



Geochemistry of Middle Jurassic mudstones (Kraków–Częstochowa area, southern Poland): interpretation of the depositional redox conditions

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Middle Bathonian iron-bearing dark grey mudstones and claystones from the Kraków–Częstochowa Upland (southern Poland) were subjected to geochemical and mineralogical study in order to evaluate palaeo-redox conditions of their deposition and diagenesis. They are mainly composed of kaolinite, with smaller amounts of other clay minerals and detrital quartz. Organic matter is composed of type III and/or IV kerogen and its $\delta^{13}\text{C}$ is between -23 and -24% , suggesting a mainly terrigenous source, with a possible admixture of marine input. Most geochemical parameters: (total organic carbon) TOC/S, U/Th, Ni/Co, V/Cr, (Cu+Mo)/Zn ratios, authigenic uranium content, and Fe-TOC-S relationship, indicate deposition under oxygenated bottom water conditions. By contrast, DOP (degree of pyritization) and V/V+Ni indices suggest a dysoxic environment. However, DOP probably reflects redox conditions in the sediment during diagenesis rather than in the overlying water column. The composition of the organic matter and the domination of pyrite euhedra over framboids indicates that the V/V+Ni ratio may not be reliable for determination of redox conditions in the rocks studied. There is no significant difference between the geochemical indices of host rocks with nodules and those without them.

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INTRODUCTION

Many major and trace elements and their ratios can be used for recognition of palaeo-redox environmental conditions and chemistry of bottom water and sediment (e.g. Condie, 1981; Lewan and Maynard, 1982; Jones and Manning, 1994; Quinby-Hunt and Wilde, 1994; Vetö *et al.*, 1997). We evaluated several widely used inorganic geochemical indices (U/Th, V/V+Ni, V/Cr, Ni/Co, (Cu+Mo)/Zn, Fe_{Tot} , S, TOC — total organic carbon, DOP — degree of pyritization, TOC/S), in an attempt to interpret redox conditions during deposition of dark-coloured epicontinental marine mudstones. The origin of organic matter in the deposits studied was determined using Rock-Eval and $^{13}\text{C}_{\text{org}}$ analyses.

This paper forms part of multidisciplinary studies that have been performed on the Middle Jurassic rocks from the Kraków–Częstochowa Upland (see Gedl *et al.*, 2006). The aim of this study was a reconstruction of palaeoenvironmental conditions during deposition of the Bathonian mudstones, using geochemical and mineralogical methods, and their comparison with

sedimentological and palaeontological data. We also attempted to evaluate the possible influence of common siderite nodule horizons on the environmental geochemical indices of the host rocks. The Gnaszyn section, which belongs to the lower part of the Częstochowa Ore (Fe)-bearing Clay Formation (the abbreviated term Częstochowa Clay Fm. will be used throughout the paper), was chosen for study due to its representative character. This is the first study of its kind on these deposits.

GEOLOGICAL SETTING

The Middle Jurassic in the area between Wieluń and Kraków rests upon the Lower Jurassic and is covered by thin Quaternary sediments or outcrops at the surface (Dayczak-Calikowska and Kopik, 1976). Significant differences in stratigraphical and facial development on the Kraków–Częstochowa Upland were the basis for distinguishing two different units: a northern unit (Wieluń–Częstochowa–Zawiercie) and a southern one (Ogrodzieniec–Kraków; Różycki, 1953). The studied area of the

Częstochowa Clay Fm. belongs to the northern unit which is characterized by low facies variability and relatively thick deposits resulting from monotonous and rapid sedimentation. The Formation rests on the Kościelisko Beds (Aalenian-lower Bajocian; Różycki, 1953) being separated by a hiatus (the lowermost upper Bajocian; Dayczak-Calikowska and Kopik, 1976). Deposits of the Częstochowa Clay Fm. were deposited in a large epicontinental basin during the Mid Jurassic transgression. It is represented by a succession of dark grey claystones, mudstones and sandstones with several interbedded siderite nodule levels (Ratajczak, 1998). Siderite horizons and nodules of the Częstochowa Clay Fm. were used as a source of iron and exploited from the Middle Ages up to the early 1980's (Różycki, 1960). Facially and stratigraphically this formation is comparable to the famous iron-bearing Jurassic deposits of Lorraine and Alsace (the "Minette" deposits; Guilbert and Park, 1986).

The Gnaszyn section belongs to, and is typical of, the lower part of the Częstochowa Clay Fm. With reference to its stratigraphical and facial development the area studied belongs to a northern unit of the Middle Jurassic deposits of the Kraków–Częstochowa Upland and it comprises the easternmost part of the Fore-Sudetic Monocline (Różycki, 1953). It represents the southern marginal part of the epicontinental basin extending during the Mid Jurassic throughout nearly the whole Polish Lowlands area (Dayczak-Calikowska and Kopik, 1976).

The palaeoenvironmental conditions during sedimentation of the deposits in the Gnaszyn clay-pit were discussed by Gedl *et al.* (2003, 2006), mainly from a palaeontological point of view. Sedimentation took place in generally oxic conditions. It was characterized by increased input of terrestrial material into the basin, leading to some changes both in the bottom water environment (opportunistic benthic assemblage tolerant of lower oxygen

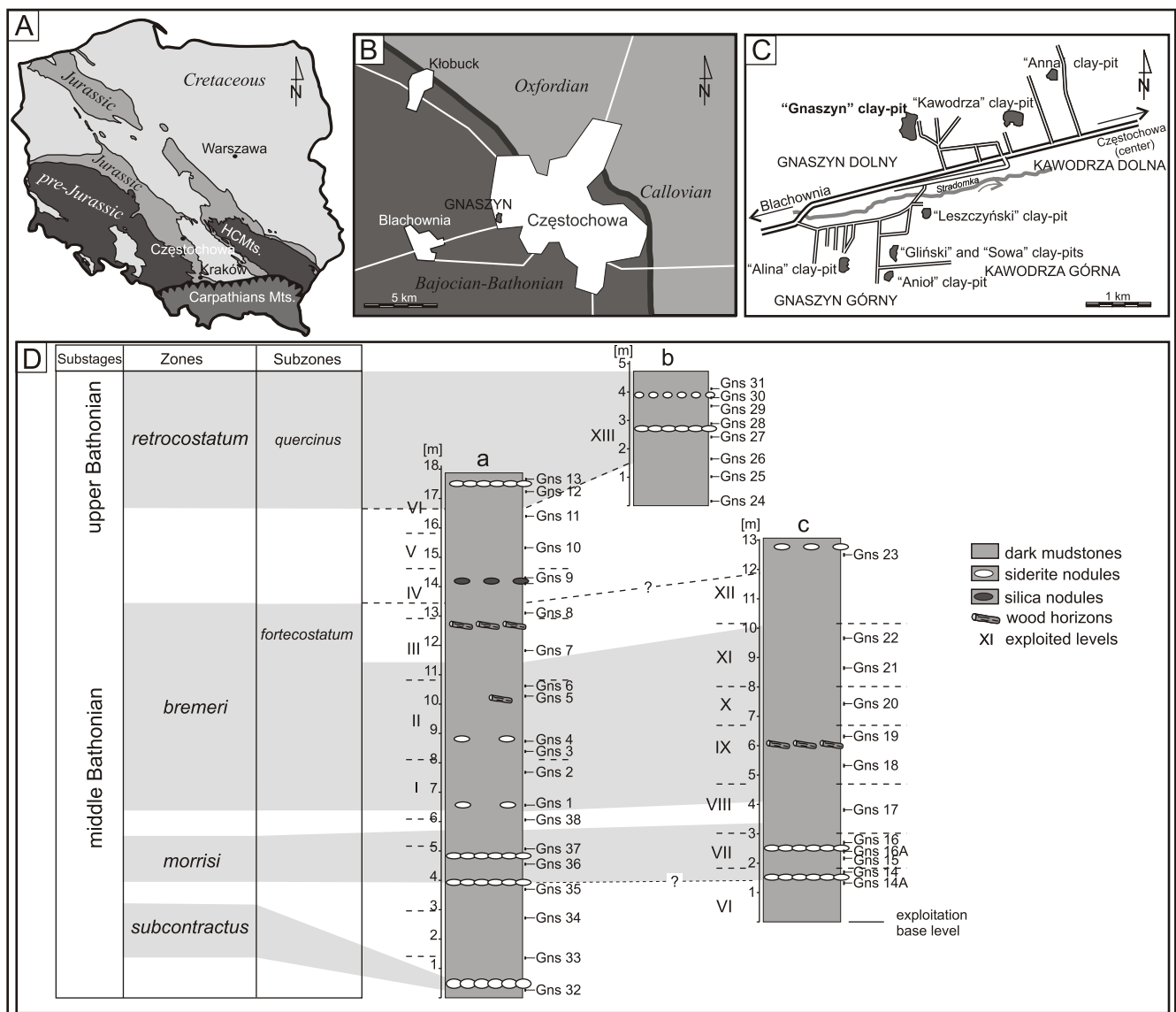


Fig. 1. The Gnaszyn section — location and samples

A — Geological map of Poland without Cenozoic cover (simplified after Dadlez *et al.*, 2000); B — geological setting of the studied area (after Majewski, 2000); C — location of the Gnaszyn clay-pit (after Matyja and Wierzbowski, 2003); D — three-part section of mudstones exposed in Gnaszyn clay-pit and its correspondence to ammonite zones (according to Matyja and Wierzbowski, 2006): a — coordinates N 501 48' 03.8'', E 191 02' 36.9'', b — coordinates N 501 48' 04.7'', E 191 02' 44.3'', c — coordinates N 501 48' 12.8'', E 191 02' 25.4''; the section originally drawn by P. Gedl, published with permission

content) as well as in the surface water (stress-indicating plankton assemblage). These changes were consequences of variable terrestrial input into the basin (a high frequency of land-derived phytoclasts and “sunken-wood” associations) and may have been caused by sea level fluctuations. The climatic evidence is conflicting. The clay mineral assemblage, which is largely of detrital origin, indicates rather cool (and/or dry) climatic conditions facilitating mechanical erosion of the source rocks. By contrast, the frequent occurrence of Araucariaceae pollen grains points rather to a warm climate. The common intervals with siderite nodules coincide with periods of relatively slower and more quieter sedimentation, which is reflected in more diversified benthic and planktonic fossils (Gedl *et al.*, 2006).

The sampled section in Gnaszyn Dolny, further simplified to Gnaszyn, is owned and mined by the Wienerberger Cegielnie Lębork Company and situated at a western suburb of Częstochowa, Poland (Fig. 1A–C). The three-part open pit exposes *ca.* 30 metres-thick sequence of marine claystones and mudstones, interbedded with eleven siderite nodule levels and one silica nodule level (Fig. 1D). The dark grey deposits are bioturbated and contain an abundant and variable fauna of ammonites, belemnites, foraminifera, bivalves, scaphopods, gastropods, and microfossils represented by foraminifera, ostracods, small gastropods and fragments of echinoderms (Gedl *et al.*, 2003). The biostratigraphy is based mainly on the ammonite fauna suggesting a middle-upper Bathonian age (Matyja and Wierzbowski, 2003, 2006).

MATERIALS AND METHODS

The majority of samples from the vertical section studied are dark grey and macroscopically uniform, except for the presence of nodules at some horizons. The samples from the highest part of the section (Gns 27–31) are yellow-red. Mineralogical study suggests that they are weathered and therefore they have not been taken into account in the palaeoenvironmental evaluation.

The mineralogical composition was studied using X-ray powder diffraction (*XRD Philips X Pert ADP PW 1830*, Institute of Geological Sciences, Jagiellonian University).

Concentrations of major (Al, Ca, Mg, Na, K, Ti, Fe, P) and trace elements (Mn, Cr, Rb, Sr, Y, Nb, Cu, Zn, Pb, Co, Ni, V, and REE) were determined by INAA and ICP-AES (ACTLABS, Canada).

Contents of total organic carbon (TOC) and total sulphur were obtained using a *LECO* analyzer. Rock-Eval pyrolysis was performed on a *Rock-Eval II* analyzer and was used to identify the type and maturity of organic matter contained in the rock samples studied.

The degree of pyritization (DOP) was calculated according to the formula described by Raiswell and Berner (1985, 1986) and Leventhal and Taylor (1990): $DOP = Fe_{Py} / [Fe_{Py} + Fe_{HCl}]$, where Fe_{Py} is the percent of pyrite iron (calculated by multiplying total S [%] \times 0.871 and Fe_{HCl} is the percent of reactive iron). Reactive iron (Fe_{HCl}), representing the Fe that has the potential to react with dissolved sulphide to form monosulphides and pyrite (Berner, 1970; Raiswell *et al.*, 1988), was extracted from 100 mg of powdered sample by 1N HCl during 24 hours in

room temperature (Leventhal and Taylor, 1990) and measured by F-AAS (*Philips 9200C*).

The $\delta^{13}C_{org}$ values were determined on the whole-sediment samples. The carbonate-free samples were oxidised with CuO at 900°C and the resultant CO₂ was separated by fractional sublimation and analyzed isotopically for $\delta^{13}C_{org}$ with a *ThermoFinnigan 252* mass-spectrometer (University of Erlangen).

CHARACTERISTICS OF INDICES AND RESULTS

MINERALOGY

The samples studied are generally uniform throughout the lithological column (Fig. 2) and represent dark grey claystones and mudstones. They are mainly composed of clay minerals (dominant kaolinite, with smaller amounts of illite/muscovite and chlorite) and detrital quartz. Subordinate amounts of feldspars (orthoclase), pyrite and siderite are present. Eleven levels of siderite nodules and one level of siliceous nodules occur within the section studied.

GEOCHEMISTRY

For the palaeoenvironmental investigation numerous useful geochemical redox parameters have been chosen. The values are given in Table 1 and Figure 2.

ORGANIC MATTER

Total organic carbon (TOC = C_{org}) varies from 0.01% to more than 10% C_{org} in sediment (Romankevich, 1984). Rock-Eval pyrolysis is a method to evaluate the thermal maturity (T_{max}) of the rocks, and the quality and origin of the organic matter. The results of Rock-Eval pyrolysis are usually displayed in a van Krevelen-type diagram of HI vs. OI values which roughly correspond to the H/C vs. O/C atomic ratio. The hydrogen index (HI) values provide information about the type and preservation of organic matter and the oxygen index (OI) value informs about the oxidation degree of organic matter. These elemental parameters can also be used to determine the terrestrial, lacustrine or marine origin of the organic matter (Espitalié *et al.*, 1973; Orr, 1983; Leventhal, 1986).

Results of the Rock-Eval pyrolysis show that the organic matter in the samples studied is depleted in hydrogen and enriched in oxygen (Table 2). Hydrogen index (HI) values are very low, ranging between 11 and 34 (mg HC/g TOC). The oxygen index (OI) ranges between 40 to 157 mg CO₂/g TOC. The total organic carbon contents of the samples studied ranges from 1.5 to 2.5 wt. %. Maximum Rock-Eval pyrolysis temperatures (T_{max}) vary from 388 to 435°C. These data were plotted on a HI/OI diagram (Fig. 3) and suggest the terrigenous origin of the organic matter (kerogen type III and/or IV) dominated by plant remains (Espitalié *et al.*, 1973; Tissot *et al.*, 1984; Leventhal, 1986).

STABLE CARBON ISOTOPES

Organic carbon isotopes can be used to determine the source/origin of different types of organic matter in sedimen-

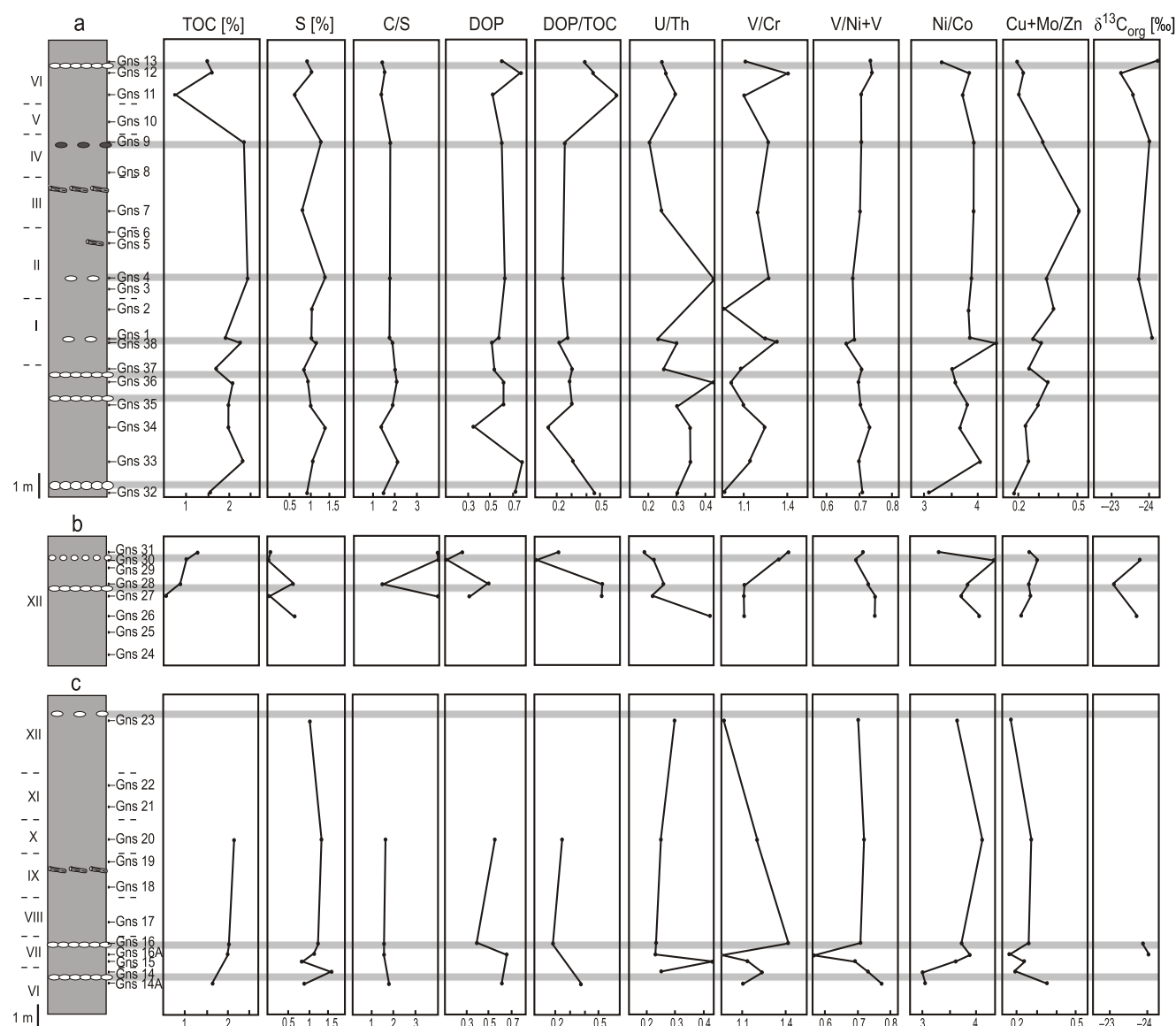


Fig. 2. Variation of geochemical data in the lithological column from Gnaszyn

Explanations as in Figure 1

tary rocks (e.g. Meyers, 1997). The differences in $\delta^{13}\text{C}$ values of organic matter may result from diagenesis, variations in plankton taxa, atmospheric CO_2 concentration, global seawater $\delta^{13}\text{C}$, selective preservation or CO_2 source (see Arthur *et al.*, 1985; Dean *et al.*, 1986; Meyers, 1997). It is important to note that the isotopic signature of organic carbon in the ancient rocks is substantially different from that in modern sediments.

According to the results presented by Hofmann *et al.* (2000) from Mid-Cretaceous black shales, isotopically light kerogen ($\delta^{13}\text{C}$ values around -29%) consist mainly of marine-derived liptinite, while isotopically heavy kerogens are dominated by land-derived vitrinite ($\delta^{13}\text{C}$ values around -23.3%). Langrock *et al.* (2003) observed that deposits rich in marine organic matter are characterized by $\delta^{13}\text{C}$ values from -25 to -30% , whereas the sequences rich in terrestrial organic components show values from -20 to -25% . The variation in carbon isotope values may reflect a mixing between marine and terrigenous end members.

The organic matter of the rocks studied show generally uniform $\delta^{13}\text{C}$ values around -23.3 to -24.4% PDB (Table 1), indicating mainly input of terrigenous material, possibly with some admixture of marine organic matter.

TOC/S (C/S) RATIO

In most marine environments the amount of TOC, not iron or sulphate availability, is the factor limiting the formation of sulphides. Organic carbon *vs.* sulphur (TOC/S) plots can be useful in characterizing modern and ancient depositional environments (Leventhal, 1983, 1987). They have been used to distinguish nonmarine *vs.* marine environments or oxic *vs.* anoxic or euxinic depositional environments (marine $0.5 < \text{TOC/S} < 5$; non-marine $\text{TOC/S} > 10$; Berner and Raiswell, 1984; Raiswell and Berner, 1985, 1986; Raiswell and Al-Biatty, 1989; Leventhal, 1987). Shallowly buried normal marine mudrocks have TOC/S values of 2.8 ± 0.8 , and this value decreases during

Table 1

Selected geochemical parameters characterizing the palaeoenvironmental conditions at Gnaszyn

Sample number	TOC [%]	S [%]	TOC/S	DOP	DOP/TOC	Fe _{Tot} [%]	Fe _{HCl} [%]	U/Th	Ni/Co	V/Cr	V/V+Ni	Cu+Mo/Zn	δ ¹³ C _{org} [‰]
Gns 1	1.97	1.06	1.84	0.58	0.29	3.4	0.66	0.24	3.8	1.25	0.69	0.28	-24.04
Gns 2	nd	1.06	nd	nd	nd	2.32	nd	0.49	3.7	0.51	0.66	0.39	nd
Gns 4	2.55	1.39	1.83	0.65	0.25	3.37	0.62	0.21	3.8	1.29	0.68	0.34	-23.75
Gns 7	nd	0.78	nd	nd	nd	2.26	nd	0.25	3.9	1.20	0.71	0.51	nd
Gns 9	2.43	1.30	1.86	0.61	0.25	3.25	0.72	0.22	3.9	1.29	0.71	0.33	-24.05
Gns 11	0.79	0.64	1.23	0.54	0.68	2.35	0.54	0.30	3.75	1.04	0.71	0.21	-23.64
Gns 12	1.62	1.01	1.59	0.73	0.45	2.62	0.31	0.26	3.7	1.41	0.74	0.23	-24.33
Gns 13	1.51	0.92	1.63	0.61	0.40	2.38	0.55	0.25	3.36	1.22	0.73	0.20	-24.31
Gns 14	nd	1.66	nd	nd	nd	2.87	nd	0.25	3.0	1.24	0.73	0.19	nd
Gns 14A	1.66	0.90	1.85	0.63	0.38	2.37	0.63	nd	3.13	1.03	0.77	0.35	nd
Gns 15	nd	0.86	nd	nd	nd	2.69	nd	0.43	3.61	1.13	0.69	0.22	nd
Gns 16	2.02	1.24	1.62	0.39	0.19	3.64	1.63	0.23	3.7	1.42	0.71	0.23	-24.04
Gns 16A	2.00	1.14	1.75	0.65	0.32	2.70	0.59	0.24	3.85	0.41	0.42	0.18	nd
Gns 20	2.17	1.29	1.68	0.56	0.25	3.43	0.87	0.25	4.2	1.20	0.72	0.27	-23.81
Gns 23	nd	1.03	nd	nd	nd	2.87	nd	0.31	3.64	0.98	0.70	0.18	nd
Gns 26	nd	0.66	nd	nd	nd	2.12	nd	0.43	4.11	1.14	0.70	0.22	nd
Gns 27	0.60	0.13	4.61	0.33	0.55	1.80	0.22	0.22	3.7	1.11	0.75	0.28	-23.75
Gns 28	0.97	0.61	1.57	0.53	0.54	2.10	0.47	0.26	3.8	1.11	0.73	0.27	-23.21
Gns 30	1.06	0.03	33.12	0.09	0.08	3.91	0.19	0.23	4.46	1.36	0.69	0.30	-23.82
Gns 31	1.27	0.15	8.69	0.28	0.22	2.53	0.14	0.19	3.3	1.42	0.72	0.27	nd
Gns 32	1.53	0.98	1.57	0.72	0.47	2.51	0.34	0.31	3.15	0.88	0.71	0.19	-23.65
Gns 33	2.46	1.12	2.19	0.77	0.31	2.95	0.28	0.35	4.17	1.15	0.70	0.25	nd
Gns 34	2.04	1.40	1.45	0.35	0.17	2.86	0.65	0.35	3.67	1.25	0.73	0.22	nd
Gns 35	2.01	1.06	1.90	0.63	0.31	2.94	0.55	0.31	3.83	1.10	0.71	0.30	nd
Gns 36	2.10	0.98	2.14	0.62	0.29	2.42	0.53	0.49	3.58	1.03	0.70	0.35	nd
Gns 37	1.74	0.84	2.08	0.56	0.32	2.32	0.57	0.27	3.54	1.09	0.71	0.26	nd
Gns 38	2.37	1.20	1.97	0.53	0.22	3.58	0.94	0.30	5.28	1.33	0.66	0.31	-24.03

nd — not determined

Table 2

Results of the Rock-Eval analyses of Gnaszyn samples

Sample number	T _{max} [°C]	S ₁	S ₂	S ₃	PI	HI	OI
Gns 1	423	0.12	0.52	0.95	0.19	33	61
Gns 4	421	0.02	0.42	0.72	0.05	23	40
Gns 9	422	0.04	0.35	0.69	0.10	26	50
Gns 11	401?	0.05	0.08?	0.72	0.38	17	157
Gns 13	421	0.04	0.28	0.56	0.13	34	67
Gns 20	422	0.06	0.50	0.92	0.11	30	56
Gns 28	435?	0.04	0.03?	0.75	0.57	11	278
Gns 30	388?	0.10	0.14 ?	0.99	0.42	22	152

? — defines unreliable determination

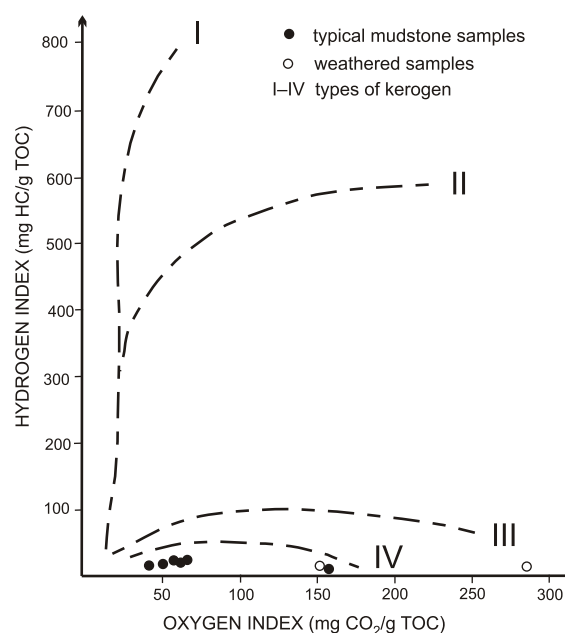


Fig. 3. Rock-Eval results for Gnaszyn samples

burial due to organic matter maturation (Raiswell and Berner, 1987). In marine deposits underlying oxic water, pyrite is formed in the sediments during early diagenesis (Goldhaber and Kaplan, 1974; Berner, 1984). Ancient mudstones from an oxic (normal marine) environment show a good correlation between organic carbon and sulphur because pyrite production is usually limited by the availability of biologically metabolizable organic matter (Berner, 1984), and sulphide retention and carbon preservation are often coupled (Berner and Westrich, 1985). Intersection of the S axis on the TOC-S plot and the curve of the slope may also characterize a palaeoenvironment (Berner and Raiswell, 1983; Leventhal, 1983). Mudstones deposited under oxic conditions tend to have a TOC-S plot with regress through the origin. The TOC/S ratio for samples deposited under euxinic (anoxic-sulphidic water column) conditions decreases (with a positive S intercept; Raiswell and Berner, 1986; Leventhal, 1983, 1987, 1995).

The samples studied show a generally positive TOC-S correlation and fall in the region of normal marine environments on the TOC/S plot (Fig. 4; Wignall, 1994; and references cited therein). The low TOC/S ratios found in this study (1.57–1.86) indicate marine environments (Leventhal 1983; Raiswell and Berner, 1985). A positive correlation between TOC and pyritic sulphur and the intercept on the origin represents normal marine conditions (Berner, 1984), and thus may suggest organic matter as the limiting factor for pyrite formation.

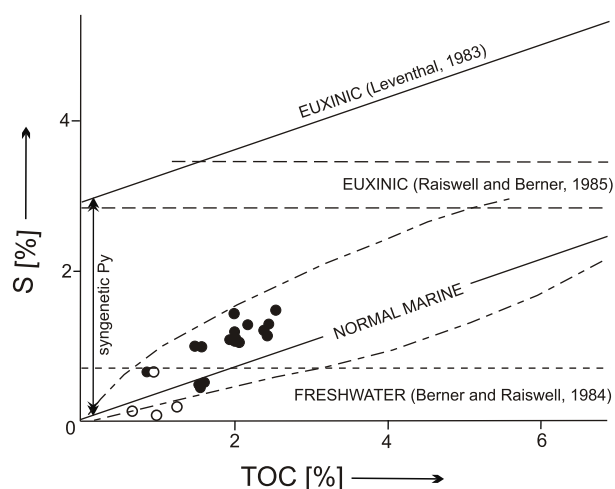


Fig. 4. Organic carbon vs. pyrite sulphur plot (from Wignall, 1994) for selected samples from Gnaszyn

Typical fields for normal (oxic) marine, euxinic water column and freshwater settings are indicated; other explanations as in Figure 3

DOP

Pyrite morphology and degree of pyritization (DOP) are often applied for evaluation of palaeo-depositional redox conditions in marine environments. DOP is defined as the proportion of pyrite Fe (Fe_{Py} , fraction of iron associated with pyrite) relative to pyrite Fe plus acid-soluble Fe (Fe_{HCL} fraction of iron that easily reacts with dissolved sulphide to produce iron monosulphides and pyrite; Berner, 1970; Raiswell *et al.*, 1988). According to Raiswell *et al.* (1988) in fine-grained sediments DOP values of <0.46, 0.46–0.75 and >0.75 indicate aerobic,

dysoxic or restricted, and anoxic sediments with dissolved H_2S in bottom waters, respectively. DOP demonstrates also iron or sulphur limitation in pyrite formation. DOP values approaching unity indicate iron-limiting conditions, which commonly occurred in ancient euxinic or semi-euxinic sedimentary environments (Raiswell and Berner, 1985).

DOP values for samples from Gnaszyn vary between 0.53 and 0.73 (except Gns 16 = 0.33), indicating dysoxic conditions (Raiswell *et al.*, 1988). A low DOP index for Gns 16 sample may result from incorporation of iron into the siderite concretions (the sample was taken from mudstones between siderite levels).

TOC-Fe-S RELATIONSHIP

Raiswell and Berner (1985) suggested a relationship between TOC vs. Fe vs. S as useful to distinguish environments of pyrite formation, where limiting factors are organic carbon or iron. In normal marine environments organic matter may be a factor restricting bacterial sulphate reduction (BSR), which is reflected in a positive correlation between TOC and pyrite sulphur (Berner and Raiswell, 1983; Berner, 1984; Raiswell and Berner, 1986). On the other hand, reactive iron may be a restricting factor for pyrite formation in euxinic environments (Raiswell and Berner, 1985) where H_2S production is much higher than Fe availability. The relatively high DOP values of sediments and the absence of a relationship between DOP and organic carbon contents may suggest iron limitation in pyrite formation (Raiswell and Berner, 1985; Lyons and Berner, 1992).

The data for the samples studied are plotted on a TOC-Fe-S ternary diagram (Fig. 5). The diagram displays the limiting factors for pyrite formation to evaluate the depositional conditions (e.g. Berner and Raiswell, 1983; Berner, 1984; Brumsack, 1988; Dean and Arthur, 1989; Hofmann *et al.*, 2000). Formation of pyrite below the stoichiometric pyrite ratio line ($S/Fe = 1.15$) is limited mostly by reactive iron and reflects anoxic conditions. Above the line, pyrite formation is limited by the amount or specific composition of organic matter.

The TOC-Fe-S diagram shown on Figure 5 provides insights into the controls on pyrite formation in the Gnaszyn sections. Most points plot within a relatively narrow field (Fig. 5), reflecting a low variability between the parameters. The Gnaszyn samples cluster along a line with a constant TOC/S ratio of 2, indicating deposition in normal marine environments, under oxic or suboxic conditions (Berner and Raiswell, 1985; Dean and Arthur, 1989). The position of the samples above the $S/Fe = 1.15$ line (Fig. 5) suggests that the pyrite formation was probably limited by the availability of labile hydrogen-rich organic matter (comp. Hoffman *et al.*, 2000).

Samples from the highest part of the section reveal TOC/S ratios above 4.6 (except GNS 28; open circles on Fig. 5) which would correspond to a freshwater environment (Berner and Raiswell, 1984). However, this parameter is not useful here because the samples are weathered.

PYRITE

Pyrite framboid size distribution has been shown to be a suitable indicator of ancient oxygen levels, with euxinic conditions having a particularly diagnostic size distribution (Wilkin

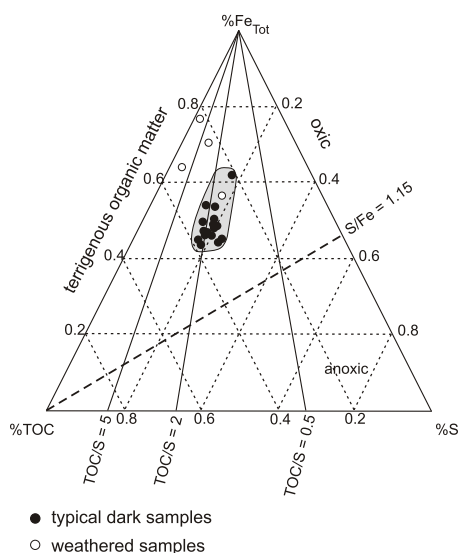


Fig. 5. Fe-TOC-S ternary diagram (based on Dean and Arthur, 1989) from Gnaszyn samples

According to Berner and Raiswell (1984) area between $0.5 < \text{TOC/S} < 5$ represents marine environments (with $\text{TOC/S} = 2$ for normal marine Upper Cretaceous shale); the $\text{TOC/S} = 5$ line is the boundary between fresh vs. marine systems; dashed line represents a stoichiometric pyrite ratio ($\text{S/Fe} = 1.15$)

et al., 1996; Wignall and Newton, 1998). Pyrite is common in the samples studied. It occurs in various morphological forms; the majority as euhedra, with aggregates and framboids in minor amounts, both in the deposits and in microfossils. Most pyrite is found inside shelly microfossils and this cannot be used for the interpretation of the depositional palaeoenvironment because its formation strictly depends on the chemistry of the microenvironment inside the organic-rich skeletons. The size of pyrite framboids in the deposits studied is generally between 5 to 25 μm , occasionally reaching 50 μm . The wide range of pyrite framboid sizes suggests that they did not form in a euxinic water column.

TRACE ELEMENTS

The V/Cr ratio has been suggested as an index of palaeo-oxidation in many studies (e.g., Ernst, 1970; Dill, 1986; Dill *et al.*, 1988). This parameter may be dependent on grain size and on carbonate content (Ernst, 1970). Values of $\text{V/Cr} > 2$ indicate anoxic depositional conditions, with H_2S present in the water overlying the sediment, whereas values of < 1 indicate normal oxic conditions (Ernst, 1970; Krejci-Graf, 1975; Dill, 1986). On the other hand, Jones and Manning (1994) suggested a V/Cr ratio of ~ 4.25 as indicating the dysoxic to oxic transition. The V/Cr ratio of the samples studied is between 1.1 and 1.4, and suggests relatively oxidizing conditions.

The Ni/Co ratio has often been used as a redox index (e.g. Dypvik, 1984; Dill, 1986). In mudstones deposited beneath an oxic water column the Ni/Co ratio is usually < 5 , with values of 5–7 indicative of a dysoxic water column. A Ni/Co ratio around 7 indicates a transition from dysoxic to suboxic and anoxic water column conditions (Jones and Manning, 1994). Samples from Gnaszyn have Ni/Co values between 3.3 and 4.46, indicating deposition beneath a relatively oxic water column.

The whole-rock V/Ni+V ratio has been used as a parameter distinguishing oxic and anoxic bottom waters by Hatch and Leventhal (1992). It is dependent on pH, Eh and sulphur contents (Lewan, 1984). Vanadium accumulates in strongly reducing environments (Lewan, 1984; Emerson and Huested, 1991), being concentrated usually in organic matter but occasionally also in detrital silicate minerals (Glikson *et al.*, 1985). As vanadium is associated with organic matter it correlates with TOC. Ni content is controlled by the sulphide content (e.g., Ni residing in framboidal pyrite) and co-varies with sulphur (Jones and Manning, 1994), but occasionally can reside in organic matter as nickel porphyrins (e.g. Sawłowicz, 1986). According to Hatch and Leventhal (1992) a high V/V+Ni ratio (> 0.84) indicates the presence of H_2S in the water column (euxinic conditions); a ratio between 0.54 to 0.82 and 0.46–0.60 represents anoxic and dysoxic water conditions, respectively. In samples from Gnaszyn the V/Ni+V ratios are generally uniform and relatively high (0.68–0.75), suggesting anoxic environments.

Thorium and uranium contents and the U/Th or Th/U ratios have been used as a measure of redox conditions in the depositional environment. According to Jones and Manning (1994) the U/Th ratio is generally a more reliable redox indicator than the V/Cr and Ni/Co ratios. Uranium is commonly associated with the organic carbon fraction (e.g. Leventhal, 1981; Hammer *et al.*, 1990; Jones and Manning, 1994). Therefore, the U/Th ratio has been applied as a redox indicator, with low values (< 0.75) typical of more oxic settings and high values reflecting dysoxic (0.75–1.25) and suboxic-anoxic (> 1.25) depositional conditions (Jones and Manning, 1994). Normal marine mudrocks deposited beneath oxygenated bottom waters typically have Th/U ratios between 3 and 5, and lower ratios ($\text{Th/U} < 2$) generally coincide with dysaerobic biofacies (Myers and Wignall, 1987; Wignall and Myers, 1988; Wignall, 1994). Authigenic U ($U_{\text{aut}} = U_{\text{tot}} - \text{Th}/3$) is a suitable indicator of benthic redox conditions. Its values below 5.5 to 12, and above 12 indicate an oxygenated, dysoxic, and suboxic to anoxic water column, respectively (Myers and Wignall, 1987; Jones and Manning, 1994). Th/U (3.7–5.2) and U/Th (0.19–0.49) ratios and the lack of authigenic U in the Gnaszyn samples suggest oxic conditions of mudstone deposition.

The ratio $(\text{Cu} + \text{Mo})/\text{Zn}$ has been proposed by Hallberg (1976, 1982) and Dypvik (1984) as an indicator of the oxygenation of bottom waters. The values of this parameter increase under reducing conditions and decrease when the environment is more oxidizing (e.g., a range between 0.1 and 6 was recorded for the Baltic Sea; Hallberg, 1976, 1982). The ratios $(\text{Cu} + \text{Mo})/\text{Zn}$ for the samples from Gnaszyn are low (0.23–0.34) and suggest oxygenated bottom waters conditions.

DISCUSSION

The succession exposed in Gnaszyn is relatively uniform and monotonous in respect to mineralogy, with the notable exception of siderite and silica nodule levels.

The geochemical parameters are also relatively similar throughout the lithological column and suggest little redox change during deposition and early diagenesis. Determination

of palaeoenvironment is not easy, especially when the different groups of parameters give conflicting results. In our case the majority of the environmental indices: TOC/S, Ni/Co, V/Cr, U/Th, (Cu+Mo)/Zn ratios, content of authigenic uranium, and relationship between TOC-Fe-S, point to oxic conditions during deposition. The geochemical data span a relatively large range but always fit well with deposition under oxygenated waters and their position is never close to the dysoxic boundary. Comparison with sedimentological and palaeontological observations on the same Gnaszyn section (Gedl *et al.*, 2003, 2006) suggests that although the latter also indicate oxic conditions they are more precise than geochemical indices in determining subtle changes in temporarily stressed environments.

On the other hand, the DOP and V/V+Ni indices point to a dysoxic/anoxic environment. The latter indices were probably influenced by diagenetic processes. Generally, conditions in the sediment during diagenesis change towards more reduced, compared with the overlying water column. In the environment of the Jurassic rocks studied where pyrite forms only diagenetically, the DOP would reflect redox conditions in the sediment during diagenesis rather than in the overlying water column. This also agrees with the conclusion of Roychoudhury *et al.* (2003) who stated that DOP values reflect the chemistry of the sediment and its pore waters rather than conditions in the water column during deposition and pyrite formation. The significance of the V/V+Ni ratio for determination of redox conditions in the rocks studied is disputable. The V/V+Ni ratio works well mainly when vanadium is accumulated by organic matter as vanadyl-porphyrins (Lewan, 1984) in an anoxic environment and the Ni content is relatively stable and independent of redox conditions. A high V/V+Ni ratio originates either from high V or low Ni contents. When the nickel content is relatively low the high V/V+Ni ratio will show a false picture of redox conditions. Two nickel carriers are important in dark sediments: organic matter (Ni-porphyrins) and pyrite. In the rocks studied Ni probably did not accumulate as porphyrins because of their low preservation potential in an environment where mainly terrigenous organic matter is preserved. Korolev (1958) showed experimentally that coarsely crystalline pyrite in contrast to fine-grained and framboidal pyrite had only minor amounts of Mo due to its loss in the aging process and suggested that a similar process would be important for Ni and Co. In the samples studied pyrite euhedra dominate and we expect a low content of Ni in pyrite. A low content of Ni in the rocks studied is confirmed by geochemical data. The average content of Ni is 46 ppm (V = 115 ppm), being lower not only in comparison to the Atlantic Cretaceous black shales (av. Ni = 186 ppm, av. V = 822 ppm; Brumsack, 1980) but also to the "average" shale (av. Ni = 68 ppm, av. V = 130 ppm; Wedepohl, 1970). In conclusion we doubt in the significance of the V/V+Ni ratio for determination of redox conditions in the rocks studied.

The pyrite framboids generally show large dimensions and a wide size range. This suggests that they did not form in a euxinic water column but during early diagenesis. Formation and accumulation of pyrite during early diagenesis is controlled by a number of environmental factors including the availability of iron, sulphate, organic carbon, and pyrite oxidation rate (e.g. Berner, 1970, 1984; Raiswell and Canfield, 1998). In a normal marine environment the main factor limiting

pyrite formation is organic matter (Berner, 1984), as is also confirmed by the low values of the TOC/S ratio and the TOC-S correlation, and also TOC-S-Fe relationships in the samples.

The organic matter preserved in the rocks studied is characterized by a low H/C ratio and generally high O/C values representing type III and/or IV kerogen. The type III or remnant IV kerogen can accumulate under oxic and upper dysoxic conditions, whereas types I and II are thought to require anoxic/suboxic conditions (Wignall, 1994). The $\delta^{13}\text{C}$ composition of organic carbon also reflects mainly terrigenous, though perhaps with some admixture of marine, input of organic matter. An organic geochemical study of carbonate nodules from comparable Middle Jurassic rocks from the Kraków–Częstochowa Upland also showed generally well oxygenated conditions of deposition in the sedimentary basin and a predominantly terrestrial type of organic matter (Zatoń and Marynowski, 2004). We cannot exclude primarily higher amounts of marine organic matter which is generally less resistant to decomposition than the terrigenous organic matter, especially in oxidizing conditions.

We attempted to evaluate the possible influence of the common siderite nodules horizons on environmental geochemical indices of the host rocks. There is a significant difference in the type of nodules between horizons. Their mineralogical composition varies between siderite, siderite and pyrite, and siderite, apatite and pyrite. However, we have not found any significant relationship between geochemical indices of host rocks with nodules and those without them. Although the values of the geochemical parameters of palaeoenvironment are generally similar throughout the section (note the expanded scale of concentrations and ratios of elements on Fig. 2), some of indices, especially those related to diagenesis, could have been influenced to some extent by the nodule horizons. An example could be the mudstone sample Gns 16, originating from the horizon with siderite nodules, which has a lower DOP value. This value was probably modified by incorporation of available iron in sediment into the siderite nodules. A detailed study of the relationship between the nodules and the Jurassic host sediments of the Kraków–Częstochowa Upland is under way.

The samples from the highest part of the lithological section show different values of geochemical indices in comparison to those in the lower part of the section. These values are typical of oxidizing conditions, though, the rusty colour and pseudomorphs of iron oxides after pyrite suggest secondary processes of oxidation in these samples. The weathering processes blurred the primary depositional signals and thus evaluation of the depositional conditions of the upper part of the section cannot be performed. These samples will be described in detail elsewhere.

CONCLUSIONS

Most of the geochemical environmental parameters studied from the Częstochowa Clay Fm. exposed at Gnaszyn point to deposition under oxygenated bottom water conditions. We suggest that geochemical indices are less precise than palaeontological data coupled with sedimentological ones in determining subtle changes in temporarily stressed environments.

DOP and V/V+Ni indices point to a dysoxic/anoxic environment. We assume that when pyrite forms only diagenetically, DOP would reflect redox conditions during diagenesis. High V/V+Ni ratio probably shows a false picture of redox conditions because of the relatively low nickel content.

The type III kerogen and its $\delta^{13}\text{C}$ reflect mainly terrigenous, with some admixture of marine, input of organic matter.

There is no significant difference between the geochemical indices of the host rocks with nodules and of without them.

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