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THERMAL HISTORY OF LOWER PALAEOZOIC ROCKS FROM THE EAST EUROPEAN PLATFORM MARGIN OF POLAND BASED ON K-AR AGE DATING AND ILLITE-SMECTITE PALAEOTHERMOMETRY

Sylwia KOWALSKA[1*], Artur WÓJTOWICZ[2], Stanisław HAŁAS†[2], Klaus WEMMER[3], Zbigniew MIKOŁAJEWSKI[4] & Arkadiusz BUNIAK[5]

† Stanisław Hałas (1945–2017)
[1]Well Logging Department, Oil and Gas Institute – National Research Institute, Lubicz 25a, 30-503 Kraków, Poland; e-mail: kowalska@inig.pl
[2]Mass Spectrometry Laboratory, Institute of Physics, Maria Curie-Skłodowska University, Maria Skłodowska-Curie Square 4, 20-031 Lublin, Poland
[3]Isotope Geology Division, Geoscience Center, University of Göttingen, Goldschmidtstr. 3,37077 Göttingen, Germany
[4]Polish Oil and Gas Company, Zielona Góra Branch, Staszica Square 9, 64-920 Piła, Poland,
[5]Orlen Upstream, Przyokopowa 31, 01-228 Warszawa, Poland
** Corresponding author*

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Abstract: Large-scale shale gas prospecting in the Polish part of the East European Platform did not discover large reserves of this resources. The article presents new research indicating that one of the reasons for the lack of shale gas relates to the thermal history of the Lower Palaeozoic rocks. Illite-smectite palaeothermometry was used to reconstruct the history of the platform and determine the maximum temperatures to which these rocks were subjected. The age of illitisation was also constrained using the K-Ar method. This method allowed precise dating of the maximum age of thermal transformations due to the deposition of numerous pyroclastic horizons (K-bentonite) throughout the entire geological profile from the Cambrian to the Silurian. Isotopic dating was made on over 53 samples of Lower Palaeozoic bentonites and low-grade metamorphic clays. These results were supplemented by analysis of the degree of thermal (smectite to illite) transformation in the profiles of 37 deep boreholes. 11 zones could be distinguished with different tectonic histories within the Polish part of the East European Platform edge. Maximum heating occurred in this region at about 320–340 Ma, corresponding to the Early Carboniferous or the turn of the Early and Late Carboniferous, phase A of the Variscan orogeny, known as the Sudetian phase. In the southern part of study area, the maximum of thermodiagenesis is slightly younger – 270–290 Ma, which responds to the Early Permian, the Asturian phase, the last phase of the Variscan orogeny. This means that the generation of hydrocarbons occurred before significant Mesozoic exhumation of the Polish part of the East European Platform, which led to the escape of a considerable amount of the gas generated. The study also presents the results of an interlaboratory comparison of illite age dating using the K-Ar and Ar-Ar methods. The comparison was conducted to find out what realistic error should be considered when interpreting geological K-Ar dating results.

Key words: Shale gas, K-Ar dating, thermal history, Variscan orogeny, Palaeozoic, East European Platform, interlaboratory comparison.

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INTRODUCTION

During 2010–2015, Poland became an area of intense exploration for unconventional hydrocarbons in the form of shale gas. The search for commercial accumulations commenced in 2009 after publications of the American consulting companies Wood McKenzie and Advanced Resources International Inc. revealed rough resource estimates for Lower Palaeozoic shale gas in slope deposits of the East European Platform in Poland of about 1.4 or even 3 trillion cubic metres (Poprawa, 2010a, b; Podhalańska *et al*., 2016). Precise estimates by the Polish Geological Institute – National Research Institute (PGI-NRI) were more conservative at only 346–768 billion cubic metres of recoverable shale gas (First Report PGI-NRI, 2012; Kiersnowski and Dyrka, 2013). These diverse assessments motivated oil and gas companies to carry out additional detailed analyses of the shale-gas-bearing sediments with the intension of establishing more accurate estimates of the hydrocarbon resources.

The investigation of areas that are prospective for hydrocarbons involves establishing the degree of thermal transformation that the source rocks experienced as well as reconstructing the thermal history, in particular the time span when the maximum palaeotemperatures occurred. Parameterising these factors allows the time range of peak hydrocarbon generation to be established. This can be used to model geochemically the amount of hydrocarbons generated, on the basis of the primary level of total organic carbon (TOC) present. Moreover, on this basis, it is possible to identify the probable locations of hydrocarbon accumulations as well as to estimate the probability of their preservation. Such models also can be used to analyse the possibility of a shale gas deposit undergoing natural fracturing after the time of hydrocarbon generation. In the case of the East European Platform slope, this issue is particularly important owing to the complicated tectonic history of the area explored. The research area (Fig. 1) is situated on the border with the Trans European Suture Zone (TESZ): a major structure constituting the contact zone between the old East European Precambrian Platform and the younger West European Palaeozoic Platform (Pharaoh, 1999).

Analysis of the smectite illitisation process is one of the ways of evaluating the maximum palaeotemperatures, to which rocks were subjected during their diagenetic history (Hower *et al*., 1976; Pollastro, 1993; Šucha *et al*., 1993; Środoń, 2007). The illite-smectite palaeothermometer exploits the phenomenon of smectite transformation, which originates at surface conditions and then alters into mixed-layer illite-smectite (I/S) minerals and finally to illite or even muscovite, if the temperature conditions are high enough. This reaction is predominantly temperature-related, although the concentration of K+ also affects the rate of reactions (Hower, 1981; Whitney, 1990; Price and McDowell, 1993; Warr *et al*., 2017). The process begins at ca. 70 ºC and continues up to at least 200 ºC. A decrease in the percentage of smectite layers in I/S is observed from 80–100 and to 0%, assuming the availability of sufficient potassium (Šucha *et al*., 1993). The reaction continues together with an increase in crystallite thickness into the range of 200–300 °C, as measured by the illite "crystallinity" (Kübler index; Kübler, 1968) method. This is commonly employed using pelitic rocks (not containing volcanogenic material) to identify the

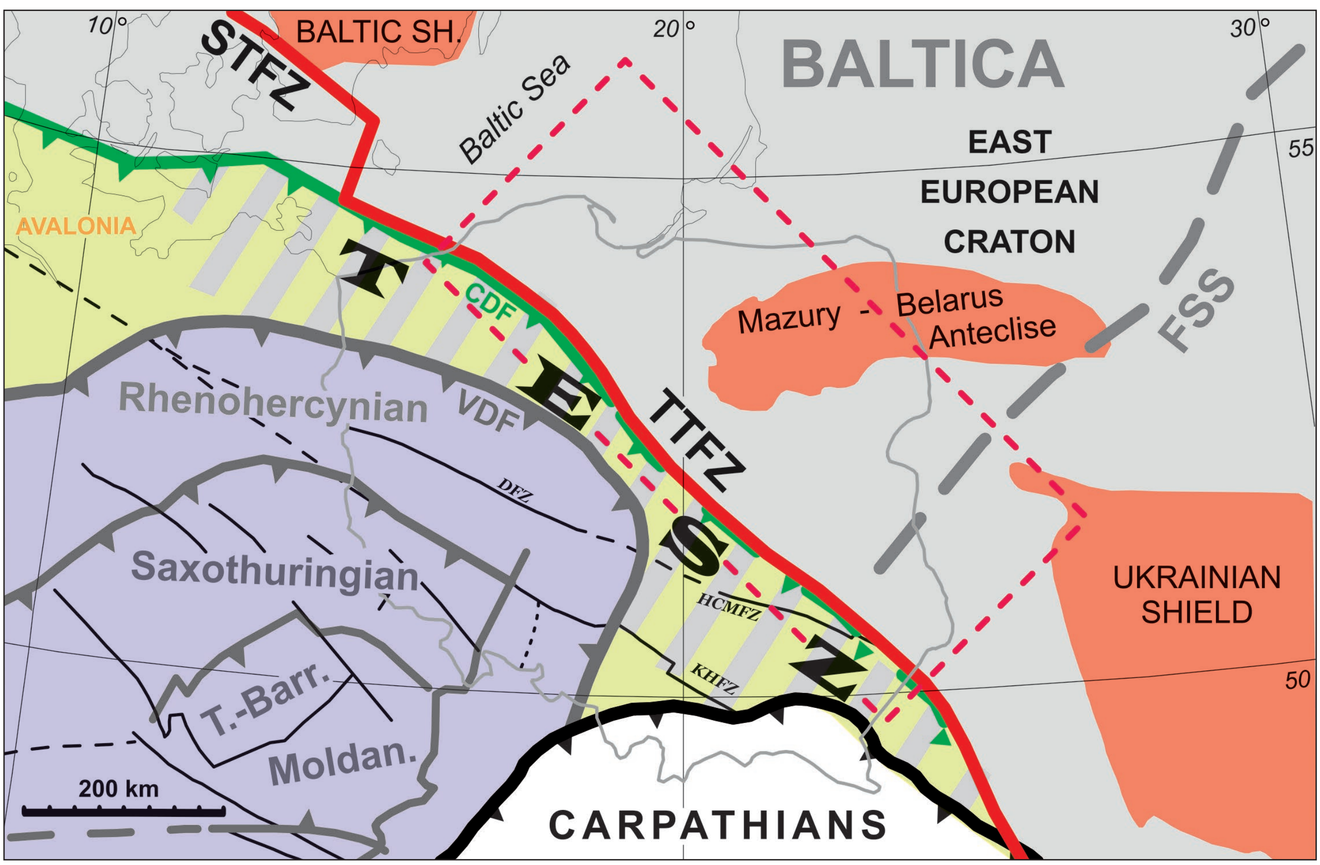

Fig. 1. Tectonic sketch map of Central Europe. Modified after Żelaźniewicz *et al*. (2011), Puziewicz *et al*. (2017), Meschede and Warr (2019). TESZ – Trans European Suture Zone (mixed grey yellow stripes); TTFZ – Teisseyre-Tornquist Fault Zone; STFZ – Sorgenfrei-Tornquist Fault Zone; FSS – Fennoscandia-Sarmatia Suture; CDF – Caledonian deformation front; VDF – Variscan deformation front; T.-Barr. – Teplá-Barrandian Unit; DFZ – Dolsk Fault Zone; HCMFZ – Holy Cross Mountains Fault Zone; KHFZ – Kraków-Hamburg Fault Zone.

stages of progressive thermal alteration from the transition from diagenesis to metamorphism (Merriman and Frey, 1999; Árkai *et al*., 2007). Illite-smectite palaeothermometry determines not only the maximum palaeotemperatures but also, in combination with the K-Ar (potassium-argon) method, the age of maximum thermodiagenesis, when either K-bentonites or anchimetamorphic mudrocks occur in the geological profile (Fig. 2).

In the case of the Silurian and Ordovician rocks, the occurrence of numerous layers of pyroclastic material offers a unique possibility of precisely determining the ages of the thermal events, to which these rocks were subjected. The reconstruction of complete thermodiagenetic profiles for selected boreholes across the region, including the Mesozoic cover, enabled the authors to evaluate the impact of thermal

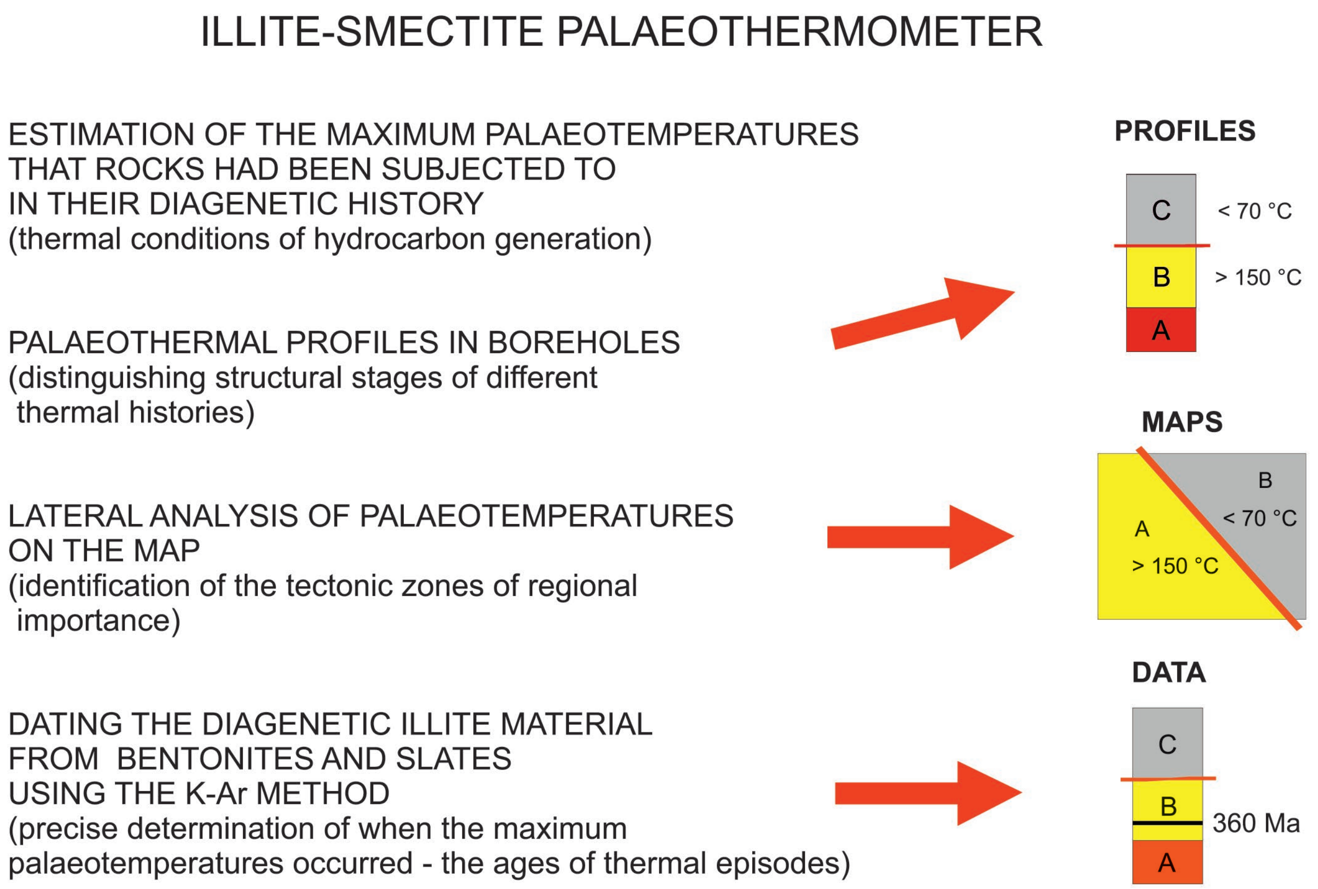

Fig. 2. Illite-smectite palaeothermometer methodology applied in the study.

The objective of this study was to provide information on the burial history of the Polish Lower Palaeozoic rocks that lie on the edge of the East European Platform and to determine the age of thermal events that can be used as constraints for modelling the maturation history of organic matter within the Baltic, Podlasie and Lublin basins (Fig. 3). The previously published data have indicated the possibility of a number of thermal events in Poland that influenced the Palaeozoic rocks during their diagenetic history: 1) a Devonian event (in the East Pomerania; Środoń and Clauer, 2001), 2) a Late Carboniferous–Early Permian event (on the Małopolska Massif; Kowalska, 2008), 3) a Triassic event (in the Polish Lowlands; Kowalska *et al*., 2015) and 4) a Jurassic–Cretaceous event (in all the above mentioned regions; Poprawa *et al*., 2010). However, previous results have been limited regionally and this has not allowed the precise determination of where and when these events took place. Their relationship to hydrocarbon generation also has remained obscure.

events on the maturation of organic matter and generation of hydrocarbons in the context of shale gas exploration.

In addition to these aspects, a number of methodological issues concerning the K-Ar age dating method were addressed in this study. Earlier works implied the necessity of carrying out measurements on four grain-size fractions and on pure bentonites (Środoń and Clauer, 2001; Środoń *et al*., 2013). It was interpreted even in terms of differences in the burial histories of sedimentary basins (Środoń *et al*., 2002; Szczerba *et al*., 2015). Such a methodology meant extensive costs, along with the necessity of conducting the measurements over a large research area. In the present study, this was the entire edge of the East European Platform in Poland. The error value that should be assumed for analysis of the results obtained in a geological interpretation was another issue to be addressed.

This paper is a significantly modified version of the book chapter by Kowalska *et al*. (2017b), published in Polish.

GEOLOGICAL SETTING

The East European Platform constitutes the sedimentary cover of the East European Craton, also known as Baltica. It extends over a considerable part of Eastern Europe and Scandinavia (Fig. 1). The craton was part of the old supercontinent Rodinia, which broke up around 750 Ma (Nawrocki and Poprawa, 2006). The basement of the craton is composed of crystalline and metamorphic rocks of Archean age (Bogdanova *et al*., 2008). After Late Proterozoic rifting, the western margin of the East European Craton evolved into a passive margin and later during the Middle Ordovician–Silurian underwent flexural bending, as a result of a collision between Baltica and Avalonia (Poprawa *et al*., 1999; Poprawa and Pacześna, 2002; Nawrocki and Poprawa, 2006). During downflexure, a sedimentary basin was formed and filled with Lower Palaeozoic sediments of Cambrian, Ordovician and Silurian age.

To the west, this basin borders with the Trans European Suture Zone (TESZ) (Pharaoh, 1999; Żelaźniewicz *et al*., 2011), the eastern margin of which is considered to be bounded by the Teisseyre-Tornquist Fault Zone (TTFZ). The TTFZ is 2,000 km long and is treated as the major tectonic line separating the European crust of Precambrian age from the younger West European Platform considered to have been consolidated during the Palaeozoic.

In the Polish part of the East European Platform margin, three smaller basins can be distinguished: the Baltic, Podlasie and Lublin basins (Fig. 3). Each basin differs in the development of Lower Palaeozoic rocks as well as the Upper Palaeozoic and Mesozoic cover (Poprawa, 2010a, 2017). In geological profiles of the Cambrian, Ordovician and Silurian strata, there are rocks rich in organic matter that constitute potential source rocks for hydrocarbons. The major part of these sequences consists of shales and mudstones with a small number of sandstone and carbonate interlayers (Porębski *et al*., 2013).

Numerous layers of volcanic material also are known among the Lower Palaeozoic sedimentary rocks (Dziadzio *et al.*, 2017; Kędzior *et al*., 2017). In the Ordovician, volcanogenic rocks were deposited during the Caradoc and during the early part of the Late Ordovician. Deposits as thick as 3 m were formed in the south of Poland and can be studied in the Lubycza Królewska-1 borehole of the Łysogóry Unit (Fig. 3). Moreover, bentonites and tuffs occur in the Silurian sequence in all stratigraphic units. Over 100 horizons of different thicknesses, ranging from <0.5 cm up to over 30 cm, have been described in recent boreholes. The stratigraphic age of these bentonites was determined using palaeontological methods (Podhalańska, 2017) as well as using the U-Pb zircon dating method (Anczkiewicz *et al*., 2017). Additionally, a 2–3 cm layer of volcanogenic material was found in the Borcz-1 borehole in the middle Cambrian sedimentary rocks of the Baltic Basin (Kowalska *et al*., 2016). The Lower Palaeozoic volcanogenic rocks represent episodes of intensive volcanic activity, recognized on a global scale (Huff, 2016).

SAMPLES

The research material, selected for the main study, consisted of 53 samples in total. These samples included mostly Lower Palaeozoic bentonites, four anchimetamorphic mudrocks (the Polik IG-1 and Bodzanów IG-1 boreholes) and one shale (the Opalino-4 borehole, for comparison), all coming from the Polish part of the East European Platform margin. The samples were collected from 14 different boreholes (Fig. 3; Tab. 1). Most of the samples are of Silurian and Ordovician ages. Only one middle Cambrian bentonite found in the Borcz-1 borehole (Kowalska *et al*., 2016) also was included in the research. Whenever it was possible, only very fine-grained bentonites were selected for K-Ar dating. Table 1 presents the mineral composition of the clay fraction <0.2 μm selected from the samples tested, the degree of illitisation determined (% S in I/S) and in the case of the metashale samples, the illite crystallinity index (IC). The bentonites analysed are of different colours from pale beige to black.

The diagenetic profiles, occurring in 37 boreholes of the research area (Fig. 3), were analysed in order to assess the maximum palaeotemperatures reached also by younger strata, what permitted better interpretation of the results of K-Ar dating. During the reconstruction of the thermal history, the results of the Blue Gas GASGEOLMOD project also were taken into account as well as unpublished data of Kowalska from earlier studies of shale gas exploration, contracted by Polish Oil and Gas Company (PGNiG; Kowalska *et al*., 2017b). Palaeotemperatures were determined only for samples of fine-grained rocks, clays and marls, in order to avoid effects, related to the sampling of different lithologies.

METHODS

Maximum palaeotemperature age dating using the K-Ar method

The determination of Ar amounts and age calculations by means of the K-Ar method were conducted for all the samples at the Mass Spectrometry Laboratory of the Maria Curie-Skłodowska University in Lublin on a MS-10 mass spectrometer (Tab. 2). This method determines the amount of radiogenic argon ($^{40}Ar^*$), i.e., originating only as a result of the decay of the ^{40}K isotope. The determination is made by measuring the amount of the total argon-40 extracted from a sample as well as desorbed from the internal surface of the apparatus and later by subtracting the amount of atmospheric argon, the presence of which is detected by identifying the ^{36}Ar isotope content in the mass spectrum (Burchart and Králĺ, 2015). The isotope ratio of atmospheric argon $^{40}Ar/^{36}Ar$ is constant and equals 298.6. The amount of K was determined in the ACTLABS laboratory in Canada for samples, fused with lithium metaborate/tetraborate. Analyses were carried out using the ICP-OES method. The dating was conducted for the clay fraction <0.2 μm, separated from the samples analysed by standard Jackson techniques (Jackson, 1974; Moore and Reynolds, 1997).

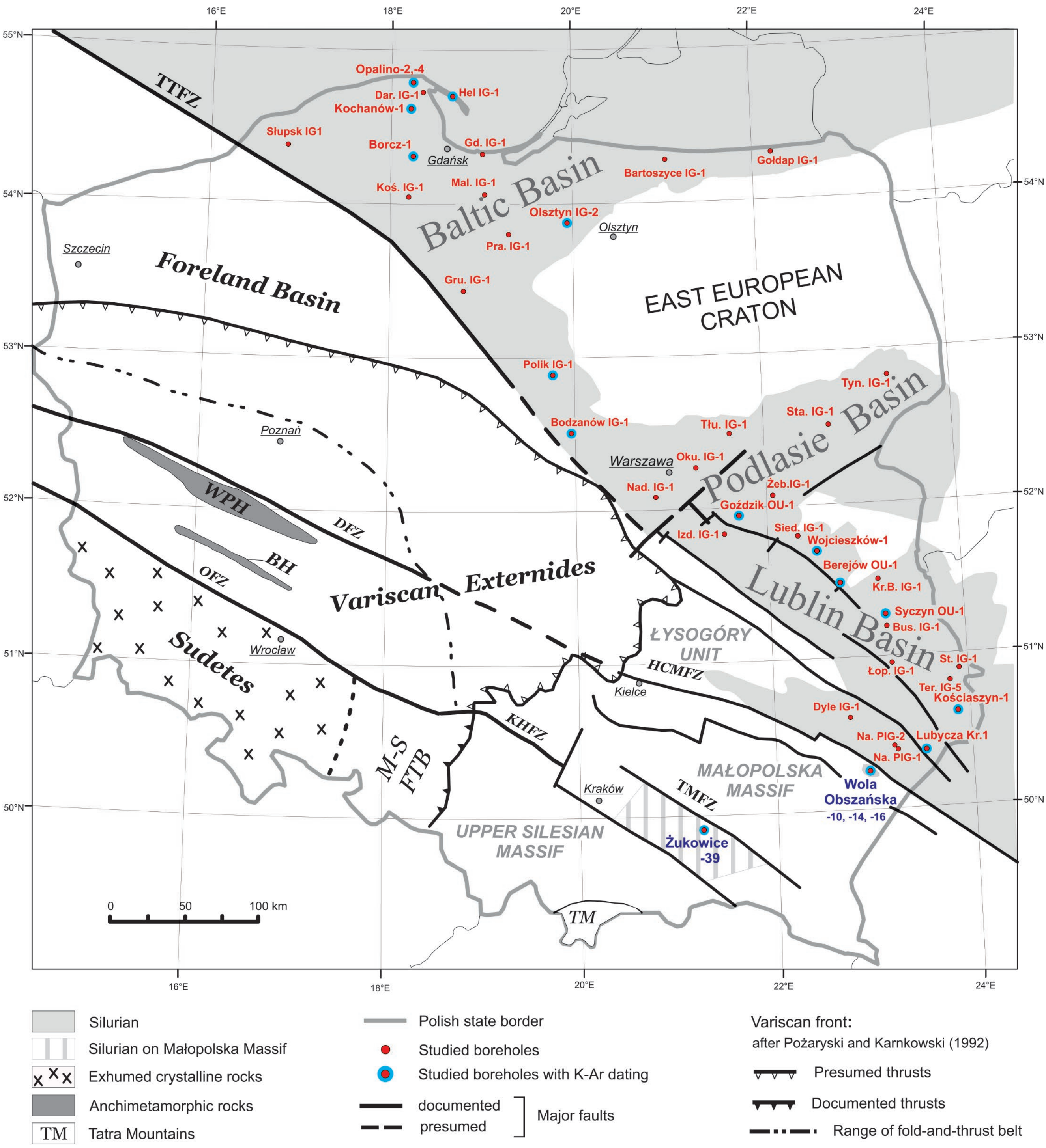

Fig. 3. Locations of boreholes from which the samples analysed were taken on the map of pericratonic Silurian basins in Poland (modified after Pożaryski and Dembowski, 1983; Poprawa, 2010a; Żelaźniewicz *et al.*, 2011).

TTFZ – Teisseyre-Tornquist Fault Zone; DFZ – Dolsk Fault Zone; OFZ – Odra Fault Zone; HCMFZ – Holy Cross Mountains Fault Zone; KHFZ – Kraków-Hamburg Fault Zone; TMFZ – Trzciana-Mielec Fault Zone; M-S FTB – Moravian-Silesian Fold and Thrust Belt; WPH – Wolsztyn-Pogorzela High; BH – Bielawy High. Abbreviation applied for boreholes: Dar. IG-1 – Darżlubie IG-1, Koś. IG-1 – Kościerzyna IG-1, Gd. IG-1 – Gdańsk IG-1, Mal. IG-1 – Malbork IG-1, Pra. IG-1 – Prabuty IG-1, Gru. IG-1 – Grudziądz IG-1, Nad. IG-1 – Nadarzyn IG-1, Oku. IG-1 – Okuniew IG-1, Tłu. IG-1 – Tłuszcz IG-1, Sta. IG-1 – Stadniki IG-1, Tyn. IG-1 – Tyniewicze IG-1, IZD. IG-1 – Izdebno IG-1, Żeb. IG-1 – Żebrak IG-1, Sied. IG-1 – Siedliska IG-1, Bus. IG-1 – Busówno IG-1, Kr.B. IG-1 – Krowie Bagno IG-1, Łop. IG-1 – Łopiennik IG-1, St. IG-1 – Strzelce IG-1, Ter. IG-5 – Terebiń IG-5, Na. PIG-1 – Narol PIG-1, Na. PIG-2 – Narol PIG-2.

Table 1

Mineralogical characteristics of illitic material present in samples selected for K-Ar dating I – illite; I/S – illite-smectite; Ch – chlorite; Kl – kaolinite. Two interpretation methods were applied: I (Dudek and Środoń, 1996) and II (Środoń, 1981), indexes 1 and 2 mark the adequate reflections used for both of them. BB1 – 001 illite peak width (Środoń, 1984). R – "Reichweite" ordering type of illitic material; IC AD – Kübler index, air-dried preparation, calibrated to the CIS scale (Warr and Ferreiro Mählmann, 2015).

No.	Borehole	Depth [m]	Strati-graphy/ Lithology	Mineralogy of clay fraction	Mineralogical characteristics of illitic material present in samples										
					Diagnostic X-ray diffraction reflections - glicolated preparation of f < 0.2 μm				BB1	% S in I/S		Mean %S	R	IC AD [Δ2θ]	T [°C]
										I[1]	II[2]				
					(5–8)	(15–17)[1]	(> 26)[1]	(31–33)[2]							
1	Opalino-2	2645.27	S bent.	I/S, tr. Kl	7.65	17.17	26.64	34.32	~ 4	14	18	16	R3		150
2		2686.10	S bent.	I/S	7.63	17.17	26.63	34.27	~ 4	14	18	16	R3		
3		2814.67	O bent.	I/S, tr. Kl	7.61	17.21	26.62	34.25	~ 4	13	18	15	R3		
4		2904.82	O bent.	I/S, tr. Ch	7.68	17.11	26.62	34.30	~ 4	15	18	16	R3		
5	Opalino-4	2782.10	S shale	I+I/S, Ch, Kl	> 7.50	> 17.00	26.78	d	< 4	-	-	< 15	R3		135
6		2768.70	S bent.	I/S, tr. Kl?	7.60	17.25	26.60	34.42	> 4	12	16	14	R3		
7		2801.25	S bent.	I/S	7.61	17.13	26.61	34.44	> 4	14	16	15	R3		
8		2860.30	O bent.	I/S, tr. Kl	7.43	17.07	26.62	~34.09	> 4	16	21	19	R2/R3		
9		2863.70	O bent.	I/S	7.36	17.10	26.62	~34.19	> 4	15	20	18	R2/R3		
10		2866.45	O bent.	I/S	7.33	17.07	26.62	~34.00	> 4	16	23	20	R2/R3		
11	Borcz-1	3454.80	S bent.	I/S, tr. Kl	7.84	17.35	26.65	34.6	< 4	10	14	12	R3		135
12		3537.20	S bent.	I/S	7.98	17.39	26.64	34.6	< 4	10	14	12	R3		
13		3643.00	S bent.	I/S, Kl	7.78	17.31	26.61	34.6	< 4	11	14	12	R3		
14		3701.40	O bent.	I/S	7.63	17.17	26.64	34.35	~ 4	14	17	15	R3		
15		3706.70	O bent.	I/S	7.37	17.10	26.69	34.2	> 4	16	20	18	R2		
16		3750.05	Cm2 bent.	I/S	7.43	17.09	26.64	34.18	> 4	17	20	20	R2/R3		
17	Kochanów-1	2984.50	S bent.	I/S, Kl	7.68	17.21	26.63	34.4	~ 4	13	17	15	R3		140
18		3027.30	S bent.	I/S, tr. Kl	7.70	17.23	26.65	34.46	~ 4	13	16	14	R3		
19		3147.80	S bent.	I/S, tr. Ch?	7.67	17.29	26.63	34.4	~ 4	12	17	14	R3		
20		3221.81	O bent.	I/S	7.68	17.17	26.66	34.39	~ 4	14	17	15	R3		
21		3233.50	O bent.	I/S	7.41	17.14	26.66	34.22	> 4	15	19	17	R2/R3		
22	Hel IG-1	2997.60	O bent.	I/S	7.32	17.04	26.67	34.19	> 4	20	20	20	R2		135
23	Olsztyn IG-2	2209.10	S bent.	I/S, Kl	7.30	17.01	26.65	34.03	> 4	18	22	20	R2		135
24	Polik IG-1	4220.00	S msh.	I, Ch	> 7.50	> 16.90	26.81	I(35.99)	< 4	-	< 10	< 10	R3	0.45	~ 200
25		4483.00	O bent.	I	8.23	17.51	26.74	35.13	< 4	-	< 10	< 10	R3		
26		4483.00	O bent.	I	8.17	17.52	26.74	35.04	< 4	-	< 10	< 10	R3		
27		4541.00	Cm2 msh.	I, Ch	> 7.50	> 16.90	26.73	I(35.90)	< 4	-	< 10	< 10	R3	0.60	
28	Bodzanów IG-1	4968.00	S msh.	I, Ch	> 7.70	> 17.30	26.78	I(35.95)	< 4	-	< 10	< 10	R3	0.44	~ 230
29		5729.00	O msh.	I, Ch	> 7.70	> 17.30	26.72	I(35.90)	< 4	-	< 10	< 10	R3	0.47	
30	Goździk OU-1	4016.50	S bent.	I/S, tr. Kl	8.02	17.37	26.61	34.82	< 4	9	10	10	R3		180
31		4059.23	S bent.	I/S, tr. Kl?	7.99	17.35	26.67	?	< 4	10	< 10	< 10	R3		
32	Berejów OU-1	2409.61	S bent.	I/S	7.75	17.14	26.63	34.44	< 4	15	16	15	R3		150
33		2409.87	S bent.	I/S, tr. Kl?	7.64	17.17	26.60	34.28	< 4	13	18	16	R3		
34	Wojcieszków-1	2550.20	S bent.	I/S, Kl	6.99	~16.83	26.53	~ 33.70	> 4	20	30	25	R1/R2		125
35		2906.05	S bent.	I/S, tr. Kl?	7.53	17.11	26.57	~34.27	> 4	17	18	17	R3		
36		2917.05	S bent.	I/S	7.69	~ 17.08	26.58	34.32	~ 4	16	18	17	R3		
37		2983.35	S bent.	I/S	7.75	~17.03	26.57	34.32	< 4	16	18	17	R3		
38		3051.00	O bent.	I/S	7.47	17.06	26.6	~33.84	> 4	17	30	23	R2/R3		
39		3051.70	O bent.	I/S, tr. Kl?	7.66	17.16	26.6	34.46	~ 4	14	16	15	R3		
40	Syczyn OU-1	2530.37	S bent.	I/S, Kl	7.8	17.26	26.61	34.66	< 4	12	13	12	R3		170
41		2644.21	S bent.	I/S	7.93	17.30	26.67	34.76	< 4	12	11	12	R3		
42	Lubycza Królewska-1	2336.60	S bent.	I/S, tr. Ch	8.07	17.48	26.66	34.93	< 4	7	8	8	R3		190
43		2385.50	S bent.	I/S, tr. Ch	> 8.00	< 17.50	26.69	34.92	< 4	< 10	8	8	R3		
44		2425.60	S bent.	I/S, tr. Ch	7.99	17.60	26.65	34.7	< 4	< 10	12	10	R3		
45		2455.60	S bent.	I/S	8.07	17.50	26.68	34.96	< 4	7	8	8	R3		
46		2661.50	S bent.	I/S	8.05	17.48	26.62	34.82	< 4	7	10	9	R3		
47		2762.60	S bent.	I/S	8.10	17.56	26.66	34.99	< 4	7	7	7	R3		
48	Kościaszyn-1	3407.35	S bent.	I/S, Ch	7.97	17.31	26.65	34.72	~ 4	12	12	12	R3		170
49		3474.67	S bent.	I/S, Ch	7.96	17.33	26.63	~34.82	< 4	~10	~10	10	R3		
50		3624.52	S bent.	I/S, Ch	7.86	17.29	26.66	~34.90	< 4	~12	~8	10	R3		
51		3678.65	S bent.	I/S, Ch	> 7.50	> 17.00	26.79	d	< 4	-	-	<15	R3		
52		3723.92	S bent.	I/S, tr. Kl	7.99	~17.37	26.65	~34.82	< 4	~9	~10	9	R3		
53		3771.05	O bent.	I/S, Kl	~7.88	> 17.00	17.34	34.72	~ 4	-	12	12	R3		

Illite-smectite palaeothermometer

At present, the illite-smectite palaeothermometer commonly is employed to evaluate the range of temperatures, to which pelitic rocks were subjected in their geological history. It allows the state of progressive shale diagenesis to be determined as well as the degree of very low-grade metamorphism (anchi- and epimethamorphism; Merriman and Frey, 1999; Árkai *et al*., 2007). Such an approach also is preferred by the Subcommission on the Systematics of Metamorphic Rocks (SCRM) of the International Union of Geological Sciences (Árkai *et al*., 2007). An X-ray diffraction phase analysis is the recommended method for estimating the degree of smectite illitisation and can be used to obtain statistically averaged results (Frey, 1987; Moore and Reynolds, 1997; Frey and Robinson, 1999).

As a result of the smectite illitisation reaction, a gradual transition can be observed from pure smectite through various types of mixed-layer minerals, known as illite-smectite (I/S). These phases also may react finally to form illite and then, with further K+ fixation and recrystallisation, change into muscovite. This process was described for the first time for Palaeogene and Neogene rocks from the Gulf of Mexico during the early stages of exploration for crude oil and natural gas (Burst, 1959; Powers, 1967). Hower *et al.* (1976) discovered in the profiles of boreholes from this region that organic matter transformation is accompanied by increases in the smectite illitisation level and the amount of chlorite and, simultaneously, by a gradual decline in potassium feldspars with burial depth.

In the study presented, a combination of two X-ray diffraction methods was applied. The methods allow the evaluation of thermal alteration within the range from 70 to 300 °C, which corresponds to the conditions of diagenesis and anchimetamorphism. The first method uses published diagrams, calculated by Środoń (1981, 1984) as well as by Dudek and Środoń (1996). These graphs are based on modelling by the NEWMOD program (Reynolds, 1985). Reflections applied to determine the percentage value of smectite layers in illite-smectite (% S in I/S) were marked on diffractograms for samples with different degrees of illitisation, presented in Figure 4. Simultaneously, two reflection sets were used each time in order to check the consistency of the results obtained and eventually, to calculate their mean value, which was assumed as the final analysis result. Figure 4 also presents an example of the palaeothermal profile, in this case from the Kościerzyna IG-1 borehole.

The second method was applied to samples influenced by temperatures around and above 200 °C. In this case, the illite "crystallinity" was used by measuring the Kübler index (Kübler, 1968), which is considered to largely reflect the thickness of the illite crystallites. This index measures the X-ray diffraction 001 peak width of illite at half its height and was determined following the procedure of Warr and Rice (1994). Details of the methodology used in this study also have been published in a monograph by Kowalska (2012).

A well-documented vertical diagenetic profile has been established for the East Slovak Basin (Šucha *et al.*, 1993; Clauer *et al.*, 1997; Środoń, 2007). This profile has been used to place temperatures for the successive stages of the illitisation process, recognized using Środoń's method (% of S in I/S; Środoń, 1981, 1984; Dudek and Środoń, 1996). In the case of the illite "crystallinity index", temperature information was drawn from the correlations, originally made by Kübler (1968). In accordance with the SCRM recommendations (Schmid *et al.*, 2007), the measured values of the Kübler index (Kübler, 1968) should be calibrated to the CIS scale (Crystallinity Index Standards), using the methodology of Warr and Rice (1994). However, recently, Warr and Ferreiro Mählmann (2015) adjusted the anchizonal boundary limits of the CIS scale to better match Kübler's original scale of measurement. Accordingly, the anchizone limits now are placed at 0.52 and 0.32 $\Delta°2\theta$, respectively.

The X-ray diffraction study was carried out, using a Philips X'Pert MPD diffractometer (X-ray tube – Cu), equipped with a stable, high-voltage generator, a θ-θ goniometer (radius 200 mm) with an electronically controlled position and a Xe-filled proportional detector. The following setup was applied: the primary beam was passed through a Soller slit with 0.04 rad and a divergence slit of 1º; the diffracted beam through an anti-scatter slit of ¼°, a receiving slit of 0.15 mm, a Soller slit of 0.04 rad and a curved graphite monochromator. For all the measurements, a voltage of 40 kV and a current of 40 mA were used. The scan range and the step size were: 2 to 50º2θ and 0.02º2θ, respectively. The analyses were carried out on fractions of < 0.2 and < 2 μm, separated by means of the standard techniques of Jackson (1974) and Moore and Reynolds (1997), using sedimented slides in air-dried (AD) and glycolated conditions (GY).

RESULTS

Results of the K-Ar dating

Interlaboratory comparison

The main reason for conducting an interlaboratory comparison of the K-Ar age-dating method was the observation that different laboratories quote varying degrees of measurement error that often ranges from 1–10 Ma (Środoń and Clauer, 2001; Kowalska, 2008; Biernacka, 2014). Knowing the absolute error involved in the K-Ar method is of key relevance, when used to make geological interpretations. The measurement error quoted by a particular laboratory refers only to the actual procedure applied and therefore interlaboratory comparisons conducted on standard materials are required for validation and error analysis, in accordance with accredited laboratories following the PN-EN ISO/IEC 17025:2015 norm.

The interlaboratory comparison also was used to assess whether measurements on the four fractions for each bentonite sample were required for an age determination, as suggested by Środoń and Clauer (2001), or whether measurement of only the < 0.2 μm fraction was sufficient. This aspect was important for reducing the cost of the analyses required for an age determination and to maximise data coverage of the entire Polish part of the East European Platform slope.

The list of scientists engaged in the interlaboratory comparison, the specifications of the instruments employed, and

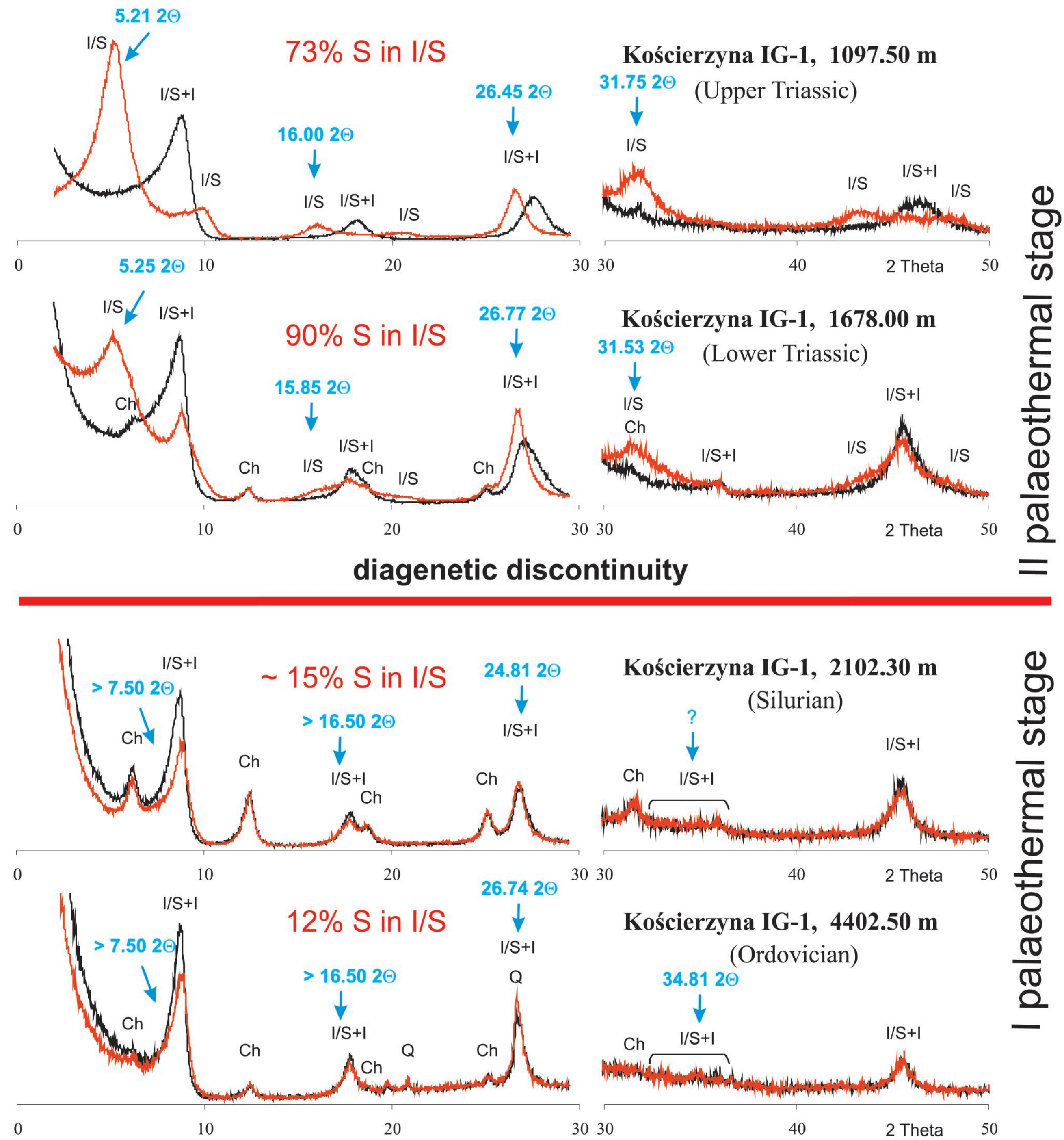

Fig. 4. The Kościerzyna IG-1 borehole thermodiagenetic profile. X-ray diffraction patterns of shales analysed with reflections used for evaluating % of smectite (S) in illite-smectite (I/S) marked.

the methodologies applied by the laboratories are presented in Table 2. The majority of laboratories (except for one) employed the K-Ar dating method. The measurement carried out in the laboratory applying the Ar-Ar method (Hall, 2013) was executed in order to evaluate the possibility of applying the method for illite dating.

For testing the interlaboratory accuracy of K-Ar age dating, Silurian bentonites were selected from three boreholes, located on the Małopolska Massif (Fig. 3; Tab. 3): 1) Wola Obszańska-10, 2) Wola Obszańska-16 and 3) Żukowice-39 (Kowalska, 2008). The purity of the diagenetic material was confirmed by an X-ray diffraction study (Fig. 5). Four different grain fractions, <0.02, 0.02–0.05, 0.05–0.2 and 0.2–2 μm, were separated from each test sample at the Institute of Geological Sciences in Kraków.

The samples were split by quartering, labelled and then dispatched to the laboratories participating in the comparison. Homogeneity of the test samples was checked by performing double measurements on some of them (Tab. 4). On the basis of this, the expanded uncertainty also could be controlled with regard to the method used for examinations in the Lublin laboratory, defined at 1.5% with a trust level/

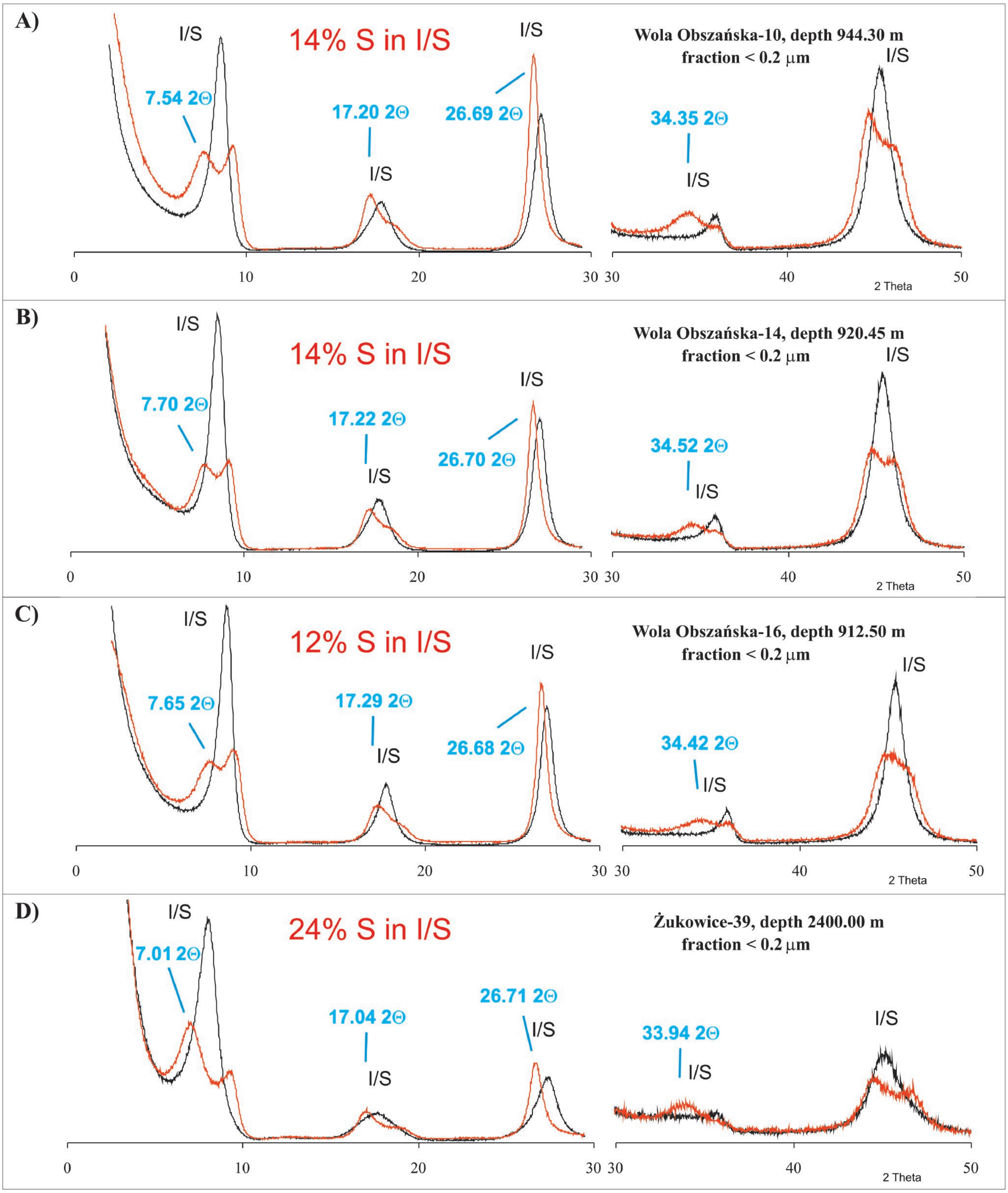

Fig. 5. X-ray diffraction patterns of Silurian bentonites from the Małopolska Massif selected for testing the interlaboratory accuracy of K-Ar age dating (after Kowalska, 2008).

confidence interval of 95% and with the assumption of a K concentration measurement error at the level of 1% (in line with the declaration of the ACTLABS laboratory).

The results of the interlaboratory comparison are presented in Table 5 and Figure 6. At a glance, it can be seen that there is a lack of the considerable differentiation of ages, obtained for the three finer fractions < 0.2 μm in the results achieved in all the laboratories, which is visible explicitly in the results of Środoń and Banaś (Tabs 2 and 5). Moreover, for all the samples, all the remaining laboratories also obtained the oldest dates for the coarsest grain fraction 0.2–2 μm, which is in line with the idea that some admixture of detrital material could be present in this fraction.

Table 2

Participants in the interlaboratory comparison with methods and instruments applied by them.

Participants	**Jan Środoń, Michał Banaś** Institute of Geological Sciences, Polish Academy of Sciences in Kraków, Poland	**Stanisław Hałas Artur Wójtowicz** Institute of Physics, Maria Curie Skłodowska University in Lublin, Poland	**Klaus Wemmer** Isotope Geology Division, Geoscience Center, University of Göttingen, Germany	**Yakov Kapusta** ACTLABS laboratory in Canada	**Chris Hall** University of Michigan, USA
Method	**K-Ar**	**K-Ar**	**K-Ar**	**K-Ar**	**Ar-Ar**
Ar measurement	**MS-20 mass spectrometer** Glauconite GLO standard	**MS-10 mass spectrometer** Glauconite GLO standard	**Thermo Scientific ARGUS VI noble gas mass spectrometer** HD-BI biotite standard	**Customer-built magnetic sector mass spectrometer (Reinolds type) with Varian CH5 magnet** LP-6 biotite standard	**Ar-Ar method with the use of the capsule technique specially adapted for very fine clay materials**
K measurement	**Sherwood 420 flame photometer** NBS 98a plastic clay (1.04% K_2O)	**K measured by ACTLABS**	**BWB-XP flame photometer** Diorite DR-N (1.70% K_2O) Mica-Fe (2.38% K_2O) Musi 7 (8.75% K_2O)	**Lithium metaborate /tetraborate fusion + ICP OES Spectrometry** NIST 694 (0.51% K) SY-4 (1.66% K) GBW (5.43% K)	

Table 3

First K-Ar results obtained for the test bentonites used in the interlaboratory comparison.

Borehole	%S in I/S	Grain size fraction [μm]	Kraków Age [Ma]	Kraków Error [Ma]	Lublin Age [Ma]	Lublin Error [Ma]	Mean
Wola Obszańska-10, depth 944.30 m	14	< 0.02	**342**	1.0	**362**	5.5	**358**
		0.05–0.02	**287**	0.8	**354**	5.3	
		0.05–0.2	**331**	0.9	**357**	5.4	
		0.2–2	**361**	1.0	**384**	5.8	
Wola Obszańska-10, depth 975.50 m	14	< 0.02	**327**	0.9	**335**	5.0	**337**
		0.05–0.02	**320**	0.9	**340**	5.1	
		0.05–0.2	**300**	0.9	**338**	5.1	
		0.2–2	**285**	0.8	**359**	5.4	
Wola Obszańska-14, depth 920.45 m	14	< 0.02	**321**	1.1	**345**	5.2	**343**
		0.05–0.02	**334**	1.2	**333**	5.0	
		0.05–0.2	**366**	1.0	**350**	5.2	
		0.2–2	**383**	1.2	**355**	5.3	
Wola Obszańska-16, depth 912.50 m	12	< 0.02	**360**	1.0	**373**	5.6	**367**
		0.05–0.02	**366**	1.1	**363**	5.4	
		0.05–0.2	**356**	0.9	**367**	5.5	
		0.2–2	**317**	0.9	**387**	5.8	
Żukowice-39, depth 2400.00 m	24	< 0.02	**311**	2.5	**190**	2.9	**199**
		0.05–0.02	-	-	**196**	2.9	
		0.05–0.2	**364**	1.9	**212**	3.2	
		0.2–2	**325**	1.8	**272**	4.1	

Very similar results were obtained with the use of the Ar-Ar method (Tab. 5; Fig. 7). In earlier publications (Kowalska *et al.*, 2017a, b), ages quoted by the University of Michigan Laboratory were much younger (about 50–80 Ma) but now have been revised after detecting a technical error. It should be emphasised that measurements were conducted on encapsulated samples. With the use of the Ar-Ar method, the K concentration is measured simultaneously on the same sample specimen from the ^{40}Ar concentration, which usually is considered to be a distinct advance with this method.

Despite the described differences, the results from the majority of laboratories did not exceed the value of +/- 10 Ma of the absolute error. Owing to a small number of observations (n < 30) in line with Student's t-distribution, the relative standard error should be assumed as the threefold standard deviation (3SEr) for the 95% confidence interval. On the basis of the analysis performed, it can be stated that the relative standard error (3SEr) is ca. 3% for K-Ar dating (Tab. 5).

In order to assess the results obtained, a statistical approach also was applied. For this purpose, parameter Z (the Z-score), commonly used for interlaboratory comparisons (International Standard ISO 13528:2015), was calculated and described by the equation,

$$Z = \frac{X_{lab} - X_{re}}{S}$$

where:

X_{lab} – results obtained by a given laboratory;

X_{ref} – the mean value after discarding the results with major errors;

S – standard deviation.

The reference value was defined as the mean of results for particular laboratories, after discarding the results with major errors. In the case of the present authors, the results obtained by the laboratory in Kraków display a major error for samples from the Żukowice-39 borehole, reaching 120–150 Ma (Tab. 5). The results from this laboratory were not taken into account, when determining the reference value. Parameter Z was calculated only for samples from Wola Obszańska-10 and Wola Obszańska-16 (Tab. 5). The analysis of results in terms of their quality is based on the following principles: the results are considered satisfactory, when the value of Z <=2; when the value of Z <=3, the results are considered questionable; and when Z is >=3, the results are considered unsatisfactory. The values implying insufficient measurement quality were marked red in Table 5; these results were obtained solely in the Kraków laboratory.

Table 4

Evaluation of the degree of homogenization of test samples.

Sample	Grain size fraction [µm]	$^{40}Ar/^{38}Ar$	$^{36}Ar/^{40}Ar$ [x1000]	$^{38}Ar_{znacz}$ [pmol]	m [mg]	$^{40}Ar_{rad}$ [%]	$^{40}Ar_{rad}$ [nmol/g]	K [%]	Age [Ma]	Error (1.5%) [±Ma]	Mean Age [Ma]
Wola Obszańska-10, depth 944.30 m	< 0.02	2.6565	0.0989	66.11	50.50	97.1	3.3762	4.83	363.8	5.5	**362.4**
		2.6496	0.0991		50.80	97.1	3.3473		361.0	5.4	
	0.05–0.02	2.6531	0.0962		50.07	97.2	3.4035	5.00	355.2	5.3	**354.3**
		2.6587	0.1169		50.15	96.5	3.3839		353.3	5.3	
	0.05–0.2	2.7599	0.0900		50.59	97.3	3.5107	5.10	358.8	5.4	**357.4**
		2.7039	0.0863		50.05	97.5	3.4805		356.0	5.3	
	0.2–2	2.9414	0.0700		50.45	97.9	3.7749	5.05	386.6	5.8	**383.6**
		2.9326	0.0698		51.16	97.9	3.7115		380.7	5.7	
Żukowice-39, depth 2400.00 m	< 0.02	1.2537	0.6055	66.11	51.46	82.1	1.3226	3.79	190.8	2.9	**189.5**
		1.2457	0.6012		51.96	82.2	1.3035		188.2	2.8	
	0.05–0.02	1.1705	0.6268		46.46	81.5	1.3572	3.79	195.5	2.9	**195.5**
	0.05–0.2	1.3469	0.5485		50.20	83.8	1.4864	3.79	213.1	3.2	**212.4**
		1.3669	0.5552		51.18	83.6	1.4762		211.7	3.2	
	0.2–2	1.6762	0.3981		50.20	88.2	1.9479	3.79	274.4	4.1	**272.1**
		1.6767	0.4044		51.05	88.0	1.9120		269.7	4.0	

The K content was measured independently in three of the labs: Kraków, ACTLABS laboratories in Canada and at the University of Göttingen (Tab. 2). The analysis of the comparison results showed that K content measurement error significantly contributes to the total measurement error. This aspect already was discussed extensively in the literature (Depciuch, 1971; Kelley, 2002; Warr *et al*., 2017). The results obtained are compared in Table 6 and graphically in Fig. 8. This clearly indicates that, in general, the results correlate with each other. Simultaneously, it is shown that the differences between them in absolute terms amount up to over 1% (which generates a relative error of over 10%). The highest K amounts were measured in the Kraków laboratory and the lowest in ACTLABS, a commercial laboratory.

In order to determine which results should be viewed as more reliable, a set of 6 NIST (National Institute of Standard and Technology) measurement standards was purchased and, after encryption, dispatched for analysis to the ACTLABS laboratory. On the basis of the results obtained as well as the data quoted in certificates to the previously mentioned measurement standards, a correlation graph was prepared and presented in Figure 9. An ideal linear relationship with the equation y = 0.9964x and the correlation coefficient R^2 0.998 point to the accuracy of

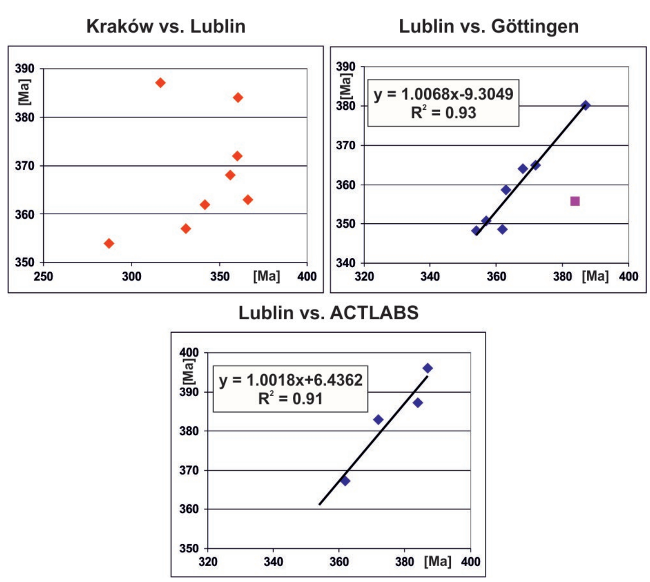

Fig. 6. Correlation of K-Ar dating results achieved by individual laboratories involved in interlaboratory comparison (see also Tabs 2 and 5).

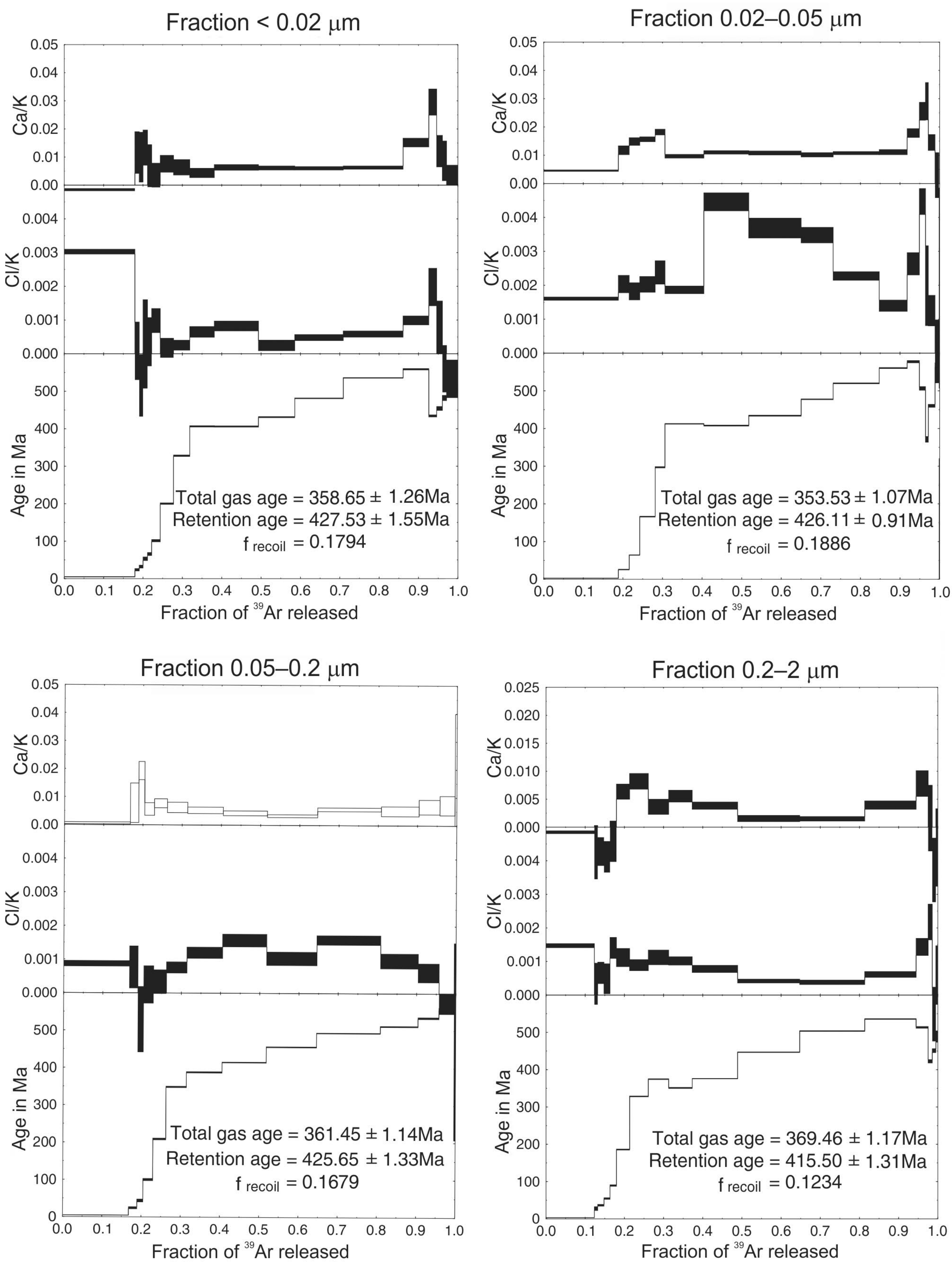

Fig. 7. Ar-Ar dating results for four grain fractions smaller than 2 μm for a sample from Wola Obszańska-10 borehole.

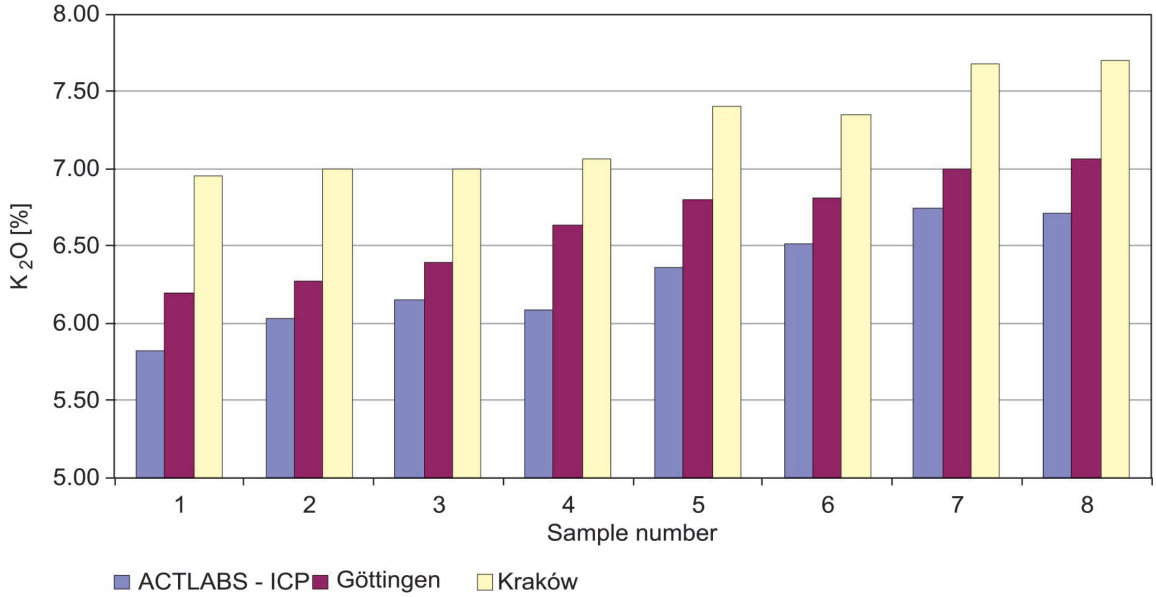

Fig. 8. Comparison of K content measurement results from three different laboratories (see also Tab. 6).

the results received from the ACTLABS laboratory; the graph also presents results for calibration measurements obtained in particular labs. However, it should be noted that the measurement error calculated on the basis of comparison measurements, conducted in such a way for the NIST standards (quoted in table on Fig. 9), considerably exceeds the value of the relative error of 1%, declared by the laboratory.

The interlaboratory comparison clearly showed that the actual relative standard error of the K-Ar method is approximately ± 3%. Comparison of the results obtained for the four fractions, using both the K-Ar and the Ar-Ar method, showed that the fraction less than 0.2 μm can be used to date the maximum heating age in the case of bentonites. The dating results of the 0.2 μm fraction are similar, considering the certain range of error involved in measuring accurately the K and Ar contents. The more minor variations can be due to some sample heterogeneity, when homogenising the samples after grain-size separation. Still, it should be emphasised that the observed major variations of results obtained for the coarsest 0.2–2 μm fraction (Tabs 4 and 5) can be related to the presence of detrital material and it seems that full homogenisation of samples is difficult to achieve in this case.

Results of maximum palaeotemperature age dating for Lower Palaeozoic bentonites from the East European Platform margin

The results of K-Ar age dating of the Silurian and Ordovician bentonite samples (< 0.2 μm fraction), collected from across the region, are presented in Table 7. The Table 7 also provides information on the thickness of bentonite layers from which the samples were taken. Overall, very consistent results were obtained for all samples. For the majority of boreholes, it was possible to determine a very narrow range of probable dates of maximum palaeotemperature. Taking into account the possibility of some detrital admixture, due to the diverse sedimentological histories of the bentonites with some possible redeposition, anomalously older ages were discarded. On the basis of the remaining results, a probable age range for the maximum stage of thermal alteration was determined. In the case of the bentonites examined, no correlation was detected between the data obtained and thickness of the layers, as suggested by Pusch and Madsen (1995).

The results clearly show a pattern of regional variability (Fig. 10). Both in the Baltic Basin as well as in the northeast part of the Lublin Basin, the maximum stage of thermal alteration occurred in the Early Carboniferous, with an age range of 320–340 Ma, which corresponds to the main Sudetian stage of the Variscan orogeny. In the southeast part of the Lublin Basin, an Early Permian thermic event is distinctly marked; the dates for the three boreholes Syczyn OU-1, Kościaszyn-1 and Lubycza Królewska-1 range from 270–290 Ma. This corresponds to a Late Variscan Austrian thermal event, often linked to granite batholith intrusion and extensional collapse of the orogen (Warr, 2012).

Diagenetic profile analysis

For the purpose of regional analysis of diagenetic profiles, the data determined in this study were combined with available archival data for the 37 boreholes selected (Kowalska, 2008; Kowalska *et al.*, 2017b). On the basis of all these data, a map was developed, presenting the maximum palaeotemperatures at the top of the Silurian strata (Fig. 11). The map, in general terms, is in agreement with the palaeotemperature map published on the basis of vitrinite reflectance values (Kiersnowski and Dyrka, 2013; Grotek, 2016).

On the basis of the diagenetic profiles, the region could be divided into eleven zones, each with a characteristic thermal history (Fig. 10). Examples of these diagenetic profiles, based on the I-S content, are presented in Figures 12–17. In this paper, the concept of a structural stage is understood as a set of layers, which were subjected to maximum temperatures at the same time. These zones are listed as follows:

Table 5

Results of the interlaboratory comparison – K-Ar and Ar-Ar dating.
Z – Z-test (values smaller than –3 are marked in red); Mean* – mean value, but without results from Kraków; S – standard deviation; SE – absolute standard error; 3SE/3SEr – threefold absolute/relative standard error for the 95% confidence interval.

Sample	Grain size fraction	Kraków		Lublin		Göttingen		Actlabs		Michigen		Mean*	S	SE	3SE	3SEr
		K-Ar	Z	K-Ar	Z	K-Ar	Z	K-Ar	Z	Ar-Ar	Z					
	[µm]	[Ma]		[Ma]		[Ma]		[Ma]		[Ma]		[Ma]	[Ma]	[Ma]	[Ma]	[%]
Wola Obszańska-10	< 0.02	**342**	-2.58	**362**	0.45	**349**	-1.51	**367**	1.21	**359**	0.00	**359**	**7.6**	**3.8**	**11.4**	**3.2**
	0.05–0.02	**287**	-23.21	**354**	0.71	**348**	-1.43			**354**	0.71	**352**	**3.5**	**2.0**	**6.0**	**1.7**
	0.2–0.05	**331**	-6.10	**357**	0.24	**351**	-1.22			**361**	1.22	**356**	**5.0**	**2.9**	**8.8**	**2.5**
	0.2–2	**361**	-1.05	**384**	0.81	**356**	-1.45	**387**	1.05	**369**	-0.40	**374**	**14.0**	**7.0**	**21.0**	**5.6**
Wola Obszańska-16	< 0.02	**360**	-2.29	**372**	1.14	**365**	-1.14					**369**	**5.0**	**3.5**	**10.6**	**2.9**
	0.050.02	**366**	2.50	**363**	1.00	**359**	-1.00					**361**	**2.8**	**2.0**	**6.0**	**1.7**
	0.2–0.05	**356**	-5.00	**368**	1.00	**364**	-1.00					**366**	**2.8**	**2.0**	**6.0**	**1.6**
	0.2–2	**317**	-22.33	**387**	1.00	**380**	-1.33					**384**	**5.0**	**3.5**	**10.6**	**2.8**
Żukowice-39	< 0.02	**311**		**190**												
	0.05–0.02	**320**		**196**						**199**		**199**				
	0.2–0.05	**364**		**212**												
	0.2–2	**325**		**272**												

Table 6

Results of the interlaboratory comparison – K content.

Sample	Grain size fraction	K_2O %		
	[µm]	Actlab	Getynga	Kraków
Wola Obszańska-10 depth 944.30 m	< 0.02	**5.82**	**6.19**	**6.95**
	0.05–0.02	**6.03**	**6.27**	**7.00**
	0.2–0.05	**6.15**	**6.39**	**7.00**
	0.2–2	**6.09**	**6.63**	**7.06**
Wola Obszańska-16 depth 912.50 m	< 0.02	**6.36**	**6.80**	**7.40**
	0.05–0.02	**6.51**	**6.81**	**7.35**
	0.2–0.05	**6.75**	**7.00**	**7.68**
	0.2–2	**6.71**	**7.06**	**7.70**

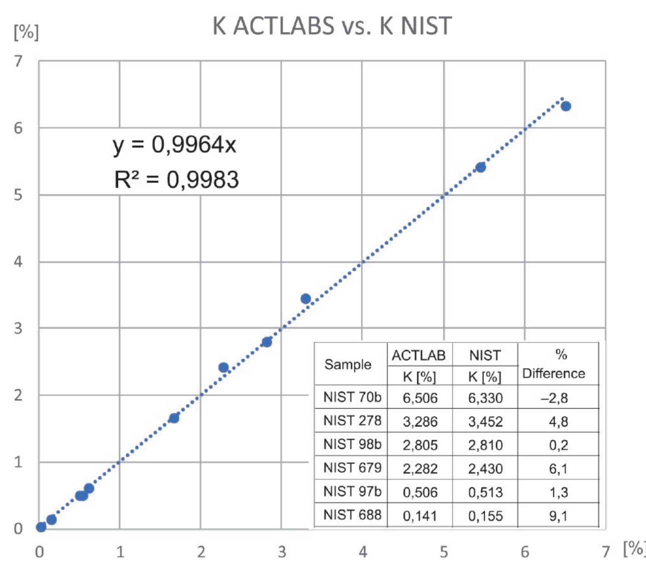

Fig. 9. Correlation of K content measurement results obtained for a set of NIST standards.

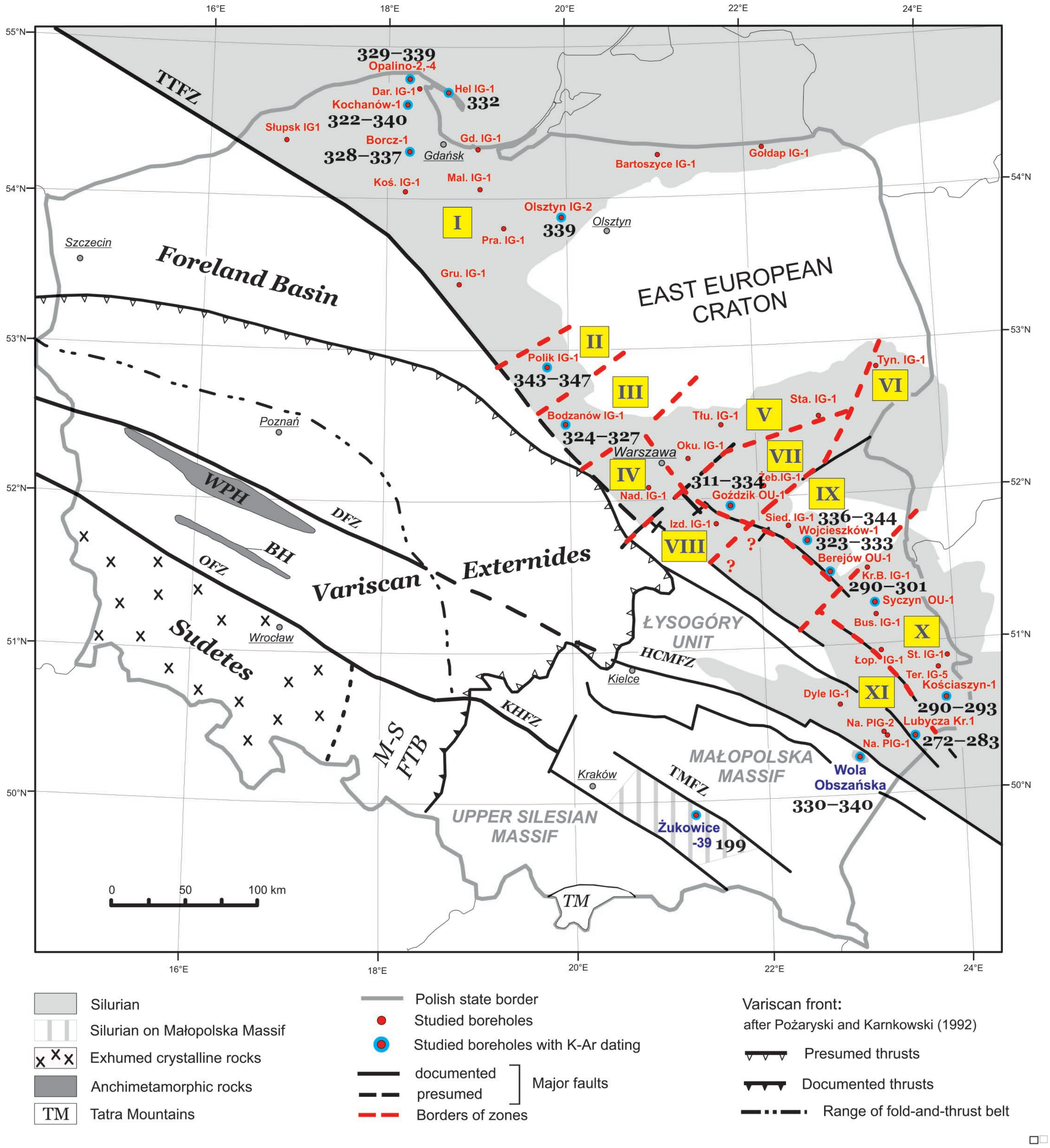

Fig. 10. Age of maximum heating dated with the K-Ar method for Lower Palaeozoic bentonites, marked on the map (dates in Ma). Zones (I - XI) distinguished with different thermal histories and possible locations of fault zones separating them.

I. Baltic Basin zone – Figure 12, boreholes: Słupsk IG-1, Hel IG-1, Darżlubie IG-1, Opalino-2, Opalino-4, Kochanowo-1, Borcz-1, Kościerzyna IG-1, Gdańsk IG-1, Malbork IG-1, Bartoszyce IG-1, Gołdap IG-1, Olsztyn IG-2, Prabuty IG-1, Grudziądz IG-1;
II. Polik zone – Figure 13, borehole: Polik IG-1;
III. Bodzanów zone – Figure 13, borehole: Bodzanów IG-1;
IV. Nadarzyn zone – Figure 14, borehole: Nadarzyn IG-1;
V. Okuniew-Stadniki zone – Figure 15, boreholes: Okuniew IG-1, Tłuszcz IG-1, Stadniki IG-1;
VI. Tyniewicze zone – Figure 15, borehole: Tyniewicze IG-1;
VII. Żebrak zone – Figure 16, boreholes: Żebrak IG-1, Goździk OU-1;
VIII. Izdebno zone – Figure 14, borehole: Izdebno IG-1;
IX. Siedliska zone – Figure 16, boreholes: Siedliska IG-1, Wojcieszków-1, Berejów OU-1;

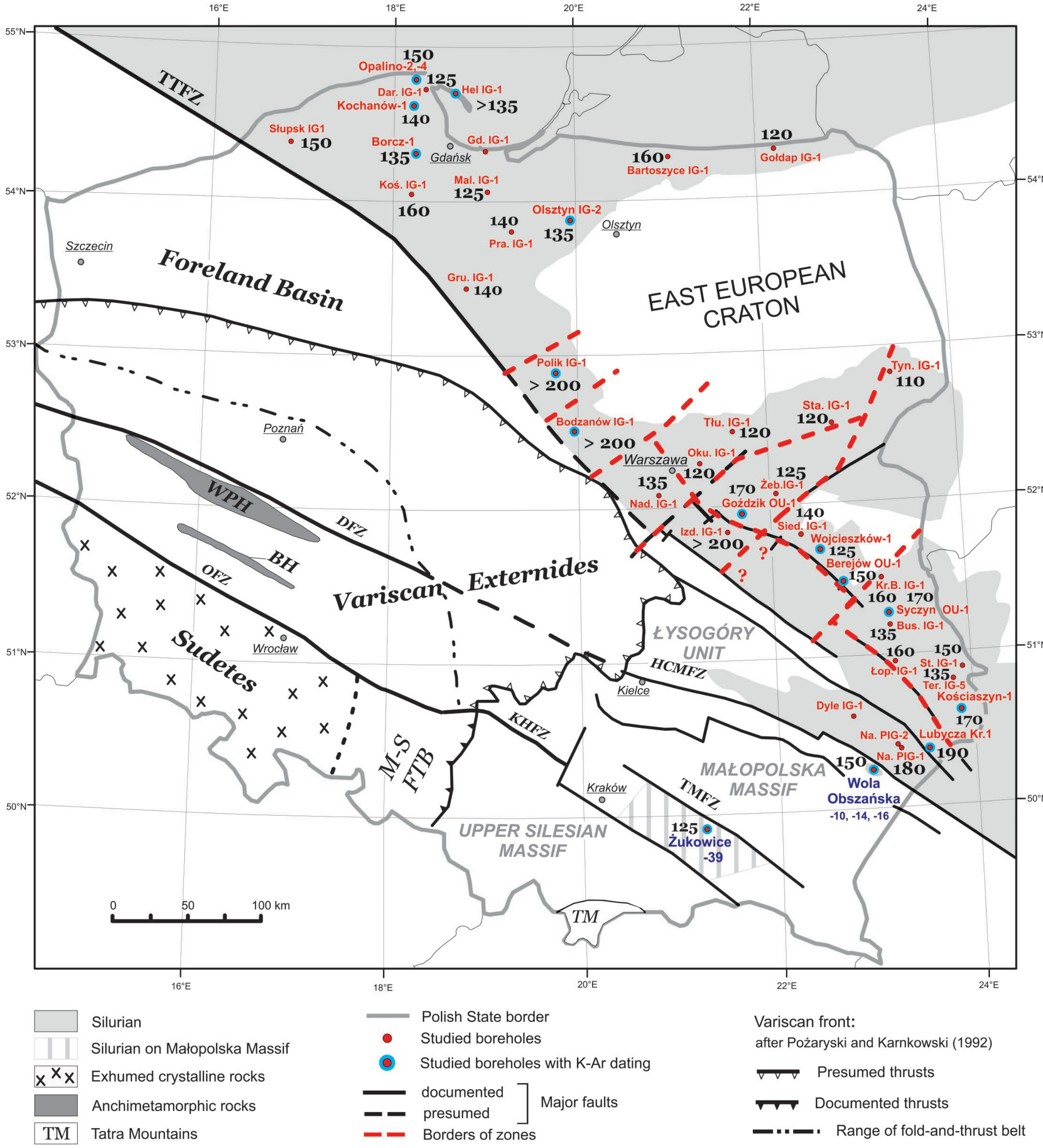

Fig. 11. Map of palaeotemperatures at the top of the Silurian complex (temperatures in degrees Celsius, °C).

X. Busówno-Terebiń zone – Figure 17, boreholes: Syczyn OU-1, Busówno IG-1, Krowie Bagno IG-1; Łopiennik IG-1, Strzelce IG-1, Terebiń IG-5, Kościaszyn-1;

XI. Narol region – Figure 17, boreholes: Lubycza Królewska-1, Narol IG-1, Narol IG-2, Dyle IG-1.

Palaeothermal history of the zones identified

The location of the 11 areas with characteristic palaeothermal histories, identified on the edge of the East European Platform, along with the location of the fault zones separating them, are shown in Figure 10. The characteristics of the tectonic zones identified are summarized below.

Zone I – the Baltic Basin (Fig. 12)

In the region of the Baltic Basin, two structural stages were identified in the geological profile of all boreholes: a Palaeozoic stage, comprising Ediacaran up to Silurian sediments as well as a Permian–Mesozoic stage. Both stages differ in the degree of thermal alteration incurred.

Table 7

Results of the dating of maximum heating by the K-Ar method for Lower Palaeozoic samples from the Polish margin of the East European Platform (data used in the calculation of the mean value are marked in red). Thickness* – thickness of bentonite layers.

No.	Borehole	Depth [m]	Strat./ Lith.	$^{40}Ar/^{38}Ar$	$^{36}Ar/^{40}Ar$ [x1000]	$^{38}Ar_{znacz}$ [pmol]	m [mg]	% $^{40}Ar_{rad}$	$^{40}Ar_{rad}$ [nmol/g]	K [%]	Age [Ma]	Error [Ma]	Mean	Thick-ness* [cm]
1	**Opalino-2**	2645.27	S bent.	2.2878	0.1379	66.05	45.27	95.9	3.2022	4.91	**341.6**	4.7	**334.9**	4
2		2686.10	S bent.	2.735	0.1790		52.29	94.7	3.2722	5.15	**333.6**	4.6		2
3		2814.67	O bent.	2.4223	0.1383		46.88	95.9	3.2736	5.24	**328.5**	4.6		2
4		2904.82	O bent.	2.3211	0.1648		46.97	95.1	3.1053	4.85	**335.9**	4.7		2
5	**Opalino-4**	2782.10	S shale	1.9692	0.1666	66.07	42.44	95.1	2.9149	4.17	***363.8***	5.0	**343.0**	*shale*
6		2768.70	S bent.	2.2174	0.1265		41.28	96.3	3.4166	5.29	**338.6**	4.7		-
7		2801.25	S bent.	2.3608	0.1577		41.07	95.3	3.6211	5.37	**352.2**	4.7		-
8		2860.30	O bent.	2.1264	0.2026		42.73	94.0	3.0914	4.74	**341.6**	4.7		-
9		2863.70	O bent.	2.2828	0.1777		46.71	94.8	3.0597	4.65	**344.4**	4.7		-
10		2866.45	O bent.	2.0422	0.1947		41.84	94.2	3.0395	4.71	**338.4**	4.7		-
11	**Borcz-1**	3454.80	S bent.	2.4754	0.0587	66.06	45.22	98.3	3.5536	5.28	**351.6**	4.8	**346.2**	2
12		3537.20	S bent.	2.4372	0.0707		45.82	97.9	3.4405	5.38	**335.6**	4.6		1.5
13		3643.00	S bent.	2.6028	0.1118		45.33	96.7	3.6679	5.33	**358.7**	4.9		2
14		3701.40	O bent.	1.9673	0.1285	66.05	45.34	96.2	2.7573	4.42	**328.0**	4.6		5
15		3706.70	O bent.	2.2208	0.1195		48.01	96.5	2.9475	4.49	**343.7**	4.8		10
16		3750.05	Cm2 b.	2.2506	0.1823		46.63	94.6	3.0164	4.37	**359.7**	5.0		2.5
17	**Kochanowo-1**	2984.50	S bent.	2.3129	0.0547	66.05	45.28	98.4	3.3193	4.96	**349.7**	4.8	**337.4**	3
18		3027.30	S bent.	2.4460	0.1027		46.44	97.0	3.3734	5.26	**336.5**	4.6		1.5
19		3147.80	S bent.	2.5782	0.1577		46.6	95.3	3.4843	5.38	**339.5**	4.7		1.5
20		3221.81	O bent.	2.1309	0.1941		48.04	94.3	2.7619	4.52	**321.9**	4.5		3
21		3233.50	O bent.	2.4078	0.1926		50.32	94.3	2.9809	4.60	**339.6**	4.7		9.5
22	**Hel IG-1**	2997.60	O bent.	2.5297	0.1642	66.05	52.94	95.1	3.0033	4.76	**331.5**	4.5		100
23	**Olsztyn IG-2**	2209.10	S bent.	2.2602	0.1246	66.05	46.65	96.3	3.0825	4.77	**338.8**	4.7		2
24	**Polik IG-1**	4220.00	S mcl.	2.7306	0.0835	66.05	45.39	97.5	3.8739	5.11	**391.3**	5.3	**344.8**	*anchi*
25		4483.00	O bent.	3.0188	0.1052	66.02	48.81	96.9	3.9582	6.05	**342.6**	4.7		-
26		4483.00	O bent.	2.9438	0.0690		47.38	98.0	4.0203	6.06	**347.0**	4.7		-
27		4541.00	Cm2 mcl	3.0849	0.0776	66.05	46.08	97.7	4.3186	5.80	**385.1**	5.2		*anchi*
28	**Bodzanów IG-1**	4968.00	S mcl.	2.7346	0.1230	66.02	48.39	96.4	3.5956	5.78	**327.4**	4.5	**325.6**	*anchi*
29		5729.00	O mcl.	2.6951	0.1111		46.21	96.7	3.7244	6.06	**323.7**	4.5		*anchi*
30	**Goździk OU-1**	4016.50	S bent.	2.3378	0.0917	66.06	45.45	97.3	3.306	5.19	**334.4**	4.6		-
31		4059.23	S bent.	2.3584	0.0990		45.57	97.1	3.319	5.64	**311.0**	4.3		-
32	**Berejów OU-1**	2409.61	S bent.	2.1885	0.1198	66.06	45.98	96.5	3.0330	4.95	**322.7**	4.5	**327.9**	-
33		2409.87	S bent.	2.1908	0.1075		46.04	96.8	3.0437	4.80	**333.0**	4.6		-
34	**Wojcieszków-1**	2550.20	S bent.	1.9879	0.3709	66.08	42.09	89.0	2.7793	4.34	**336.0**	4.7	**350.8**	-
35		2906.05	S bent.	2.3521	0.3231		41.07	90.5	3.4235	5.21	**344.0**	4.8		-
36		2917.05	S bent.	2.2443	0.3678		40.76	89.1	3.2435	4.58	**368.2**	5.1		-
37		2983.35	S bent.	2.1565	0.1858		41.93	94.5	3.2122	4.9	**343.2**	4.8		-
38		3051.00	O bent.	2.4278	0.2098		42.8	93.8	3.5163	5.15	**356.2**	4.9		-
39		3051.70	O bent.	1.6669	0.1969		40.97	94.2	2.5323	4.88	**356.9**	4.9		-
40	**Syczyn OU-1**	2530.37	S bent.	2.0911	0.0947	66.06	45.91	97.2	2.9248	5.38	**289.1**	4.1	**289.1**	-
41		2644.21	S bent.	2.2123	0.1195		45.68	96.5	3.0864	5.44	**300.7**	4.2		-
42	**Lubycza Królewska-1**	2336.60	S bent.	2.4723	0.0598	66.06	47.25	98.2	3.3955	6.20	**291.1**	4.0	**287.1**	15
43		2385.50	S bent.	2.2361	0.0735		45.54	97.8	3.1733	6.23	**272.2**	3.8		3.5
44		2425.60	S bent.	2.1577	0.0550		45.73	98.4	3.0663	5.84	**279.9**	3.9		1.5
45		2455.60	S bent.	2.2146	0.0547		45.43	98.4	3.1683	5.97	**282.7**	4.0		150
46		2661.50	S bent.	2.3206	0.0653		46.35	98.1	3.2437	5.77	**298.2**	4.2		10
47		2762.60	S bent.	2.2919	0.0718		44.73	97.9	3.3131	5.89	**298.3**	4.2		20-30
48	**Kościaszyn-1**	3407.35	S bent.	1.8377	0.1411	66.07	42.43	95.8	2.7424	5.42	**270.5**	3.9	**286.5**	> 15
49		3474.67	S bent.	1.9800	0.1206		43.74	96.4	2.8844	5.34	**287.4**	4.0		1
50		3624.52	S bent.	2.0324	0.1431		42.84	95.8	3.0022	5.55	**287.7**	4.1		3-4.
51		3678.65	S bent.	2.0719	0.1521		42.1	95.5	3.1055	5.63	**293.0**	4.1		1
52		3723.92	S bent.	2.8831	0.8582		43.39	74.6	3.2784	6.00	**290.4**	4.1		2
53		3771.05	O bent.	2.1598	0.1732		43.33	94.9	3.1249	5.73	**289.9**	4.1		2

The Palaeozoic rocks in their geological history were heated up to temperatures in the range of 120–160 °C. The degree of the thermal alteration is seen to decrease from the west to the east (Fig. 11). In contrast, the overlying Permian–Mesozoic rocks were not heated above 70 °C, which corresponds to the thermal conditions at their present burial depth (see also Fig. 4). The K-Ar dates for the Silurian and Ordovician bentonites fall into the narrow range of 322–340 Ma and imply an Early Carboniferous age of maximum palaeotemperatures. The Cambrian rocks underwent maximal heating at the same time. For the middle Cambrian bentonite from the Borcz-1 borehole, the age of 360 Ma was obtained, which is approximately the same as for Silurian and Ordovician bentonites (Tab. 7).

Zone II – Polik (Fig. 13)

Two thermal stages also were identified in the Polik IG-1 borehole: Cambrian–Silurian and Permian–Mesozoic stages. The Silurian and older rocks underwent anchimetamorphism, with Kübler index values of 0.45-0.60º$\Delta 2\theta$ (air-dried preparation, calibrated to the CIS scale; Warr and Ferreiro Mählmann, 2015). The maximum palaeotemperatures for this structural stage are considered to have exceeded 200 ºC. Dating the age of the temperatures mentioned above on two Ordovician bentonites gave very consistent results of 342–347 Ma (Early Carboniferous; Tab. 7). The Permian–Mesozoic stage also underwent thermodiagenesis, however, in temperatures ranging between 100 and 110 ºC. In this case, the maximum temperatures are considered to have occurred in the Cretaceous. The Polik region is one of the rare locations on the edge of the East European Platform, where a Cretaceous thermal event could be detected.

Zone III – Bodzanów (Fig. 13)

In the Bodzanów zone, three thermal stages can be distinguished: one older than the Silurian, an Upper Carboniferous–Lower Triassic and a Middle Triassic–Cretaceous one. Two thermal events were encountered here: an Early Carboniferous event and an Early Triassic one. The Triassic episode in the area of the Fore-Sudetic Monocline is well documented (Kowalska *et al.*, 2015, as well as unpublished materials). As in the Polik zone, the Silurian and older rocks form the lowest structural unit in the Bodzanów IG-1 borehole underwent anchimetamorphism in the range of the lower anchizone, about 230 ºC – Kübler index 0.44–0.47º$\Delta 2\theta$ (air-dried preparation, calibrated to the CIS scale). Anchimetamorphism age dating was carried out on metashales, establishing an age close to that recorded in the Baltic Basin at ca. 324–327 Ma (the latest Early Carboniferous) – Table 7. The second thermal stage involved heating up to ca. 140 ºC and the third stage recorded in its bottom part with the temperatures corresponding to the present geothermal gradient (ca. 80 ºC, 3 km deep).

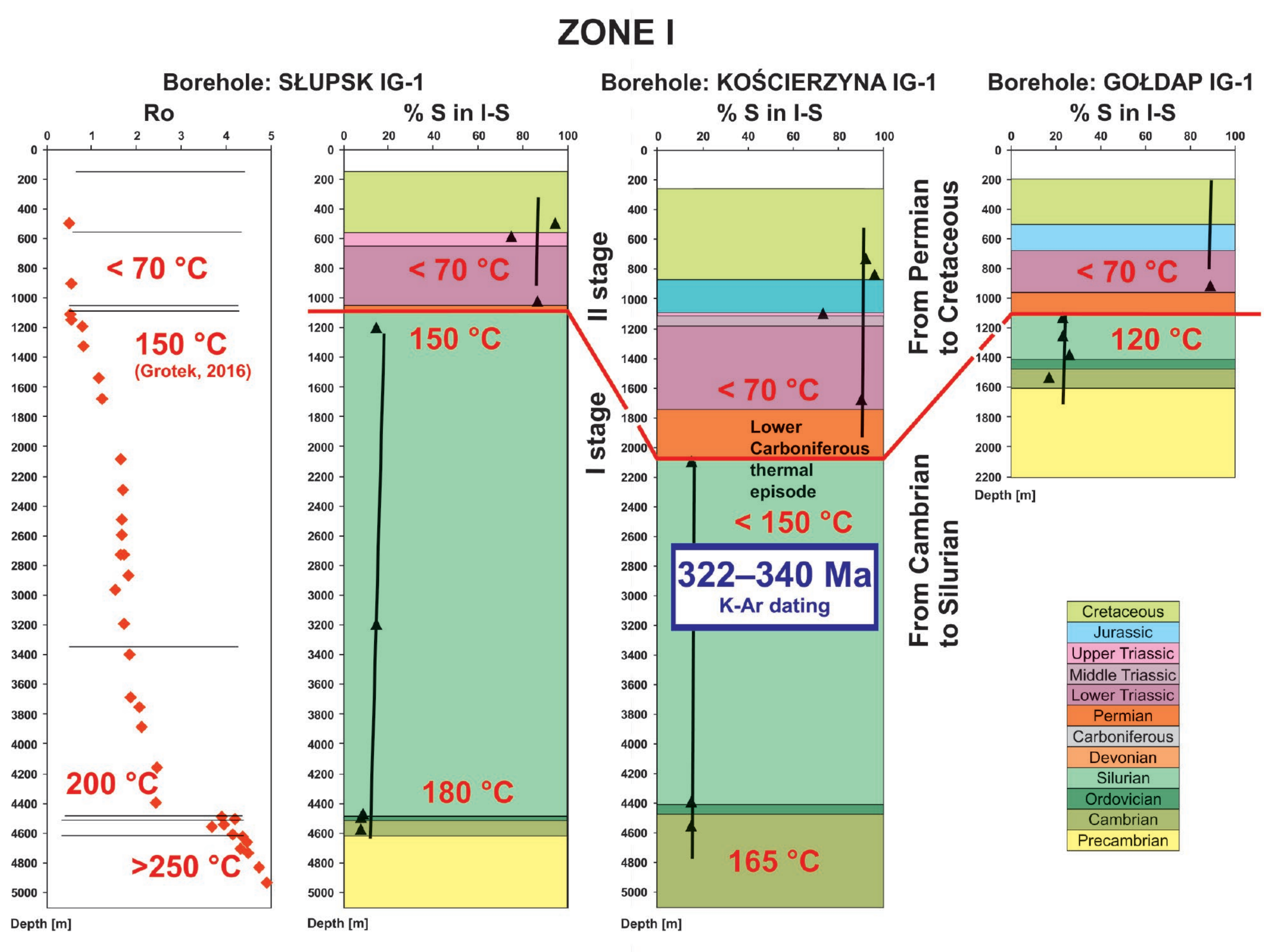

Fig. 12. Thermodiagenetic profile typical of the Baltic Basin – zone I.

Zone IV – Nadarzyn (Fig. 14)

In the Nadarzyn zone, there also are three thermal stages of the same time span, represented by different degrees of smectite illitisation. The Silurian rocks in the top part of the first stage reached maximum palaeotemperatures of 140 ºC. The age of maximum of thermodiagenesis can be dated as Early Carboniferous, on the basis of the presence of a diagenetic discordance between the Silurian and the Upper Carboniferous rocks as well as by comparison with neighbouring areas. Another thermal event occurred in the Early Triassic. In the profile of the Nadarzyn IG-1 borehole, a diagenetic discordance can be observed between the Lower and Middle Triassic rocks. Palaeotemperatures between the top and the bottom of the second thermal stage

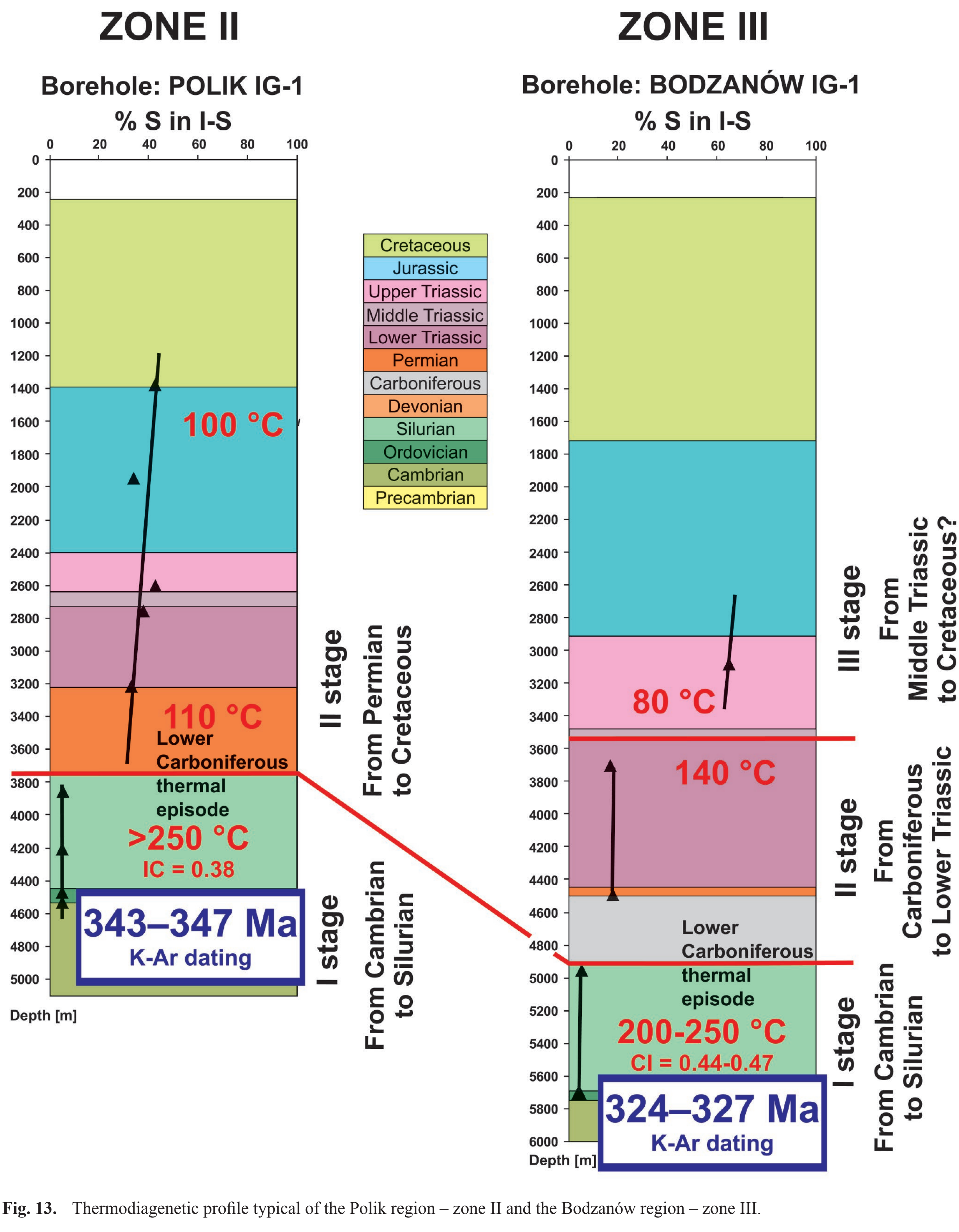

Fig. 13. Thermodiagenetic profile typical of the Polik region – zone II and the Bodzanów region – zone III.

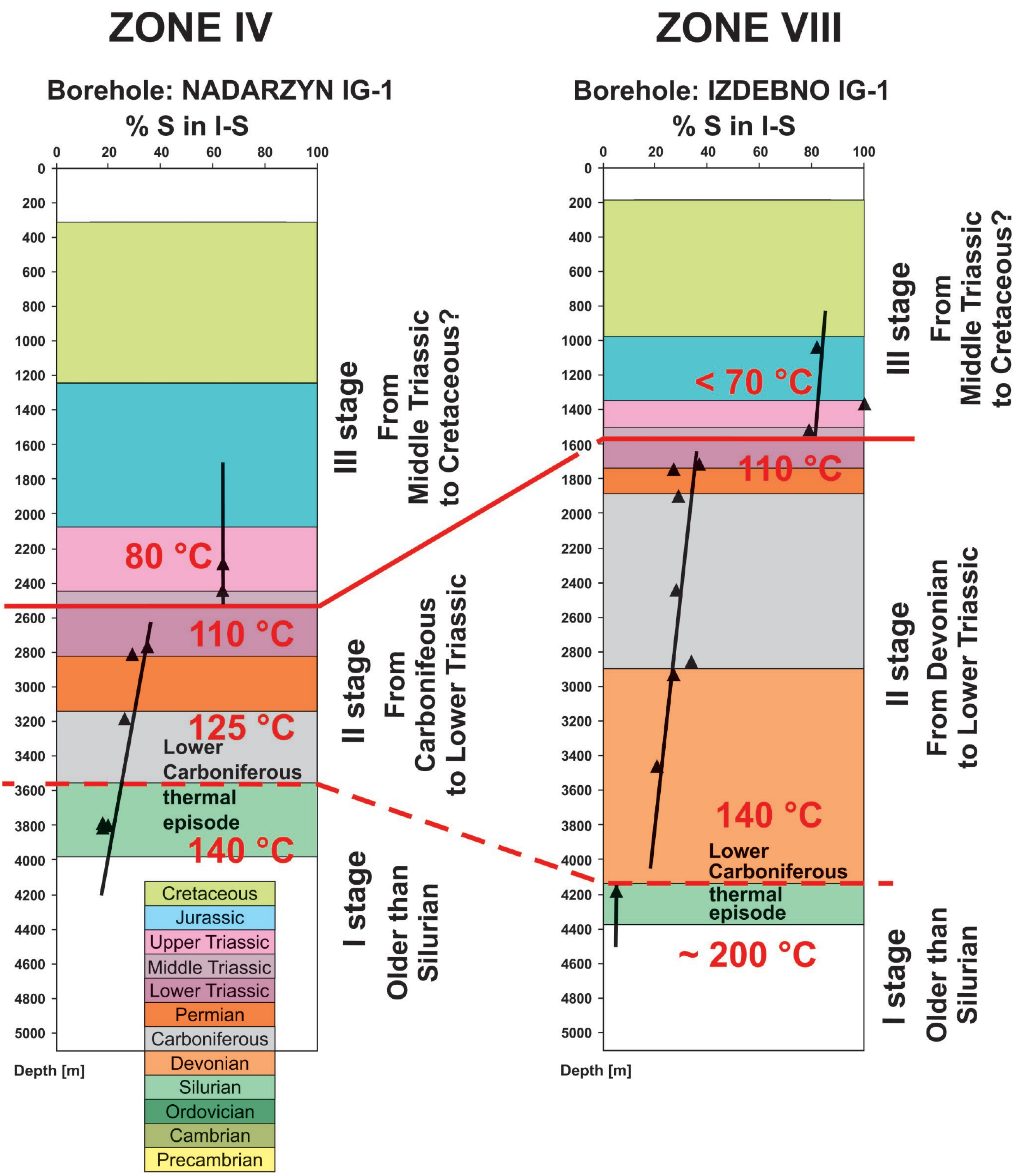

Fig. 14. Thermodiagenetic profile typical of the Nadarzyn region – zone IV and the Izdebno region – zone VIII.

range from 110 to 125 ºC. Owing to the slight difference in maximum palaeotemperatures detected between the Carboniferous and Silurian rocks, taking into account the distance between the samples examined in the geological profile, thermal continuity between these rocks cannot be excluded. However, the assumption that the Silurian rocks underwent deeper diagenesis only in the Triassic is very unlikely on the basis of the results from neighbouring areas. The third thermal stage again contains sediments from the Middle Triassic to the Cretaceous. The maximum palaeotemperatures determined for the Middle Triassic rocks are approximately 80 ºC.

Zone V – Okuniew-Stadniki (Fig. 15)

In the Okuniew-Stadniki zone, two thermal stages were also identified: one older than the Silurian and a Permian–

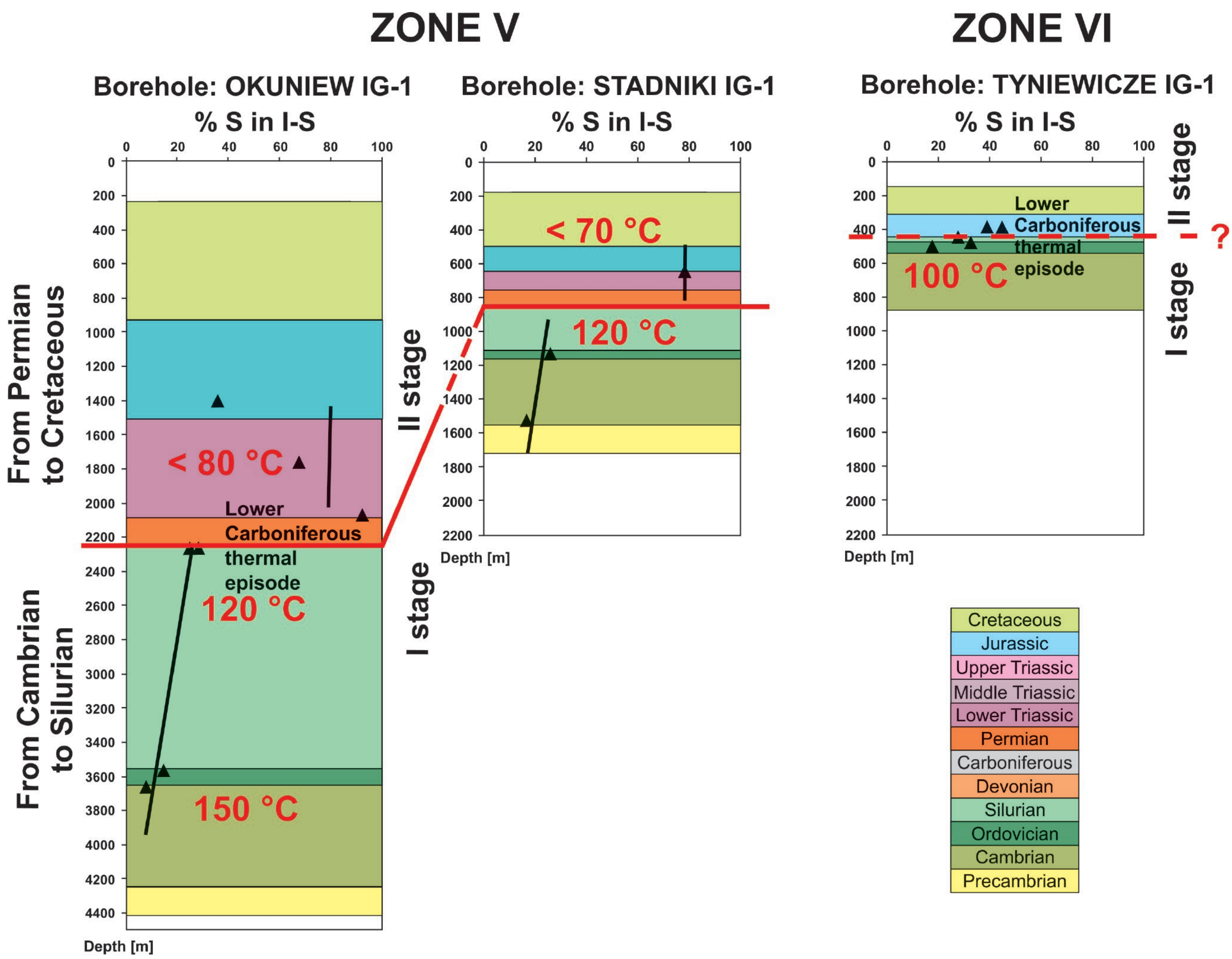

Fig. 15. Thermodiagenetic profile typical of the Okuniew-Stadniki region – zone V and the Tyniewicze region – zone VI.

Mesozoic one. The situation here is similar to that described for Baltic Basin zone. At the top of the Silurian strata, the smectite illitisation level can be observed with palaeotemperatures of ca. 120 ºC. The Mesozoic rocks show initial diagenesis with palaeotemperatures estimated at 70–80 ºC. The direct dating of the maximum of thermodiagenesis also for this zone was not possible, owing to the lack of bentonite samples. An Early Carboniferous age for the main heating phase is assumed for the Lower Palaeozoic rocks from this region and is based the relationships described in neighbouring areas.

Zone VI – Tyniewicze (Fig. 15)

The Tyniewicze zone differs from the remaining areas with respect to its burial history and the small thickness of particular stratigraphic units. The entire profile from the Carboniferous to the Cretaceous is less than 500 m in thickness. The degree of diagenesis is relatively high, considering the present burial depths, and ranged between 100 and 150 ºC. However, a significant scatter of results from 18 to 45% of the smectite layers indicates another mechanism of illitisation, known from shallow saline-water sediments (Sandler and Harlavan, 2006).

Zone VII –Żebrak (Fig. 16)

In the Żebrak zone, three thermal stages may be encountered: Ordovician–Cambrian, Upper Carboniferous–Silurian and Zechstein–Mesozoic. Also, in this case, a diagenetic discordance between the second and the third stage in the profile of the Żebrak IG-1 borehole is clear. The Zechstein Mesozoic cover was not subjected to temperatures higher than 70 ºC during its geological history. The Upper Carboniferous and Silurian rocks were altered thermally at a level of ca. 130 ºC. The age of maximum palaeotemperatures is determined to be 311 Ma, i.e., during the Late Carboniferous, on the basis of the K-Ar dating carried out for Silurian bentonites from the Goździk OU-1 borehole. It cannot be excluded that this event extends into the Early Permian, as seen in the southern part of the Lublin Basin. This is assuming a small admixture of detrital material is found in the fine fraction of the sample studied. A considerably higher degree of smectite illitisation, corresponding to palaeotemperatures of ca. 180 ºC, was observed in an Ordovician sample. Owing to the fact that only one Ordovician sample was examined, it is not clear if this represents a reliable degree of illitisation. The presence of an Ordovician thermal event in this region should be confirmed with additional research.

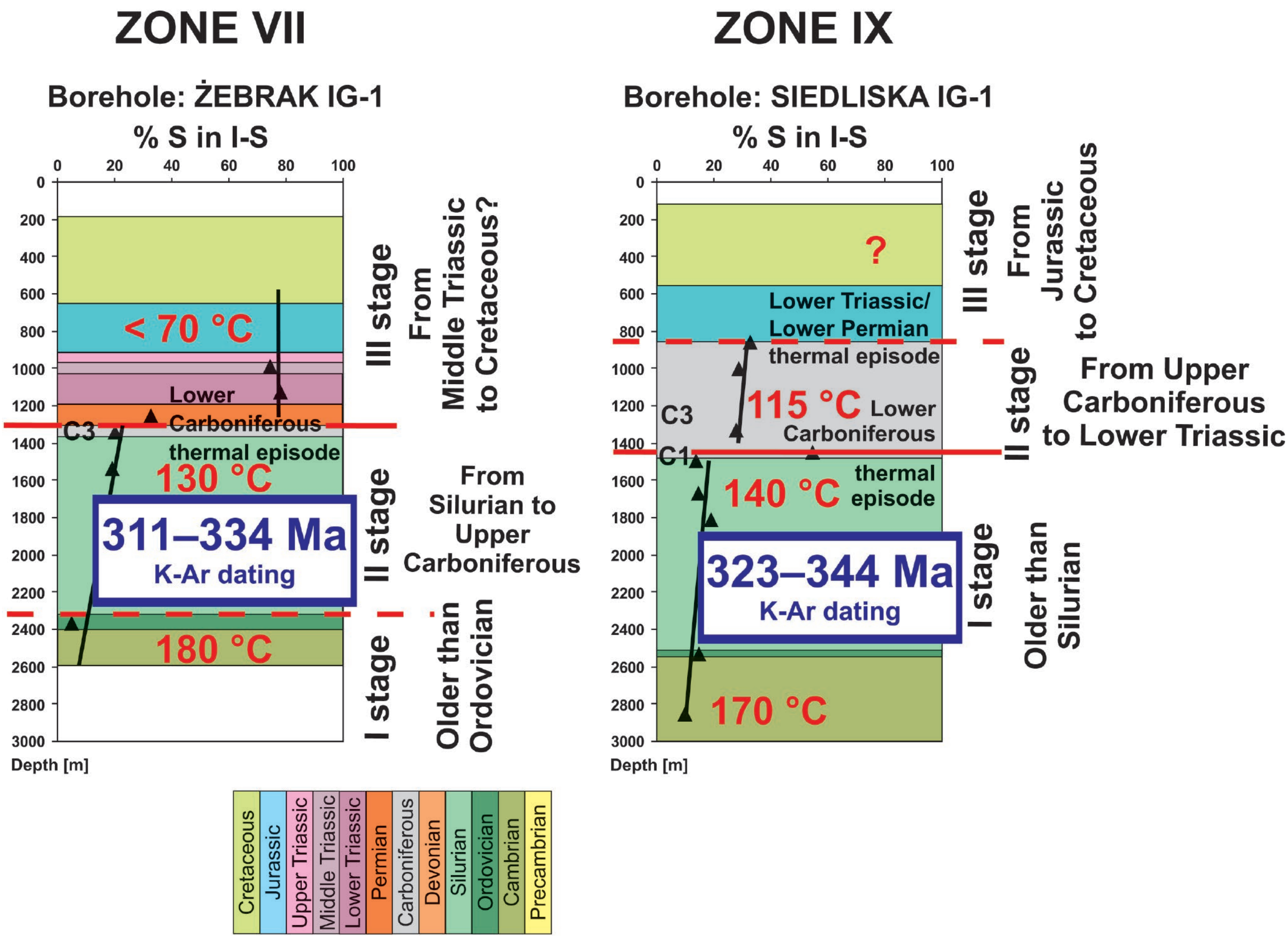

Fig. 16. Thermodiagenetic profile typical of the Żebrak region – zone VII and the Siedliska region – zone IX.

Zone VIII – Izdebno (Fig. 14)

The Izdebno zone differs from the others with the presence of a Late Silurian–Early Devonian thermal event. In the Izdebno IG-1 borehole, three thermal stages were identified. The first one comprises Silurian rocks and exhibits a degree of thermal alteration close to anchimetamorphism (5% of smectite layers in illite-smectite, maximum palaeotemperatures ca. 200 ºC). The overlying Upper Devonian, Carboniferous, Permian and Lower Triassic rocks show a considerably lower degree of thermal alteration from 130 ºC at the bottom to 110 ºC at the top of the rock complex mentioned above. The maximum of diagenesis occurred after the Early Triassic, as observed in other zones. The very low degree of burial diagenesis, with temperatures lower than 70 ºC, is characteristic for the remaining Mesozoic rocks.

Zone IX – Siedliska (Fig. 16)

In the Siedliska zone, three thermal stages are proposed. The K-Ar dating, carried out for Silurian bentonites from the Berejów OU-1 borehole, denotes that the Silurian rocks underwent maximum of thermodiagenesis in the Early Carboniferous, at ca. 323–333 Ma (Tab. 7). Thus, the first thermal stage would comprise rocks older than the Lower Carboniferous. The Upper Carboniferous sediments also were subjected to more advanced diagenesis than present burial would imply, where the maximum palaeotemperatures reached 115 ºC at the top of the rock sequence. Today, the present burial depth is only ca. 850 m. It can be assumed that the second thermal stage of alteration occurred in the Early Permian or Early Triassic, similar to that of neighbouring areas as well as taking into account a significant stratigraphic gap between the Upper Carboniferous and its Jurassic–Cretaceous cover. Although no Jurassic and Cretaceous shale samples were available, a low degree of diagenesis for these rocks can be assumed, on the basis of the results from neighbouring areas.

Zone X – Busówno-Terebiń (Fig. 17)

In the Busówno-Terebiń zone, two thermal stages were confirmed. Layers from the Ediacaran to the Upper Carboniferous were maximally heated in the Early Permian. Apart from a visible leap in the degree of diagenesis in the Terebiń IG-5 borehole profile, the occurrence of maximum palaeotemperatures in the Early Permian was confirmed by K-Ar dating of Silurian and Ordovician bentonites from the boreholes Syczyn OU-1 (289 Ma) and Kościaszyn-1 (270–288 Ma) – Table 7. A relatively high degree of heating of the Jurassic–Cretaceous cover, ca. 100 ºC and ca. 550 m deep, indicating deeper burial, should also be verified. As in the case of the Siedliska zone, owing to specific lithology, the result mentioned above requires confirmation with a greater number of samples.

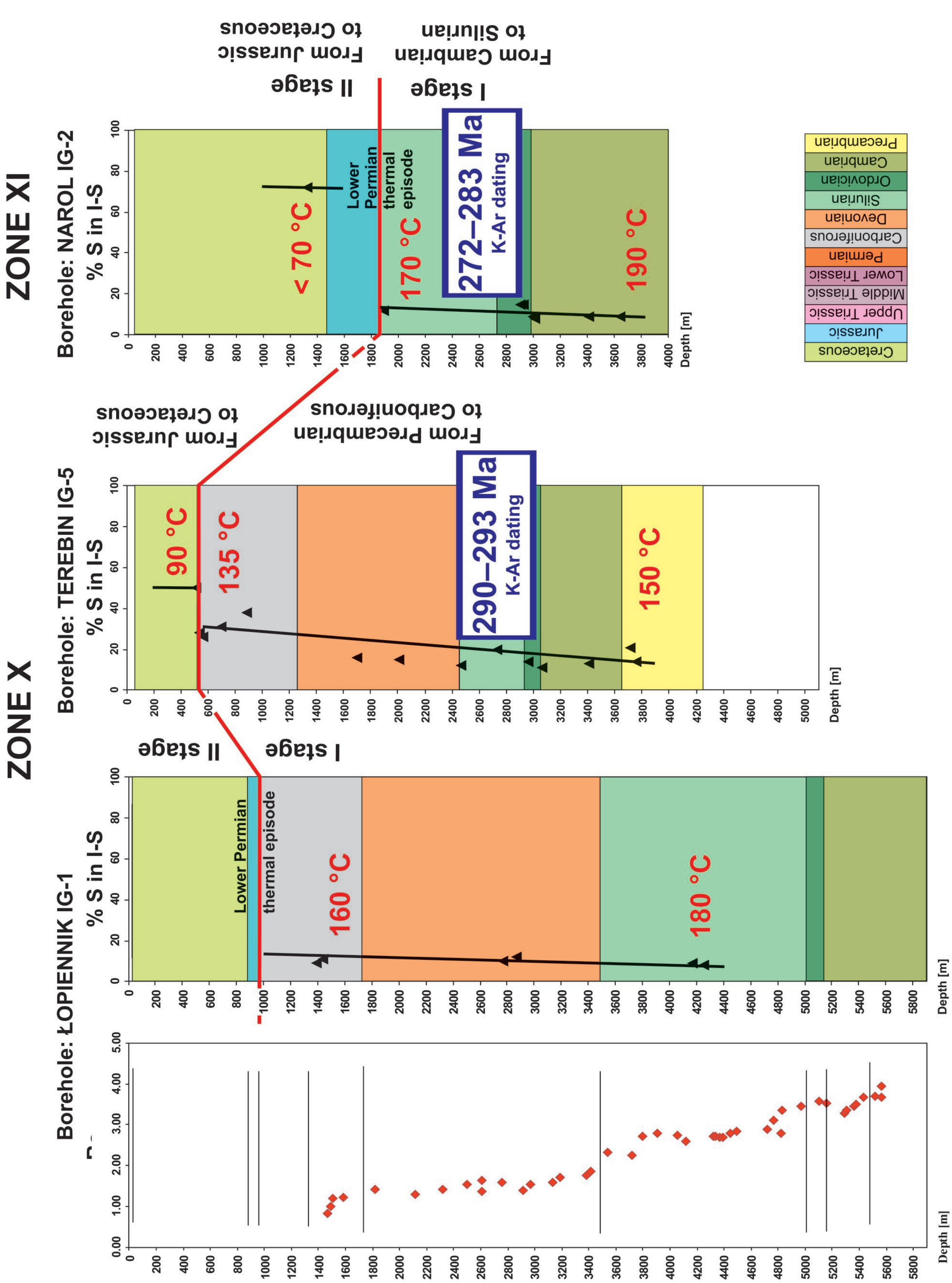

Fig. 17. Thermodiagenetic profile typical of the Busówno-Terebiń region – zone X and the Narol region – zone XI.

Zone XI – Narol (Fig. 17)

In the Narol zone, a similar situation can be observed to that in the Busówno-Terebiń zone. The maximum thermal events affecting the Silurian, Ordovician and Cambrian rocks occurred in the Early Permian. This was established from K-Ar dating executed for Silurian bentonites from the Lubycza Królewska-1 borehole, with a similar age range of 272–283 Ma (Tab. 7). Unlike the previous zone, the Silurian strata are not overlain here with Carboniferous sediments but directly with a Jurassic–Cretaceous cover. In this case, a low degree of thermodiagenesis of the cover is well documented (Fig. 17).

DISCUSSION

Previous studies

In the light of the new data, the Lower Palaeozoic rocks of the Baltic Basin were subjected to maximum palaeotemperatures in the Early Carboniferous or at the turn of the Early and Late Carboniferous, 320–340 Ma. The Devonian age of maximum heating in the region of the Baltic Basin, postulated by Środoń and Clauer (2001), has not been confirmed despite the dating of over 20 bentonites from the boreholes Borcz-1, Kochanów-1 and Opalino-2 and Opalino-4, located near the Lębork IG-1 borehole. Among all the samples dated by the authors mentioned above, there were only three bentonite samples included in their study. Mudstones generally are not suitable for determining the age of diagenesis, owing to the almost certain presence of a detrital material admixture, even in the smallest grain fraction. For the only bentonite from the Lębork IG-1 borehole, Środoń and Clauer (2001) obtained dates in the range of 366–387 Ma.

On the other hand, taking into account the results obtained for samples from the Opalino-4 borehole (Tab. 7), it can be stated that a detrital material admixture in the finest grain fraction does not have always to be meaningful, even in the case of shales. Dating the age of diagenesis for the 0.2 μm fraction of the shale sample gave a result not much higher than the one obtained for bentonites. This can be due to a generally large amount of pyroclastic material in the Silurian rocks of this region, resulting from very intense volcanic phenomena at that time as well as from mainly the coarse-grained character of the detrital material in this particular shale layer. However, this situation is rather exceptional.

In the case of samples from the Polik IG-1 borehole, the difference between the results obtained for bentonites and metashales is clearly visible (Tab. 7). Only a thermal reset allows the use of metashales, when heated above 250–270 °C, for dating exact thermal events (McDowell and Elders, 1980). This can be observed for samples from the Bodzanów IG-1 borehole, although the temperature recognized is lower than 250 °C. However, owing to the degree of tectonic complication in the research area, the present authors cannot be fully certain at this stage of the studies that the reset was completed. Very consistent results obtained for two entirely different metashale samples – 323–327 Ma – can make a case for completion of the reset. The results are also in line with the ones noted in the Baltic Basin in zone I. Still, doubts can be raised by the fact that in the neighbouring areas farther south the maximal heating age can be significantly younger (even 270–290 Ma).

In the southern part of the research area in Poland, dating the period of thermodiagenesis so far has not been carried out on bentonites. The only information concerning the age of diagenesis on the Małopolska Massif comes from the Wola Obszańska area (Kowalska, 2008), the information having been verified as part of the present work (currently 340–350 Ma; Tabl. 3), as well as from the results of research on the Dniester region of the Ukrainian part of the East European Platform margin (Środoń *et al*., 2013). On the basis of the verified K-Ar dating methodology, it was assumed that only dates consistent for all fractions smaller than 0.2 μm can be considered reliable. After such a selection of results, the data from the above publication (Środoń *et al*., 2013) seems to indicate a fairly unambiguous age of thermodiagenesis for the Silurian rocks of the Dniester region – 340–350 Ma – analogous to the date obtained for the Wola Obszańska region, also corresponding to the Early Carboniferous.

Variscan orogeny and volcanism

The results obtained show explicitly that maturity of Palaeozoic rocks at the East European Platform margin was affected mainly by phenomena related to the Variscan orogeny (Warr, 2012; Franke *et al*., 2017). The Early Carboniferous age of maximum palaeotemperatures is correlated with the age of Lower Carboniferous igneous rocks, occurring at the edge of the East European Platform (338–348 Ma) and described by Demaiffe *et al.* (2013) for rocks from the northeastern region of Poland and by Pańczyk and Nawrocki (2015) for rocks from the Lublin Basin. The maximum heating age about 270–290 Ma, found in the southern part of the study area (zones X and XI; Fig. 17), is most probably associated with Early Permian volcanism, the closest signs of which can be observed in the Kraków region (Nawrocki *et al*., 2007, 2008, 2010).

Intensified volcanic activity also was linked with the increase in geothermal palaeogradient in the entire research area (Karnkowski, 2003). For this reason, a palaeotemperature rise did not require deep, sedimentary burial; an overburden 3 km thick is sufficient to reach a temperature of 150 °C with a palaeogradient of almost 50 °C per 1 km. The presence of a tectonic overburden cannot be excluded, taking into account the fact that the extent of the Variscan front in Poland has been a matter of controversy for years (Karnkowski, 2008).

Comparison with other methods

The results obtained are generally in agreement with the results of research on the thermal transformation of organic matter (Grotek, 2016; Botor *et al*., 2017b, 2019b) and with the results of low-temperature thermochronology (Botor *et al*., 2017a, 2019a). The map presented in Figure 10 easily can be compared with maps of palaeotemperature distribution at the top of the Silurian strata, based on vitrinite reflectance measurements, published by Poprawa (2010a), Kiersnowski and Dyrka (2013; fig. 2) and Grotek (2016). However, taking the present results into account, it seems that palaeotemperature distribution was controlled not only sedimentologically, but mainly results from the tectonics, as a consequence of the location of this region at the East European Platform margin.

It should be kept in mind, however, that the thermal transformation of organic matter is much more kinetically controlled, according to the Arrhenius equation, than can be observed in the case of smectite illitisation process. The structural stages, described on the basis of clay minerals transformation analysis, and the discontinuities between them in the diagenetic profiles, however, are marked less evidently on the profiles of organic matter maturation from the same boreholes (Figs 12, 17). This is mainly due to differences in organic matter content and change in its type in the geological profile, which is clearly visible in the Ro profile (vitrinite reflectance) for the Łopiennik IG-1 borehole (Fig. 17). The Ro values differ considerably for the stratigraphic levels identified and simultaneously, for example, in the Carboniferous rocks, show significant differentiation in a short profile interval. Land Permian and Triassic formations are a good example of a situation, where practically no organic matter has been preserved. In the case of vitrinite reflectance, there is still another problem- the absence of vitrinite in Silurian and older rocks. The profile of thermal transformations involving rocks containing different types of organic matter inevitably is burdened with this type of measurement uncertainty. This is exactly the case in point – the profile of the East European Craton cover contains Precambrian to Cretaceous rocks.

Implications for regional geology

The identified zones with diversified thermal histories are clearly visible on the maps of geophysical potential field anomaly for Poland, especially on the map of magnetic anomaly reduced to the pole (fig. 3 in Mikołajczak *et al.*, 2019). The fault zones, possibly constituting their borders, correlate well with the borders of blocks with different geophysical characteristics, seen on the map mentioned above (Fig. 10). This confirms the tectonic basis for the variation in thermal history, presented here.

Ages related to the Early Carboniferous Variscan orogeny phases predominate in the Baltic Basin as well as in the Podlasie Basin, namely zones I, II, III and IX (Fig. 10). In the Lublin Basin (zone X), the impact of rift phenomena related to the declining phase of the Variscan orogeny (290 Ma) is marked. An even younger age of maximum palaeotemperatures (270–280 Ma) was recorded for the Łysogóry Unit, already referable to the TESZ (zone XI). In the thermodiagenetic profiles at the very edge of the Platform (zones II, III, IV, VIII and IX), the presence of younger thermal episodes of the Triassic and Cretaceous ages also is seen. However, these episodes did not have any impact on the degree of thermal maturity of the Lower Palaeozoic rocks, as the heating temperatures were much lower than the Carboniferous ones.

Early Carboniferous Variscan ages of the maximum of thermodiagenesis also were recorded for the Lower Palaeozoic rocks in the northeastern part of the Małopolska Massif. On the basis of verified data for the test samples used in the interlaboratory comparison, a marked difference should be noted in the maximum palaeotemperature ages of the Silurian rocks, occurring in the area of the Małopolska Massif. In the eastern part, the Silurian rocks were subjected to the maximum of thermodiagenesis occurring ca. 340–350 Ma in the area of Wola Obszańska and in its western part ca. 190–200 Ma in the area of Żukowice-39 (Fig. 10). On the basis of observations both of the degree of diagenesis in the area of the Małopolska Massif as well as of the mineralogical variability of rocks drilled within the Massif (Kowalska, 2012), it might be supposed that the extension of the Kraków-Lubliniec Zone, being a part of the Kraków-Hamburg Fault Zone, may be in line with the northern border of the Trzciana-Mielec Fault Zone (Maksym *et al.*, 1998), to the north of the Żukowice-39 borehole, rather than in the zone proposed by Buła *et al.* (2008) and Żelaźniewicz *et al.* (2011).

The maximum palaeotemperatures of Silurian rocks occurring in the western part of the Małopolska Massif in the area of Żukowice-39 (ca. 190–200 Ma) correspond to thermal phenomena, related to the breakup of Pangea and an enhanced geothermal gradient before the opening of the Atlantic Ocean (Gaupp *et al.*, 1993; Liewig and Clauer, 2000). The phenomenon is also associated with the precipitation of authigenic illite, common in Permian sandstones, also in the Polish Basin (Biernacka, 2014).

CONCLUSIONS

1. In general, the Lower Palaeozoic rocks in almost all the Polish part of the East European Platform slope reached maximum palaeotemperatures in the Early Carboniferous or at the turn of the Early and Late Carboniferous (K-Ar dates of 320–340 Ma). Only in the southern part of the Lublin Basin and in the Łysogóry Unit, the age of maximum palaeotemperatures differs; in the Early Permian, the K-Ar dates obtained range from 270 to 290 Ma, responding to volcanic activity of the same age, occurring in a considerable part of Poland (near Kraków, in the Sudetic Mountains and in the Fore-Sudetic Monocline). The 340–350 Ma age of thermodiagenesis, determined in the area of Wola Obszańska on the Małopolska Massif, is most probably in accordance with the age of thermodiagenesis on the Dniester Slope in Ukraine.
2. The younger thermal events had no impact on the generation of hydrocarbons in the Lower Palaeozoic rocks, as temperatures accompanying them were lower than the Variscan ones and the presence of such episodes is visible only in geological profiles of the younger rock sequences. A Cretaceous thermal event (Poprawa *et al.*, 2010) occurred most probably only in the Polik zone. A Triassic thermal event marked its presence in several zones: Bodzanów (zone III), Nadarzyn (zone IV), Izdebno (zone VIII) and possibly, Siedliska (zone IX).
3. After a period of maximum palaeotemperatures in the Early Carboniferous, during Carboniferous and Permian time, a long-lasting stage of uplift and erosion affected the entire area of the East European Platform edge,

as indicated by significant stratigraphic gaps that are noticeable in stratigraphic profiles of the boreholes examined (Figs 12–17). In the most perspective region of the Baltic Basin, Permian–Mesozoic sediments rest directly on Silurian strata; in the southern part of the Lublin Basin, Upper Jurassic and Cretaceous carbonate rocks directly overlie Silurian strata. The complex thermal and tectonic history of this area most probably led to the deformation and breakage of hydrocarbon trap seals, which enabled considerable amounts of the hydrocarbons generated to escape.

4. On the basis of the value of maximum palaeotemperatures at the top of the Silurian strata, it is likely that the Devonian–Carboniferous cover existed across the entire research area. The thickness of this cover is, however, difficult to estimate. The age of maximum palaeotemperatures correlates with an increase in volcanic activity. Therefore, it can be assumed that maximum palaeotemperatures relate largely to increases in the geothermal palaeogradient and less to an increase in burial depth. With the palaeogradient reaching 50–60 ºC, the Devonian–Carboniferous cover might not have exceeded 3 km of thickness in most places.
5. The Late Carboniferous–Early Permian age of maximum palaeotemperatures reveals that most of the hydrocarbons had been generated prior to major exhumation of the East European Platform edge, which markedly limits the possibility of hydrocarbon deposits being preserved today. Simultaneously, a dense network of faults and fractures, which accompanied these post-Variscan tectonic movements, resulted in the escape of the gas that had accumulated in unconventional reservoirs.
6. An interlaboratory comparison of the K-Ar clearly indicated a relative error of ca. ± 3%. Comparing the results obtained for four fractions, both with the K-Ar method and the Ar-Ar one, demonstrates that the fraction < 0.2 µm can be used for maximum palaeotemperature age dating. The split of this fraction is not necessary for bentonites and earlier reported age differentiation among the finer fractions rather was related to measurement errors. The greater 0.2–2 µm grain fraction, in the majority of cases, shows impurity caused by detrital material admixture and therefore the dates obtained are significantly older. It was also demonstrated that both thin and thicker bentonites are suitable for dating the age of thermodiagenesis.
7. In the light of the research conducted, it should be stated that the age dating of maximum palaeotemperature, carried out for the Dniester region and the Baltic zone, requires verification. It should be emphasised that, also in this case, obtaining a high degree of thermal alteration, most probably was not related to deep burial.
8. In the area of the Małopolska Massif, an explicit differentiation was identified in the maximum palaeotemperature ages of Silurian rocks between the northeastern and the southwestern parts: 340–350 Ma in the Wola Obszańska area and 190–200 Ma in the Żukowice area. This implies the presence of a significant tectonic zone between these regions. It is possible that the northern border of the Trzciana-Mielec Fault Zone may constitute the extension of the Kraków-Lubliniec Fault Zone, which is a part of the Hamburg-Kraków Fault Zone.

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