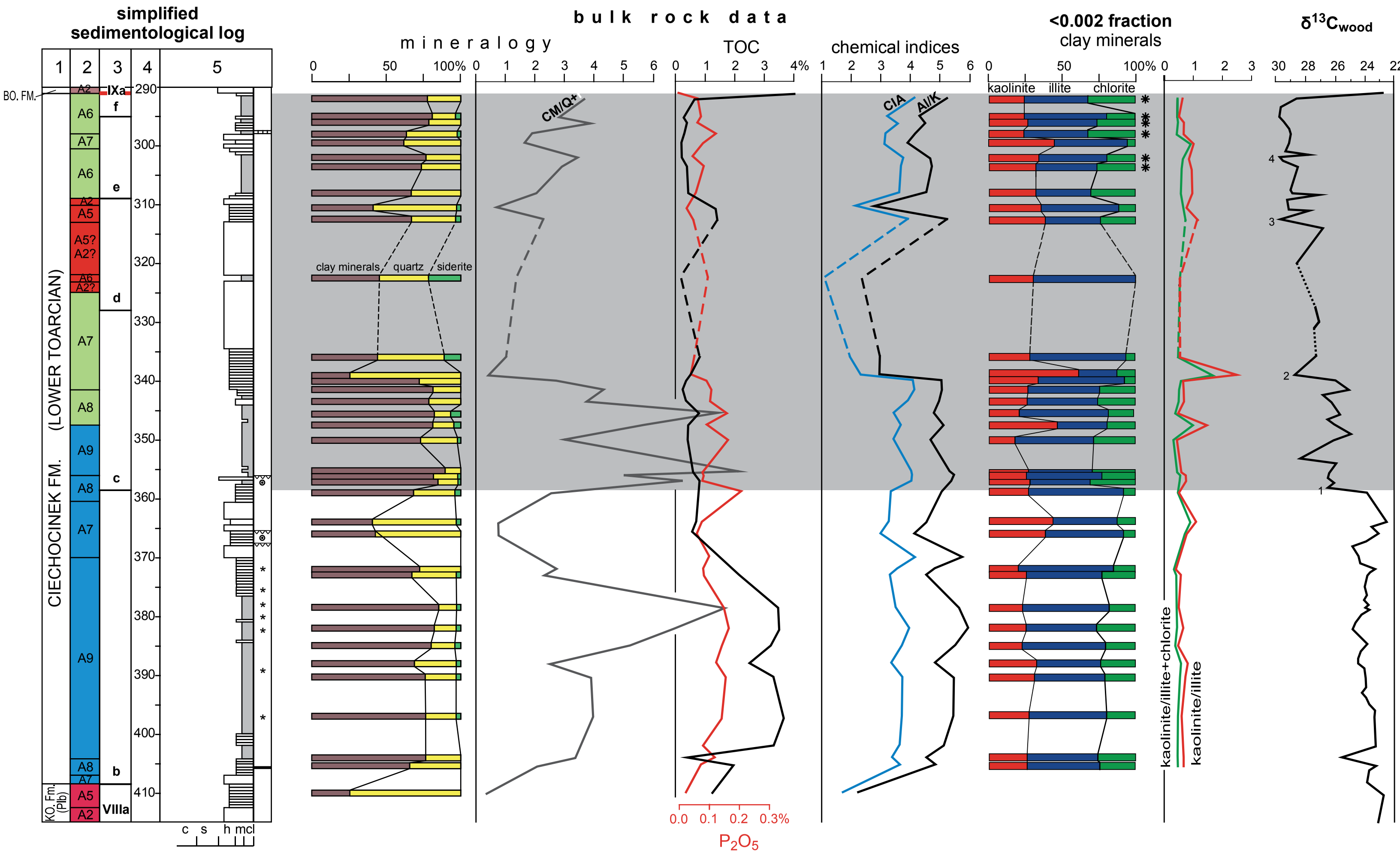

Fig. 5. Bulk rock and <2 µm fraction data from Ciechocinek Fm. in Mechowo IG 1 borehole plotted against a simplified sedimentological log.

Clay index (CI=CM/Q+F) spikes are consistent with offshore deposition and a more distal detrital source. TOC content is highest during transgressive phase. Note that the P_2O_5 proportion rises at the top of VIIIb parasequence (inferred onset of global warming), opposite to the TOC content. In the middle part of the section a distinct increase in kaolinite content is observed, due to the onset of global warming. Note that the first kaolinite peak (~365 m) slightly precedes the onset of CIE (~358.5 m). Note the rhythmic changes in kaolinite content as well. In the upper part of the section the kaolinite proportion seems to diminish. Asterix (*) denote small admixtures of I-S mixed-layers (with > 90% illite content).

All simplified sedimentological logs (Fig. 5–8) are mostly adopted from Pieńkowski (2004) with some modifications from Hesselbo, Pieńkowski (2011) and the present author (unpublished paper). Carbon-isotope curves with the numbers of CIE steps are from Hesselbo, Pieńkowski (2011). Bulk rock data (mineralogy, TOC content, P_2O_5 content and selected chemical indices) and clay mineral data (clay mineral composition, kaolinite/illite ratio and kaolinite/illite+ chlorite ratio) are from this study. The grey bands (Fig. 5–8) indicate an equivalent of the T-OAE interval that corresponds to negative CIE (according to Hesselbo, Pieńkowski, 2011). CM/Q+F – clay minerals/quartz+ feldspar ("clay index" – CI). CIA – chemical index of alternation after Goldberg, Humayun (2010)

For other explanations see Fig. 7

68%). Quartz is generally less abundant but occurs in varied amounts (10–69%). In almost all samples, minor amounts of feldspars (1–6%) were observed. The quartz + feldspar content reach 28% on average. In most samples, siderite was observed with proportions of 2–4% (maximum as much as 21%). Sporadically (at depth 356–359 meters), pyrite appears in an accessory amount. The clay index (CI) fluctuates in a range of 0.3 to 8.8 (with an average of 3.4). It increases in the lower and middle parts of VIIIb parasequence (from 2 up to 8), but rapidly falls beneath 0.7 in the upper part. In the VIIIc parasequence, an abrupt twofold rise of CI (up to 8.8) is observed but it immediately drops below 1.0 in the upper part of this unit and stays low in VIIId parasequence (Fig. 5). In the upper part of the section (VIIIe-f parasequences), the CI progressively increases once again and reaches 3 to 4 values. The distribution in the organic matter is variable in the section and the total organic carbon (TOC) content ranges from 0.20 to 3.56% (with an average of 1.17%). TOC content exceeds 3% in the lower part of the VIIIb parasequence, then gradually decreases to less than 1% in it upper part, and remains low (<1%) to the end of the section (Fig. 5). Interestingly, the phosphorous content slightly decreases in the upper part of VIIIb parasequence (P_2O_5 <0.1%), then abruptly increases at its top (P_2O_5 exceed 0.2%) (Fig. 5). It remains relatively high in the VIIIc parasequence (P_2O_5 above 0.1%), but generally decreases in the upper part of the section (P_2O_5 mostly below 0.1%). It should be emphasized that amounts of P_2O_5 change rhythmically in the middle part of the section.

Chemical indexes of alternation (CIA*) change in the limits of 1.1–4.1 (average of 3.4). The Al/K index ranges from 2.3 to 5.8 (with an average of 4.6).

The composition of the clay mineral assemblages is very diverse. Generally, the clay fraction is dominated by illite (26–70%, with an average of 50%) with subdominant amounts of kaolinite (18–61, with an average of 30%) and subsidiary, but mostly significant, amounts of chlorite (0–33%, average of 20%). Smectite appears only exceptionally; however the samples from upper part of the section (VIIIe-f parasequences) contain some illite-smectite mixed-layer admixtures. Kaolinite/illite (0.3–2.4, average of 0.7) and kaolinite/illite+chlorite (0.2–1.6, average of 0.5) ratios reflect the varied clay mineral composition and general illite predominance. In the lowest part of the Ciechocinek Fm, the kaolinite content in <0.002 mm fraction is low (K/I in order 0.6), but it is distinctly higher at the top of VIIIb parasequence (K/I ~1.0). Next, the kaolinite content increases within VIIIc parasequence and achieves maximum values (K/I up to 2.4); however in VIIId–f parasequence decreased again (K/I not exceed 1.0) (Fig. 5). It should be noticed that in the Mechowo borehole a few cyclic variations at the 10–20 m scale in kaolinite/illite ratios were observed.

GORZÓW WLKP. IG 1

Seventeen fine-grained rock samples were taken to study from the Gorzów Wlkp. borehole core in the Fore-Sudetic Monocline (Fig. 3). Clastic material to the Gorzów Wlkp. area was derived from Sudety Land (Pieńkowski, 2004). The bulk rock samples consist here predominantly of phyllosilicates (54–84%, with an average of 72%). Quartz is generally less abundant but occurs in varied amounts (8–37%). The presence of feldspar is significant (3–10%). The average content of quartz + feldspar amounts to 24%. The main components are accompanied by siderite – up to 16% in VIIId parasequence (about 3% in average) and goethite and hematite in negligible amounts (~ 2%). In a single sample, traces of dolomite were noticed (at depth of 798.0 m). The clay index (CI) ranges from 1.2 to 9.4 (average of 3.6) and distinctly increases in VIIIb and especially VIIIc parasequences, where it exceeds amounts 5 and 9, respectively, and next decreases in the VIIId parasequence (Fig. 6). The total organic carbon was not examined in this borehole. The chemical indices of alternation (CIA and CIA*) are included in the range 68–79 and 2.1–3.7 (average of 3.1), respectively. The Al/K index varies from 4.6 to 6.1 (with an average of 5.3%).

The clay fraction from the Ciechocinek formation is characterised by a similar content of illite (with smectite) and kaolinite (28–55%, with an average of 44%, and 30–55%, with an average of 43%, respectively). The presence of chlorite is more subordinate (4–21%, with an average of 13%). It should be emphasized that the Gorzów Wlkp. is the only section studied where subsidiary amounts of smectite commonly occur (usually less than 10%). The relations between the main clay mineral assemblages reflect the kaolinite/illite + smectite ratio (1.1 in average). The proportion of kaolinite tends to slightly increase up to the VIIIc/VIIId parasequence boundary, partly at the expense of illite (K/I + Sm maximum – 1.6); then it clearly diminishes (K/I + Sm drops to 0.5) and increases again in the upper part of VIIId parasequence (Fig. 6).

SULISZOWICE 38 BN

Twelve fine-grained rock samples were obtained from the Suliszowice borehole core in the Częstochowa region (Fig. 3). Clastic material to the Suliszowice area was mostly derived from Fore-Carpathian Land (Pieńkowski, 2004). Phyllosilicates and quartz are the dominant minerals with proportions ranging from 56 to 82%, (average of 68%) and from 17 to 40%, (average of 27%) respectively. In the majority of samples, minor amounts of feldspar (2–5%) were observed. Siderite frequently appears up to 8% (average of 2%). At 334.5m of depth, a little gypsum admixture (~2%)

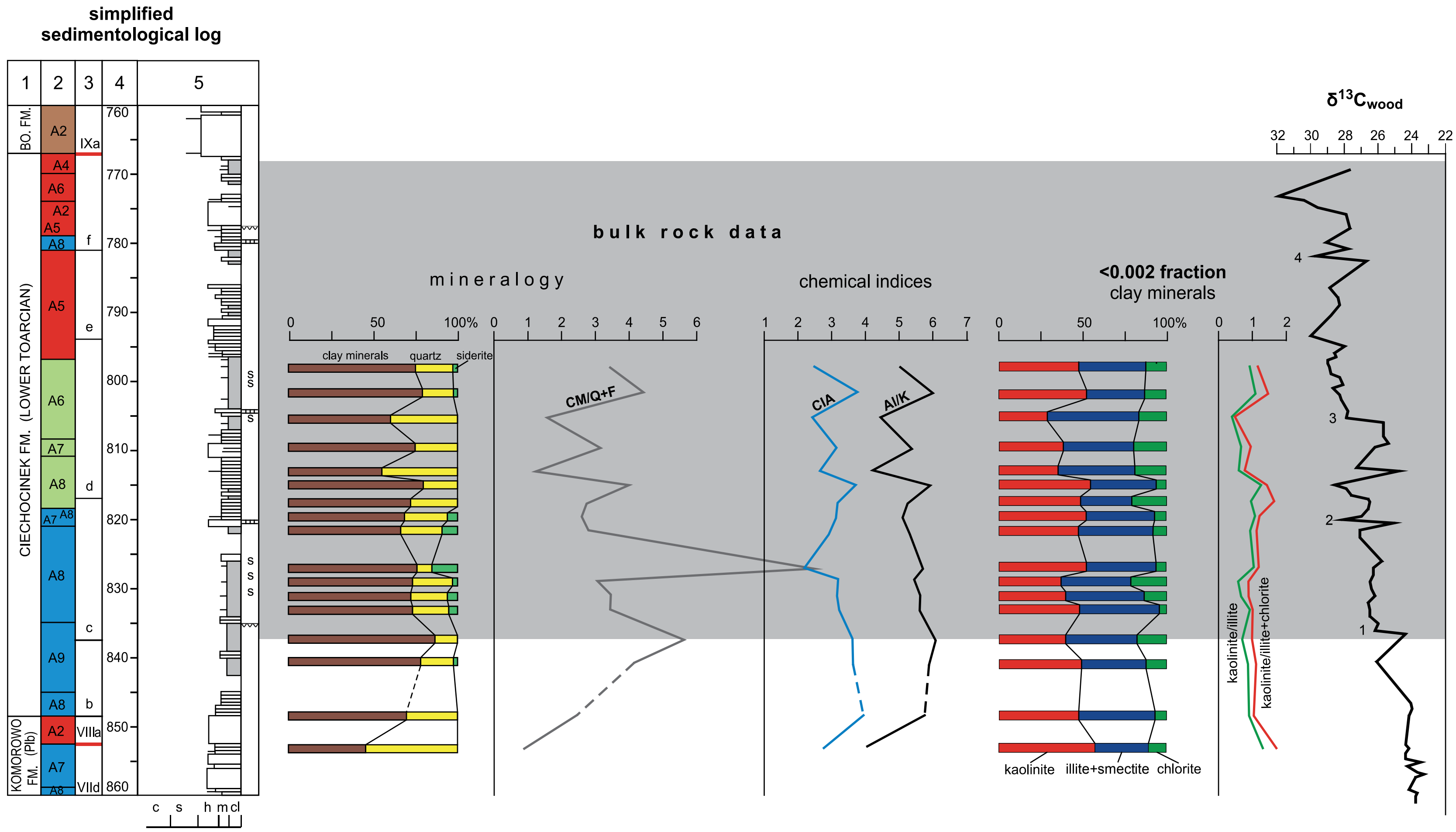

Fig. 6. Bulk rock data and clay mineral (<0.002 mm fraction) from the Ciechocinek Fm. in Gorzów Wlkp. IG 1 borehole plotted against a simplified sedimentological log

The higher CI values coincide mostly with offshore deposition and more distal detrital source. The kaolinite content slightly increases in the middle part of section. Illite is here accompanied by subsidiary smectite (most probably derived from Sudety Land as a ferromagnesian silicate weathering product)

For explanation see Fig. 7

was observed (Fig. 7). The clay index (CI) markedly increases from the base of the Ciechocinek Fm., exceeds 4 units in lower part of the VIIIb parasequence, diminishes in the VIIIb and VIIIc parasequences (~1–2), and sharply increases again in the VIIId parasequence (up to the value 4.8). Total organic carbon was not examined in this borehole. The chemical index of alternation (CIA*) ranges from 3.3 to 4.5 (with an average almost of 3.9). The Al/K index changes from 4.4 to 6.3 (with an average of 5.4). It should be noticed that highest values of weathering indices agree exactly with the maxima of CI (Fig. 7).

For the clay fraction from the Suliszowice section illite usually prevails (33–50%, with an average of 40%) with a varied proportion of kaolinite (16–54%, with an average of 35%). The chlorite content is fairly high but also very diverse (13–44%, with an average of 25%). Both smectite and illite-smectite mixed-layers are absent in this section. Kaolinite/illite and kaolinite/illite+chlorite ratios range from 0.4 to 1.6 (average of 0.9) and 0.2 to1.2 (average of 0.6), respectively. In principle, the kaolinite content increases gradually from the base of Ciechocinek Fm. to the lowest part of parasequence VIIId in the Suliszowice section and then it probably decreases. Nevertheless, the kaolinite maximum is well expressed in the curves of the all mineralogical indices, at depth 321.5 m (Fig. 7). The first rise of the kaolinite content was observed already in the upper part of VIIIb parasequence (at depth 328.6 m), but kaolinite prevails over illite only in the VIIIc-d parasequences.

BRODY-LUBIENIA BL 1

A set of 19 claystone samples was taken from Brody-Lubienia borehole core, which represents the Holy Cross Mts. region of the Polish Basin (Fig. 3). Clastic material to the Brody-Lubienia area was derived from the East European Craton (Lublin Land – Pieńkowski, 2004). Like in the other sections, the bulk rock samples from this borehole are mainly composed of phyllosilicates (55–73%, average of 66%) with subsidiary amounts of quartz (17–46%, average of 25%). The presence of feldspar is common (2–5%, average of 4%). In the some samples the main components are accompanied by siderite up to 18% (mostly 2–5%). The sample from the lowest part of Ciechocinek Fm. (depth of 181.1 m) contains, exceptionally, calcite in a proportion as much as 12%, and a trace amount of gypsum (Fig. 8). The clay index rises rhythmically from the base of formation to the VIIId parasequence (from the value 1.9 to 3.9), and then falls gradually to the value 1.1 at the top of the section (Fig. 8). The studied samples contain also organic matter, but the content of total organic carbon is usually less than 1% (0.10–1.63%, with an average of 0.74%). Distribution of the organic matter is not random. TOC content exceeds 1% in the lowest part of the section but in the upper part of VIIIb parasequence it tends to decrease and then stays low (Fig. 8). In turn, the phosphorous content is low at the base of Ciechocinek Fm. (P_2O_5 <0.1%), then it increases rhythmically up to VIIId parasequence (P_2O_5 reaches almost 0.2%) and next decreases again (P_2O_5 <0.1%) (Fig. 8). CIA change from 77 to 82 (with an average of 80), and CIA* is contained in the limits of 3.5–5.4 (average of 4.5). Al/K index range from 4.3 to 6.6 (with an average of 5.7).

The clay fraction of the Ciechocinek Fm. samples from the Brody-Lubienia borehole is clearly dominated by kaolinite (33–82%, with an average of 52%), with subdominant illite content (14–62 with an average of 35%) and a minor proportion of chlorite (0–29, with an average of 13%). Both smectite and illite-smectite mixed-layers are absent in all samples. Kaolinite predominance is mirrored by the average kaolinite/illite and kaolinite/illite+chlorite ratios (1.83 and 1.32, respectively). In the lowest part of the Ciechocinek Fm. illite predominates and the kaolinite content is moderate (below 40 %, with exception of the sample from depth 176.1 m). But already at the top of VIIIb parasequence a surge of kaolinite (up to 82%) is observed offset by a significant depletion of illite (~14%) and chlorite (~4%). The kaolinite spike at 159.0 m is very well marked in the curves of the kaolinite/illite and kaolinite/illite+chlorite ratios (6.0 and 4.6, respectively) (Fig. 8). The abundance of fine-grained degraded kaolinite is revealed also in the SEM observations (see fig. 8 in Brański, 2010). The kaolinite content is still very high in the VIIIc parasequence (K/I ratio achieve the values of 2.3–3.7), but in the upper part of the section it slightly decreases (K/I ratio range from 1.2 to 2.1) (Fig. 8). Regardless of the depicted trend, a few cyclic variations at the ~10 meters scale in kaolinite/illite ratios are observed in the middle part of the Ciechocinek Fm. in the Brody-Lubienia section.

SUMMARY

The studied bulk rock samples of claystones and mudstones are mainly composed of phyllosilicates. Quartz is generally less abundant but occurs in varied amounts and minor amounts of feldspar are commonly observed. In most cases, subordinate siderite is observed in various proportions. Other minerals (calcite, dolomite, gypsum, pyrite, hematite and goethite) appear sporadically and mostly in accessory amounts. In the four studied boreholes, illite or kaolinite predominates whereas chlorite is very minor. Subsidiary amounts of smectite were only observed in one borehole – Gorzów Wlkp. IG 1. The general clay mineral assemblages of the Ciechocinek Fm. are similar basin-wide, but the average content of kaolinite and other clay minerals is different in <2 μm fraction

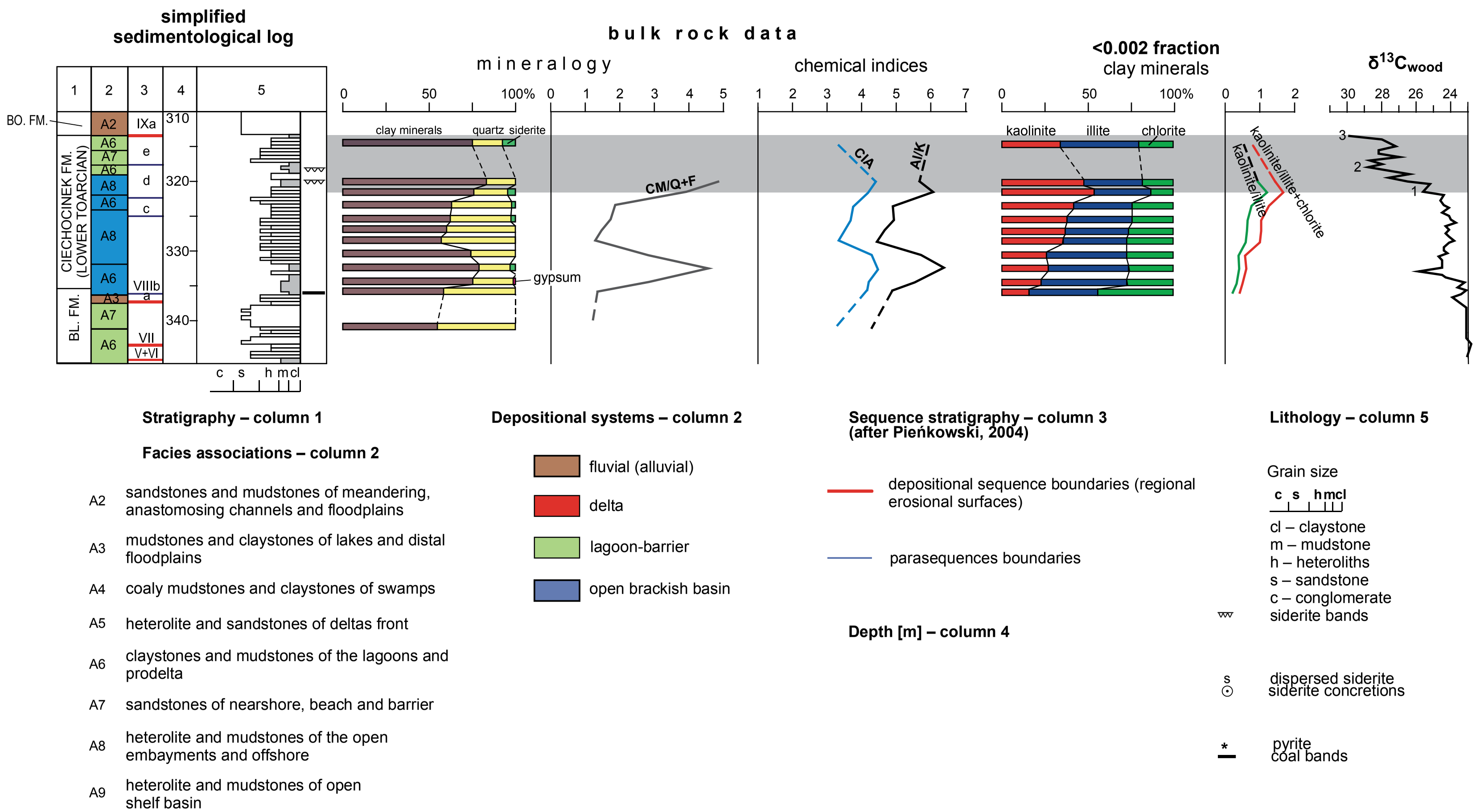

Fig. 7. Bulk rock data and clay mineral (<0.002 mm fraction) from the Ciechocinek Fm. in Suliszowice 38 BN borehole plotted against a simplified sedimentological log

The CI values coincide mostly with the maximum floodings of VIIIb and VIIId parasequences. Note that the peaks of the chemical indices are in concordance with CI peaks. Note the kaolinite increase just after first CIE (at the Pliensbachian-Toarcian boundary) and the gradual rise in kaolinite content that precede the onset of the main second CIE

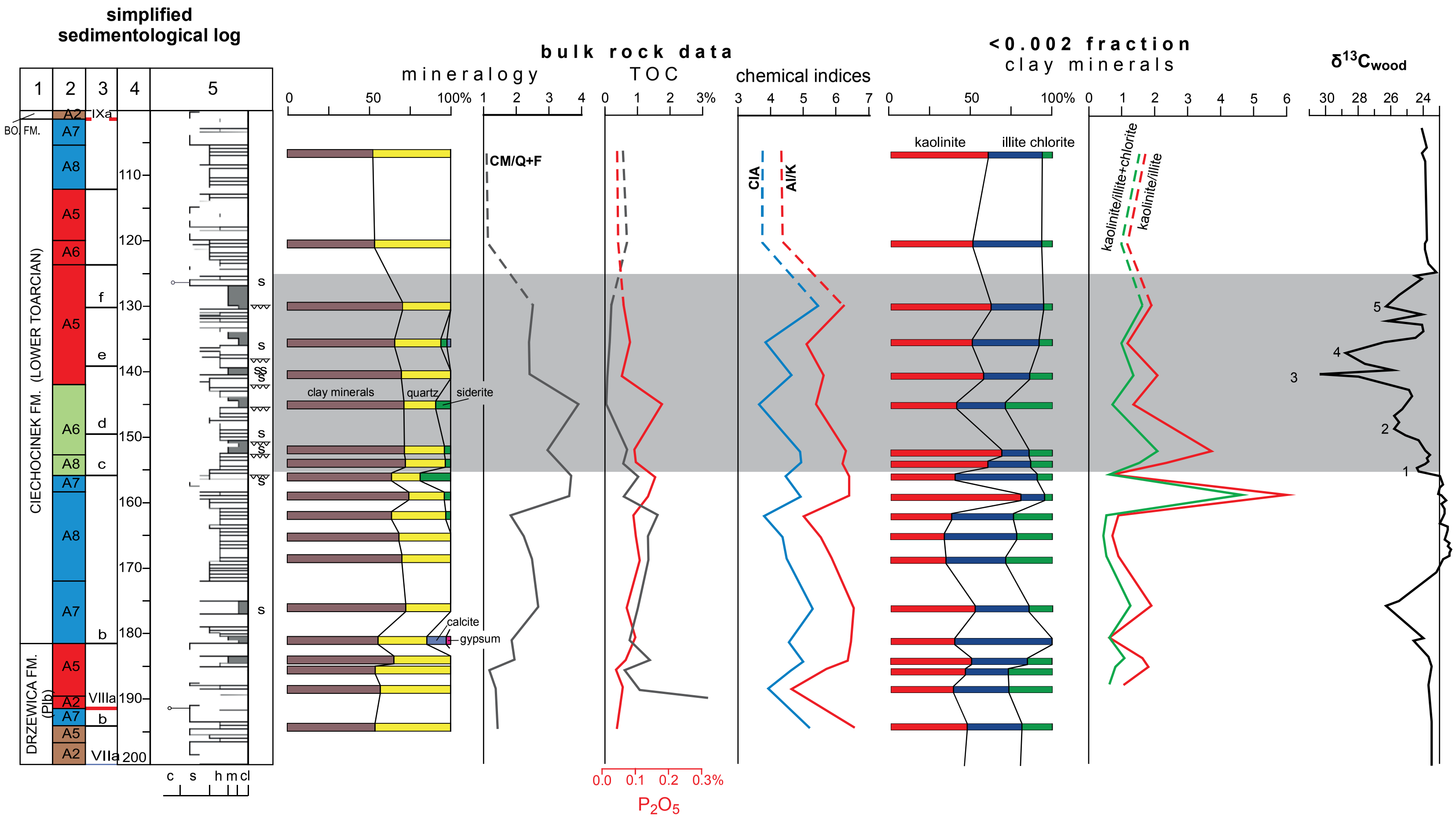

Fig. 8. Bulk rock data and clay minerals (<0.002 mm fraction) from the Ciechocinek Fm. in Brody–Lubienia BL-1 borehole plotted against a simplified sedimentological log

Note the calcite and accessory gypsum at the Toarcian transgressive surface. The CI rise is mostly related to restriction of the brackish-marine basin. Note that the P_2O_5 proportion rises at the top of "b" parasequence (inferred onset of global warming), opposite to the TOC content. A distinct cyclic increase in kaolinite content is visible in the middle part of the section. Note the profound kaolinite spike (~159 m) that slightly precedes the onset of CIE (~155,5 m)

For explanation see Fig. 7

depending on borehole localisation. In stratigraphic order (vertically) such characteristics are visible:

- the proportion of phyllosilicates fluctuates (CI), but it is greater in the lower and/or middle intervals of the Ciechocinek Fm.;
- siderite content is the greatest in the middle part of the Early Toarcian profile (in the lower part of second CIE = TOAE);
- Organic matter content is relatively high in the lower interval of the Ciechocinek Fm., but diminishes in its middle part (at the beginning of second CIE);
- the changes in phosphorus content are more complex. One may cautiously suggest two events in the phosphorus cycle: slight rises in P_2O_5 content are observed at the Pliensbachian-Toarcian boundary (during or after the first CIE = Pl/To event). Next, a distinct increase is observed at a top of VIIIb parasequence that is on the beginning of main second CIE;
- geochemical weathering indices (CIA and Al/K) do not reveal distinct trends but closely correlate each other, indicating low content of Na and Ca. The lack of expected distinct correlation between geochemical and mineralogical weathering indices is observed;
- a very similar vertical trend in kaolinite content is observed in all boreholes. It increases slightly from the lower to the middle part of the Ciechocinek Fm. and becomes stable in its upper part;
- the first negative CIE (at the bottom of formation studied close to the Pliensbachian-Toarcian boundary) is accompanied by a kaolinite increase only in Suliszowice borehole. In the middle part of the formation (lower part of second CIE, and just below) the distinct positive anomalies in the K/I index are commonly observed. The kaolinite maximum falls in VIIIc parasequence.

INTERPRETATION AND DISCUSSION

RELIABILITY OF MINERALOGICAL AND GEOCHEMICAL DATA AS PALAEOCLIMATE PROXIES

The mineralogical and geochemical data may be used for the interpretation of weathering conditions in the source area. As the end product of continental weathering processes, detrital clay minerals are a key to understanding past changes in weathering regime and palaeoclimate (*e.g.* Singer, 1984; Chamley, 1989; Robert, Kennett, 1994; Thiry, 2000; Adatte *et al.*, 2002, John *et al.*, 2006; Schnyder *et al.*, 2006; Raucsik, Varga, 2008; Hesselbo *et al.*, 2009). On the other hand, it should be remembered that the present clay mineral content (and generally mineralogical and geochemical composition) of sedimentary rocks may be also controlled by the lithology of provenance, depositional environment and sedimentary regime, and finally diagenesis.

Diagenesis

Before making any palaeoenvironmental interpretation of clay mineral assemblages, it is necessary to estimate the potential overprint of diagenesis. There is no distinct and systematic evolution of clay-mineral assemblages from bottom to top of the studied boreholes that would be indicative of burial diagenesis. The significant diagenetic overprint (especially illitization of smectite) starts when burial depth exceeds about 2000 m (Chamley, 1989). The succession has probably not been buried to more than 1500–2000 m (Fig. 9), indicating that Toarcian sediments studied were not significantly modified by thermal diagenesis, especially in the closed diagenetic system (Środoń, 1996). Here, we mainly focus on the kaolinite content because of its strong climatic dependence and significant resistance under moderate diagenetic conditions. The alternation of kaolinite to illite occurs commonly at temperatures of 120–140°C that correspond roughly to 4000 m of burial depth (Bjorlykke, Aagard, 1992; Kozłowska, 2004). It is likely therefore that burial diagenesis of the Toarcian deposits was never strong enough to transform the initial kaolinite into illite and/or chlorite. Moreover, previous SEM observations indicate that clay minerals of the Ciechocinek Fm. are mainly detrital and present a weak diagenetic overprint (Brański, 2007, 2010). Fibrous illite was not observed at all. Also, the organic matter is generally immature in the whole Lower Jurassic series of the Polish Basin, as indicated by the low Thermal Alteration Index of palynomorphs (the background ‘thermal’ colours of Early Jurassic palynomorphs are dark yellow to pale orange, *i.e.* thermal index = 2, rarely 2.5–3.0 (Pieńkowski, Waksmundzka, 2009)), and biomarkers have been recovered with biological configurations (Marynowski, Simoneit, 2009). Summing up, relative variations in the mineralogical assemblage most likely preserved a primary signal driven by palaeoclimatic and palaeoenvironmental changes, although local influence of diagenesis is possible to some extent.

Sedimentary regime and provenance diversity

Besides the climate, other palaeoenvironmental factors control the mineralogy and geochemistry of the Lower Toarcian. Especially in bulk rock data, sea-level changes and terrigenous supply variations are reflected above all. Even though the average bulk rock composition of claystones and

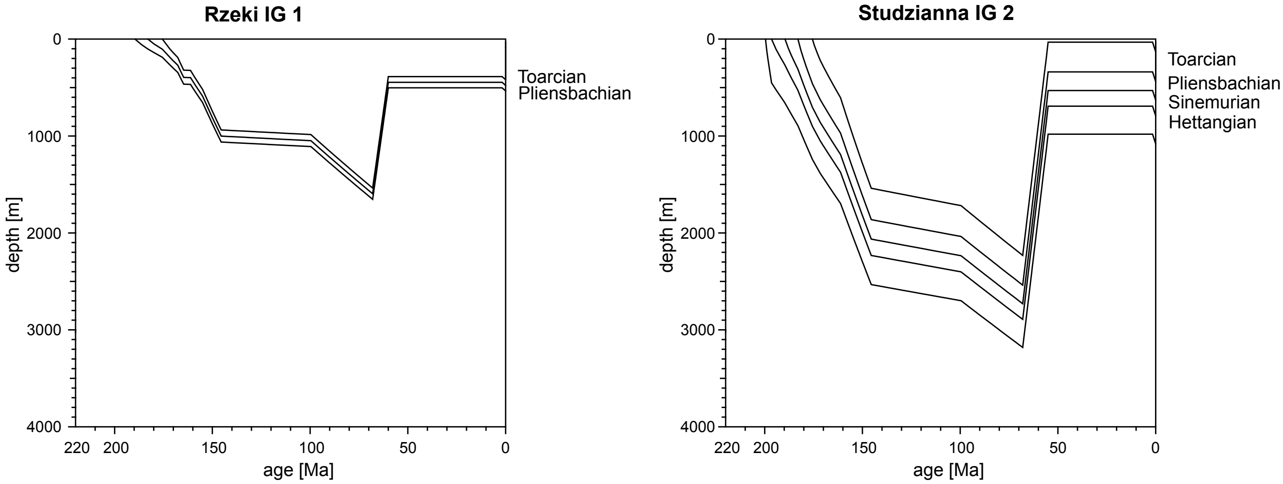

Fig. 9. Burial history of the Lower Jurassic deposits drilled in the Polish Basin within the Mid-Polish Trough (right) and outside of it (left) (backstripped by P. Poprawa using BasinMod program)

mudstones is very similar in all studied boreholes (Tab. 2), the comparison with sedimentological logs (Figs 5–8) suggests that the bulk rock mineralogy and clay index (CI) values are mainly influenced by sea-level changes and to lesser extent by climate variations. The clay minerals to quartz (and feldspar) ratio reflects changes in the energy of the sedimentary environment, shoreline proximity, and terrigenous supply. Rising total clay mineral content (CI increase) indicates mainly a more distal detrital source, decreased erosion and deeper water conditions, or deposition in a restricted (low-energy) part of the basin. The highest CI values coincide with offshore environments especially in the Mechowo and Gorzów Wlkp. sections (Figs 5, 6) or with restricted lagoons as in the Brody-Lubienia section (Fig. 8) and locally in other boreholes. A rising quartz and feldspar content (CI decrease) reflects generally a more proximal detrital source, increasing erosion and shallower (high-energy) water conditions.

Moreover, the TOC content in the Early Toarcian deposits seem to be not connected with climate changes as well. In the case of the epicontinental Polish Basin, the high TOC amounts are associated with the influx and burial of terrestrial organic matter. In boreholes studied, organic coal was accumulated mostly in the lower part of the Ciechocinek Fm., thus under moderate climate conditions, and the TOC content decreases in the middle part of the section with the onset of warming (Figs 5, 8). One may suppose that in this case, organic matter enrichment is first of all connected with the marine flooding due to the Early Toarcian transgression and with reworking of the swampy lowland deposits. However, sampling of a higher resolution would be required to solve the uneven distribution of organic matter throughout the profiles studied.

There is a lack of any expected distinct correlation between the geochemical and mineralogical weathering indices. The main chemical indices suggest moderate weathering, predominantly the opposite of the clay mineral ratios. Surprisingly, CIA and Al/K seem also to correlate mostly with sea-level changes, not climatic variations. This is particularly visible in the Suliszowice section (Fig. 7), and links spresumably to the so-called "non-steady-state weathering" (Nesbitt *et al*., 1997). The Early Toarcian was mostly a time of enhanced erosion and runoff. Definitely reversal conditions alter rates of chemical weathering and physical erosion on the surrounding landmasses, resulting in the exposure of differently weathered zones or bedrocks. Such conditions may result in the delivery of sediments with diverse mineralogies to the marine basin, reflecting incipiently-to-highly weathered zones (*cf.* Nesbitt *et al*., 1997). It should be noticed that unweathered feldspar admixture is common in claystones and mudstones from all the studied boreholes. In any case, the chemical indices are not accurate indicators of the weathering regime and climatic conditions for the Lower Toarcian deposits in the Polish Basin.

The average content of kaolinite and other clay minerals is different in the Ciechocinek Fm. deposits depending on borehole localisation (Tab. 2). Such spatial diversity in the clay mineral assemblage may be influenced by differences in continental proximity and source area lithology. For example, the Brody-Lubienia borehole represents a kaolinite-rich (on average) Toarcian succession due to the more proximal environments and reworking of nearby well developed soil profiles from the East European Craton. The kaolinite content might be increased by differential settling in the shallow marine environments near to the continent. Moreover, kaolinite enrichment might be locally enhanced by erosion and reworking not only of contemporary tropical soils but also of pre-Jurassic rocks rich in kaolinite. The more illite-rich Mechowo section represents more offshore environments.

A significant smectite admixture is observed only in the Gorzów Wlkp. borehole and its presence indicates environmental rather than climatic causes. Smectite was probably derived from Sudety Land as a product of chemical weathering of a parent ferromagnesian silicate under the same climatic conditions (*cf.* Liu *et al*., 2009). Volcanic rocks weather preferentially into smectite regardless of climate conditions if there is sufficient water to allow hydrolytic processes (Chamley, 1989; Liu *et al*., 2012). Small I-S mixed-layer admixtures in the progradational upper part of Mechowo section (Fig. 5) seem to be related to neoformation (pedogenic) processes in swampy or marshy environments.

Weathering regime

Generally, the clay mineral assemblages of the Ciechocinek Fm. are quite similar across the Polish Basin and show identical vertical trends. This suggests that the difference in the observed vertical clay mineral distribution can be attributed to the intensity of chemical weathering or transport, rather than dissimilarities in parent lithology. The degree of weathering increases with high mean annual temperature and precipitation which control the rate of chemical weathering reactions and ion exchange. CIA and Al/K closely correlate indicating low content of sodium and calcium. An increase of hydrolysis intensity and ionic subtraction during weathering of the parent rocks leads to secondary minerals that become more and more depleted in mobile cations. Kaolinite typically dominates in those mature soils that develop as a result of intense biochemical weathering in tropical or humid-subtropical climate with perennial rainfall (Singer, 1984; Hallam, 1984; Chamley, 1989; Weaver, 1989; Ruffel *et al*., 2002); and its formation requires a minimum soil temperature of ~15°C (Gaucher, 1981). Illite (with subsidiary chlorite) could have been derived from physical erosion of various parent rocks located on the hinterland. Illite is considered as a primary mineral, which reflects decreased hydrolytic processes in continental weathering and increased direct rock erosion under cool and/or arid climatic conditions (Singer, 1984; Chamley, 1989; Weaver, 1989). An increased chlorite content may also support the transformation of mafic minerals (Weaver, 1989). It should be noticed that kaolinite/illite or kaolinite/illite +chlorite ratios have been used by many authors for palaeoclimatic reconstructions (*e.g*. Robert, Kennett, 1994; Adatte *et al*., 2002; Deconinck *et al*., 2003; Raucsik, Varga, 2008; Hesselbo *et al*., 2009; Rostasi *et al*., 2011; Duchamp-Alphonse *et al*., 2011). Especially, the vertical clay mineral distribution in the <2 μm fraction is related to the changes of chemical weathering intensity in the aftermath of climate fluctuations. The occurrence of smectite in the Polish Basin is sparse and seems to be controlled by local conditions mentioned above.

Another controversial problem is the delay between the time of clay mineral formation on continents and their marine deposition. According to Thiry (2000), the delay may be quite significant and exceed 1 Ma. I think that such a long time may be connected with the peculiarly thick weathering covers. Recently, Dera *et al*. (2009a) suggest that the formation of kaolinite in tropical soils and its deposition in marine sediments could be almost contemporaneous during the Early Jurassic in the Peritethyan domain (less than 100 ky).

PALAEOCLIMATE CHANGES IN THE TOARCIAN

In many European sections as well as in the Polish Basin, a distinct short-term negative C-isotope excursion records a greenhouse gas release triggered by a very short-lived warming event just at the Pliensbachian-Toarcian boundary (Hesselbo *et al*., 2007; Suan *et al*., 2008; Pieńkowski, Hesselbo, 2011). This event is poorly reflected in the present clay mineral data because of the rare sampling of the boundary interval. Only in Suliszowice borehole (Fig. 7) is the kaolinite increase observed just after the first negative CIE. Moreover, slight rises in phosphorus content are observed during or just after this short-term excursion (Figs 5, 8). Beyond this episode, illite and chlorite are predominant in the lower part of the Ciechocinek Fm. (Figs 5–8). These coeval kaolinite depletions counterbalanced by higher illite proportions in the lower interval of all the sections studied would indicate a moderately warm climate marked by a low hydrolysis rate. In other words, these data would suggest a possible cooling event accompanied by a reduced humidity during the deposition of the lower part of the Ciechocinek Fm. A relatively short phase of cooler and drier conditions is also indicated for the lower *tenuicostatum* Zone by isotope and micropaleontological data (*e.g*. Suan *et al*., 2008; Mattioli *et al*., 2008; Pieńkowski, Hesselbo, 2011), following the mentioned humid episode across the Pliensbachian-Toarcian boundary interval.

All profiles analyzed from the Polish Basin show the same well-developed second carbon isotope excursion towards exceptionally light isotopic values that started from VIIIc parasequence (*cf.* Hesselbo, Pieńkowski, 2011).

The results of clay mineral analyses are generally consistent with the carbon isotope record in marine and terrestrial materials measured in sections in the Polish Basin and in different parts of the world. However, some differences are also visible. Firstly, the clay mineral evidence from the Polish Basin confirms the view of some authors (*e.g*. Cohen *et al*., 2007; Hermoso *et al*., 2012) that environmental and climatic changes slightly preceded the main carbon cycle perturbations – the first kaolinite increase is observed below the main second CIE. It may express a precursor warming episode to the T-OAE. Interestingly, the phosphorus record in sections from the Polish basin also starts to increase again before the onset of the second CIE (Figs 5, 8). This more distinct increase in P_2O_5 content is observed at the top of VIIIb parasequence (Figs 5, 8). This means that we can suspect two events in the Early Toarcian phosphorous cycle. Phosphorus represents an essential nutrient for living organisms. A change from less humid to more humid climate at the VIIIb/VIIIc parasequence boundary, accompanied by an increased input of terrigenous material from fluvio-deltaic runoff, could be the cause of the increased amount of phosphorus delivery to the basin in the later *tenuicostatum* Zone. That is in accordance with Mattioli *et al*. (2008), who infer high surface water fertility in the interval below the main isotope excursion of the T-OAE. Recently, high resolution research from the Paris Basin enabled the recognition of the precursor phases of CO_2 injection, *c*. 130 kyr in advance of the major negative CIE (Hermoso *et al*., 2012). This indicates the environmental perturbations that predate the first step towards relatively light carbon isotopes in carbonate and organic matter. According to Cohen *et al*. (2007), an earlier thermal increase with an enhanced hydrological cycle may have been an precursor of the Toarcian OAE before the emplacement of the Karoo-Ferrar province. Similar phenomena were also observed for other well-known warming events (*cf*. Slujis, 2007), suspect that the initial warming was linked to an intrusive phase of LIP development (*cf*. McElwain *et al*., 2005; Svensen *et al*., 2007), and could trigger off a positive feedback mechanism, that in turn caused the Toarcian super-greenhouse/anoxic event.

In the middle part of the Ciechocinek Fm., kaolinite becomes dominant by comparison with illite. In the Brody-Lubienia borehole, the initially illite-rich sedimentation was interrupted by sudden kaolinite inputs at the top of VIIIb parasequence (Fig. 8). In Mechowo borehole, kaolinite increases by fluctuating (Fig. 5). More gradual mineralogical changes were also recorded in the Suliszowice and Gorzów Wielkopolski boreholes (Figs 6, 7). Nevertheless, the kaolinite contents increased at approximately the similar time (*i.e*., mostly below the VIIIb/VIIIc parasequence boundary) and its maximal content is reached in the VIIIc parasequence in all sections studied. Warm and humid climate conditions combined with low-relief and intense vegetation encourage strong chemical weathering processes. A similar subtropical climate along with similar hydrologic conditions caused a comparable weathering intensity in all the source areas. The high kaolinite/illite ratio in this part of the Ciechocinek Fm. suggests extreme continental weathering under a humid subtropical climate related to the main phase of the global warming event that is identified by European oxygen isotope data in the upper part of the *tenuicostatum* Zone (see "Introduction" and references therein). Moreover, one may observe deposits representing a conspicuous shallowing event noticeable througout the whole basin, connected with the decreasing of the basin depth as a result of enhanced continental weathering and sediment supply (Pieńkowski, 2004; Cohen *et al*., 2004; Pieńkowski, Schudack, 2008). The shallowing and oxygen depletion are also confirmed by an increase in the siderite content (Figs 5–8). Most probably, this shallowing event is linked with the Early Toarcian global greenhouse warming, but misleadingly simulates the effects of sea-level fall (Hesselbo *et al*., 2007; Hesselbo, Pieńkowski 2011). These latter authors suggest that four progradational parasequences (VIIIc–f) fall within the T-OAE (Figs 5–8).

One particularly important feature of all carbon isotope profiles of the Lower Toarcian in the Polish Basin is the development of a number of abrupt steps leading up to the climax of the negative excursion (Hesselbo, Pieńkowski, 2011). The stepped nature of the main negative CIE, previously only known from marine materials (Kemp *et al*., 2005; Suan *et al*., 2008; Sabatino *et al*., 2009) was recently confirmed in terrestrial organic matter. Hesselbo and Pieńkowski (2011) correlate their step 3 with step A of Kemp *et al*. (2005) (Fig. 2). These results provide strong support for the orbitally and climatically controlled release of isotopically light carbon from marine methane gas hydrates into the ocean–atmosphere system in a series of rapid bursts (Kemp *et al*., 2005, 2011; Cohen *et al*., 2007; Hesselbo, Pieńkowski, 2011). Moreover, the greenhouse gas content was most probably enhanced by methane emission from the magma-intruded organic-rich sedimentary rocks (McElwain *et al*., 2005; Svensen *et al*., 2007; Aarnes *et al*., 2011) and wetlands. I wish to pay attention to presumable additional methane emission from melting ice-sheets and permafrost thaw (*cf*. Anthony *et al*., 2012), that might have been inherited after the Latest Pliensbachian glaciations. Each step has been interpreted as a phase of rapid and voluminous release of isotopically light carbon from an external source, with pacing modulated by climatic forcing at an astronomical frequency (Kemp *et al*., 2005, 2011; Wignall *et al*., 2005; Suan *et al*., 2008; Sabatino *et al*., 2009; Hesselbo, Pieńkowski, 2011). Clay mineral evidence from the Polish Basin confirms the stepped nature of the super-greenhouse event in the Early Toarcian. Especially in the Mechowo and Brody-Lubienia boreholes, a number of cyclic, short time-scale fluctuations of the clay mineral composition and in the values of the mineralogical weathering indices were observed (Figs 5, 8). The multiple kaolinite spikes indicate steps of rising warming and humidity that most probably correspond to Milankovitch cycles. As already mentioned, the formation of kaolinite on continents and its deposition in marine sediments seems to be almost contemporaneous during the Early Jurassic (*cf.* Dera *et al*., 2009a).

Hesselbo and Pieńkowski (2011) suggest that each 100-kyr cycle in carbon-isotope values was characterized by increasingly severe palaeoclimatic change, culminating in extremely hot and humid conditions co-incident with the peak of the most negative carbon-isotope excursion. Clay mineral evidence from the Polish Basin seems to be not entirely consistent with a permanent increase in relative humidity during the T-OAE, but their composition suggests to some extent the stabilisation or transient decrease in precipitation. The kaolinite content in all sections studied seems to diminish slightly in the upper part of Ciechocinek Fm., which may be interpreted as a trend towards hot but less humid conditions that somewhat restrain chemical weathering. The content of P_2O_5 reaches a maximum at the interval where the initial negative anomalies of the carbon isotope curves and the high kaolinite content are registered, and then return to background values (Figs 5, 8). It may suggest some decrease in nutrient delivery to the basin. Studies of other global warming events have provided ambiguous evidence for precipitation change. Data from the Paleocene-Eocene Thermal Maximum (PETM) are not particularly consistent with a single, large increase in atmospheric moisture, and lend support to variable hydrologic conditions (*e.g.* Smith *et al*., 2007; Storme *et al*., 2012). On the other hand palynological evident indicates still hot and humid climate conditions. Megaspores in the Ciechocinek Fm. are derived from the hydrophilic plant groups Lycopsida and Isoetaceae (Marcinkiewicz, 1971; Hesselbo, Pieńkowski, 2011). Taking this into consideration, some decrease of the kaolinite in relation to the illite content may rather reflect the interruption in the weathering cycle or a change in the source of clay minerals. Erosion and run-off can expose the unaltered rock surfaces and deliver more primary minerals that were then transported rapidly to river deltas without strong chemical alteration, which would have required more time. In other words, intense erosion in adjacent continental landmasses would have mixed the clay particles derived to the basin from diverse soils and substrates. Regardless of this, it should be noticed that upper part of Ciechocinek Fm. was rarely sampled for clay mineral analyses.

The new data presented in this paper are also consistent with the results of most recent clay mineral studies on Toarcian deposits from other parts of Europe (*cf.* Raucsik, Varga, 2008; Dera *et al*., 2009a). According to Dera *et al*. (2009a), a distinct palaeolatitudinal distribution in detrital clay mineralogy of the Lower Toarcian is observed. Major kaolinite enrichments in the northern parts of the Peritethyan Realm indicate a warm humid climate and imply enhanced runoffs on continental landmasses that reworked kaolinite-rich sediments from subtropical soils. Cohen *et al*. (2004) reported an $^{187}Os/^{188}Os$ excursion during the Toarcian OAE and suggested that this was linked to a 400 to 800% sudden increase in global weathering at the negative carbon isotope shift of the Early Toarcian. Waltham and Gröcke (2006) however questioned the validity of such a dramatic increase in the weathering rate. On the other hand, Dera and Donnadieu (2012) modeled recently the Early Toarcian warming event and showed rises in of 0 to +15 cm/year in runoff. Summing up, the increase in kaolinite input into the basin was related to the warm event in the late *tenuicostatum* Zone, which generated wetter conditions, more rainfall and intensified continental runoff.

CONCLUSIONS

The aim of present research was to recognize the rapid climatic changes during the Early Toarcian in the hinterland of the Polish Basin by means of clay mineral data. The results complete the patterns highlighted by Dera *et al*. (2009a) for the whole of Tethys due to the high sampling resolution, which allows a better timing. The samples studied do not show any significant diagenetic overprint as a result of low or moderate burial and a closed hydrologic system. The detrital clay mineral composition of the fine-grained deposit (<2 μm fraction) in the Ciechocinek Fm. from the Polish Basin and the vertical variations in kaolinite content were mostly controlled by the weathering regime linked to the climatic conditions. The changes in the kaolinite/illite ratio recorded especially rainfall fluctuations. New data presented in this paper are in accordance with the results of most recent clay mineral studies on Toarcian deposits from the other parts of Europe and confirm the presence of a warm humid climate and enhanced runoffs on continental landmasses in northern parts of the Peritethyan Realm. The results of clay minerals analyses presented are also generally consistent with the carbon isotope record in marine and terrestrial materials received from both the sections in the Polish Basin and in different parts of the world. In particular the following conclusions are highlighted:

- the Early Toarcian warming (with year-round humidity) is recorded almost synchronously in clay mineral and carbon isotope data from the Polish Basin (and is supported by other evidence such as palynological results);

- clay mineral evidence from the Polish Basin confirms the stepped nature of the super-greenhouse/anoxic event in the Early Toarcian and supports indirectly the supposition for orbitally and climatically controlled rapid bursts of isotopically light carbon most probably from methane hydrates;
- illite predominance in the lower part of the Ciechocinek Fm. (early *tenuicostatum* Zone) suggest the absence of extended hydrolysis due to the still moderate climate;
- kaolinite abundance in the middle part of Ciechocinek Fm. (later *tenuicostatum* Zone) indicates rapid weathering due to the humid subtropical or tropical climate;
- the onset of warming (with high rainfall) slightly preceded the main carbon cycle perturbations – the first kaolinite spike is observed below the CIE;
- stabilization or transient decrease in kaolinite content in upper part of the Ciechocinek Fm. (most probably early *falciferum* Zone) may be interpreted as a trend towards hot but less humid conditions, but more probably, some kaolinite depletion reflects the interruption in the weathering cycle by erosion and runoff.

Besides the climate, other palaeoenvironmental factors controlled the mineralogy and geochemistry of the Lower Toarcian deposits in the Polish Basin to some extent. First of all, the sea-level changes and terrigenous supply variations are reflected in the bulk rock data. Moreover, even though clay mineral assemblages were controlled mostly by the weathering regime, the spatial diversity in clay mineral proportions may have been influenced by differences in continental proximity and source area lithology.

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