

Kaolinite peaks in early Toarcian profiles from the Polish Basin – an inferred record of global warming

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In lower Toarcian clay deposits (Ciechocinek Fm., VIII depositional sequence of the Lower Jurassic) from three boreholes from the Polish Basin, illite-dominated sedimentation representing the lower part of studied interval was interrupted by enhanced kaolinite input. Levels of high kaolinite/illite ratio at the VIIIb/VIIIc parasequence boundary suggest strong continental weathering in a humid-subtropical to tropical climate related to the phase of the early Toarcian global warming recorded at the top of the *tenuicostatum* Zone and correlated with isotope curves from a number of European sections. Kaolinite enrichment may be locally enhanced by reworking of pre-Jurassic kaolinitic rocks and differential settling. Diagenetic processes were not sufficient enough to transform the initial kaolinite, but may have altered smectite and mixed-layers into illite and/or chlorite.

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Key words: lower Toarcian, Ciechocinek Fm., Polish Basin, kaolinite content, palaeoclimate, global warming.

INTRODUCTION

The early Toarcian (Early Jurassic, ~183 Ma ago) was a critical time in Earth history, characterized by pronounced negative carbon isotope excursion (CIE) recorded in marine organic matter, marine carbonate and terrestrial wood (e.g., Hesselbo et al., 2000, 2007; Schouten et al., 2000; Röhl et al., 2001; Jenkyns et al., 2002; Kemp et al., 2005; Hermoso et al., 2009) as well as perturbations to other isotopic systems. The disruptions were associated with an oceanic anoxic event – the Toarcian OAE (Jenkyns, 1988), a pronounced transgression (Hallam, 1997, 2001), carbon production crises (e.g., Mattioli et al., 2004, 2009; Tremolada et al., 2005), an increase in atmospheric CO₂ content, global greenhouse warming (Bailey et al., 2003; Cohen et al., 2004; McElwain et al., 2005; Hesselbo et al., 2007), and a second-order global mass extinction (e.g., Little and Benton, 1995; Pálfy and Smith, 2000; Wignall et al., 2005). Brief but extreme climatic events spanning mainly the tenuicostatum-falciferum biochronozonal transition were related to massive injections of isotopically light carbon most probably from oceanic methane hydrate and/or intense volcanic degassing in the Karoo-Ferrar large igneous province of southern Gondwana (Hesselbo et al., 2000, 2007; Pálfy and Smith, 2000; Kemp et al., 2005; Suan et al., 2008). Some authors point to thermal metamorphism of organic-rich deposits (McElwain et al., 2005; Svensen et al., 2007), changes in palaeoceanography (Bailey et al., 2003; van de Schootbrugge et al., 2005; Wignall et al., 2005) or extensive biomass burning (Finkelstein et al., 2006) as a main reason. The substantial increase in global temperature (McArthur et al., 2000; Bailey et al., 2003; Rosales et al., 2004; Suan et al., 2008) and abundant rainfall caused a substantial increase in continental weathering and in sediment supply (Bailey et al., 2003; Cohen et al., 2004, 2007; Hesselbo et al., 2007).

Marine clays represent a final product of the continental weathering process and may reveal global climatic fluctuations. Clay mineralogy has been successfully used in palaeoclimate interpretations especially of Mesozoic rocks (e.g., Singer, 1984; Chamley, 1989; Ruffell *et al.*, 2002; Ahlberg *et al.*, 2003; Deconinck *et al.*, 2003; Schnyder *et al.*, 2006; Raucsik and Varga, 2008; Godet *et al.*, 2008; Dera *et al.*, 2009; Hesselbo *et al.*, 2009). Recently, the present author used clay minerals in Hettangian palaeoclimate interpretation (Bra ski, 2009). The present paper comprises the results of clay mineralogical research into lower Toarcian successions in two boreholes (Brody-Lubienia BL-1 and Suliszowice 38 BN; Fig. 1) from the southern marginal part of the Polish Basin and additionally of the Mechowo IG 1 borehole in its central part (Pomerania region).

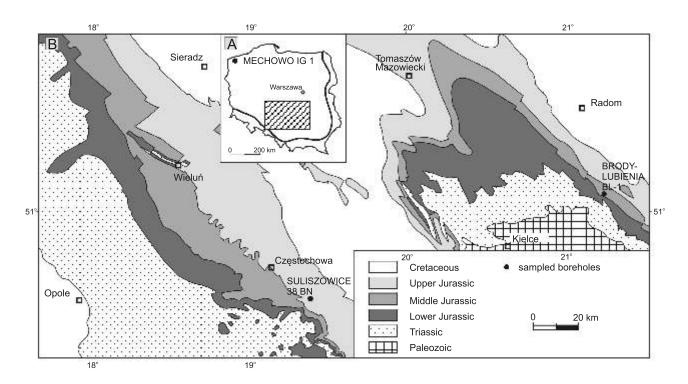


Fig. 1. Location of boreholes examined

A – area shown on Figure 1B and the extent of the Toarcian basin in Poland (after Pie kowski, 2004); **B** – geological sketch map of Southern Poland without Cenozoic deposits (after Dadlez *et al.*, 2000, simplified)

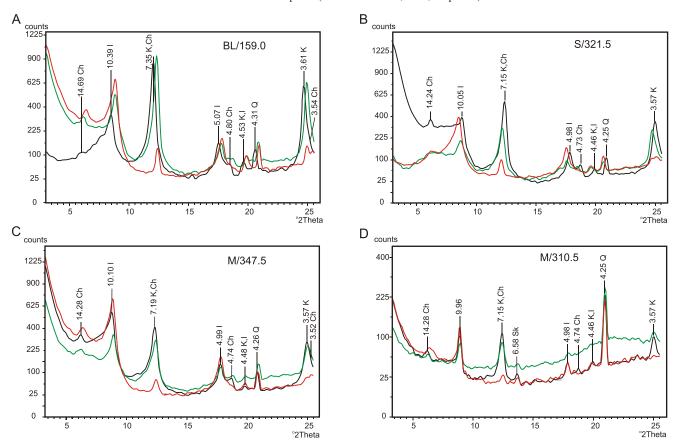


Fig. 2. Selected X-ray diagrams of lower Toarcian samples (<0.002 mm fraction) (carried out by W. Narkiewicz)

 ${\bf A}$ – kaolinite-dominated claystone with very subordinate illite and only trace amount of chlorite (Brody-Lubienia borehole, depth 159.0 m); ${\bf B}$ – kaolinite-dominated claystone with subordinate illite and chlorite (Suliszowice borehole, depth 321.5 m); ${\bf C}$ – kaolinite-dominated claystone with subordinate illite and chlorite (Mechowo borehole, depth 347.5 m); ${\bf D}$ – 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 (550°C)

EXPLANATION OF THE PROFILES

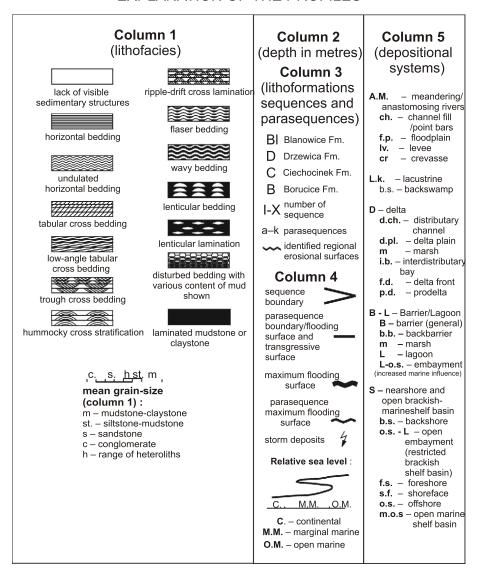


Fig. 3. Explanations for the sedimentological profiles on Figures 4, 5 and 6 (after Pieńkowski, 2004, modified)

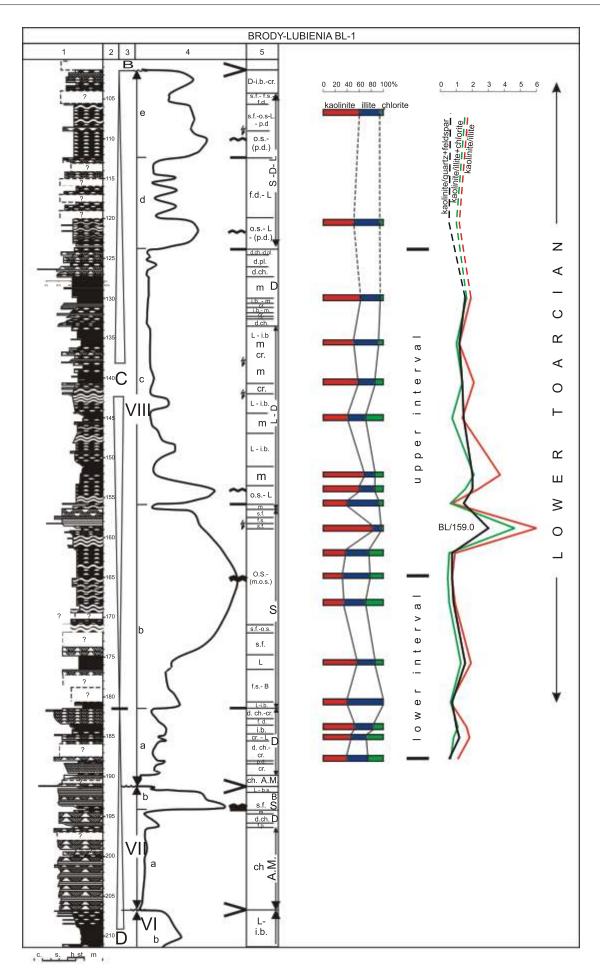
MATERIAL AND METHODS

In the present study 64 samples from clay-rich lower Toarcian beds were examined using X-ray diffraction (*Phillips PW* diffractometer with CuKa radiation) in the laboratory of the Polish Geological Institute – National Research Institute. The analyses ran on untreated, glycolated and heated samples of the <2 µm fraction (Fig. 2). Clay mineral identification was made according to the procedure of Moore and Reynolds (1997). Afterwards, the present author calculated the indices: kaolinite/illite (K/I), kaolinite/illite+chlorite (K/I+Ch) and kaolinite/quartz+feldspar (K/Q+F). SEM analyses were also performed.

RESULTS

According to Pieńkowski (2004), greenish-grey mudstones, claystones and heterolithic deposits of the Ciechocinek Fm. (lower Toarcian – VIII depositional sequence) were developed in a large, shallow, brackish-marine embayment and in lagoons (see for details Figs. 3–6).

Previous mineralogical analyses lower Toarcian claystone and mudstones performed on bulk rock samples only from Southern Poland showed a distinct predominance illite over kaolinite (Kozydra, 1968; Maliszewska, 1968; Leonowicz, 2005). They were briefly summarized by the present author (Brański, 2007).



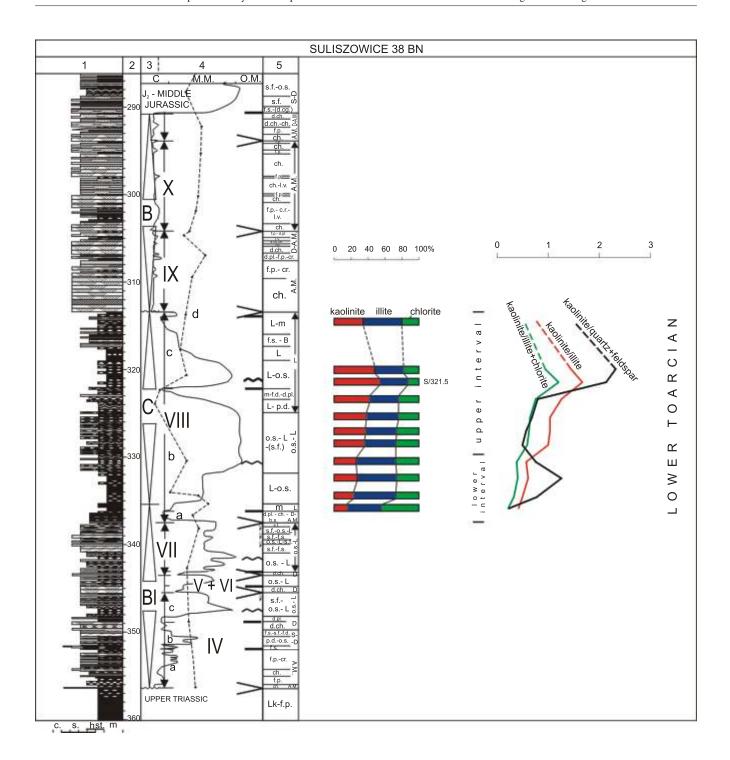
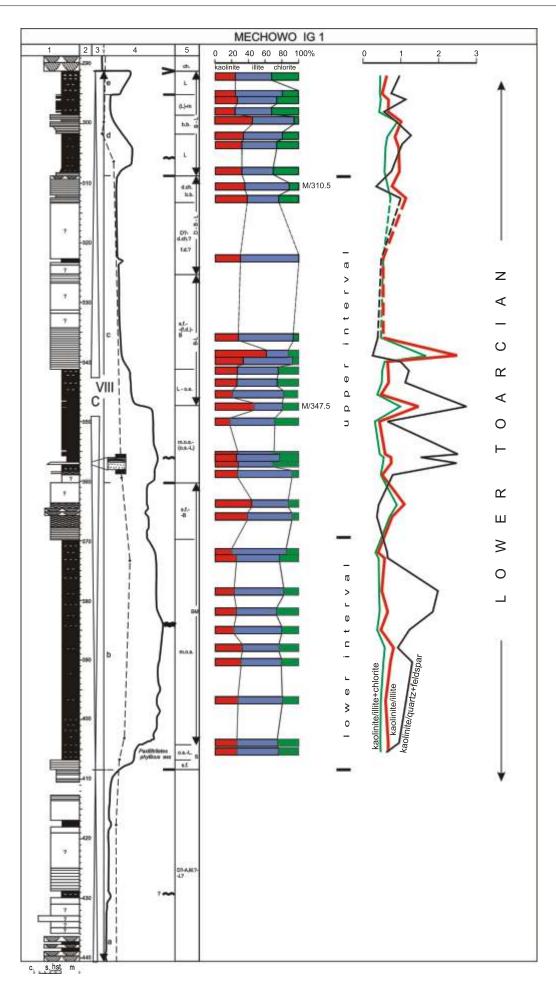


Fig. 5. Lower Toarcian clay min eralcom po si tionand min er al og i daldi cestrom the Suliszowice borehole (with detailed sedimentological profile after Pieñkowski, 2004)

Note the gradual increase in kaolinite content but well expressed kaolinite maximum above the VIIIb-VIIIc parasequence boundary; for explanations see Figure 3

Fig. 4. Lower Toarcian clay min eralcom po si tionand min er al og i daldi cefrom the Brody-Lubienia borehole (with detailed sedimentological profile after Pieñkowski, 2004)

Note a kaolinite spike at 159.0 m suggesting extreme continental weathering in a humid-subtropical to tropical climate (most probably related to the onset of the main phase of early Toarcian global warming); for explanations see Figure 3

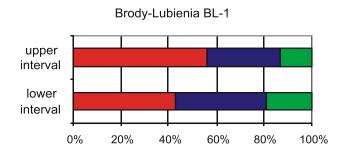


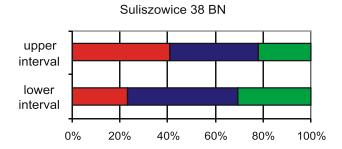
The clay fraction of recently examined samples comprises kaolinite (16-82%), illite (14-70%) and chlorite (0-44%). Smectite was almost never observed. The section corresponding to the VIIIb and VIIIc parasequences was especially examined (Figs. 3–6). The age of parasequence VIIIb represents the tenuicostatum Zone, and parasequence VIIIc is roughly comprised of falciferum Zone deposits (Pie kowski, 2004). It should be noticed that a difference in clay mineral distribution occurs between the lower interval of the sections (approximately from the sequence boundary located at the Pliensbachian/Toarcian boundary to the maximum flooding surface) and the upper interval (up to the VIIIc/VIIId parasequence boundary; Figs. 4-7; Table 1). In the lower interval the average kaolinite amounts are minor (~23% in Suliszowice and ~ 26% in Mechowo to ~43% in Brody-Lubienia) while those of illite are major (between 38 and 53%). In the upper interval kaolinite becomes dominant (on average 33% in Mechowo and 41% in Suliszowice to ~56% in Brody-Lubienia) by comparison with illite (50 and 37%, and 31%, respectively). The content of chlorite is considerable and ranges from 13-19% (in Brody-Lubienia) and 17-21 (in Mechowo) to 22–31% (in Suliszowice).

At the base of the upper interval in Brody-Lubienia profile there is a surge of kaolinite (up to 82%) offset by a significant depletion of illite (~14%) and chlorite (~4%; Fig. 2A). The kaolinite spike at 159.0 m is very well marked in the curves of the kaolinite/illite and kaolinite/illite+chlorite ratios (Fig. 4). The abundance of fine-grained degraded kaolinite is shown also via SEM observations (Fig. 8A and B). In the Suliszowice section, the kaolinite content increases more gradually from the base of Ciechocinek Fm. to the lower part of the parasequence VIIIc (Fig. 5). The kaolinite maximum, though, (Fig. 2B) is well expressed in the curves of the all mineralogical indices. In Mechowo borehole a few cyclic variations at the 10-20 m scale in kaolinite/illite ratios are observed, but the most distinct increase in kaolinite content is seen in the lower part of the parasequence VIIIc (Figs. 2C and 6). It is noteworthy that, in all sections, the interval with the highest kaolinite content is represented mostly by open embayment deposits punctuated by prograding nearshore sediments (Pie kowski, 2004).

INTERPRETATION AND DISCUSSION

The author focuses on kaolinite content because of its strong climatic dependence and significant resistance under moderate diagenetic conditions. Kaolinite typically dominates in mature soils that develop as a result of intense chemical weathering in a tropical or humid-subtropical climate. The detrital clay mineral suites in the Toarcian mudstone and shale samples show a weak diagenetic overprint due to low (Suliszowice) or moderate (Brody-Lubienia, Mechowo) burial and to closed diagenetic systems (Bra ski, 2008). The burial





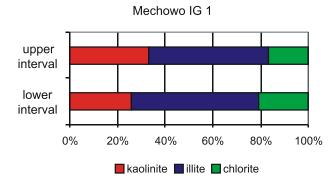


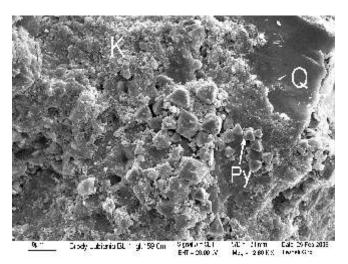
Fig. 7. Average clay mineral compositions in the early Toarcian claystones and mudstones from lower and upper intervals in the boreholes studied

Note the enhanced kaolinite enrichment in the Brody-Lubienia borehole and the predominance of kaolinite in the upper interval of all studied sections; for "lower" and "upper" intervals see Figures 4–6 and explanations in text

diagenesis was never strong enough to transform the initial kaolinite into illite and/or chlorite, but part of the illite and chlorite may have come from transformation of smectite (cf. Dera et al., 2009).

In the most cases isotope and micropalaeontological data from the *tenuicostatum* Zone suggest moderate climate control (e.g., Suan *et al.*, 2008; Mattioli *et al.*, 2008), although there is a distinct negative C-isotope excursion correlated with a positive O-isotope excursion, that record a short-lived warming just at the Pliensbachian–Toarcian boundary (Hesselbo *et al.*, 2007;

Fig. 6. Lower Toarcian clay min eralcom po si tionand min er al og i daldi cefrom the Mechowo borehole (with detailed sedimentological profile after Pieñkowski, 2004)



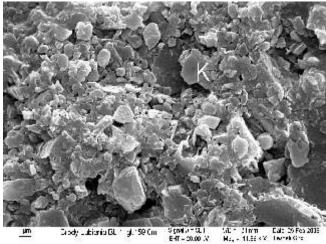


Fig. 8. SEM images of kaolinite clay specimen from the Brody-Lubienia BL-1 borehole, depth 159.0 m (taken by L. Giro)

Note very fine (0.2-2.0 μm) degraded kaolinite plates and crystals of pyrite; K - kaolinite, Q - quartz, Py - pyrite

Suan *et al.*, 2008). The moderate climate coincides with the higher illite and chlorite content in the lower interval studied due to prevention from extended hydrolysis. In the upper part of the lower Toarcian interval kaolinite becomes the dominant clay mineral, suggesting mostly warm and humid climate conditions (Figs. 4–7; Table 1).

In the Brody-Lubienia borehole initially illite-rich sedimentation was interrupted by a sudden amplified kaolinite input at the top of the VIIIb parasequence (Figs. 2A, 4 and 8). A more gradual mineralogical change was also recorded in Suliszowice borehole (Fig. 5). In the Mechowo borehole the kaolinite increase is oscillatory (Fig. 6). In this part of the Ciechocinek Fm. one may observe deposits representing a conspicuous shallowing event marked in the whole basin (Figs. 4–6), that was connected with a decrease in the basin depth as a result of enhanced continental weathering and sediment supply (Pie kowski, 2004; Cohen *et al.*, 2004; Pie kowski and Schudack, 2008). It is compatible with the idea (Hesselbo *et al.*, 2007), that the shallowing event at the *tenuicostatum-falciferum* biochronozonal transition may be

linked with early Toarcian global greenhouse warming, but may misleadingly simulate the effects of sea level fall. 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 and Varga, 2008; Dera et al., 2009). Levels of the high (up to 6.0!) kaolinite/illite ratio at the VIIIb/VIIIc parasequence boundary interval (Fig. 4) suggest extreme continental weathering in a humid-subtropical to tropical climate related to the onset of the main phase of global warming that was recorded in Europe on many isotope curves at the top of the tenuicostatum Zone. In the more densely sampled Mechowo borehole we may suspect the effects of brief palaeoclimatic fluctuations (Fig. 6) that most probably correspond to Milankovitch cycles. The evolution of kaolinite content in the deposits may correspond to these short-term climate variations because the formation of kaolinite on continents and its deposition in marine sediments seems to have been almost contemporaneous during the Early Jurassic (Dera et al., 2009). Kaolinite enrichment may be locally enhanced by erosion and reworking of pre-Jurassic kaolinitic rocks and proximal deposi-

Table 1

Av er agælay min er alsom po si tioand min er al og i daldi cesin the early Toarcian claystones and mudstones from studied boreholes

Profile		Composition and indices					
		K [%]	I [%]	Ch [%]	K/I	K/I+Ch	K/Q+F
Brody-Lubienia BL-1	upper interval	56	31	13	2.25	1.58	1.65
	lower interval	43	38	19	1.24	0.79	0.86
Suliszowice 38 BN	upper interval	41	37	22	1.14	0.73	1.19
	lower interval	23	46	31	0.49	0.30	0.73
Mechowo IG 1	upper interval	33	50	17	0.74	0.54	1.03
	lower interval	26	53	21	0.51	0.36	1.03

K - kaolinite, I - illite, Ch - chlorite, Q - quartz, F - feldspar; for "lower" and "upper" intervals see Figures 4–6 and explanations in text

tion of kaolinite due to differential settling in shallow marine environments surrounded by continents. Some decrease of kaolinite relative to the illite content above the kaolinitic interval discussed may reflect an interruption in the weathering cycle or a change in the source of clay minerals as a result of erosion. Alternatively it may reflect hot but less humid climatic conditions that may have slowed chemical weathering.

CONCLUSIONS

Distinct changes in the clay mineral contents in the Brody-Lubienia, Suliszowice and Mechowo boreholes reflect marked climatic change during the early Toarcian. Other factors (provenance, differential settling and diagenetic transformation of smectites) may, though, cloud the palaeoclimate signal. However, an increase in kaolinite content is inferred to be a direct result of amplified chemical weathering even though part of kaolinite was derived from older sedimentary rocks. Kaolinite abundance at the VIIIb/VIIIc parasequence boundary

reflects an increase in temperature and especially in year-round rainfall related to the onset of the early Toarcian global warming that was recorded at the top of the *tenuicostatum* Zone on isotope curves in other European sections. The kaolinite pulses in the upper interval of the lower Toarcian (Mechowo borehole) were possibly controlled by astronomically forced changes in climate, superimposed upon longer-term global warming.

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