Acta Geologica Polonica, Vol. 76 (2026), No. 1, e74
DOI: 10.24425/agp.2026.158188

Geochemical peculiarities of the Lower–Middle Devonian transition in the Jurkowice block (Holy Cross Mountains, Poland) and the problem of the Devonian "ore-bearing horizon"

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ABSTRACT:

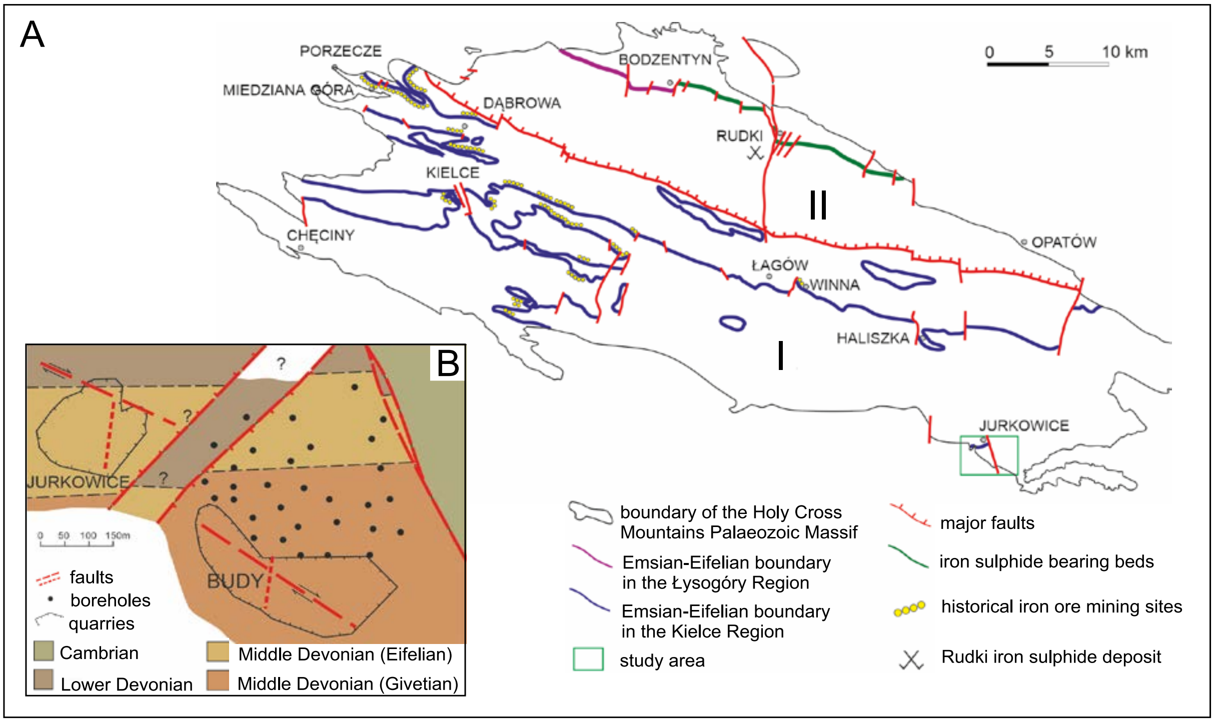
Nieć, M. and Sermet, E. 2026. Geochemical peculiarities of the Lower–Middle Devonian transition in the Jurkowice block (Holy Cross Mountains, Poland) and the problem of the Devonian "ore-bearing horizon". *Acta Geologica Polonica*, **76** (1), e74.

The deposits of the Emsian to the Eifelian period in the Holy Cross Mountains are of interest due to the occurrence of the "ore-bearing horizon" composed of clays with nested iron ores at their outcrops. In boreholes drilled in the vicinity of sites of ore occurrence no ore is found at depth but only pyrite-bearing clay-mudstones. Exposures of these deposits in the dolomite quarry in Jurkowice have allowed the authors to study their sedimentological features and geochemical properties. There are present here deposits of the upper part of the Winna Formation: red sandy mudstones and hematite-bearing clays, followed by grey-black tuffitic mudstone with disseminated iron sulphide, overlaid by laminated heterolithic clayey and sandy sediments with intercalations of quarzitic sandstone. They are strongly convolute-folded, in their uppermost part and covered by quartz-dolomitic sandstone, followed by the carbonate rock series. Chemical analyses reveal a considerably elevated rare-earth elements content in the grey heteroliths. The convex-upwards MREE distribution pattern suggests their supply by hydrothermal mineralizing fluids. The hematite and iron sulphide-bearing rocks with signs of hydrothermal activity allow us to assume that the "ore-bearing horizon" at the Emsian-Eifelian boundary encompasses the upper part of the Winna Formation. The siderite appearing in the neighbouring limestones was a product of their alteration by iron sulphites produced during the weathering of iron sulphides.

Key words: Emsian-Eifelian boundary, REE distribution, Iron ores, Holy Cross Mountains.

INTRODUCTION

At the Emsian to Eifelian boundary in the Holy Cross Mountains, a fundamental change in sedimentation conditions occurred, related to the progress of the transgression of the Devonian sea (Szulczewski 1995; Racki and Narkiewicz 2000; Belka and Narkiewicz 2008). The continental and marginal marine deposition of the clastic series was succeeded by carbonate platform development. It was a period of much diversified terrigenous-carbonate sedimentation caused by the varied morphology of the sea margin and repeated transgressive-regressive events and associated sea level fluctuations (Malec 2005; Wójcik 2015). The later sedimentation on the carbonate platform led to the formation of the Eifelian



Text-fig. 1. Geological setting. A – Middle Devonian boundary and “ore bearing horizon” in the Holy Cross Mountains (after Czarnocki 1956, modified); I – Kielce Region, II – Łysogóry Region. B – geology of the Jurkowice area without Neogene cover (after Nieć *et al.* 2024).

dolomites (Skompski and Szulczewski 1994; Malec 2005; Narkiewicz *et al.* 2006; Wójcik 2015).

The deposits of the Late Emsian to Eifelian transition are of particular interest due to their facies variations, which makes it challenging to correlate recognized formations and members of local and supra-local extent. Attempts at such correlations have been presented by Tarnowska (1983), Malec (2005), Skompski and Szulczewski (1994), Szulczewski (1995), Fijałkowska-Mader and Malec, (2011) and Wójcik (2015). Czarnocki (1923, 1951, and 1956) pointed to the particular importance of the deposits at the Early-Middle Devonian boundary in the Holy Cross Mountains, especially in the Western part of Kielce region. These deposits, formed by iron-ore-bearing, often variegated clays, were distinguished by him as the” Kuwin” beds in accordance with the stratigraphic terminology used at that time, as well as the “ore-bearing horizon” located between quarzitic sandstones and carbonate rocks. Within this ore-bearing horizon, in numerous sites along the approximately 30-km-long zone between the Ławeczno–Miedziana Góra area and the vicinity of Łagów nested and lenticular occurrences of limonite and, more rarely, hematite and siderite were found (Text-fig. 1A). Such iron ores were exploited in many places until the beginning of the 19th century (Czarnocki 1956; Rubinowski *et al.* 1966; Kozak *et al.* 2025).

The reported occurrences of iron ores within the sediments at the Early to Middle Devonian boundary prompted the search in the 20th century for their deposits. Such attempts were ultimately unsuccessful. Drilling carried out in the second half of the 20th century as part of large-scale research revealed either the absence of ore-bearing clays or the presence of only pyrite-bearing clay-mudstones (Tarnowska 1969a, 1983; Kowalczewski and Wróblewski 1974), which were transformed to limonite contained in the weathering zone.

Claystones at the Emsian-Eifelian boundary are characterized by an increased Cu, Pb, Zn, Ni, and Co content (Lenartowicz 1999). In the pyrite-bearing rocks, sulphides of Zn, Pb, and Cu were also found (Kowalczewski and Wróblewski 1974; Wróblewski 1973b, 1988; Tarnowska 1969b) and their increased radioactivity was often recorded (Borucki *et al.* 1967, Kasza and Król 2019). Such features make the transitional formations of the Lower to Middle Devonian an important component of the metallogeny of the Holy Cross Mountains representing a probable site of synsedimentary ore accumulation (Czarnocki 1951, 1956). The “ore-bearing clays” were also considered

Text-fig. 2. North-western part of the Jurkowice Quarry (photo made in 2014).

a potential source of metals for the widespread ore occurrences in younger rock formations whose hydrothermal origin is unquestionable (Kowalczewski and Wróblewski 1974).

In the eastern part of the Kielce Region, ore-bearing or pyrite-bearing clays have not been identified. Based on detailed studies of borehole profiles, the Late Emsian rock suite below the Eifelian carbonates was described by Tarnowska (1983) as the Winna Formation. It is formed of a complex of variegated mudstones occurring above white quarzitic sandstones and below the overlying, partly dolomitic, sandstones ("upper sandstones"), which often contain sulphide mineralization (Tarnowska 1969a, 1970). A characteristic feature of this formation is the presence of two tuffitic beds, T-3 and T-4, considered to be regional correlation horizons (Tarnowska 1999). The complex of carbonate rocks that overlies the Winna Formation was named the Łagów Formation by Tarnowska (1983) and the Barania Góra Formation by Wójcik (2015). In the Western part of the Kielce region, pyrite-bearing clays were defined by Wójcik (2015) as the Porzecze Member, located at the base of the Barania Góra Formation. It occurs directly over the mudstones of the Winna Formation identified by the presence of the T-4 tuffite bed (Tarnowska and Malec 1987).

The sparse and fragmentary exposures of deposits at the Lower to Middle Devonian transition make their study difficult and most investigations have therefore relied on borehole data often with deficiencies in core recovery. Between 2014 and 2019, however, these deposits were exposed on a large area in the northern part of the dolomite quarry in Jurkowice. This allowed observations of their sedimentological features and study of their geochemical properties, characterized by a noteworthy increased REE content (Musiał *et al.* 2017) and signs of supposed synsedimentary hydrothermal activity. Their results prompted discussion of the relationship between the "ore bearing horizon" and the Winna Formation. The mine closure and filling of the open pit with crushed dolomite waste has now made the described formations inaccessible.

GEOLOGY OF STUDIED AREA

The recently closed Jurkowice dolomite open cast mine (quarry) is located in the southern wing of the Klimontów Anticlinorium, within a tectonic half-graben exposed over a small area at the southern border of the Paleozoic massif of the Holy Cross Mountains plunging under Miocene sediments of the Carpathian Foredeep. The exposed fragment of Devonian deposits (Text-fig. 1B) is referred to as the Jurkowice Block or Element (Romanek 1977). The quarry is located in the western part of this block, which is cut by a meridional dislocation zone. Within its boundaries, the Eifelian dolomites of the Barania Góra formation predominantly occur. Their detailed

Text-fig. 3. Strike-slip fault zone (A), and associated contractionally folded marly dolomites of unit "H" (B) and tuffitic mudstones of unit "C" (C).

lithology and stratigraphic position were described by Narkiewicz *et al.* (1981) and Wójcik (2015).

In the northwestern part of the quarry, the rocks of the Winna Formation were exposed (Text-fig. 2), cut by an NWW-SEE dextral strike-slip fault (Text-fig. 3A). Within the dislocation zone, clay and carbonate formations are contractionally folded (Text-fig. 3B, C), similar to such structures associated with strike-slip faults recorded in other parts of the Holy Cross Mountains, studied by Konon (2007).

MATERIALS AND STUDY METHODS

The field work was carried out in Jurkowice quarry during its period of activity. Detailed geological mapping of the quarry walls (Text-fig. 2) enabled the study of the lithology and sedimentological features of the complete rock succession from the Early to Middle Devonian (Text-fig. 4). Each macroscopically distinct rock variety was sampled for standard petrographical study using thin sections, and for chemical analysis, some of which were supported by X-ray investigation. The age of the exposed rocks was not determined, but based on lithological analogy to well-studied similar rocks in boreholes located northward in Haliszka and Łagów locality (Tarnowska 1969a 1976), they may be recognized as representing Upper Emsian Winna Formation. The Lower Eifelian age of overlying carbonate rocks was demonstrated by Narkiewicz *et al.* (1981) and Wójcik (2015).

Chemical analysis were performed in the AcmeLabs laboratory. Samples of approximately 1 kg were crushed to 2 mm grain size, and after homogenization, 250 g was pulverized to achieve 85% below 75 µm. For the analytical procedure, 0.5 g of pulverized material was used. It was decomposed by lithium borate fusion, and analyzed by IPC-ES/MS following standard AcmeLabs procedures (LF 200 and A 200).

Tab. 1. Chemical analyses. 1, 2 – quarzitic sandstones (unit "A"); 3 – hematite bearing sandy mudstone (unit "B"); 4 – hematite bearing laminated sandy mudstone (unit "B"); 5 – tuffitic mudstone (unit "C"); 6, 7 – laminated clay-muddy-sandy hetorolite (unit "D"); 8 – quarzitic sandstone within hetorolite (unit "D"); 9 – upper quartz-dolomitic sandstone (unit "F"); 10 – limestone (unit "G"); 11, 14 – marly dolomites (unit "H"); 12, 13 – clayey mudstones, tuffitic (unit "J"); 15 – limestone, siderite bearing (in unit "H"), 16–19 – dolomites, Jurkowce Member (unit "K").

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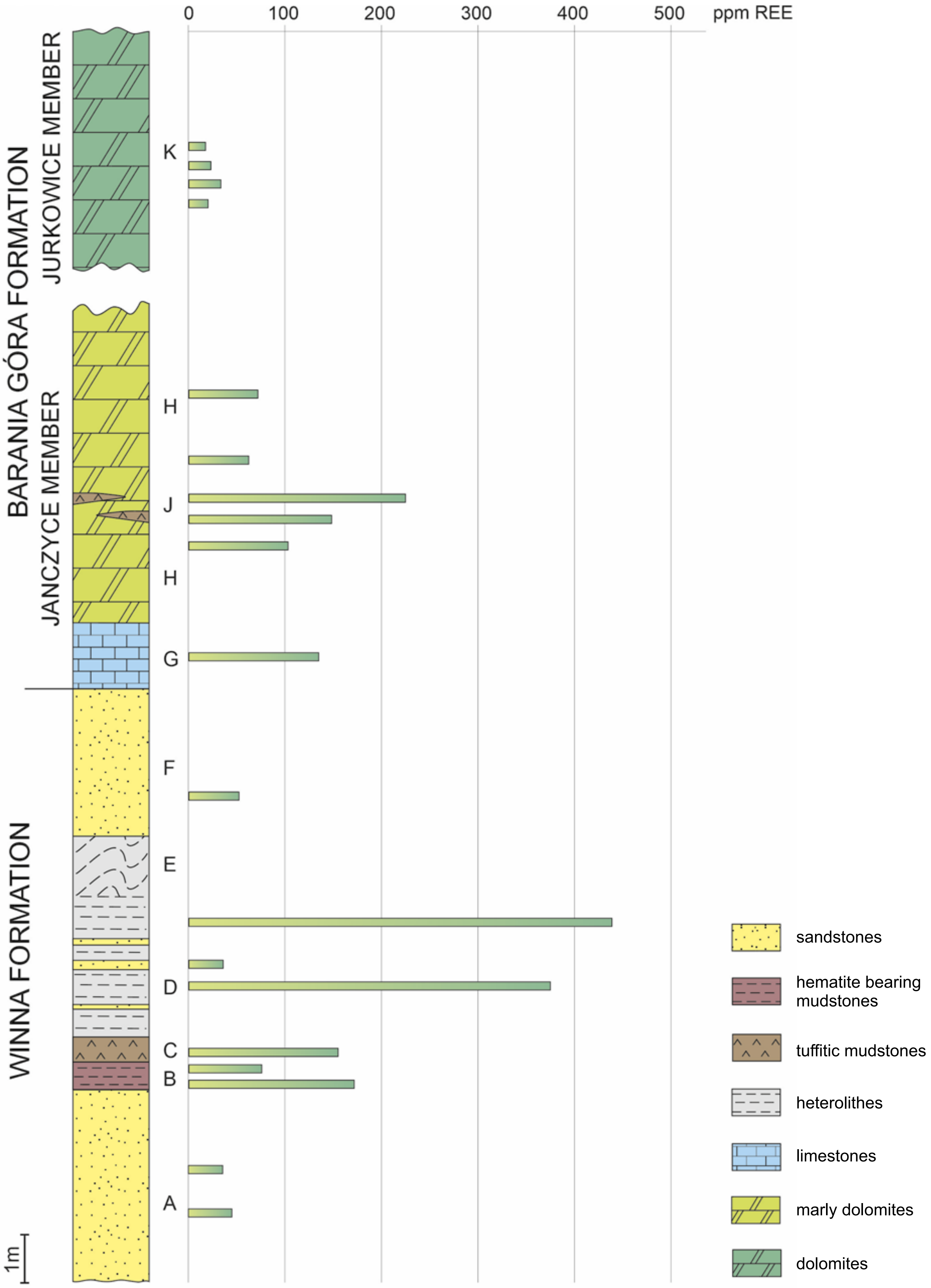
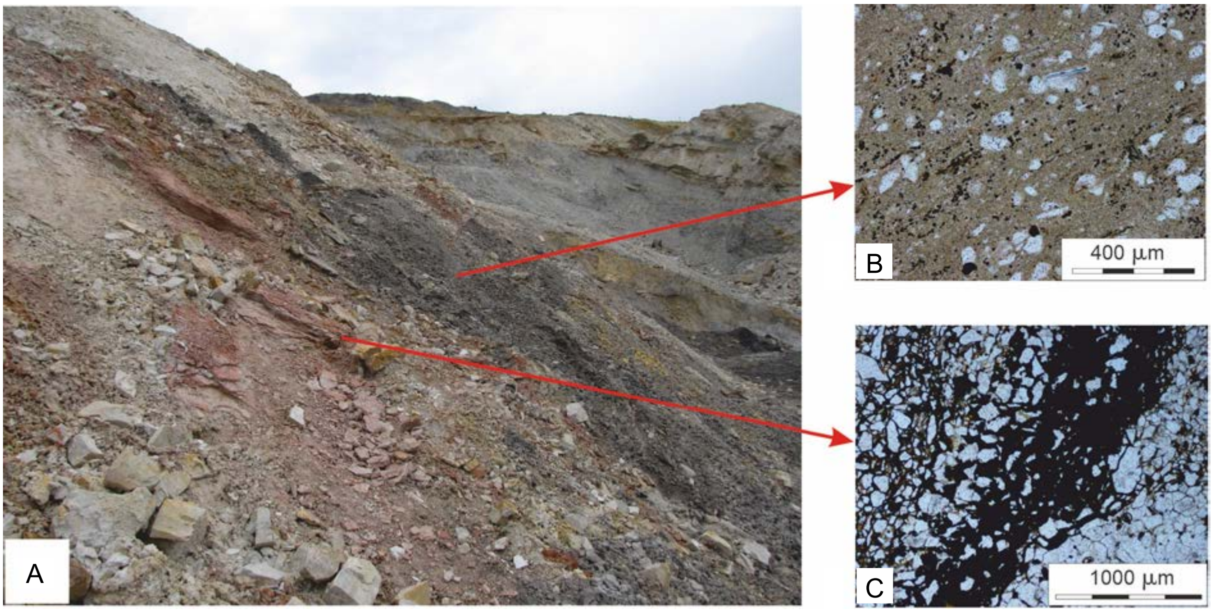
	Winna Formation									Barania Góra Formation									
										Janczyce Member						Jurkowice Member			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SiO_2 %	98.21	97.64	87.65	38.3	53.18	72	65.31	96.03	96.61	4.15	9.05	57.55	51.2	6.75	3.94	2	5.47	1.19	1.72
Al_2O_3	0.53	0.93	4.95	12.48	20.84	15.2	18.65	0.6	1.01	1.78	1.22	10.48	22.9	1.93	1.06	0.61	1.71	0.57	0.6
Fe_2O_3	0.52	0.73	2.59	33.56	5.43	1.58	1.86	1.99	0.45	1.25	0.66	18.68	3.22	0.8	2.22	0.43	0.84	1.02	0.4
MgO	0.05	0.06	0.3	1.29	1.45	0.81	1.04	0.05	0.24	7.11	18.5	1.12	3.55	18.44	8	20.78	19.84	19.1	20.82
CaO	0.07	0.02	0.04	0.49	0.21	0.23	0.3	0.06	0.35	42.3	26.6	0.34	1.04	26.61	41.16	30.06	28.22	31.83	29.92
Na_2O	<0.01	<0.01	0.03	0.03	0.07	0.09	0.1	<0.01	<0.01	0.02	0.04	0.05	0.04	0.04	0.02	0.02	0.03	0.02	0.03
K_2O	0.07	0.18	1	2.52	4.08	4.05	4.68	0.06	0.27	0.54	0.36	2.9	5.87	0.64	0.3	0.21	0.64	0.17	0.19
TiO_2	0.24	0.1	0.72	0.3	0.82	0.87	1.03	0.07	0.11	0.08	0.06	0.62	0.24	0.09	0.05	0.03	0.07	0.03	0.03
P_2O_5	<0.01	<0.01	0.03	0.03	0.02	0.04	0.05	0.02	0.01	0.06	0.03	0.12	0.05	0.02	0.01	<0.01	0.02	<0.01	<0.01
MnO	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.04	0.03	0.25	0.04	0.02	0.03	0.02	0.03	0.1	0.03
Cr_2O_3	0.006	0.004	0.011	0.026	0.014	0.01	0.015	0.002	<0.001	<0.002	<0.002	0.011	0.003	<0.002	<0.002	<0.002	0.003	<0.002	<0.002
LOI	0.2	0.3	2.5	10.8	13.7	5	6.7	1.1	0.9	42.5	43.1	7.7	11.6	44.3	43.1	45.8	43.1	45.9	46.2
TOT/S	<0.02	<0.02	0.05	0.08	3.05	<0.02	0.15	<0.02	<0.02	<0.02	0.03	0.05	<0.02	0.02	<0.02	0.12	0.34	<0.02	<0.02
Sc ppm	<1	<1	4	15	11	13	18	<1	<1	4	3	17	12	3	3	1	2	1	<1
Ni	4	5.6	4.6	8.6	89.2	77	97.1	20.6	1.6	9.8	15.2	86	29.8	5.6	7.8	2.9	7.2	6.6	3
Ba	33	66	186	102	225	425	525	26	39	34	23	346	95	32	25	14	28	30	10
Be	<1	<1	2	<1	3	3	2	<1	1	1	<1	4	1	1	1	<1	<1	<1	<1
Co	0.8	1.7	1.5	3.5	31.5	38.6	61.4	5.3	0.9	1.9	3.3	25.2	14	1.1	2	2.7	1.7	1.1	0.5
Cs	0.2	0.5	1.7	10.3	9.7	7.7	12.3	0.1	0.5	1.8	0.8	7.6	25.2	2	1.6	0.3	1	0.2	0.3
Ga	0.5	1	5.3	13.1	17.5	16.3	20.8	<0.5	0.7	1.4	1.2	12.2	25.2	2.1	0.6	1	1.7	<0.5	<0.5
Hf	18.1	3.7	20.8	4.8	6.3	9.5	9.4	3.8	3.9	0.6	0.8	7.7	14.4	0.5	0.3	0.2	0.5	0.3	0.2
Nb	3.2	1.8	12.1	14.3	14.2	15	19	1.5	2	2.4	1.4	10.5	29	1.9	0.7	0.6	1.4	0.6	0.5
Rb	2.2	4.9	30.7	68.9	133.3	120	152.6	1.5	7.7	17.8	10.8	99.8	135	21.1	10.8	6.4	17.5	4.5	5.6
Sn	<1	<1	1	4	3	3	3	<1	<1	<1	<1	2	9	<1	<1	<1	<1	<1	<1
Sr	6.8	12.2	21.3	16.9	47.4	63.9	82.2	5.7	124	54.3	64.1	42.9	17.5	78.2	42.1	105.4	84	78.9	84.6
Ta	0.3	0.2	0.8	1.4	0.9	1	1.3	<0.1	0.2	0.1	0.1	0.7	5.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Th	2.8	1.6	10.7	25.7	12.8	13.4	16.6	0.9	1.8	2.2	2.1	13.5	55.7	1.5	1.7	0.4	1	0.5	0.4
U	1.4	0.5	3.2	10.7	7.4	3.6	9.2	1.1	0.6	1.2	2	3.7	6.2	1.3	0.7	2.1	1.7	2.7	2.2
V	<8	11	39	161	115	90	117	<8	10	17	16	99	33	19	14	12	13	14	11
W	<0.5	<0.5	2	0.6	1.7	1.4	1.5	<0.5	<0.5	0.6	<0.5	1.2	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	12.2
Zr	763.8	145.8	844	132.5	224.8	338	340.5	165.5	156.3	22.2	26.3	283.1	264	18.6	10.3	6.4	16.9	7.6	7.8
Y	9.3	3.6	23.9	5	11.3	42.9	55.9	2.2	4.9	22	10	35	16.1	6.8	11.6	2.2	4.3	3	1.8
La	7.3	6	30	14.5	33.7	66.5	81.8	8	8.9	23.3	15.3	49.7	18.7	8.1	9.9	2.8	5.3	3	2.4
Ce	16.1	14.1	62	30.2	64.9	138	160.3	9.9	21.2	35.9	36.5	94.9	69	17.6	22.1	4.7	9.6	6.1	4.4
Pr	1.79	1.59	6.54	3.73	6.7	15.2	17.92	1.71	2.19	5.84	4.58	13.87	6.65	2.16	2.79	0.59	1.17	0.74	0.5
Nd	7.4	5.9	25.6	14.1	22.3	61	69.1	6.4	7.7	23.9	19.7	56.9	22.4	9.7	13.2	2	4.2	2.9	1.9
Sm	1.31	1.13	4.44	3.21	3.69	11.5	13.07	0.84	1.35	5.12	4.68	11	4.14	2.12	3.13	0.34	0.76	0.44	0.32
Eu	0.24	0.22	0.63	0.55	0.65	2.32	2.9	0.17	0.25	0.92	0.88	2.25	0.44	0.41	0.62	0.09	0.17	0.1	0.08
Gd	1.34	0.86	3.79	1.86	2.7	11.1	13.74	0.71	1.05	4.82	4.07	10.02	3.52	1.91	3.22	0.36	0.78	0.54	0.34
Tb	0.2	0.11	0.64	0.27	0.42	1.65	2.08	0.09	0.16	0.72	0.55	1.57	0.62	0.28	0.47	0.06	0.13	0.08	0.05
Dy	1.29	0.44	4.09	1.37	2.27	8.5	11.18	0.43	0.81	4.08	2.6	7.82	3.46	1.68	2.49	0.3	0.73	0.43	0.25
Ho	0.31	0.12	0.87	0.2	0.44	1.54	2.09	0.07	0.16	0.69	0.45	1.49	0.63	0.27	0.43	0.08	0.14	0.1	0.06
Er	1.08	0.41	2.57	0.64	1.53	4.24	5.44	0.24	0.5	1.84	0.95	3.79	1.82	0.7	1.06	0.17	0.38	0.27	0.16
Tm	0.18	0.05	0.42	0.1	0.23	0.61	0.77	0.03	0.08	0.23	0.14	0.49	0.27	0.1	0.14	0.03	0.06	0.04	0.02
Yb	1.21	0.4	2.9	0.7	1.63	3.84	4.82	0.26	0.54	1.46	0.87	3.23	1.76	0.62	0.81	0.17	0.34	0.22	0.16
Lu	0.22	0.07	0.49	0.1	0.25	0.59	0.74	0.04	0.08	0.19	0.1	0.46	0.26	0.08	0.11	0.02	0.05	0.03	0.02
Mo	1.1	1	0.5	7.7	1	<0.1	0.2	2	0.3	0.2	0.4	2.5	1.2	<0.1	0.6	1	0.7	0.5	0.3
Cu	6.5	10.3	4.4	32.8	218.9	12.7	17.6	77.3	13	1.9	4.2	26.6	52.8	4.6	2.2	4.9	6.9	0.9	1.8
Pb	3.5	8.5	9.8	16.8	81.8	4.5	4.7	13.1	3.1	1.9	7.1	71	128	6.2	1.5	5.8	19.8	1	1.9
Zn	7	2	37	278	259	31	50	70	6	34	208	39	389	76	26	41	177	11	13
As	0.8	1.2	5.8	111.6	46.7	8.4	6.4	11.2	1.1	3.2	2.6	106.2	40.3	<0.5	<0.5	4.5	8.7	1.6	0.7
Cd	<0.1	<0.1	<0.1	0.1	0.8	<0.1	<0.1	0.1	<0.1	0.4	0.2	0.2	<0.1	<0.1	<0.1	<0.1	0.5	<0.1	<0.1
Sb	<0.1	0.1	<0.1	0.4	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.1	<0.1	<0.1	0.5	0.3	0.2	0.3	<0.1	<0.1	<0.1	<0.1	0.2	1.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Au ppb	<0.5	1.4	<0.5	3.3	<0.5	1.8	<0.5	3.2	1	3.5	<0.5	0.7	4.3	<0.5	1.2	<0.5	1.5	1.2	1
Hg ppm	<0.01	0.02	0.03	0.07	0.04	0.01	0.01	<0.01	0.01	<0.01	<0.01	0.03	0.07	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Tl	<0.1	<0.1	0.1	0.1	0.4	0.6	1.4	<0.1	<0.1	<0.1	<0.1	0.9	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	<0.5	<0.5	0.5	2.5	4.8	<0.5	<0.5	1.8	<0.1	<0.5	<0.5	0.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5



Text-fig. 4. Generalized profile of studied rocks and REE content.



Text-fig. 5. The hematite-bearing sandy mudstones (A, C) and the overlying tuffitic mudstones (A, B); B, C photos in transmitted light.

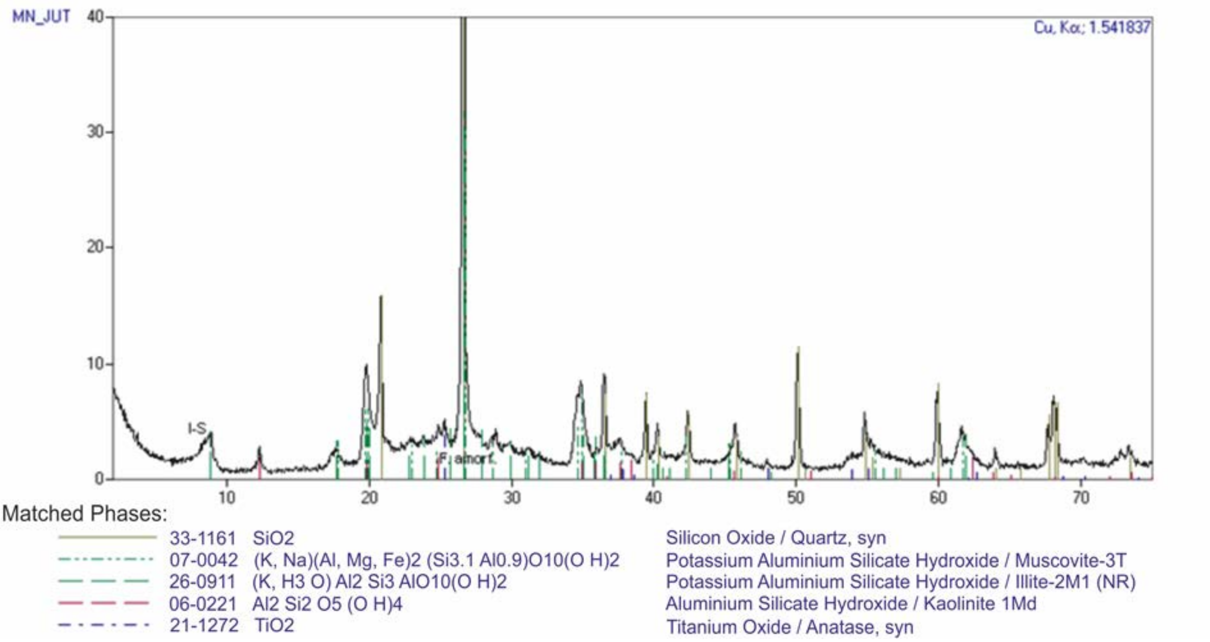
The results of chemical analysis (Table 1), in particular the rare-earth elements (REE) content, were normalized in relation to the Post Archean Australian Shale (PAAS). They differ insignificantly from the normalized to the Upper Continental Crust (UCC) and North American Shale Composite (NASC), respectively (Piper and Bau 2013, Rudnick and Gao 2003).

STUDY RESULTS

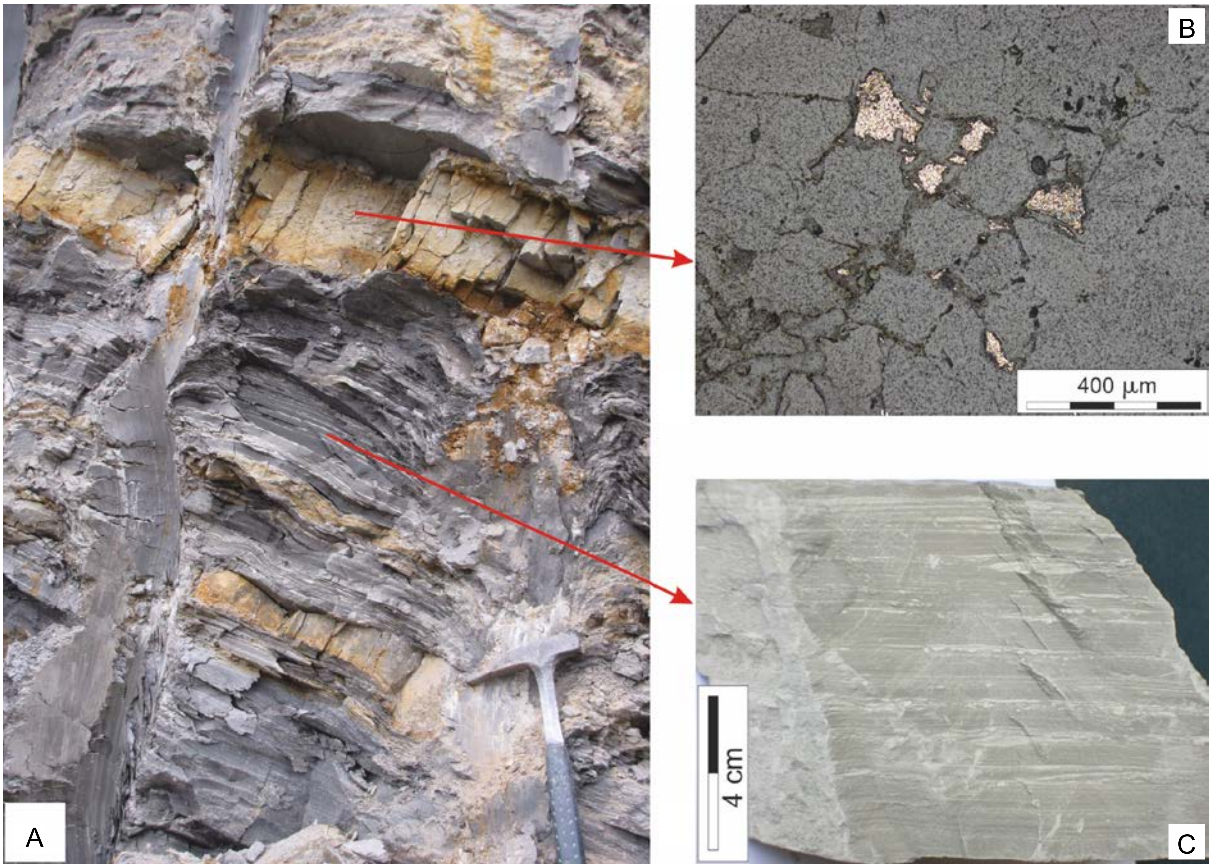
Lithology of studied transitional formations from the Lower to Middle Devonian

Early and Middle Devonian rocks were exposed on the north-western walls of Jurkowice quarry, reaching depths of up to 30 m below the original ground level. The presence of a strike-slip fault complicates continuous observation of the exposed rock sequences, making it difficult to trace the complete profile of strata continuously. However, the broad exposure of these deposits on the quarry walls – locally up to approximately 10 m high – made it possible to combine fragmentary sections into a synthetic one (Text-fig. 4).

The exposed suite of rocks (units “A”–“K” on Text-fig. 4) begins with white quarzitic sandstones of about five meters of visible thickness. They are massive and compact, in colour passing upwards from white to bright gray, slightly beige. Cross-bedding is locally visible, and there are ripple marks and irregular bioturbations on some bedding planes. The white sandstones (unit “A”) are overlain by red, hematite-stained, massive, sandy mudstones (unit “B”). Their average thickness does not exceed 0.5 m. They pass upwards into a laminated series of beds, composed of graded sandy-mud layers separated by thin irregular ferruginous haematitic bands (Text-fig. 5C). The Fe_2O_3 content in hand-size samples may be up to about 30%. The red-stained and laminated sandy mudstones pass upwards to gray-black clays and tuffitic mudstones (unit “C”), brown, limonite-stained if weathered (Text-fig. 3C). Their characteristic feature is high porosity when air-dried. The rock is composed of angular quartz silt with accompanying muscovite dispersed in structureless clayey material of mixed-layered composition (Text-fig. 5B and 6). The rock contains a few percent of dispersed iron sulphide and carbonaceous material. Overlying this interval is an approximately 8-m-thick suite of laminated heterolithic sediments (unit “D”), composed of alternating millimetric bands of gray silty clay



Text-fig. 6. X-ray diagram of the tuffitic mudstone (unit "C").



Text-fig. 7. Heterolithic mudstones (A, C) with quarzitic sandstone interlayers (B) with disseminated iron sulphide; B photo in reflected light.

Text-fig. 8. Earthquake-induced folded mudstone (unit "E"), below a flat-lying quarzitic sandstone (unit "F")

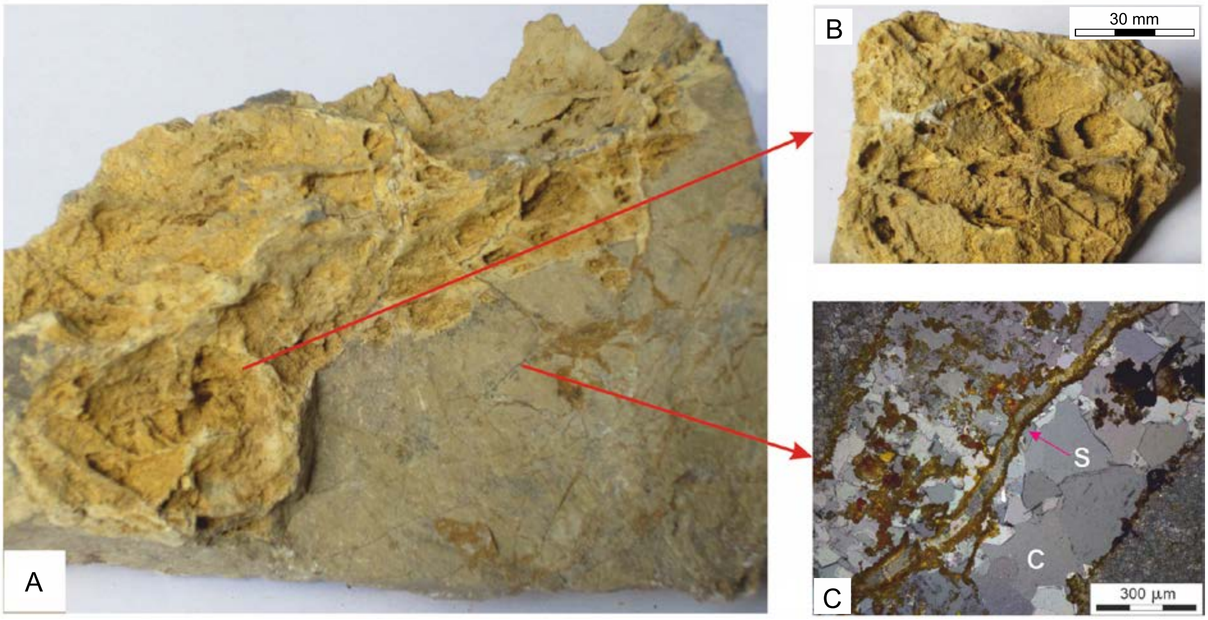
and white, fine-grained sand, sometimes cross-bedded and with a few intercalations of quarzitic sandstone up to about ten centimeters thick (Text-fig. 7) The sedimentary features of the heterolithic rock suite suggest a shallow-water epicontinental tidal flat or a lagoonal suboxic depositional environment (Terwindt 1981, Gradziński *et al.* 1986, Gao 2019).

The uppermost part of this heterolithic rock suite (unit "E"), about 1.5 m thick, is strongly distorted by convolute bedding, locally folded (Text-fig. 8) below a planar footwall of the overlying sandstone. The forms and sizes of the distortions suggest a seismic episode in their formation (Sims 1973, Shanmugam. 2016). The upper quarzitic sandstone (unit "F"), about 5 m thick, is locally darkly laminated, dolomitic, and with *Cylindrichinus* burrows in the upper part. The overlying rocks are limestones (unit "G") passing upwards into fine-bedded micritic marly dolomites (unit "H"), with lenticular interlayers of greenish claystone (unit "J"), transformed to rusty-brown due to weathering (Text-fig. 9). A noteworthy feature is a brown band, a few centimetres thick, located about 10 m above the base of the carbonate sequence, formed of recrystallized micritic limestone with disseminated siderite grains, replaced by goethite. The siliciclastic rocks are free of macrofossils. Within the overlying carbonate rocks, poorly preserved, undetermined fragments of brachiopods| and probable gastropods are occasionally visible.

The location of silt-clay sediments with a tuffitic horizon (units "B"–"E" on Text-fig. 4) situated above quarzitic sandstones and below quartz-dolomitic sandstones (unit "F"), which underlie the sequence of carbonate sediments, allows these formations to be identified as the upper part of the Winna Formation (Tarnowska 1971). The bed of pyroclastic composition occurring within this interval can be identified as a T-4 tuffitic horizon, considered a regional correlation marker (Tarnowska 1999). The above-lying limestones, marly dolomites and thin bedded dolomites, represent the Janczyce Member of the Barania Góra Formation defined by Wójcik (2015). The discontinuous lenticular interlayers of greenish-rusty silty clay enriched in oxidized FeS2 may be identified as the T-5 and T-6 tuffitic horizons of Tarnowska (1999).

The uppermost part of the carbonate rock (unit "K") series consists of gray, medium to thick bedded dolomites distinguished by Wójcik (2015) as the Jurkowice Member.Within this unit, a bed of bentonite was found (Czermiński and Ryka 1962), which may be identified as a T-7 tuffitic horizon.

Text-fig. 9. Clayey mudstone (unit “J”) a supposed tuffitic T-5 level within marly dolomites of Janczyce Member beds (unit “H”).



Text-fig. 10. Boxwork structure of weathered siderite-bearing limestone (A, B) and siderite veinlets (C); s – siderite; c – calcite.

The strike-slip fault places the silty-clay formations in direct contact with the carbonate formations. A characteristic feature of limestones in contact with mudstones is their particular cavernosity. Cavities up to a few centimeters in size are edged with limonite. Their internal boxwork cellular structure (Text-fig. 10A, B) is similar to that of limonite formed as a result of siderite weathering (Blanchard 1968). The rock is also cut with thin siderite veinlets up to about 1 mm thick (Text-fig. 10C).

Geochemical features of the studied formations

Chemical analysis reveals a number of peculiar features of the studied rocks. First of all there is the varied content of rare earth elements (REE), particularly enriched in the gray heteroliths (Text-fig. 4). The REE contents in the quarzitic sandstones located at the base of the studied rock series are lower compared to Post Archean Australian Shale (PAAS) (Text-fig. 11). However, there is a clear, more than two-fold increase in the heavy rare-earth elements (HREE) content compared to that of light rare-earth elements (LREE). Noteworthy is a simultaneous high content of zircon, estimated in thin section at approximately 1% by volume. It may be accompanied by the xenotime as the HREE carrier, which is indistinguishable from zircon because of its similar optical properties.

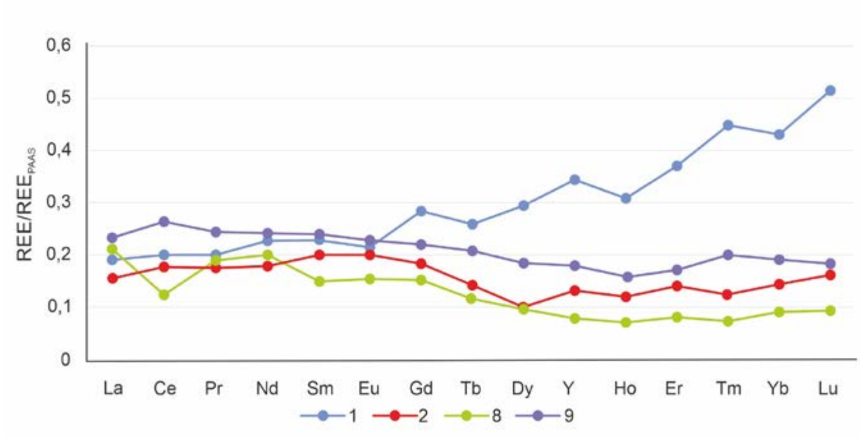
In the hematite-bearing unit "B" and in the overlying tuffitic mudstones unit "C", the REE contents are slightly lower compared with PAAS (Text-fig. 12). However, in the younger gray heterolithics, the REE content is considerably higher, with a characteristic increased intermediate or middle rare-earth elements (MREEnorm) content compared to LREEnorm and HREEnorm. The distribution of the REE content in the limestone layer above the heterolithic complex is similar. In the overlying marly dolomites, as we move away from the top of the heterolithics, the REEnorm contents gradually decrease in relation to PAAS, and the contrast of LREE, MREE, and HREE contents diminishes (Text-fig. 13). In the younger dolomites of the Jurkowice member, REE contents are more uniform and much lower than PAAS, but their local increase in the fault zone cutting them has been noticed (Nieć *et al*. 2024).

DISCUSSION

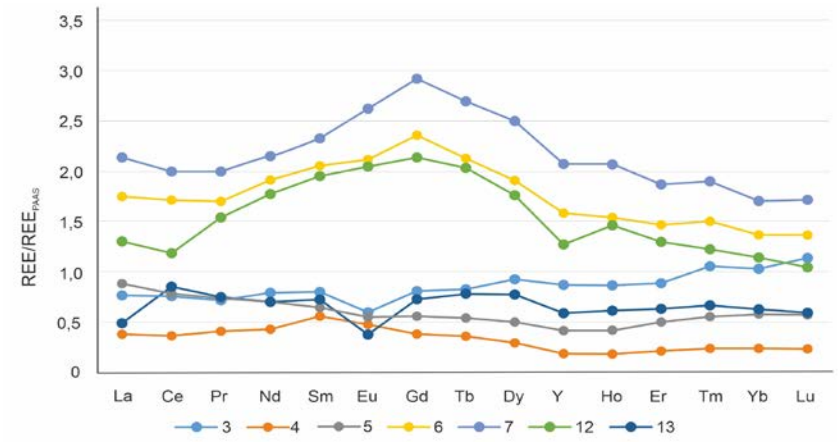
The lithological features of the studied rocks at the Early to Middle Devonian boundary exposed in Jurkowice indicate a marginal marine environment for their deposition, being a transition from beach through tidal flat or lagoonal sedimentation to a carbonate platform. An environment of coastal-marine sedimentation with freshwater inflow are suggested by the low Y/Ho ratio of 25–30 (Nozaki *et al.* 1997; Frimmel 2009). The variable values of the Ce/Ce* anomalies 0.84–1.10 indicate the varied pH and redox potential of this environment (Tostevin *et al.* 2016). A pronounced negative Ce/Ce* anomaly of 0.61, evidently indicating an oxidized environment, appears only in the sandstone interlayers in the heterolithic rock suite and in the limestone with siderite, both altered by weathering. Terrigenous supply of clay, silt, and sand to the sedimentary basin is evidenced by the correlation of Al and Zr, as well as the Th in the accumulated sediments (Text-fig. 14). The correlated REE content should follow the PAAS pattern. However, in the sequence of the studied rocks, the Zr-REE relationship reveals three different trends (Text-fig. 15).

Emsian quarzitic sandstones and mudstones are exceptionally Zr-rich and have moderate REE content. This may be explained by the wave-induced accumulation of heavy mineral fractions in the beach environment. The mudstones located over the basal quarzitic sandstones contain 140 to about 340 ppm of Zr, clearly correlated with the REE content varying from about 30–440 ppm with a correlation coefficient of 0.94. The variation in REE contents in the profile of this rock series differs characteristically from PAAS. The MREEnorm content in the tuffitic mudstone is slightly reduced. The grey heterolithic clay mud-sandy rocks lying above display enrichment in MREE, as evidenced by the REE convex- upwards distribution pattern. Such enrichment of MREE is considered to be the result of their delivery by hydrothermal mineralizing fluids (Hecht *etal.* 1999; Frimmel and Lane 2005; Boulvais *et al.* 2006; Frimmel 2009), or by remobilization from the bedrocks (Sawłowicz 2013; Bechtel *et al.* 2001; Oszczepalski *et al.* 2016). Remobilization is hardly demonstrated in the case of the studied rocks, and their supply by hydrothermal fluids from external sources seems more probable; however, their location remains enigmatic. The close Zr-REE correlation suggests that these hydrothermal fluids introduced also a part of the Zr content (Rubin *et al.* 1993).

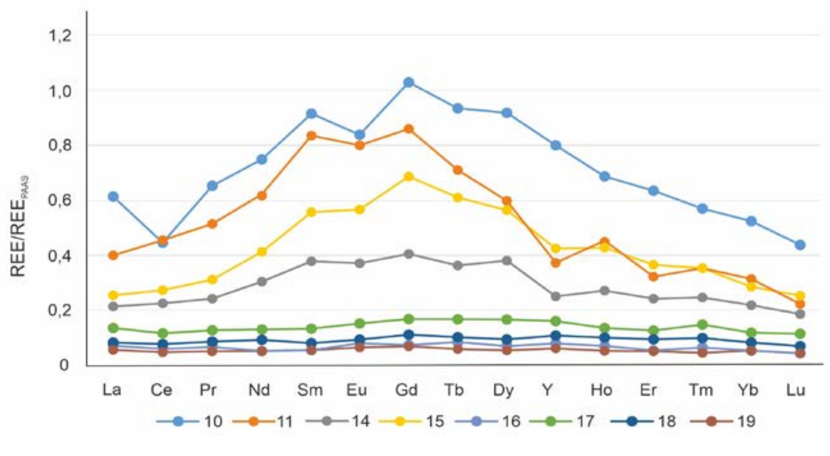
A bell-shaped distribution of REE content appears also in the lower part of the carbonate rock series (Janczyce Member). However, it varies in the upward rock sequence and is characterized by a negative Eu anomaly. Initially, the REE content is similar to that of the underlying heterolithes but gradually changes in younger beds by a decrease in the MREE content



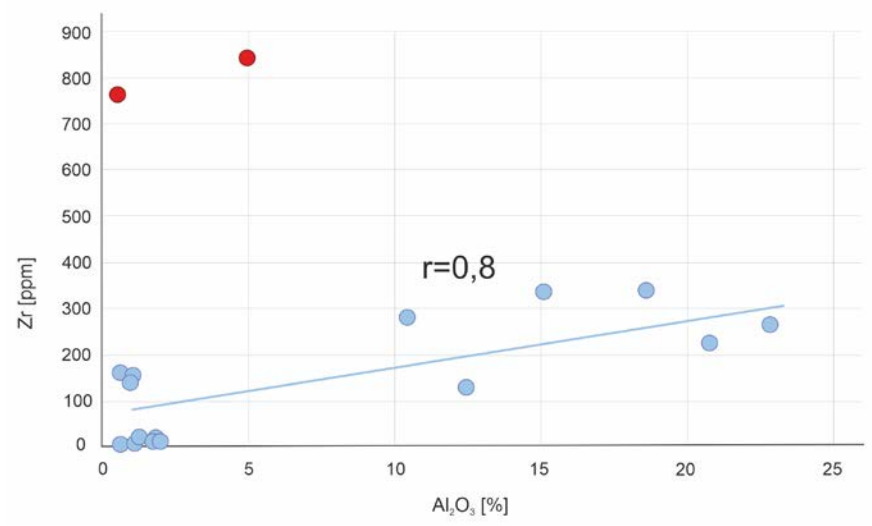
Text-fig. 11. PAAS normalized REE content in sandstones (sample numbers as in Table 1, lithologic units as in Text-fig. 4). 1, 2 – Emsian quarzitic sandstone (unit "A"); 8 – quarzitic sandstone within heterolithic mudstones of Winna Formation (unit "D"); 9 – sandstone at the top of Winna Formation (unit "F").



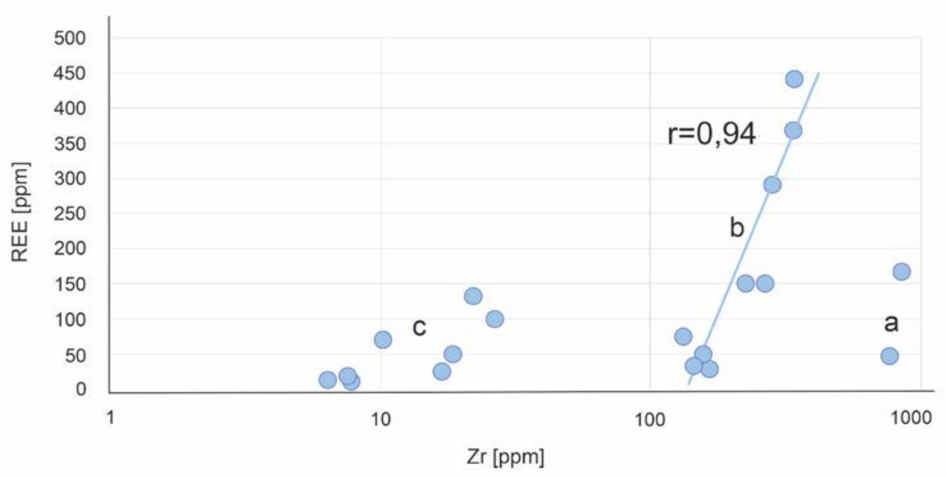
Text-fig. 12. PAAS normalized REE content in mudstones and claystones (sample numbers as in Table 1, lithologic units as in Text-fig. 4). 3, 4 – hematitic mudstones (unit "B"); 5 – tuffitic mudstone (unit "C"); 6, 7 – heterolithic mudstones, Winna Formation (unit "D"); 12, 13 – claystones (tuffitic T-5 and T-6 horizons, unit "J") within carbonate rocks of Janczyce Member.



Text-fig. 13. PAAS normalized REE content in carbonate rocks (sample numbers as in Table 1, lithologic units as in Text-fig. 4). 10–15 – limestones (unit "G") and marly dolomites (unit "H"), Janczyce Member; 16–19 – dolomites (unit"K"), Jurkowice Member.



Text-fig. 14. Zr – Al_2O_3 correlation in the studied rock samples presented in Table 1. Red dots – heterolithic mudstones (unit "D").

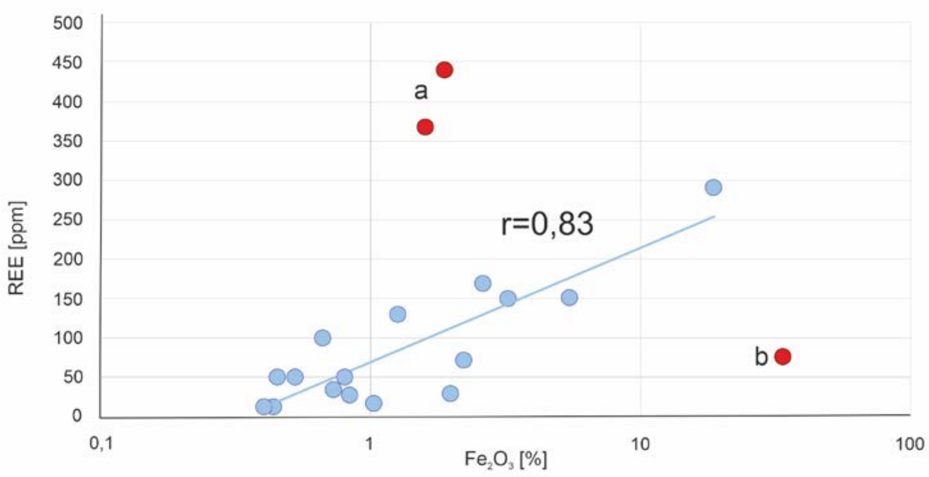


Text-fig. 15. Zr – REE relationship. a – quarzitic sandstone (unit "A") at the bottom of the Winna Formation, b – mudstones (units "B"–"E") of Winna Formation, c – carbonate rocks of Barania Góra Formation, Janczyce (unit "G", "H") and Jurkowice (unit "K") Members.

indicating either a gradual cessation of hydrothermal processes, or a decreasing share of redeposited sediments with elevated REE content, from the surroundings into the area of the carbonate platform. The enriched REE content and bell-shaped distribution in the supposed tuffitic T5 interlayer (Text-fig. 12) advocates for hydrothermal processes.

The distribution of the REE content in the younger Eifelian dolomites of the Jurkowice Member is similar to PAAS, with their total amount significantly reduced. There is a slightly lower total content of LREE than HREE. These carbonate rocks are characterized by low Zr content, below 30 ppm, and show a weaker correlation with the REE, with correlation coefficient r = 0.79.

A conspicuous feature of the studied siliciclastic formations of silty-clay composition (units "B"–"E") is the content of finely dispersed iron-bearing components, although often in small quantities. In the bottom part of the Emsian-Eifelian transitional beds, there are mudstones (unit "B"), colored red by finely dispersed hematite, with thin centimetric iron ore interlayers with up to 30% Fe_2O_3. In the overlaying tuffitic horizon (T-4, unit "C"), iron sulphides appear in the amount of about a few percent. The organic carbon content has also increased here up to about 1%, and the



Text-fig. 16. Fe_2O_3 – REE content relationship in the studied rock samples; red dots: a – heterolithes (unit "D") and b – hematite-bearing mudstone (unit "B"), respectively.

increased content of Cu (219 ppm), Pb (82 ppm), and Zn (250 ppm) is noteworthy. The fall of volcanic ash forming the tuffitic horizon changed the sedimentary environment from an oxidizing to a reducing, euxinic one. In the heterolithic rock suite (unit "D") lying above the tuffitic horizon, dispersed iron sulphides appear in silty-clay laminae. Iron sulphides are present also in the sandstone interlayers, where they are dispersed in the quartz grain cement and the filling of cracks (Text-fig. 7B) although they are now largely replaced by hydrated Fe oxides.

In the studied formations, excluding the heterolithic rock series and the sandy mudstones with hematite-rich lamina, REE is clearly correlated with the Fe (Fe_2O_3) content, with a correlation coefficient of r = 0.83 (Text-fig. 16). This allows us to assume that they were either jointly supplied to the sediments or the REEs were accumulated by colloidal Fe compounds. The high REE contents in the heterolithes evidently deviate from this relationship, which is consistent with the assumption that they were introduced by hydrothermal solutions. Sandy mudstones rich in Fe_2O_3 with hematite-hydrohematite interlayers also do not fit into this relationship. The form of the iron-oxide accumulation at the bottom of graded-bedded sandy mud laminae (Text-fig. 5C) suggests that it was of the bog ore type, formed in the nearshore swamp environment. Their special feature is an increased arsenic content (111 ppm) accumulated in the colloid-ochreous precipitate.

The lithological features of the studied complex of mudstone-clayey-sandy rocks in the transition zone from the Early to Middle Devonian formations exposed in the Jurkowice quarry, together with their geochemical features indicating possible hydrothermal activity during their deposition, provide a basis for a discussion of the "Devonian ore-bearing horizon" defined by Czarnocki (1923, 1951). This horizon, situated between the Emsian quarzitic sandstones and younger carbonate rocks, conventionally assigned to the Eifelian[1], may thus be reconsidered in light of the new observations. The "ore bearing" rocks are claystones with limonite accumulations and supposed siderite below the zone of weathering. The deposit in Dąbrowa near Kielce was considered a model site of siderite occurrence within deposits at the Emsian to Eifelian boundary (Czarnocki 1951). However, drilling studies conducted to the East and West of the place of former iron ore exploitation revealed that at the Emsian to Eifelian boundary only the pyrite-bearing clays are present, sometimes enriched with sulphides of Zn, Pb, and Cu (Nieć 1966; Wróblewski 1980; Kowalczewski and Wróblewski 1974). Siderite accumulation outside the Dąbrowa deposit has not been found. Sometimes only disseminated siderite has been detected (Tarnowska 1976; Malec and Studencki 1988) or its presence has been supposed by the occurrences of limonite concretions (Kozak *et al.* 2025).

Geochemical studies of black clay rocks from the Lower to Middle Devonian boundary zone in the

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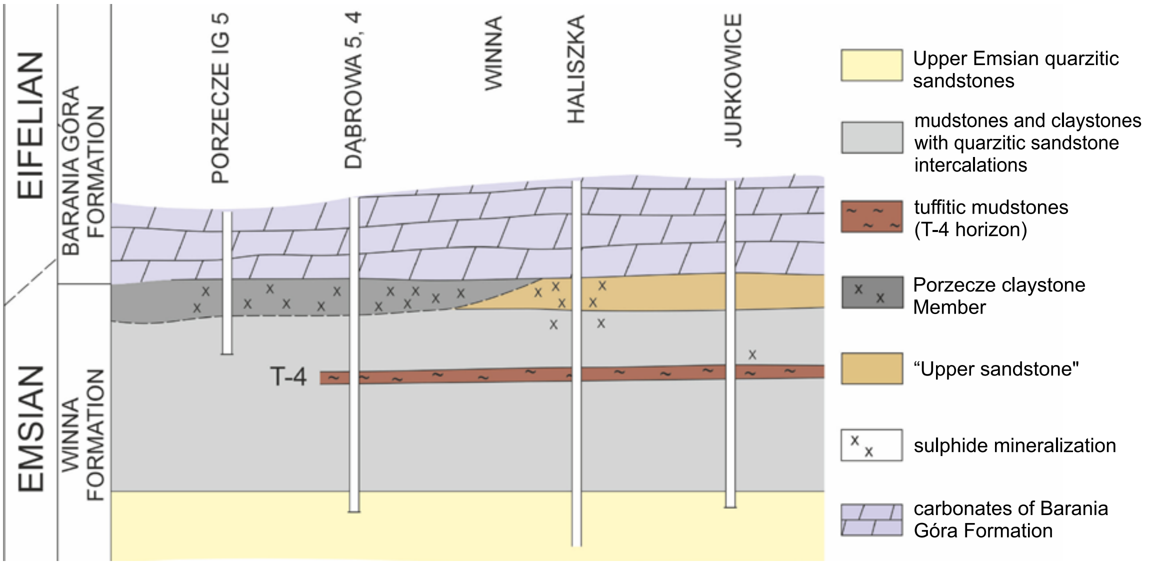
[1] Detailed chronostratigraphic studies indicate that the transition from clastics to carbonates is diachronous to the Emsian-Eifelian boundary. The carbonate sedimentation began at the end of the Emsian in some areas (Fijałkowska-Mader and Malec 2011). In Dąbrowa (D5 borehole) Emsian-Eifelian boundary is located within the pyrite bearing clays (Tarnowska and Malec 1985).



Text-fig. 17. Lithostratigraphical scheme of the Upper Emsian and Eifelian in the Kielce Region.

Western part of the Holy Cross Mountains in Dąbrowa, Miedziana Góra and Porzecze (Sadłowska and Lenik 2018) have revealed a convex-upwards REE PAAS normalized distribution pattern with increased MREE content, which suggests their hydrothermal supply to the sedimentary basin. The "pyrite-bearing clays", named the Porzecze Member by Wójcik (2015), were assigned to the base of the carbonate Barania Góra Formation. Fijałkowska-Mader and Malec (2011) located them above the "upper sandstone" horizon of the Winna formation. In the Western part of the Kielce region, the "upper sandstone" is missing and "pyrite bearing ("ore-bearing") clays" appears directly over the mudstones of the Winna Formation in Dąbrowa (Tarnowska and Malec 1987) and in Porzecze (Wójcik 2015). From a lithological point of view they may be considered to be the youngest member of this formation according to the rules of lithostratigraphy (Alexandrowicz *et al.* 1975; Racki and Narkiewicz 2006). Tarnowska and Malec (1987) have found in the Dabrowa (D5 borehole) the Emsian–Eifelian boundary located within the pyrite bearing clays.

In the Eastern part of the Kielce region, pyrite-bearing clays were not detected, but dolomitic sandstones finishing the sedimentation of the Winna formation were recorded below the younger carbonate rocks (Tarnowska 1969a, 1981). These "Upper sandstones" of the Winna Formation, which contain sulphides (Tarnowska 1969a), seem to be coeval with the pyrite bearing clays of the Porzecze Member, as both units occur above the T-4 tuffitic horizon and below younger carbonate formations (Text-fig. 17). In the Winna vicinity the pyrite-bearing clays found in outcrops between quartzites and dolomites (Czarnocki 1939; Rubinowski *et al.* 1966) appear close to the site of occurrence of the "upper sandstones", detected by boreholes (Tarnowska 1976).

In Jurkowice the hematite accumulations and the presence of iron sulphides, replaced in the weathering zone by hydrated Fe oxides ("limonite"), make the studied rocks similar to the those forming the "ore-bearing clays" horizon in the which occurrences of hematite and "limonitic" ores (as a product of iron sulphide weathering) on former mining sites were reported by Czarnocki (1923, 1956). Such features of the studied rocks allow us to assume that the "ore-bearing clays horizon" includes a complex of variegated claystone of the Winna Formation and overlying clayey formations or dolomitic sandstones, as previously suggested by Dowgiałło (1970) and Kowalczewski (1971), covered with various members of carbonate formations of the Late Emsian or Lower Eifelian (Text-fig. 17).

The pyrite-bearing clays, or limonite-bearing at outcrops, are also present in the Western part of the Łysogóry region (eastward from Bodzentyn) above the Late Emsian quarzitic sandstones of the Zagórze Formation and below various members of the carbonate formations (Pajchlowa 1957; Wróblewski 1968; Bzowska 1970; Wróblewski 1983; Fijałkowska-Mader and Malec 2011). They were informally named the Tarczek Member (Malec 2001). Such claystones dragged into the transversal dislocation zone, surround the part of the iron sulphide deposit at Rudki (Czarnocki 1950; Jaskólski *et al.* 1953; Nieć 1968).

Despite numerous studies of the deposits in the Early to Middle Devonian transition beds, the genesis of their mineralization is still unclear. A volcanogenic-sedimentary origin of sulphide mineralization has been suggested (Kowalczewski and Wróblewski 1974). The elevated REE content and their bell-shaped distribution in the transition formation from Emsian to Eifelian, suggesting their supply by hydrothermal solutions, support such previous assumptions. The source of the hydrothermal solutions is unknown. These could be heated formation waters of deep circulation or juveniles associated with the magmatic processes periodically repeated since the late Ludlowian up to the Late Carboniferous (Migaszewski 2002; Nawrocki *et al.* 2013; Krzemińska and Krzemiński 2019). The varied positions of the pyrite-bearing rocks may be a result of local variation of the sedimentation environment and localized pulses of supposed hydrothermal activity.

The submarine inflow of hydrothermal mineralizing solutions may have been related to the volcanic activity and seismic events evidenced in Jurkowice by the intensively convolute disturbed mudstone and clay layers. Similar phenomena are recorded today in coastal and marine formations in Mexico (Nuñez-Cornu *et al.* 2000) and Papua New Guinea (Pichler *et al.* 1999). Noteworthy is the occurrence of iron sulphide mineralization in the clays deposited at boundary between the Lower and Middle Devonian located in the vicinity of fault zones, in Winna and Belno in the Kielce region (Czarnocki 1939; Tarnowska 1969b). They might be the sites of discharge of hydrothermal solutions. A special case presents the iron sulphide deposit at Rudki located in the transversal fault zone (the Świętokrzyski Fault), partly within the claystones below the Eifelian dolomites. Its volcanogenic-sedimentary origin (SEDEX) was suggested by Gruszczyk (1961) but the presence of stockwork iron sulphide mineralization also in the Givetian dolomites indicates a younger hydrothermal deposit genesis (Nieć 1968). Hydrothermal remobilization of a former one is also possible.

The occurrence of siderite in the ore-bearing horizon is a special question. It occurs in the Dąbrowa deposit near Kielce (currently the Słoneczne Wzgórza estate in the urban area of Kielce). Czarnocki (1951) presented a description of it, based on available historical mine documents, as a model example of the sedimentary iron ores in the "Kuwin" beds. It was also described earlier by Pusch (1833), according to his direct observations in a mine active during his time. He reported gradual transitions from limestone to siderite, which suggests a metasomatic rather than sedimentary origin. Apart from the deposit in Dąbrowa, no siderite has been found in clays and mudstones deposited from the Emsian to Eifelian (Wróblewski 1980), but concretions interpreted as oxidized siderite have been reported in Szydłówek and Porzecze (Malec and Studencki 1988). The variegated clays with limonite iron ores found in transitional beds on the Early to Middle Devonian boundary in the other sites are, according to Czarnocki (1923), "a product of the decomposition of dolomitic marls and dolomites". This type of iron ore occurrence led Bohdanowicz (1934) to assume that the formation of siderite "may be the result of a wide underground circulation of mineralized water from the surface...".

The mode of occurrence of siderite in Jurkowice gives arguments against its sedimentary formation. Limestones in tectonic contact with the iron sulphide bearing mudstone-clay formations contain numerous centimetric nests of limonite whose boxwork structure suggests formation through the weathering of siderite (Blanchard 1968). Siderite also appears in thin veinlets. The siderite was probably formed by the reaction of iron sulphites produced through iron sulphide weathering, with calcium carbonate, and simultaneous removal of calcium sulphite formed in an acidic environment (Smirow 1956; Blanchard 1968).

$$\mathrm{FeSO_4 + CaCO_3 = FeCO_3 + CaSO_4}$$

Minute, fine gypsum crystals remain visible at the border of limonite nests formed in place of supposed former siderite.

These observations support the assumption regarding the epigenetic genesis of siderite in the Dąbrowa deposit (Wróblewski 1980) suggested by gradual transitions from siderite to limestone noted by Pusch (1833). The replacement of limestone by siderite there, may be explained by the process related to iron sulphide weathering. The same genesis of siderite present in the Rudki deposit is also possible (Nieć 1968).

CONCLUSIONS

Signs of hydrothermal activity during deposition of the Winna Formation allow us to assume that the "ore-bearing horizon" on the Emsian to the Eifelian boundary comprises the youngest elements of this formation and the overlying "pyrite-bearing clays" distinguished in the Kielce region as the Porzecze Member. Their common feature is varied iron sulphide content which is replaced by spotty, streaky and nested concentrations of hydrated iron oxides in the weathering zone. They are accompanied by hematite, which is also present in unweathered rocks. The siderite appearing in these formations and their vicinity is most probably a product of replacement of limestones or dolomites as the result of their reaction with Fe sulphates formed due to the oxidation of iron sulphides. The increased REE content which characterizes the clay-silt deposits of the Winna formation merits attention because it suggests the possibility of their higher concentrations in other areas of the occurrence of these deposits.

The widespread area of mineralization at the Early to Middle Devonian boundary in the Holy Cross Mountains is interesting as it is located on the periphery of the "Devonian Mineral Belt" which extends from Western Germany up to Romania (Amstutz *et al.* 1971). Numerous ore deposits considered to be of volcanogenic-sedimentary origin (e.g. Meggen, Rammelsberg in Germany, Poiana Rusca in Romania) are located here, suggesting the existence of a long-lasting, probably deep-seated sources of mineralizing solutions.

Acknowledgements

The Authors are thankful to the Jurkowice Mine management for allowing them to work in the quarry and for their kind support in the field. We address special thanks to the reviewers for their valuable remarks, which motivated us to revise the presentation of the results of our study and make the conclusions, we hope, clearer, however we admit that some of these may be disputable.

REFERENCES

Alexandrowicz, S., Birkenmajer, K., Burchart, J., Cieśliński, S., Dadlez, R., Kutek, J., Nowak, W., Orłowski, S., Szulczewski, M. and Teller, L. 1975. Zasady polskiej klasyfikacji, terminologii i nomenklatury stratygraficznej. Instrukcje i Metody Badań Geologicznych, 33. Wydawnictwa Geologiczne, Warszawa.

Amstutz, G.C. Zimmermann, R.A. and Schot, E.H. 1971. The Devonian Mineral Belt of Wester Germany, Geotectonic Framework. Sedimentology Congress Guidebook VIII, Sedimentology of parts of Central Europe, 253–254.

Bechtel, A. Ghazi, A.M., Elliott, W.C. and Oszczepalski, S. 2001. The occurrences of the rare earth elements and the platinum group elements in relation to base metal zoning in the vicinity of Rote Fäule in the Kupferschiefer of Poland. *Applied Geochemistry*, **16**, 375–386.

Belka, Z. and Narkiewicz, M. 2008. Devonian. In: T. McCann (Ed.) The Geology of Central Europe Volume 1: Precambrian and Palaeozoic, 383–410

Blanchard, R. 1968. Interpretation of leached outcrops. *Nevada Bureau of Mines Bulletin*, **66**, 8–196.

Bohdanowicz, K. 1934. Zagadnienia poszukiwań rud żelaznych na obszarze świętokrzyskim. Naczelne Archiwum Geologiczne, Państwowy Instytut Geologiczny, 17 pp.

Borucki, J., Głowacki, Z., Masłowski, W., Sałdan, M., Uberna, J. and Zajączkowski, W. 1967. Ocena perspektyw poszukiwawczych złóż rud uranu w Polsce. *Prace Instytutu Geologicznego*, 93 pp.

Boulvais, P., De Parseval, P., D'Hulst, A.D. and Paris, P. 2006. Carbonate alteration associated with talc-chlorite mineralization in the eastern Pyrenees, with emphasis on the St. Barthelemy Massif. *Mineralogy and Petrology*, **88**, 499–526.

Bzowska, R. 1970. Objawy mineralizacji kruszcowej w otworach Chełmowa 4, Chełmowa 3 i Modrzewie 1. *Kwartalnik Geologiczny,* **14**, 928–929.

Czarnocki, J. 1923. O rudach żelaznych paleozoicznych w środkowej części Gór Świętokrzyskich. *Posiedzenia Naukowe Państwowego Instytutu Geologicznego*, **6**, 14–15.

Czarnocki, J. 1939. Piryt w okolicy Winnej pod Łagowem. *Biuletyn Państwowego Instytutu Geologicznego*, **15**, 8.

Czarnocki, J. 1950. Geologia regionu łysogórskiego w związku z zagadnieniem złoża rud żelaza w Rudkach. *Prace Państwowego Instytutu Geologicznego*, 1, 15–404.

Czarnocki, J. 1951. Złoże rud żelaza w Dąbrowie pod Kielcami w związku z zagadnieniem rud dewońskich w Świętokrzyskim. Księga Pamiątkowa ku czci prof. Karola Bohdanowicza. *Prace Państwowego Instytutu Geologicznego*, **7**, 95–114.

Czarnocki, J. 1956. Złoża rud żelaza, kruszców ołowiu i miedzi w regionie świętokrzyskim. Jan Czarnocki Prace geologiczne t. V, Surowce mineralne w Górach Świętokrzyskich, *Prace Państwowego Instytutu Geologicznego,* 100–108.

Czermiński, J. and Ryka, W. 1962. Bentonites in Eifelian dolomites at Jurkowice near Klimontów. *Kwartalnik Geologiczny*, **6**, 8–20 [In Polish with English summary].

Dowgiałło, D. 1970. Wyniki wierceń geologicznych wykonanych w Paśmie Bielińskim i Wale Małacentowskim w Górach Świętokrzyskich. *Kwartalnik Geologiczny*, **14**, 924–925.

Fijałkowska-Mader, A. and Malec, J. 2011. Biostratigraphy of the Emsian to Eifelian in the Holy Cross Mountains (Poland). *Geological Quarterly,* **55,** 109–138.

Frimmel, H.E. 2009. Trace element distribution in Neoproterozoic carbonates as paleoenvironmental indicator. *Chemical Geology,* **258**, 338–353.

Frimmel, H.E. and Lane, K. 2005. Geochemistry of carbonate beds in the Neoproterozoic Rosh Pinah Formation, Namibia; implications on depositional setting and hydrothermal ore formation. *South African Journal of Geology*, **108,** 5–18.

Gao, S. 2019. Geology and sedimentology of tidal flats. *Coastal Wetlands,* **17***,* 359–381. Elsevier.

Gradziński, R., Kostecka, A., Radomski, A. and Unrug, R. 1986. Zarys sedymentologii. Wydawnictwa Geologiczne, Warszawa.

Gruszczyk, H. 1961. Jeszcze w sprawie poszukiwań rud metali. *Przegląd Geologiczny*, **9**, 7–9.

Hecht, L., Freiberger, R., Gilg, A.H., Grundmann, G. and Kostisyn, Y.A. 1999. Rare earth element and isotope (C, O, Sr) characteristics of hydrothermal carbonates: genetic implications for dolomite-hosted talc mineralization at Göpfersgrün, (Fichtelgebirge, Germany). *Chemical Geology*, **155**, 115–130.

Jaskólski, S., Poborski, C. and Goerlich, E. 1953. Złoże pirytu i rud żelaznych kopalni „Staszic" w Górach Świętokrzyskich. *Biuletyn Instytutu Geologicznego*, 122 pp.

Kasza A. and Król P. 2019. Poszukiwania uranu w okolicach Daleszyc i Łagowa. *Studia Muzealno-Historyczne*, **11**, 139–148.

Konon, A. 2007. Strike-slip faulting in the Kielce unit, Holy Cross Mountains, central Poland. *Acta Geologica Polonica*, **57**, 415–441.

Kowalczewski, Z. 1971. Main geological problems of the Lower Devonian in the Świętokrzyskie Mts. *Kwartalnik Geologiczny*, **15**, 263–282 [in Polish with English summary].

Kowalczewski, Z. and Wróblewski, T. 1974. Problem of ore contents in sediments in the light of diastrophism and volcanism in the Świętokrzyskie Mts. *Kwartalnik Geologiczny,***18**, 537–561 [In Polish with English summary].

Kozak B., Fijałkowska-Mader A. and Rutkiewicz P. 2025. Historia eksploatacji rud żelaza w północnym skrzydle synkliny daleszyckiej (Góry Świętokrzyskie). *Przegląd Geologiczny*, **73**, 98–106.

Krzemińska, E. and Krzemiński, L. 2019. Magmatic episodes in the Holy Cross Mountains, Poland – A new contribution from multi-age zircon populations. *Biuletyn Państwowego Instytutu* Geologicznego, **474**, 43–58.

Lenartowicz, L. 1999. Regionalny profil geochemiczny utworów dewonu w Górach Świętokrzyskich. Materiały konferencyjne: Geologia i sozologia w regionie świętokrzyskim u schyłku XX wieku. Polskie Towarzystwo Geologiczne, Odział Świętokrzyski, Kielce, 17–41.

Malec, J. 2001. Litostratygrafia osadów na pograniczu dewonu dolnego i środkowego w regionie łysogórskim Gór Świętokrzyskich.. *Posiedzenia Naukowe Prace Państwowego Instytutu Geologicznego*, **57**, 102–106.

Malec, J. 2005. Lithostratygraphy of the Lower and Middle Devonian boundary interval in the Łysogóry region of the Holy Cross Mts. (Poland). *Biuletyn Państwowego Instytutu* Geologicznego*,* **415**, 5–59 [In Polish with English summary].

Malec J. and Studencki M. 1988. Lower Eifelian at Szydłówek in Kielce. *Biuletyn Państwowego Instytutu* Geologicznego, **358**, 73–92 [in Polish with English summary].

Migaszewski Z.M, 2002. Datowanie diabazów i lamprofirów świętokrzyskich metodą K-Ar i Ar-Ar. *Przegląd Geologiczny*, **50**, 227–229.

Musiał, A., Sermet, E. and Nieć, M. 2017. Rare earth elements in the rock sequence from Lower to Middle Devonian in the Holy Cross Mountains, Poland. 17 International Mutidisciplinary Scientific Geo-Conference SGEM, 1–7.

Narkiewicz, M., Olkowicz-Paprocka, I. and Romanek, A. 1981. Jurkowice – Kamieniołom dolomitów marglistych środkowego dewonu. Przewodnik LIII Zjazdu PTG, Kielce, Wydawnictwa Geologiczne Warszawa, 271–276.

Narkiewicz, M., Racki, G., Skompski, S. and Szulczewski, M. 2006. Zapis procesów i zdarzeń w dewonie i karbonie Gór Świętokrzyskich. LXXVII Zjazd Naukowy Polskiego Towarzystwa Geologicznego; Procesy i zdarzenia w historii geologicznej Gór Świętokrzyskich. Państwowy Instytut Geologiczny, Warszawa, 51–62.

Nawrocki, J., Salwa S. and Pańczyk, M. 2013. New ^{40}Ar^{39}Ar age constrains for magmatic and hydrothermal activity in the Holy Cross Mts. (southern Poland). *Geological Quarterly*, **57**, 551–560.

Nieć, M. 1966. Metasomatyczne złoża syderytu i hematytu w Górach Świętokrzyskich i perspektywy poszukiwań złóż tego typu. *Zeszyty Naukowe AGH, XIV Sesja Naukowa*, **139**, 253–262.

Nieć, M. 1968. Mineralization of the deposit of iron sulphides and siderite at Rudki in the Holy Cross Mountains. *Prace Geologiczne PAN*, **46**, 7–82 [in Polish with English summary].

Nieć, M., Pawlikowski, M. and Sermet, E. 2024. Multi-stage fault formation and REE distribution in surrounding Devonian dolomites in the South-Eastern Part of Holy Cross Mountains (Poland). *Geology, Geophysics and Environment*, **50**, 77–92.

Nozaki, Y., Zhang, J. and Amakawa, H. 1997. The fractionation between Y and Ho in the marine environment. *Earth and Planetary Science Letters*, **148**, 329–340.

Nuñez-Cornu, F.J., Prol-Ladesma, R.M., Cupul-Magaña, A. and Suarez-Plascencia, C. 2000. Near shore submarine hydrothermal activity in Bahia Banderas, Western Mexico. *Geofisica Internacional*, **39**, 171–178.

Oszczepalski, S., Chmielewski, A. and Mikulski, S. 2016. Controls on the distribution of rare earth elements in the Kupferschiefer series of SW Poland. *Geological Quarterly,* **60**, 811–826.

Pajchlowa, M. 1957. Dewon w profile Grzegorzowice–Skały. *Biuletyn Instytutu Geologicznego*, 122, Z badań geologicznych regionu świętokrzyskiego T. II, 145–254.

Pichler, T., Giggenbach, W.F., McInnes B.I., Buhl, D. and Duck, B. 1999. Fe sulphide formation in the seawater-gas-sediment interaction in a shallow-water hydrothermal system at Lihir Island, Papua, New Guinea. *Economic Geology,* **94**, 281–288.

Piper, D.Z. and Bau, M. 2013. Normalized Rare Earth Elements in water, sediments and wine: identifying sources and environmental redox conditions. *American Journal of Analytical Chemistry*, **4**, 69–83.

Pusch, G.G. 1833. Geognostische Beschreibung von Polen so wie Ubrigen Nordkarpathen Länder, Stuttgart u. Tübingen, 216 pp.

Racki, G. and Narkiewicz, M. 2000. Tectonic versus eustatic controls of sedimentary development of the Devonian in the Holy Cross Mts., Central Poland. *Przegląd Geologiczny*, **48**, 65–76 [In Polish with English summary].

Romanek, A. 1977. Objaśnienia do szczegółowej mapy geologicznej Polski, arkusz Klimontów (887). Instytut Geologiczny, Wydawnictwa Geologiczne, Warszawa.

Rubin J.N., Henry C.D. and Price J.G. 1993. The mobility of zirconium and other "immobile" elements during hydrothermal alteration. *Chemical Geology,* **110**, 29–47.

Rubinowski, Z., Kowalczewski, Z., Lenartowicz, L. and Wróblewski, T. 1966. Metalogeneza trzonu paleozoicznego Gór Świętokrzyskich. *Prace Instytutu Geologicznego*, 378 pp.

Rudnick, R.L. and Gao, S. 2003. Composition of the continental crust. *Treatise on Geochemistry*, **3**, 1–64.

Sadłowska, K. and Lenik, P. 2018. Geochemia czarnych łupków w strefie przejściowej dewonu dolnego i środkowego Gór Świętokrzyskich. Kongres Surowcowy, V Konferencja: Złoża Kopalin – Aktualne Problemy Prac poszukiwawczych, badawczych i dokumentacyjnych. Kraków, 56–58.

Sawłowicz, Z. 2013. REE and their relevance to the development of the Kupferschiefer copper deposit in Poland. *Ore Geology Reviews*, **55**, 176–186.

Shanmugam G. 2016. The seismite problem. *Journal of Paleogeography*, 5, 318–362.

Sims J.D. 1973. Earthquake induced structures in sediments of Van Norman Lake, San Fernando, California. *Science*, **182**, 161–163.

Skompski, S. and Szulczewski, M. 1994. Tide-dominated Middle Devonian sequence from the northern part of the Holy Cross Mountains (Central Poland). *Facies*, **30**, 247–265.

Smirnow, S.O. 1956. Strefa utlenienia złóż siarczkowych. Wydawnictwa Geologiczne, Warszawa, 317 pp.

Studencka, J. 1983. *Chimaerothyris dombrowiensis* (Gürich) from Lower Eifelian in the Góry Świętokrzyskie Mts. *Kwartalnik Geologiczny*, **27**, 471–490 [In Polish with English summary].

Szulczewski, M. 1995. Depositional evolution of the Holy Cross Mts. (Poland) in the Devonian and Carboniferous – a review. *Geological Quarterly*, **39**, 471–488.

Tarnowska, M. 1969a. Wstępne dane o mineralizacji warstw przejściowych emsu i eiflu w strefie Łagów – Iwaniska w Górach Świętokrzyskich. *Rocznik Polskiego Towarzystwa Geologicznego*, **39**, 727–731.

Tarnowska, M. 1969b. Iły z pogranicza emsu i eiflu w otworze Belno-1 w Górach Świętokrzyskich. *Kwartalnik Geologiczny*, **13**, 945–947.

Tarnowska, M. 1970. Kruszcowa mineralizacja impregnacyjna w profilu emsu i eiflu w regionie kieleckim. *Kwartalnik Geologiczny*, **22**, 936–937.

Tarnowska, M. 1971. Polymictic and tuphogene deposits of Lower Devonian in the Kielce region in the Świętokrzyskie Mts. *Kwartalnik Geologiczny*, **15**, 569–586 [In Polish with English summary].

Tarnowska, M. 1976. Lithological structure and correlation of the Lower Devonian in the Eastern part of the Góry Świętokrzyskie. *Biuletyn Instytutu Geologicznego,* **296**, 75–128 [In Polish with English summary].

Tarnowska, M. 1981. Dewon dolny w centralnej części Gór Świętokrzyskich. Przewodnik LIII Zjazdu PTG, Kielce, Wydawnictwa Geologiczne, Warszawa, 57–68.

Tarnowska, M. 1983. Litostratygrafia niższego dewonu w regionie kieleckim Gór Świętokrzyskich. Archiwum NAG, Warszawa, 140 pp.

Tarnowska, M. 1999. Schemat dewońskiego wulkanizmu piroklastycznego w Górach Świętokrzyskich. Geologia i sozologia w regionie świętokrzyskim u schyłku XX wieku. X Konferencja sozologiczna PTG-PIG, Kielce, 43–54.

Tarnowska, M. and Malec, J. 1987. Osady pogranicza emsu i eiflu w otworze wiertniczym Dąbrowa D5 k. Kielc. *Kwartalnik Geologiczny*, **31**, 510–511.

Terwindt J. H. J. 1981. Palaeo-tidal reconstructions of inshore tidal depositional environment. In: R L. de Boer A., van Gelder and S. D. Nio (Eds) Tide-Influenced Sedimentary Environment and Facies. D. Reidel Publishing Company, Dordrecht, 233–263.

Tostewin, R., Shields, G.A., Tarbuck, G.M., Clarson, M.O. and Wood, R.A. 2016. Effective use of cerium anomalies as a redox proxy in carbonate dominated marine settings *Chemical Geology*, **438**, 146–162.

Wójcik, K. 2015. The uppermost Emsian and lower Eifelian in the Kielce Region of the Holy Cross Mts. Part I: Lithostratigraphy. *Acta Geologica Polonica*, **65**, 141–179.

Wróblewski, T. 1973a. Uwagi w sprawie genezy mineralizacji złoża „Staszic" w Górach Świętokrzyskich. *Kwartalnik Geologiczny*, **17**, 661.

Wróblewski, T. 1973b. Nowy punkt występowania ciemnych iłów pirytonośnych w dewonie antykliny bielińskiej w Górach Świętokrzyskich. *Kwartalnik Geologiczny*, **17**, 956–957.

Wróblewski, T. 1980. Rudy żelaza w Dąbrowie w świetle wyników wiercenia Stara Góra IG-1. *Kwartalnik Geologiczny*, **24**, 975–976.

Wróblewski, T. 1983. Mineralizacja siarczkowa skał dewonu środkowej i wschodniej części synkliny bodzentyńskiej Gór Świętokrzyskich. *Kwartalnik Geologiczny*, **27**, 881–883.

Wróblewski, T. 1988. Siarczki metali w ciemnych skałach świętokrzyskiego dewonu. *Kwartalnik Geologiczny*, **32**, 759–760.

Manuscript submitted: 6th June 2025
Revised version accepted: 3rd March 2026