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K-Ar DATING OF BENTONITE DIAGENESIS IN ACCRETIONARY-WEDGE TURBIDITES: CASE STUDY FROM WESTERN OUTER CARPATHIANS

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Abstract: Sixteen bentonite layers of Eocene–Oligocene age were sampled at thirteen sites in accretionary-wedge turbidite sequences, in the three innermost nappes of the Western Outer Carpathians. K-Ar dating was carried out for five of these layers to obtain the maximum burial ages. All of the ages obtained are older than the stratigraphic ages of the host strata. This relationship is due to significant contamination of the bentonites with non-authigenic minerals. This contamination resulted from rapid sedimentation during synsedimentary folding, which is a common feature in accretionary wedges. It follows that the K-Ar dating of bentonite layers in the turbidite sequences of accretionary wedges should be largely restricted to the very distal facies of turbidites or to pelitic intercalations within the turbidites.

Key words: Bentonites, illite-smectite, K-Ar dating, accretionary-wedge turbidites, Western Outer Carpathians.

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INTRODUCTION

The main aim of the present study is the reconstruction of the development of the thermal structure in the Polish segment of the Western Outer Carpathians (WOC). This structure is fairly well recognized from extensive studies of illite-smectite claystones (Dudek *et al.*, 2000, 2004; Kotarba, 2003, Świerczewska *et al.*, 2003, 2007a, b; Świerczewska 2005). The thermal structure is largely the result of folding and subsequent thrusting (Świerczewska, 2005). However, no attempt was made to date the maximum palaeotemperatures which affected the WOC strata. This presents a serious gap in the knowledge of the thermal development of the WOC and in consequence, hampers the understanding of WOC tectonics. Therefore, the main objective of the research reported was to close this gap. The results of this research have been only partly successful, as the authors were able to date the maximum palaeotemperatures for only a few of the samples analysed (Świerczewska *et al.*, 2012). In this contribution, the authors explain the possible reasons for this failure. The Eocene and Oligocene strata were chosen by the authors as the object of study for two reasons. Within the WOC, (1) bentonite layers are most numerous in strata of this age range (Wieser, 1985) and (2) the bentonites that are Eocene and Oligocene in age have been studied most extensively (Van Couvering *et al.*, 1981; Wieser, 1985 and references therein; Cieszkowski *et al.*, 2006 and references therein).

During the burial of siliciclastic strata, mixed-layer illite-smectite (I-S) forms in the course of progressive smectite diagenesis. This transformation starts at a temperature of about 70–80°C (e.g., Jennings and Thompson, 1986). The transformation of smectite to illite is a one-way reaction, involving K enrichment within the newly formed diagenetic I-S. In claystones, the degree of transformation from smectite to illite, expressed by % S in I-S can be correlated with the maximum palaeotemperature, which affected the claystones. Therefore, I-S is useful for dating of the maximum burial of siliciclastic strata (e.g., Clauer *et al.*, 1997; Środoń and Clauer, 2001; Środoń *et al.*, 2006b, 2009). However, there are some factors, which can mo- dify the relationship between the degree of transformation from smectite to illite, expressed by % S in I-S, and the estimated palaeotemperature. First of all, the degree of transformation from smectite to illite depends also on the availability of K in the diagenetic system. For example, in a bentonite-

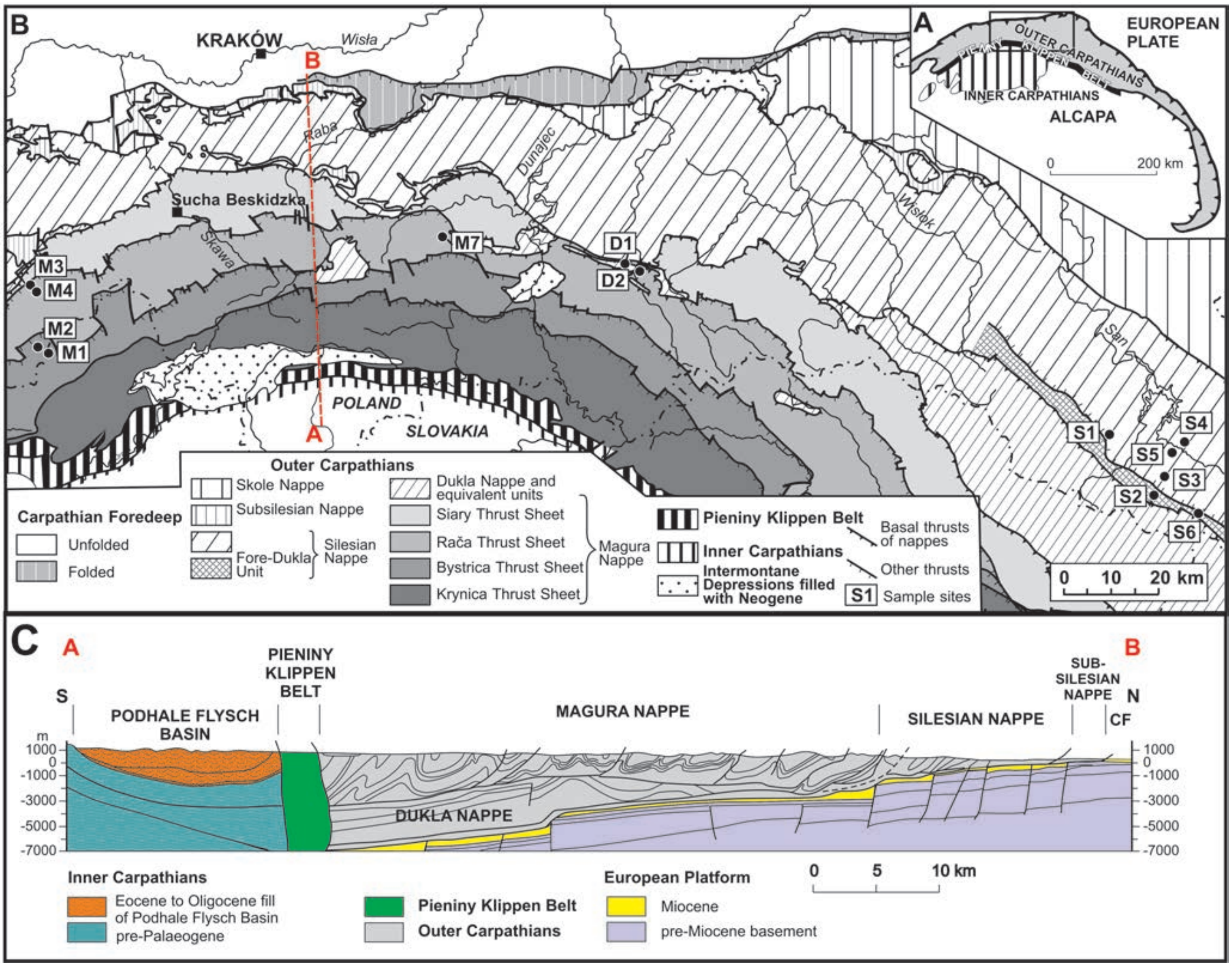

Fig. 1. Geology of study area and location of bentonite sites sampled. **A.** Geological sketch map of central Europe, showing location of area studied. **B.** Polish sector of the Western Outer Carpathians (modified after Żytko *et al.*, 1989, and Świerczewska, 2005) showing location of bentonite sites sampled; S – Silesian Nappe sites; D – Dukla Nappe sites; M – Magura Nappe sites. **C.** Cross-section through the Carpathians (after Oszczypko, 2006, modified); CF – Carpathian Foredeep.

claystone sequence, the transformation from smectite to illite can be more advanced in claystone, because of a local source of potassium (Altaner *et al.*, 1984; Šucha *et al.*, 1993). Furthermore, a longer duration of burial may result in the co-existence of diagenetic I-S, which show different ages ("mixed ages" of Środoń *et al.*, 2002).

The claystones studied for the reconstruction of the WOC thermal structure contain K-bearing minerals, both detrital and authigenic. The occurrence of the former excludes the claystones from the K-Ar dating of diagenesis. Therefore, the authors decided to use bentonites for the dating. However, bentonites also may contain non-authigenic K-bearing minerals of both detrital and volcanic origins. The contamination of bentonites by K-bearing non-authigenic minerals, especially by the $2M_1$ polytype of illite, results in the ages measured being a mixture of pre-diagenetic and diagenetic K-Ar ages. Therefore, only bentonites devoid of non-authigenic K-bearing minerals are appropriate for K-Ar dating of the maximum burial.

GEOLOGICAL SETTING

The Polish segment of the WOC is composed of five north-verging, rootless nappes, from north to south: the Skole, Sub-Silesian, Silesian, Dukla and Magura nappes (Fig. 1). The nappes consist largely of Lower Cretaceous to lower Miocene flysch sequences. To the north, the WOC are thrust over the Carpathian Foredeep, filled with Neogene strata (e.g., Oszczypko, 2006 and references therein). To the south, the WOC are separated from the Inner Carpathians by the Pieniny Klippen Belt, a narrow zone of extreme shortening and wrenching (Birkenmajer, 1986; Plašienka and Mikuš, 2010). Although debates on several issues still continue, there is broad agreement that the main tectonic features of the WOC were formed largely during the Palaeogene–Neogene, owing to the southward-directed subduction of the oceanic or sub-oceanic crust at the southern margin of the European plate below the continental crust of the ALCAPA (Alps-Carpathian-Pannonian) unit

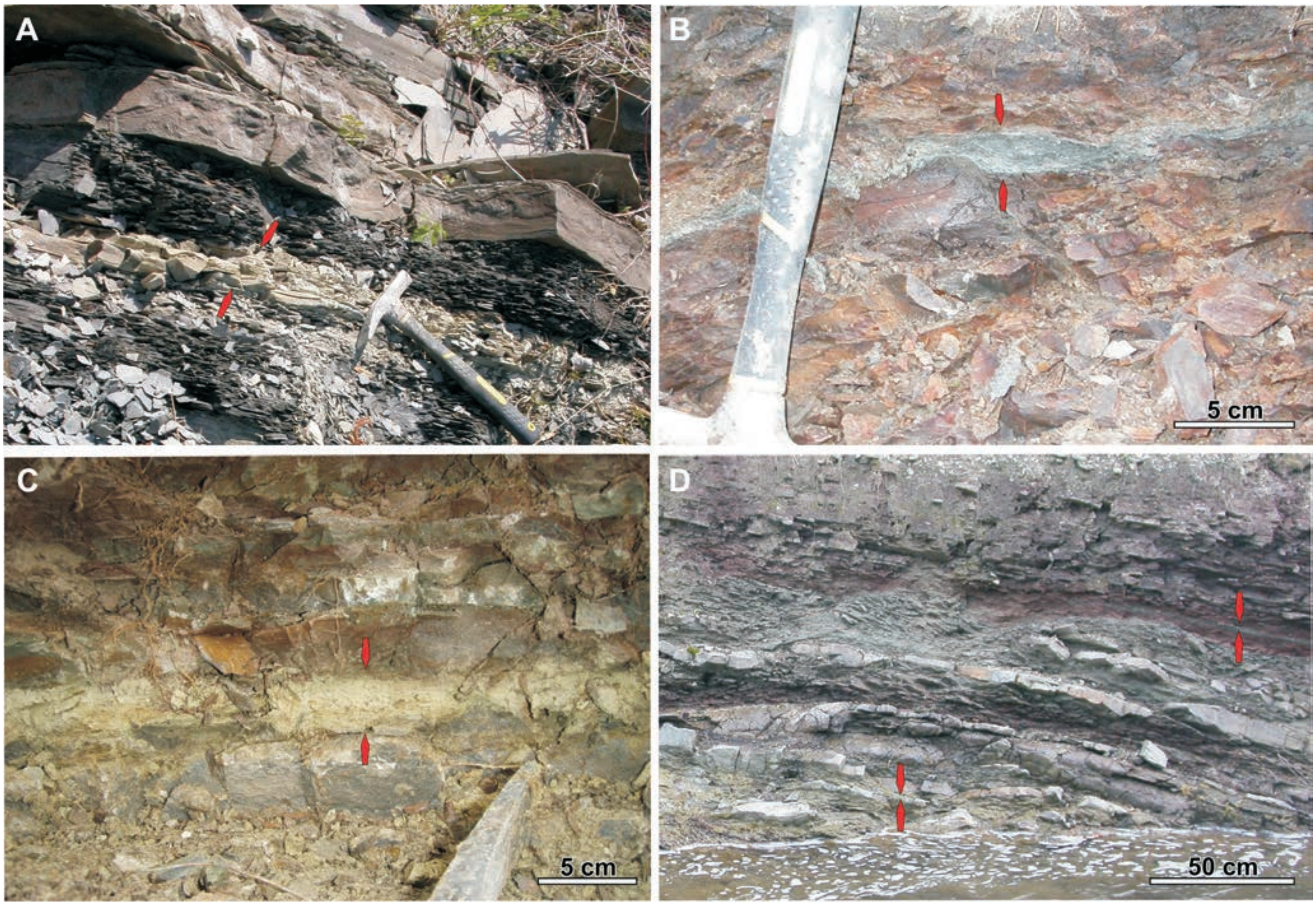

Fig. 2. Typical exposures of bentonite layers (arrowed). **A.** Bentonite layer in the Cergowa Beds, site D1 (hammer is 32 cm long). **B.** Bentonite lenses in the Zembrzyce Beds, close to sites M3 and M4. **C.** Bentonite layer in the Beloveža Beds, site M1 (note gradational upward transition of bentonite into claystone). **D.** Bentonite layers in the Beloveža Beds, close to sites M1 and M2).

(for review see: Picha *et al.*, 2005; Fig. 1A). During those times, the WOC were an orogenic wedge, whereas the Pieniny Klippen Belt acted as a back-stop, inwards of which the Podhale Flysch fore-arc basin was located, filled mainly with Oligocene flysch strata (Gedl, 2000).

MATERIAL

Bentonites were reported from numerous sites in the sedimentary sequences in the Polish segment of the WOC (Cieszkowski *et al.*, 2006 and references therein). They occur in all five nappes, exclusively in thin-bedded turbidites or hemipelagic claystones (Wieser, 1985; cf. Ślączka *et al.*, 2005). In the present account, the authors use the term "bentonite" in a general sense. It denotes a rock, which shows the following features: (1) it is very fine-grained, (2) it is non-carbonate rock, and (3) it is very light in colour, strikingly different from the host strata. Moreover, some of the studied "bentonites" swell in water.

When choosing sampling sites, the authors were restricted by two factors. One was the occurrence of bentonite layers within the strata, which had been subjected to a palaeotemperature of more than 100°C. The results of previous studies of the Carpathian bentonites (Šucha *et al.*, 1993; cf. Cieszkowski *et al.*, 2006) showed that such a temperature is necessary for the initiation of the transformation of smectite to illite in bentonites. It follows, that only strata affected by temperatures of more than 100°C may contain bentonites with diagenetic I-S, appropriate for K-Ar dating of the maximum palaeotemperature affecting the strata. Following this requirement, the authors decided to leave out the Skole and Subsilesian nappes (cf. Świerczewska, 2005) and restrict the sampling to particular parts of the Silesian, Dukla and Magura nappes (Fig. 1, Tab. 1). Secondly, the authors were restricted by the quantity of material necessary for all projected laboratory studies. Therefore, thick and continuous bentonite layers were sampled.

According to Wieser (1985), in the Eocene and Oligocene strata of the nappes studied, bentonite layers occur at several isochronous levels. There are six such levels in the Magura Nappe, three levels in the Dukla Nappe and five levels in the Silesian Nappe. The sampling was most widespread in the Magura Nappe, where the Eocene Beloveža and Zembrzyce beds were sampled in the western part of the nappe, and the Eocene Beloveža Beds were sampled in the central part of the nappe. In the Dukla Nappe, only the Oligocene Cergowa Beds exposed in two tectonic windows were sampled, whereas within the Silesian Nappe, the sampling was restricted to the Oligocene Krosno Beds and the transitional beds between the Menilite and Krosno beds in the easternmost segment of the nappe. All samples were co-

Table 1

Location of sites sampled with their lithostratigraphic and stratigraphic positions, and thickness of sampled bentonites layers

Site	Tectonic subunit	Sample	Geographic coordinates		Lithostratigraphy	Stratigraphy	Thickness of bentonite layer (cm)	Sampled part of bentonite layer
			Lat. N	Lon. E				
Magura Nappe								
M1 Glinka	Bystrica Thrust Sheet	PA-457/T1	49°27.464'	19°13.591'	Beloveža Beds	Eocene	1 to 3	bulk
		PA-457/1/T1					3	bulk
M2 Glinka	Bystrica Thrust Sheet	PA-458/U	49°27.423'	19°13.170'	Beloveža Beds	Eocene	10 to 15	upper
		PA-458/L						lower
		PA-458/C						bulk
M3 Cisiec	Rača Thrust Sheet	PA-459/T	49°34.118'	19°06.146'	Zembrzyce Beds	Eocene	1	bulk
M4 Cisiec	Rača Thrust Sheet	PA-459/1	49°34.168'	19°06.198'	Zembrzyce Beds	Eocene	>100	middle
M7 Zbludza	Bystrica Thrust Sheet	PA-452/T	49°35.081'	20°21.387'	Beloveža Beds	Eocene	5	bulk
Dukla Nappe								
D1 Rzeka Biała	Grybów Sub-Nappe	PA-465/B	49°37.157'	20°56.786'	Cergowa Beds	Oligocene	10	bulk
		PA-465/1					15	bulk
D2 Grybów-Czerwony Potok	Grybów Sub-Nappe	PA-466/B	49°36.534'	20°56.119'	Cergowa Beds	Oligocene	10	bulk
Silesian Nappe								
S1 Rabe	Central Carpathian Depression	PA-479	49°18.928'	22°15.959'	Krosno Beds	Oligocene	5	bulk
S2 Wetlina	Fore Dukla Unit	PA-477	49°09.755'	22°27.505'	transitional beds*	Oligocene	15	bulk
S3 Nasiczne	Central Carpathian Depression	PA-474	49°09.202'	22°34.543'	Krosno Beds	Oligocene	40	bulk
S4 Chmiel	Central Carpathian Depression	PA-475	49°13.674'	22°35.043'	Krosno Beds	Oligocene	5	bulk
S5 Zatwarnica	Central Carpathian Depression	PA-476	49°14.160'	22°33.684'	Krosno Beds	Oligocene	10	bulk
S6 Berechy Górne	Fore Dukla Unit	PA-473	49°08.275'	22°34.288'	transitional beds*	Oligocene	10	bulk

* – "transitional beds" refer to transitional strata between the Menilite and Krosno beds (cf. Ślączka, 1993)

llected in mudstone/claystone sequences within thin- and medium-bedded turbidites (Fig. 2).

The samples discussed were collected at thirteen sites: five in the Magura Nappe, two in the Dukla Nappe and six sites in the Silesian Nappe (Fig. 1, Tab. 1). Fiveteen bentonite layers were sampled altogether. These layers ranged from 1 cm to more than 1 m thick, but layers 10 to 15 cm thick were the most common. Most of the bentonite layers pinch and swell along the strike (Fig. 2A). Most of these layers are also bedding-parallel, but some display a wavy appearance (Fig. 2B). The bentonite layers are easy to distinguish, for they show a distinct colour difference, compared to the host strata (Fig. 2). Those in the Magura and Dukla nappes are creamy, light grey and light olive, whereas those within the Silesian Nappe show a light bluish colour. All bentonite layers sampled display sharp bottom surfaces. The top surfaces of these layers are either sharp (Fig. 2A, B) or gradational into claystone (Fig. 2C). The bentonites observed at sites M2 and M4 swell in water. In the layer exposed at site M2, three samples were collected, whereas only single samples were taken from all of the other bentonite layers. Altogether, seventeen bentonite samples were collected.

At one of the sites sampled (M3), the fission-track age had been determined for zircons (Van Couvering *et al.*, 1981) and at another site (S6) the petrography of the bentonite had been studied (Koszarski *et al.*, 1960).

METHODS

The clay fraction (<0.2 μm) was separated from all of the bentonites sampled and from the claystones, associated with the bentonite layers, sampled at sites M1, M2, M7, D2, as well as from claystones exposed close (<200 m) to sites S1–S6 (Fig. 1, Tab. 1), using the procedure of Jackson (1975). Following this procedure, the Na-exchanged form of the mixed-layer minerals was obtained. For 17 bentonite

Table 2

% S measurements and ordering (R) in I/S obtained from shales and bentonites, and mineral composition of bentonites

Site	Claystone	Bentonite				
	% S in I/S	Sample	% S in I/S	R	other minerals in fraction <0.2 µm	other minerals identified in bulk rock
Magura Nappe						
M1 Glinka	28	PA-457/T1	22	R>1	I/S, I, Ch	Q, C, Pl, Ch, I, 2M1, I/S
		PA-457/1/T1	20		I/S, I, Ch	
M2 Glinka	30	PA-458/L	24	R1/ R>1	I/S, I, Ch	Q, C, Pl, Ch, I, 2M1, I/S
M3 Cisiec	35–70*	PA-459/T	40	R0	I/S, I, K, Q	Q, C, Pl, I, 2M1, I/S, K
M4 Cisiec	35–70*	PA-459/1	70	R0	I/S, I (tr), Q (tr),	
M7 Zbludza	18	PA-452/T	20	R>1	I/S, I, Ch	
Dukla Nappe						
D1 Rzeka Biała	22	PA-465/B	20	R>1	I/S, I, Ch	
		PA-465/1	22	R>1	I/S, I, Ch	Q, Pl C, D,Ch, I, 2M1, I/S
D2 Grybów-Czerwony Potok	12	PA-466/B	20	R>1	I/S, I, Ch?, K(?)	Q, Pl, Ch, I, 2M1, I/S
Silesian Nappe						
S1 Rabe	21	PA-479	19	R1/R>1	I/S, I, Ch, Q (tr)	Q, C, Ch, 2M1, Pl, I/S
S2 Wetlina	26	PA-477	23	R1	I/S, I, Ch	Q, Pl, F, 2M1, D
S3 Nasiczne	23	PA-474	12	R>1	I/S, I, Ch, Q (tr)	Q, C, D, Ch, I, 2M1, I/S
S4 Chmiel	35	PA-475	32	R0/R1	I/S, I, Ch(tr), K	Q, C, D(tr), 2M1, Pl, Py(tr), I/S
S5 Zatwarnica	23	PA-476	33	R0/R1	I/S, I, Ch(tr), K	Q, C, Ch, D(tr), 2M1
S6 Berechy Górne	26	PA-473	16	R1/R>1	I/S, I, Ch, Q (tr)	Q, C, D, Ch, I, 2M1, I/S

* – based on Świerczewska (2005); Q – quartz, Ch – chlorite, I-S – illite-smectite, I – illite, Mu – muscovite, 2M1 polytype of illite, Pl – albite, C – calcite, D – dolomite, K – kaolinite.

samples, three grain-size fractions (<0.02, 0.02–0.05 and 0.05–0.2 µm) were separated by high-speed centrifugation. Oriented air-dry and glycoled preparations of the clay fraction were analyzed by X-ray diffraction (XRD), using a Phillips diffractometer, equipped with a Cu tube and a graphite monochromator, and an ARL X'TRA diffractometer, equipped with a Si(Li) solid-state detector. To identify the mineral composition of bentonites 11 bulk rock samples (Fig. 3; Tab. 2) were also analyzed by XRD.

The degree of transformation of smectite to illite, expressed as the percentage of smectite in the mixed-layer illite-smectite (% S), was determined on the basis of the measurement of the position of the diagnostic reflections in the glycolated samples. Reflections in the range 5–8, 15–17 and 33–35°2Θ were used (Środoń, 1980, 1981, 1984; Dudek and Środoń, 1996). The maximum palaeotemperatures were calculated, using the degree of transformation of smectite to illite in the claystones (Šucha *et al.*, 1993). The correction of 10°C, suggested by Clauer *et al.* (1997), was implemented. Following Clauer *et al.* (1997) and Środoń *et al.* (2002), the K-Ar dating of the bentonite clay fraction was carried out for three clay fractions (<0.02, 0.02–0.05 and 0.05–0.2 µm) of five samples (Tab. 3), identified by XRD as being the most pure among the 17 analysed. A Sherwood Model 420 flame photometer was used for the determination of the K_2O content in all of the bentonite samples studied. The following standards were used: 76a Burnt Refractory NIST Standard Reference (1.33% K_2O) and 70a Potassium Feldspar NIST Standard Reference Material (11.80% K_2O). The authors used the Ar measurement techniques, described by Środoń *et al.* (2006a).

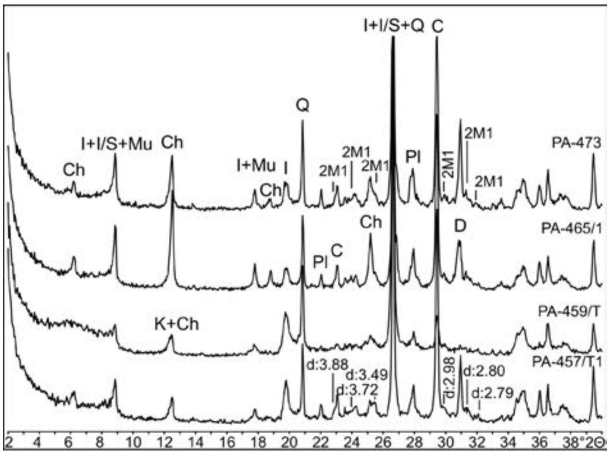

Fig. 3. Representative random XRD patterns of whole-rock bentonite samples from the Magura (PA-457/T1, PA-459/T), Dukla (PA-465/1) and Silesian (PA-473) nappes. Q – quartz, Ch – chlorite, I-S – illite-smectite, I – illite, Mu – muscovite, 2M1 polytype of illite, Pl – albite, C – calcite, D – dolomite, K – kaolinite.

Most analyses were performed in the laboratories of the Institute of Geological Sciences, Polish Academy of Sciences, Kraków. Only bulk rock XRD analyses were done in the laboratory of the Faculty of Geology, Geophysics and Environment, AGH University of Sciences and Technology, Kraków.

Table 3

Results of K-Ar dating of bentonites in three grain size fractions

Sample	Fraction (μm)	K_2O (%)	^{40}Ar (%)	^{40}Ar (pmol/g)	**Age (Ma)**	2δ (Ma)	Strat. age (Ma)	Stratigraphy
Magura Nappe								
PA-457/T1	< 0.02	5.53	58.4	491.1	**60.7**	1.1	34–38	Eocene (Priabonian)
	0.02–0.05	5.55	49.9	573.3	**70.4**	0.9		
	0.05–0.2	5.47	40.7	634.8	**78.9**	2.9		
PA-458/L	< 0.02	5.41	50.2	476.8	**60.2**	1.2	37–50	Eocene (Ypresian-Priabonian)*
	0.02–0.05	5.4	28.6	523.4	**66.1**	2.4		
	0.05–0.2	5.42	67.5	588.9	**74**	0.8		
PA-459/1	< 0.02	2.70	71.7	373.2	**93.6**	1.6	34–38	Eocene (Priabonian)
	0.02–0.05	2.88	59.4	352.7	**83.1**	3.0		
	0.05–0.2	3.66	68.6	557.6	**102.9**	1.7		
Dukla Nappe								
PA-465/1	< 0.02	5.88	54.0	478.3	**55.6**	0.8	24–30	Oligocene NP24** and NP25**
	0.02–0.05	5.95	65.5	516.0	**59.3**	0.8		
	0.05–0.2	5.96	70.4	651.3	**74.4**	0.7		
PA-466/B	< 0.02	6.61	60.6	488.4	**50.6**	0.6	24–30	Oligocene NP24** and NP25**
	0.02–0.05	6.64	78.2	640.9	**65.8**	0.7		
	0.05–0.2	6.78	75.6	588.7	**59.3**	0.5		

* – after Wagner (ed.), 2008; ** – after Oszczypko-Clowes and Ślączka, 2006

RESULTS

The bulk-rock bentonite samples contain significant amounts of non-clay minerals (Tab. 2; Fig. 3). Quartz occurs in all samples. Albite is common, while carbonates, mostly in the form of calcite, occur in most samples. Only two samples, collected at sites D2 and S2, are devoid of calcite. Dolomite was identified in six samples. Illite and I-S were observed in all samples, whereas kaolinite was identified in only one sample (site M3). The $2M_1$ polytype of illite was identified in all samples, on the basis of its characteristic reflections in the 19–35°2Θ range (Moore and Reynolds, 1997). Chlorite is common in all bentonite samples, except for those collected at sites M3 and M4.

The mineral composition of the clay fraction <0.2 μm is very similar in all bentonite samples studied (Fig.4; Tab. 2). I-S and discrete illite occur in all samples, whereas kaolinite was observed only in four samples (sampling sites M3, D2, S4 and S5) and traces of quartz were noted in five samples. Chlorite is common in all bentonite samples, except for those collected at sites M3 and M4.

The XRD analysis results of I-S composition in the claystones and bentonites are summarized in Table 2. The Oligocene claystones, sampled in the easternmost segment of the Silesian Nappe, contain I-S with 21–35% S, whereas the composition of I-S in bentonites varies there from 12 to 33% S. The Dukla Nappe Oligocene claystones were sampled in two tectonic windows. The sample from the Grybów Tectonic Window contains I-S with 12% S, whereas in the Krużlowa Tectonic Window the smectite content in I-S is 22%. The Eocene claystones sampled in the western segment of the Magura Nappe (sites M1 and M2) contain I-S with 28–30% S. On the other hand, in the same parts of this nappe, in the vicinity of sites M3 and M4 these claystones show 35–70% S in I-S (Świerczewska, 2005). The Eocene claystone sampled in the central segment of the Magura Nappe (site M5) contain I-S with 18% S.

The composition of I-S in most of the bentonites sampled is largely similar to that of I-S in the associated claystones. The only exception is the bentonite layer, more than 100 cm thick, sampled at site M4. The latter bentonite shows a significantly lower degree of transformation from smectite to illite (70% S) than the degree of this transformation in a bentonite layer, 1 cm thick, sampled at site M3 (40% S), 200 m from site M4.

K-Ar DATING RESULTS

Five Eocene and Oligocene bentonite samples, two from the Dukla Nappe and three from the Magura Nappe, were selected for K-Ar dating (Tab. 3). The dating was performed for the bentonites with the clay fraction, least contaminated by detrital minerals. The largest contamination occurs in the bentonite samples from the Silesian Nappe and, therefore, these bentonites were excluded from the K-Ar dating.

The K-Ar ages obtained for particular fractions of the bentonite samples discussed show significant scatter. The ages of the Oligocene bentonites range from 50.6 to 74.4 Ma, while those of the Eocene bentonites vary from 60.2 to 102.9 Ma. In four bentonite samples, the finest fraction shows the youngest age and the coarsest fraction displays the oldest age. In three samples (PA-457/T1, PA-458/L, PA-465/1), the K-Ar ages increase systematically with coarsening of the grain size.

DISCUSSION

The I-S composition of the claystone beds associated with the bentonites studied indicates that the maximum palaeotemperatures, which affected the bentonites, were 110 to 170°C. These temperatures involved a considerable degree of smectite-to-illite I-S transformation (12–70% S) in all of the sampled bentonites (Tab. 2). Such a degree of transformation is sufficient for the K-Ar dating of bentonite diagenesis. However, all K-Ar ages obtained are older than the stratigraphic ages of the corresponding host strata (Tab. 3). The authors believe that this relationship has resulted from the major contamination of the bentonites analysed by non-diagenetic minerals. Such contamination is evident in the results of the XRD bentonite bulk-rock analyses and in some XRD clay-fraction analyses (Fig. 3; Tab. 2). Moreover, the contamination of the WOC bentonites by non-diagenetic minerals was already reported (Koszarski *et al.*, 1960; Van Couvering *et al.*, 1981; Cieszkowski *et al.*, 2001). Nevertheless, it appeared possible that the contamination was largely restricted to the coarser fractions of the bentonites (cf. Cieszkowski *et al.*, 2001).

In all bentonite samples analyzed, the age of the 0.05–0.2 μm fraction is much older (10–20 Ma) than that of the fraction <0.02 μm (Tab. 3). This relationship shows that a depletion in some K-bearing detrital minerals took place systematically, with respect to the decrease in grain size. This can be related to the removal of mica flakes**,** the occurrence of which was also reported in bentonites from the Silesian and Magura nappes (Koszarski *et al.*, 1960; Leszczyński and Malata, 2002). Nevertheless, the K-Ar ages obtained show that not all of the K-bearing non-authigenic minerals were removed during separation of the clay fraction from the samples dated. It appears, therefore, that the ages obtained are influenced by the presence of discrete detrital illite. It is possible that in some bentonites analyzed, small amounts of discrete illite may be a product of the diagenetic alteration of kaolinite. The illitization of kaolinite may occur parallel to the illitization of smectite (cf. Środoń *et al.*, 2009**)**. In summary, the authors believe that not all of the bentonites studied were suitable for K-Ar diagenetic dating, because they are considerably contaminated by non-diagenetic minerals.

Not all of the WOC bentonites are contaminated by non-diagenetic minerals. Non-contaminated bentonites were reported from the Eocene strata of the sub-Silesian Nappe (Cieszkowski *et al.*, 2006; Fig. 1). Unfortunately, these bentonites are not suitable for the K-Ar dating of diagenesis, because they show an insufficient degree of smectite-to-illite transformation in I-S. These bentonites occur either in the very distal facies of turbidites or in the pelitic intercalations within the turbidites. The relationship between the occurrence of non-contaminated *vs.* contaminated bentonites and the type of host strata was described from the Campos Basin (offshore Brazil) by Caddah *et al.* (1998). In that area, the contaminated bentonites are associated with turbidites, whereas non-contaminated ones occur in pelitic sequences. It follows that within turbidite sequences, the bentonites occurring in pelitic intercalations or in the more distal turbidite facies are potentially more suitable for the K-Ar dating of diagenesis than those occurring in the more proximal turbidite facies.

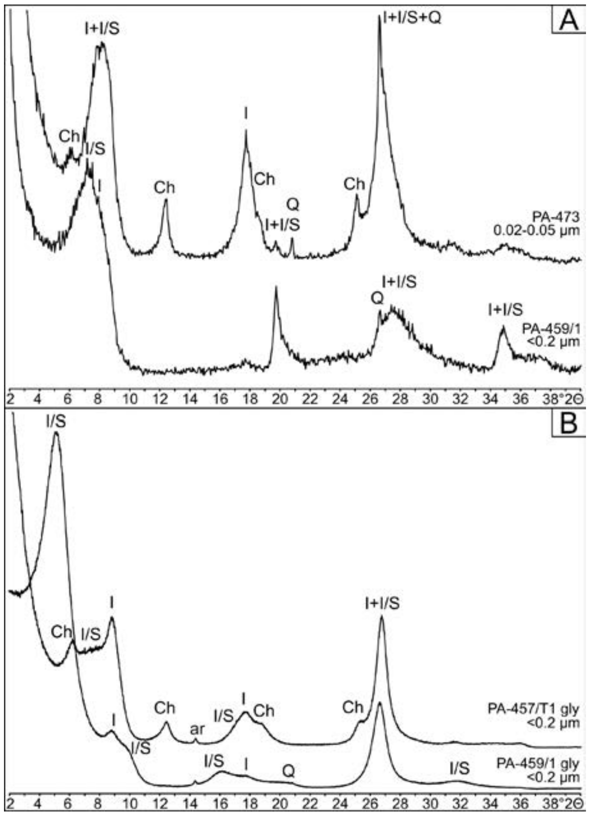

Fig. 4. Representative XRD patterns of clay fraction of bentonites (Q – quartz, Ch – chlorite, I-S – illite-smectite, I – illite, ar – oxalate crystallized during the separation of clay fraction). **A.** XRD patterns of powdered and un-oriented clay fraction of bentonites from sites M4 (PA-459/1) and S6 (PA-473). **B.** XRD patterns of oriented ethylene-glycol-saturated <0.2 μm clay fractions of bentonites from sites M1 (PA-457/T1) and M4 (PA-459/1).

Numerous bentonite layers occur within the Oligocene flysch sequence, filling the forearc Podhale Flysch Basin (Fig. 1). The bentonites mostly are not contaminated by non-authigenic minerals (Środoń *et al.*, 2006b). Unfortunately, the detailed sedimentological setting of the bentonites is not known. The authors believe that difference in the degree of contamination between the WOC bentonites and the Podhale Flysch Basin bentonites results from different tectonic processes, active in the respective regions during sedimentation of the bentonite-bearing strata. This differentiation is, in turn, due to the very different tectonic settings of the two regions.

During the Eocene–Oligocene, the WOC were an active accretionary wedge, the formation of which involved a major increase in the rate of deposition (Poprawa *et al.*, 2006) and the onset of synsedimentary folding (Świerczewska and Tokarski, 1998). This folding as well as the coeval and subsequent thrusting resulted in the formation of the WOC thrust-and-fold belt (Fig. 1C). In contrast, during Oligocene times, the Podhale Flysch Basin was a fore-arc basin, in which sedimentation was controlled largely by sea-level changes (Starek *et al.*, 2013). The Oligocene flysch sequence filling the basin was deformed into open folds. The folding largely post-dated the flysch deposition (Ludwiniak, 2010 and references therein). It follows that the degree of contamination of bentonites by non-diagenetic minerals may depend also on the tectonic setting of the bentonite-bearing basins.

The authors observed numerous hitherto unreported bentonite layers, up to over 1 m thick. This presents a significant addition to the inventory of bentonites within Polish segment of the WOC. The most important is the discovery of several bentonite layers in the easternmost part of the Silesian Nappe (Fig. 2, Tab. 1), in which up to now only a single occurrence of these rocks was reported.

CONCLUSIONS

The K-Ar diagenesis dating of WOC bentonites should be restricted to the bentonites affected by palaeotemperatures of more than 100°C.

Bentonites in the Eocene–Oligocene turbidite sequences in the WOC accretionary wedge mostly are contaminated by non-diagenetic K-bearing minerals and therefore are largely unsuitable for the K-Ar dating of diagenesis. The K-Ar dating of bentonites in the turbidite sequences of accretionary wedges should be largely restricted to the extreme distal facies of turbidites or to pelitic intercalations within the turbidites.

The degree of contamination of bentonites by non-diagenetic minerals may depend on the tectonic setting of the bentonite-bearing basins.

The discovery of several bentonite layers in a part of the Silesian Nappe, in which only a single occurrence of such rocks had been reported up to now, represents a significant addition to the inventory of bentonites within the Polish segment of the Western Outer Carpathians.

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