Ordovician Jeleniów Claystone Formation of the Holy Cross Mountains, Poland – Reconstruction of redox conditions using pyrite framboid study

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Abstract
The aim of this research is to reconstruct palaeoredox conditions during sedimentation of the Jeleniów Claystone Formation deposits, using framboid pyrite diameter measurements. Analysis of pyrite framboids diameter distribution is an effective method in the palaeoenvironmental interpretation which allow for a more detailed insight into the redox conditions, and thus the distinction between euxinic, dysoxic and anoxic conditions. Most of the samples is characterized by framboid indicators typical for anoxic/euxinic conditions in the water column, with average (mean) values ranging from 5.29 to 6.02 µm and quite low standard deviation (SD) values ranging from 1.49 to 3.0. The remaining samples have shown slightly higher values of framboid diameter typical for upper dysoxic conditions, with average values (6.37 to 7.20 µm) and low standard deviation (SD) values (1.88 to 2.88). From the depth of 75.5 m till the shallowest part of the Jeleniów Claystone Formation, two samples have been examined and no framboids has been detected. Because secondary weathering should be excluded, the lack of framboids possibly indicates oxic conditions in the water column. Oxic conditions continue within the Wólka Formation based on the lack of framboids in the ZB 51.6 sample.

Key words: Ordovician, pyrite framboids, redox conditions, Jeleniów Formation

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Introduction

Jeleniów Claystone Formation

Jeleniów Claystone Formation (JCF) is one of 17 lithographic formations distinguished in Ordovician of the Holy Cross Mountains (Trela 2006). Name of the formation comes from the town Jeleniów located approximately 3 kilometers SE of Nowa Słupia (Fig.1). Previous name, Claystone Formation from Jeleniów, was established by Bednarczyk (1981). The formation described, with a thickness of up to 120 m, consists of dark-gray, sometimes black claystones and locally occurring gray claystones with a green shade. Thin interlayers and lenses of gray marly limestone (especially in the basal part), bentonites and small phosphate concretions are also quite common (Trela 2006). The stratotype of the formation (cores from the boreholes: Jeleniów-2, Wilków IG–1 and Daromin IG–1) is stored in the archives of the Polish Geological Institute - National Research Institute, Holy Cross Mountains Branch in Kielce. For the lower boundary of the unit a thin (10 cm) layer of dark phosphate (Daromin IG-1, depth. 399.9 m) has been

indicated (see Trela et al. 2006), whereas upper contact is characterized by gradual transition to gray-green and green, bioturbated claystone and clayey mudstone (Daromin IG-1 at depth 207.0 m, Wilków IG-1 at depth 676.0 m - see Trela 2003; Trela et al. 2006). The deposits of the Jeleniów Claystone Formation occur in the Łysogóry Region and Zbrza-Brzeziny area (see Tomczyk & Turnau-Morawska 1964, 1967; Tomczykowa 1968; Deczkowski & Tomczyk 1969, Bednarczyk 1971). The age of the formation was dated on the uppermost Llanvirn/Caradoc on the basis of graptolites belonging to the *teretiusculus, gracilis, multidens, clingani* and partly *styloides* zones (Tomczyk & Turnau-Morawska 1964, 1967; Tomczykowa 1968; Deczkowski & Tomczyk 1969; Tomczykowa & Tomczyk 2000).

Pyrite framboid diameter study

Analysis of pyrite framboid diameter distribution is an effective method in the paleoenvironmental interpretation (e.g., Wignall and Newton 1998; Zatoń et al. 2008). It allows for a more detailed insight into the redox conditions, and thus the distinction between the euxinic (lower part of the column where the water is devoid of oxygen but contains hydrogen sulfide), dysoxic (oxygen-poor) or anoxic (lack of oxygen and hydrogen sulfide) conditions (see Wignall & Newton 1998). Wilkin et al. (1996) distinguished two types of framboids: syngenetic (diameter <6 μm) which are less diverse in size, forming in the water column and after reaching a critical diameter of about 5 μm (the critical weight) they begin to sink to the bottom; and diagenetic framboids (about 7 ± 4 μm in diameter), forming in the sediment under oxygenated or dysoxic water column. Importantly, syngenetic framboids do not grow following their accumulation at the sea-bottom and gradual burial, but later their size may be increased by secondary growth of euhedral pyrites. It allows to distinguish syngenetic from diagenetic framboids based on low values of the mean and the standard deviation (Wignall & Newton 1998; Zatoń et al. 2008). Moreover, the additional element that allows to distinguish anoxic from euxinic, or from more aerobic conditions is proportion of pyrite framboids to other forms of pyrite in the sample. It is known that the sediments deposited in the oxic and dysoxic environment contain much higher amount of other forms of pyrite, such as the most common euhedral pyrite crystals (Zatoń et al. 2008).

The aim of this research is to reconstruct palaeoredox conditions during sedimentation of the JCF deposits, using for the first time pyrite framboid diameter study and compare the obtained results with sedimentological and geochemical data published elsewhere (Trela 2007, Zhang et al. 2011).

Materials and methods

Ten samples were collected from the Zbrza PIG 1 borehole (Fig.1), comprising various claystones and black shales. All samples in the form of small chips were polished, and examined for pyrite framboids in uncoated state using back-scattered electron (BSE) imaging with the aid of Philips XL30 Environmental Scanning Electron Microscope (ESEM) at the Faculty of Earth Sciences (Sosnowiec, Poland). Framboid diameters (in μm) were measured using the ESEM internal measuring device. At least 100 specimens were measured (when possible) in each sample. The minimum, maximum and mean diameter of framboids in each sample, as well as their standard deviation are presented on Figures 2 and 3. Framboid size-frequency distributions are depicted in the form of box-and-whisker plots (see e.g. Wignall and Newton, 1998), and for samples we have produced histograms to better show the size-frequency of a given framboid population.

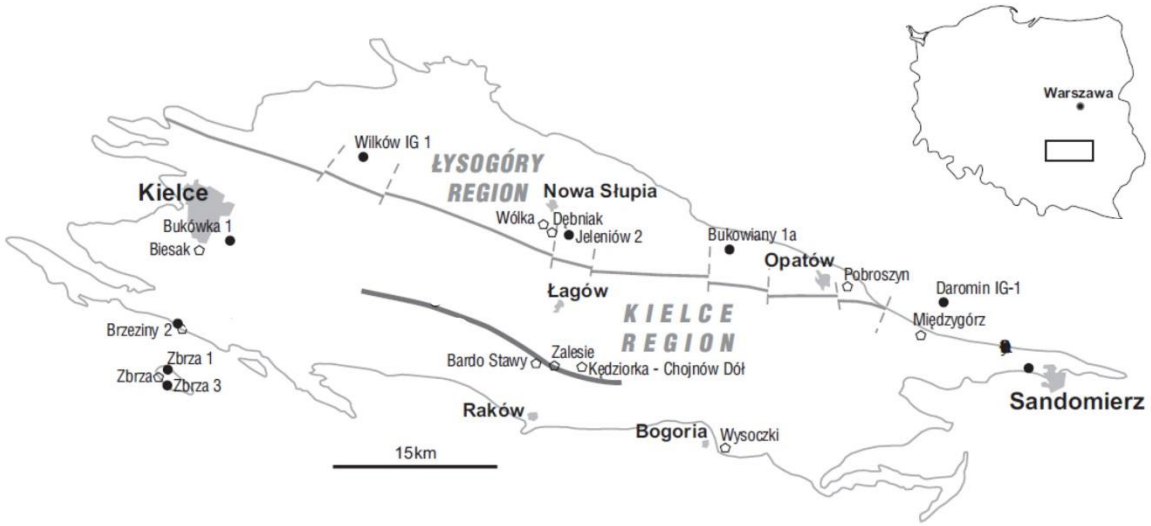

Fig.1. Location of the Zbrza PIG 1 borehole and the locations of Ordovician deposits in the Holy Cross Mts. Black circles denote boreholes, pentagons denote outcrops.

Results

Pyrite framboids are common in all the Sandbian claystones. In every sample 100 measurements have been carried out (Figs. 2-4). Most of the samples (ZB 79.8; ZB 85.5; ZB 87.2; ZB 93.0; ZB 100.0) is characterized by framboid indicators typical for anoxic/euxinic conditions in the water column, with average values ranging from 5.29 to 6.02 µm, low minimum values (Min FD) ranging from 1.83 to 3.05 µm, quite low maximum values (Max FD) from 9.61 to 27.0 µm, as well as low standard deviation (SD) values (1.49 to 3.0, Figs. 2-5). The remaining samples (ZB 76.7; ZB 90.4; ZB 98.2) have shown slightly higher values of framboid diameters typical for upper dysoxic conditions, with average values from 6.37 to 7.20 µm, low minimum values (Min FD) ranging from 2.70 to 3.58 µm, maximum values (Max FD) from 13.9 to 21.20 µm, and quite low standard deviation (SD) values from 1.88 to 2.88 (Figs. 2, 3 & 5). From the depth of 75.5 m till the shallowest part of the Jeleniów Claystone Formation, two samples (ZB 75.7; ZB 63.7) have been examined and no framboids has been detected (Fig.5). A lack of framboids suggests oxic conditions in the water column, especially that we observed no evidence for secondary weathering processes. Oxic conditions continue within the Wólka Formation based on the lack of framboids in the ZB 51.6 sample (Fig. 5)

Discussion

Pyrite framboid study of the Jeleniów Claystone Formation from the Zbrza PIG 1 borehole has shown anoxic/euxinic conditions in the water column in prevalent part of the profile (Fig.5). Based on sedimentological and stratigraphic data provided by Trela (2007), claystones from the Jeleniów Formation were accumulated in oxygen-deficient conditions, prevailing at the bottom zone of the water column, except for a brief oxygenation episode in the middle Sandbian. Single framboids with larger diameters and generally higher values of diameters measured for all framboids, can be a result of short episodes enriched in oxygen caused by changes in the sea- level. Such kind of slightly higher enrichment in oxygen has been found in samples ZB 87.2 and ZB 90.4, which can be a result of described episode.

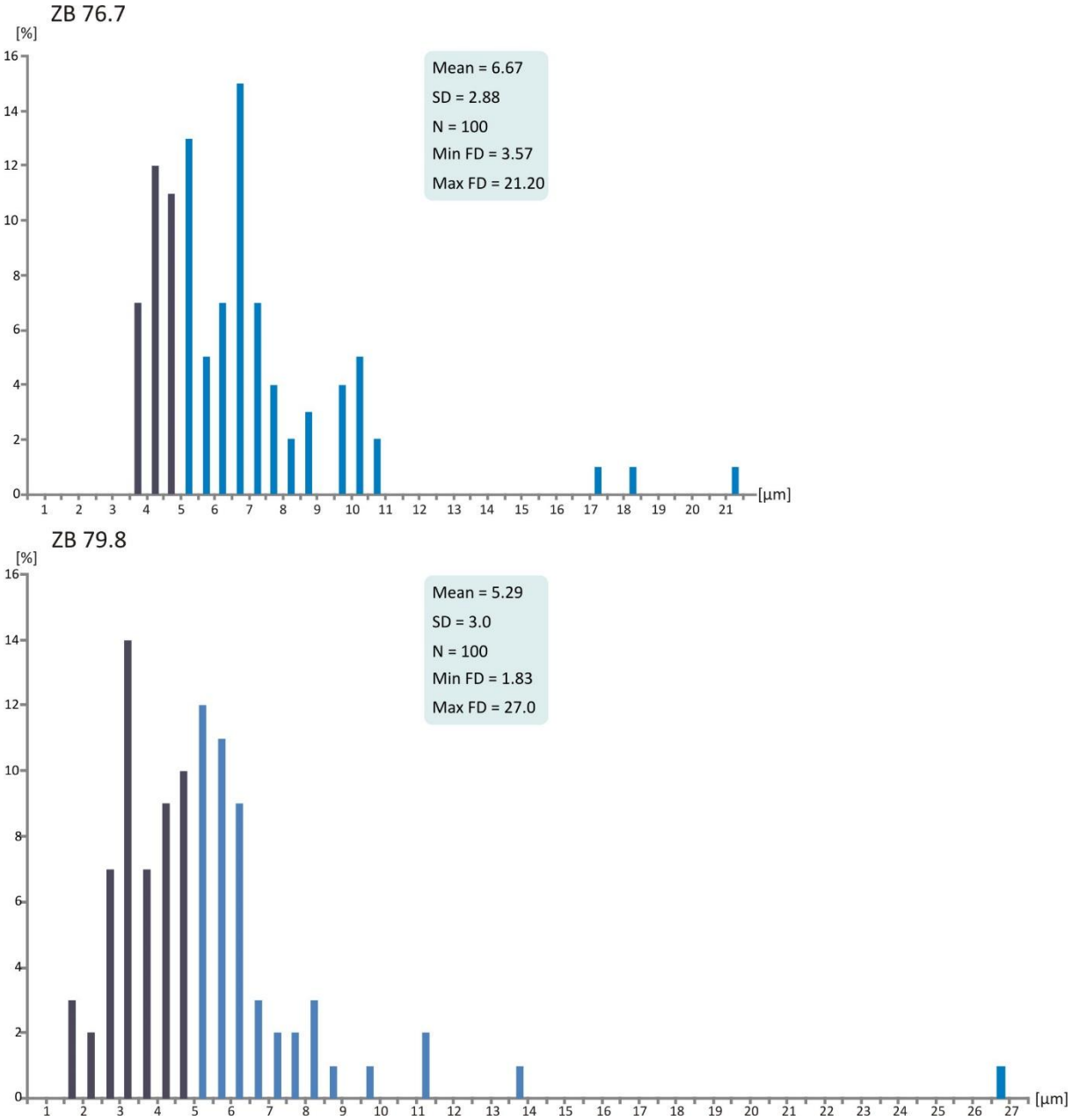

Fig.2. Histograms of samples from the Zbrza PIG 1 borehole showing the pyrite framboid size distribution; N — number of measurements, Min FD. — minimum value of framboid diameter in µm, Max FD. — maximum value of framboid diameters in µm, Mean. — mean value of framboid diameters in µm, SD — standard deviation.

Recently Zhang et al. (2011) compared geochemical results for the Jeleniów and Wólka formations from the Wilków and Daromin boreholes of the Łysogóry region (Holy Cross Mountains). They found much higher TOC and V/(V+Ni) values for the Jeleniów Formation in comparison to Wólka Formation, suggesting restricted anoxic conditions during deposition of the JCF. Sedimentation of claystones from the JCF in the Łysogóry Region was a part of the facies configuration, which was formed at the shelf of western and south-western Baltica (Thickpenny & Leggett 1987). According to the cited authors, dark shales of the Caradoc were formed in stagnant basin, which evolved as a consequence of the Tornquist Ocean closure and restriction of the Iapetus Ocean.

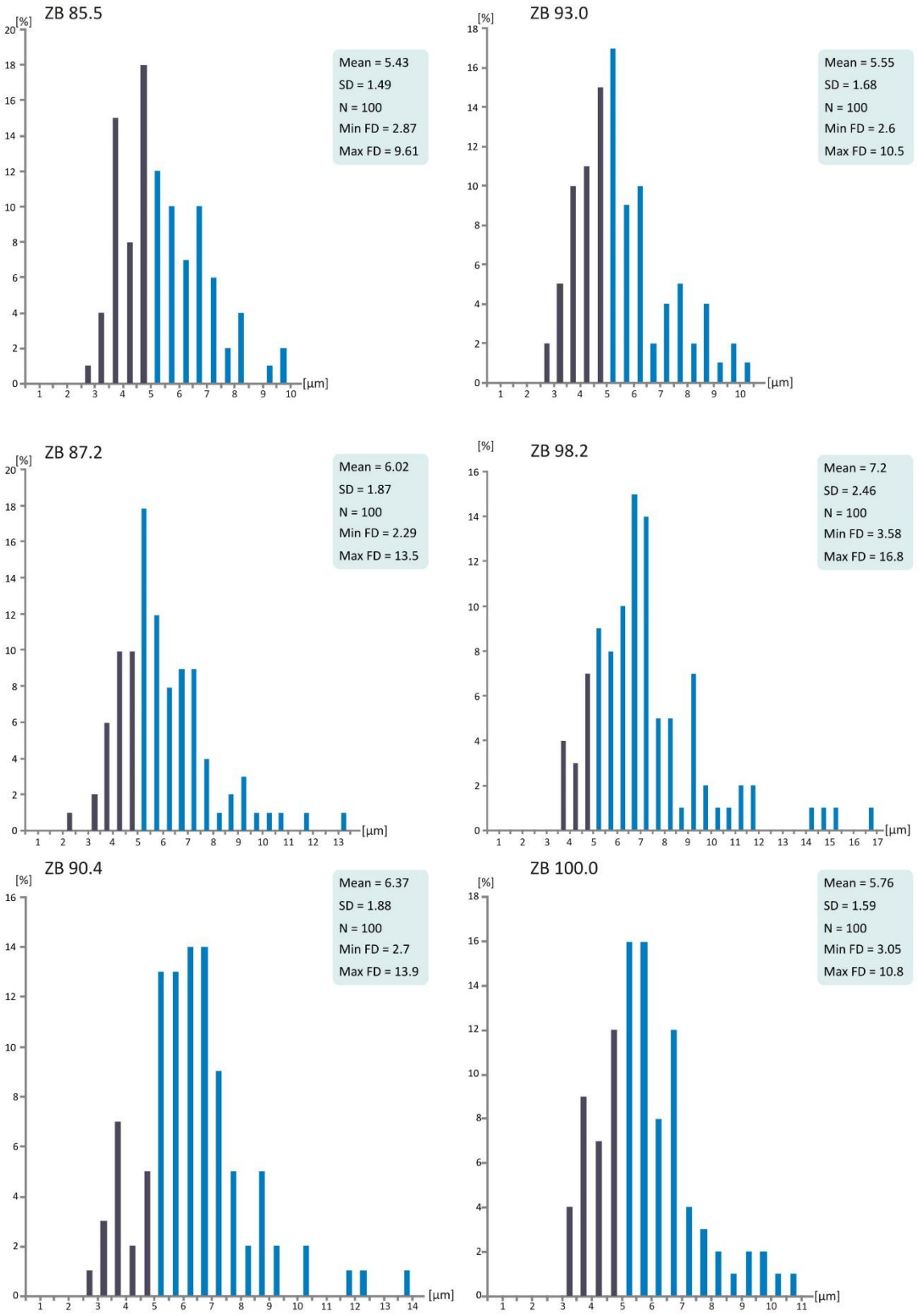

Fig.3. Histograms of samples from the Zbrza PIG 1 borehole showing the pyrite framboid size distribution; N — number of measurements, Min FD. — minimum value of framboid diameter in µm, Max FD. — maximum value of framboid diameters in µm, Mean. — mean value of framboid diameters in µm, SD — standard deviation.

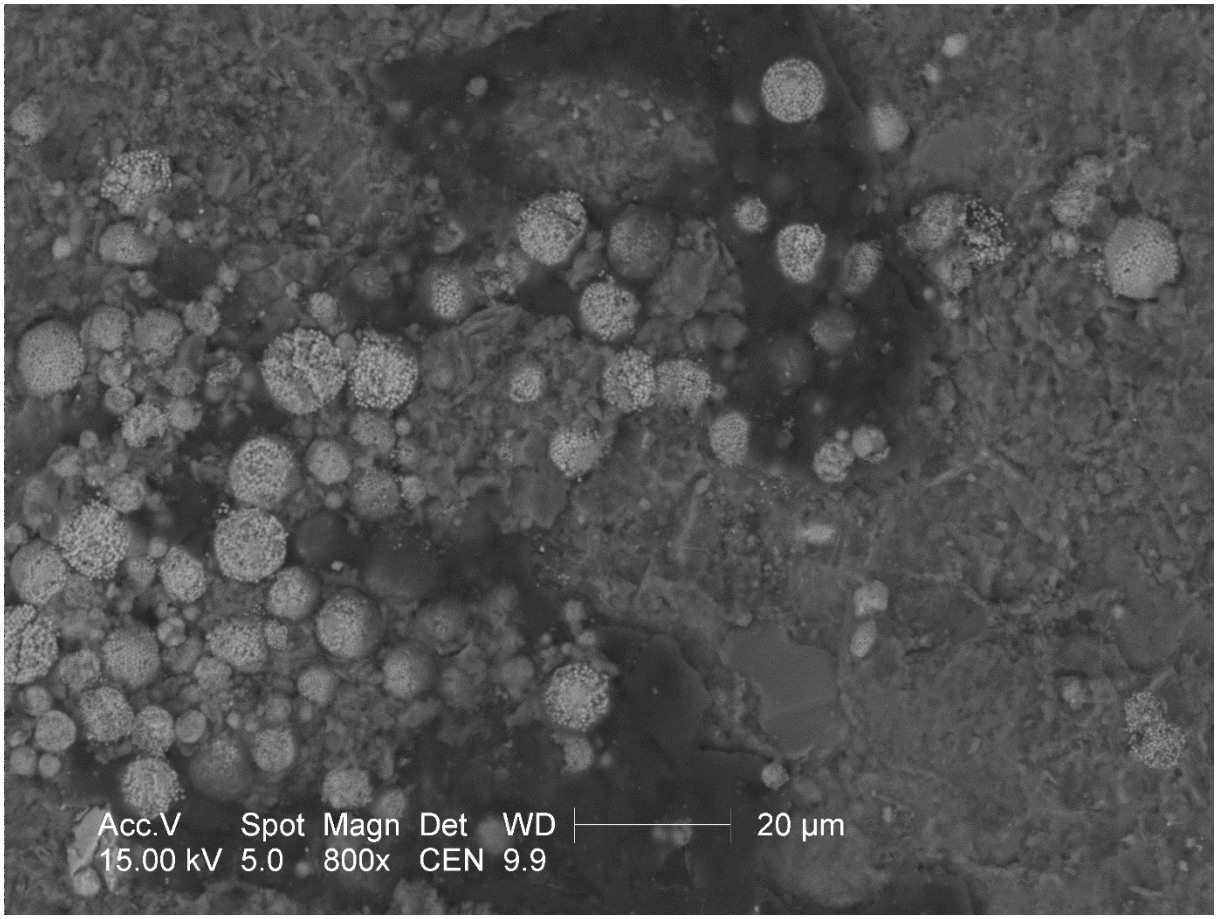

Fig.4. Example of pyrite framboids from the Zbrza PIG 1 borehole (sample ZB 76.7).

In the middle Sandbian, there was a short-lived increase of oxygen saturation of the sediment and the water column in the deeper parts of the Łysogóry basin (Trela 2007), which coincided in time with the low state of the sea-level on the Baltica (Nielsen 2004). Renewed stagnation of the Łysogóry basin at the end of Sandbian and in the early Katian (middle/late Caradoc) resulted in the return of oxygen-deficient conditions in the lower zone of the water column (Trela 2009). In view of data connecting the glacier growth of Gondwana from the late Sandbian (Pope & Read 1998), it can be assumed that these changes, also described from the Polish part of the East European Craton (Modliński 1982), resulted from different oceanographic conditions. The shallowest part of the JCF and beginning of the Wólka Formation are characterized by the lack of framboids which suggest oxic conditions in the water column (Fig.5). Sustainable growth of oxygenation in the water column has been documented by the gray-green claystone and marly mudstones from the Wólka Formation (Trela 2007, Zhang et al. 2011). Beginning of the Wólka Formation sedimentation coincides in time with the interval of low sea-level documented on the Baltica (Ashgill Lowstand Interval, see. Nielsen, 2004). Our data from the Zbrza IG1 well suggests that in the Kielce region (S part of the Holy Cross Mountains), oxygenation of water masses took place during the upper part of the Jeleniów Formation, at an earlier stage than in the Łysogóry region (N part of the Holy Cross Mountains).

Conclusions

- pyrite framboid study of the Jeleniów Claystone Formation from the Zbrza PIG 1 borehole has shown anoxic/euxinic conditions in the water column in prevalent part of the section
- slightly higher enrichment in oxygen has been detected in samples ZB 87.2 to ZB 90.4, which can be a result of brief oxygenation episode
- the shallowest part of the JCF and beginning of the Wólka Formation are characterized by the lack of framboids which indicates oxic conditions in the water column
- the oxygenation of water column in the southern Kielce region took place at an earlier stage than in the northern Łysogóry region

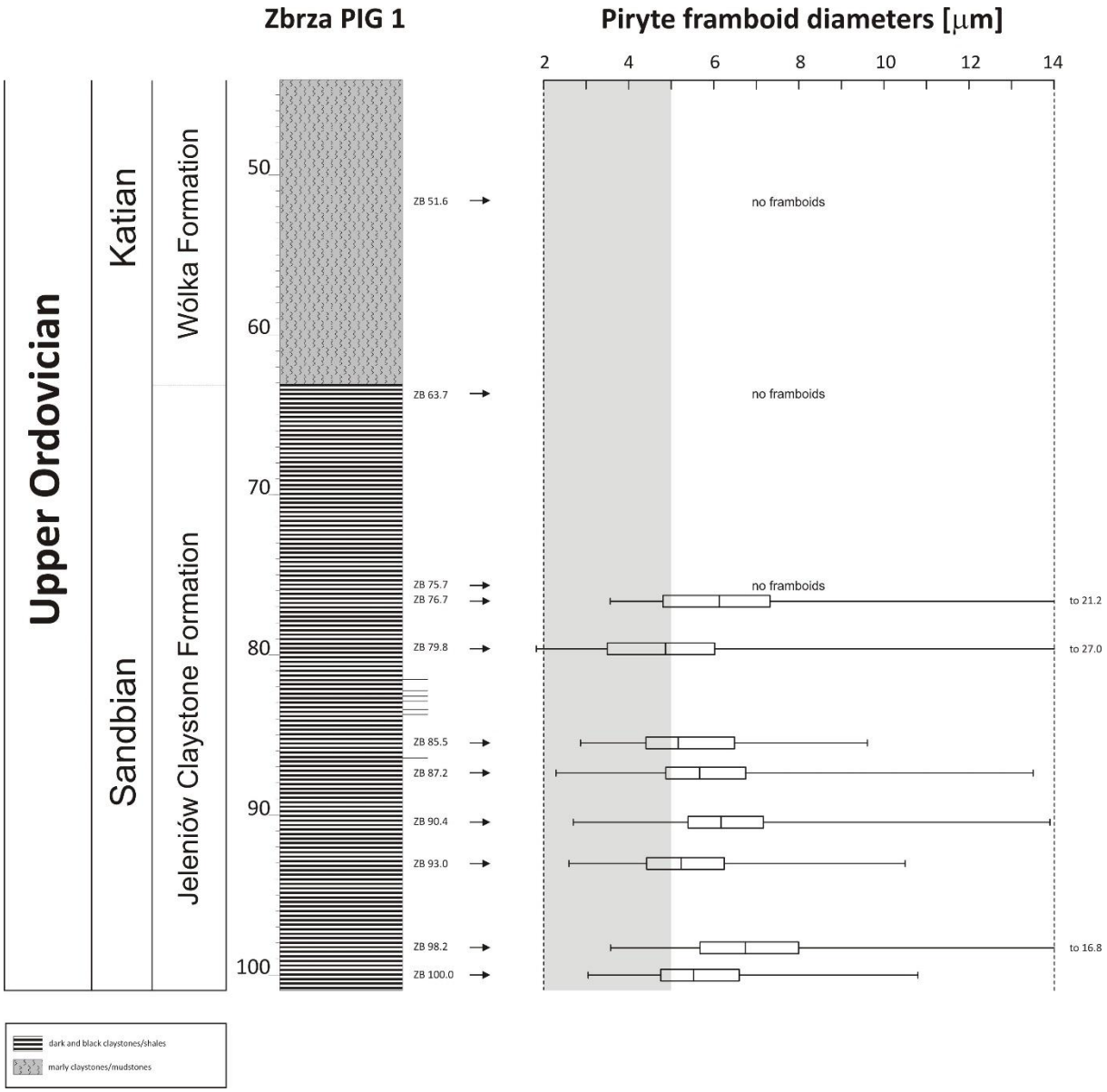

Fig.5. Lithological section of the Jeleniów Claystone Formation from the Zbrza PIG 1 borehole with the box-and-whisker plots showing the characteristics of the measured pyrite framboids.

Acknowledgements

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References

Bednarczyk W. (1971) Stratigraphy and paleogeography of the Ordovician in the Holy Cross Mountains. Acta Geol. Pol., 21: 574–616.

Bednarczyk W. (1981) Stratygrafia ordowiku Gór Świętokrzyskich. Przew. 53 Zjazdu Pol. Tow. Geol., Kielce: 35–41.

Deczkowski Z. & Tomczyk H. (1969) Budowa geologiczna antykliny zbrzańskiej w płd.–zach. części Gór Świętokrzyskich. Biul. Inst. Geol., 236: 143–175.

Modliński Z. (1982) Rozwój litofacjalny i paleotektoniczny ordowiku na obszarze platformy prekambryjskiej w Polsce. Pr. Inst. Geol.,102: 1–66.

Nielsen A.T. (2004) Ordovician sea level changes: a Baltoscandian perspective. [In:] Webby B.D., Paris F., Drosser M.L. & Persival I.G. (eds.) The Great Ordovician Biodiversification Event. Columbia University Press, New York: 84–93.

Pope M. & Read J.F. (1998) Ordovician metre-scale cycles: implication for climate and eustatic fluctuations in the central Appalachians during a global greenhouse, non-glacial to glacial transition. Palaeogeogr., Palaeoclimat., Palaeoecol., 138: 27–42.

Thickpenny A. & Leggett J.K. (1987) Stratigraphic distribution and palaeo-oceanographic significance of European early Palaeozoic organic-rich sediments. [In:] Brooks J. & Fleet A.J. (eds.),Marine Petroleum Source Rocks. Geol. Soc., Spec. Publ., 26: 231–247.

Tomczyk H. & Turnau-Morawska M. (1964) Stratygrafia i petrografia ordowiku Brzezin koło Morawicy w Gór Świętokrzyskich Acta Geol. Pol., 14: 501–546.

Tomczyk H. & Turnau-Morawska M. (1967) Zagadnienia stratygrafii i sedymentacji ordowiku Łysogór w nawiązaniu do niektórych profilów obszaru południowego. Acta Geol. Pol., 17: 1–46.

Tomczykowa E. & Tomczyk H. (2000) Starszy paleozoik z otworu Daromin IG 1 potwierdzenie budowy terranowej bloku Łysogórskiego i małopolskiego (Gór Świętokrzyskich). Biul. Państw. Inst. Geol., 393: 167–203.

Tomczykowa E. (1968) Stratygrafia osadów najwyższego kambru z Gór Świętokrzyskich. Pr. Inst. Geol., 54: 1–85.

Trela W. (2003) Sedimentological record of oxygen-depleted conditions in Upper Ordovician of central Poland (Holy Cross Mts.). [W:] G.L. Albanesi, M.S. Beresi, S.H. Perlata (eds) - Proceedings of the 9th International Symposium on the Ordovician System INSUGEO Serie Correlatión Geológica, 17: 449–455.

Trela W. (2006) Lithostratigraphy of the Ordovician in the Holy Cross Mountains. Prz. Geol., 54: 622–631.

Trela W. (2007) Upper Ordovician mudrock facies and trace fossils in the northern Holy Cross Mountains, Poland, and their relation to oxygen- and sea-level dynamics. Palaeogeogr., Palaeoclimat., Palaeoecol., 246: 488–501.

Trela W. (2009) Evolution of sedimentary environments in the Ordovician of the Łysogóry Region (northern Holy Cross Mts., Poland) in relation to the sea-level curve for Baltica. Prz. Geol., 57: 900–904.

Trela W., Szczepanik Z., Żylińska A., Salwa S. & Malec J. (2006) Stanowisko 3. Kielce - magazyn rdzeni wiertniczych Oddziału Świętokrzyskiego PIG, otwory wiertnicze: Lenarczyce PIG–1 i Daromin IG–1. Przew. 77 Zjazdu Pol. Tow. Geol.

Wignall P.B. & Newton R. (1998) Pyrite framboid diameter as a measure of oxygen deficiency in ancient mudrocks. Amer. J. Sci., 298: 537–552.

Wilkin R.T., Barnes H.L. & Brantley S.L. (1996) The size distribution of framboidal pyrite in modern sediments: an indicator of redox conditions. Geochim. Cosmochim. Acta, 60: 3897–3912.

Zatoń M., Rakociński M., Marynowski L. (2008) Pyrite framboids as paleoenvironmental indicators. Prz. Geol., 56:158–164.

Zhang T., Trela W., Jiang S-Y., Nielsen J.K., Shen Y. (2011) Major oceanic redox condition change correlated with the rebound of marine animal diversity during the Late Ordovician. Geology, 39: 675–678.