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K-Ar DATING OF AMPHIBOLES FROM ANDESITE OF COMPLEX DYKE IN DUBIE (SOUTHERN POLAND)

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Abstract: This study presents the results of radiometric K-Ar measurements on separated amphiboles from the andesite of the Dubie complex dyke. The data obtained cover the period of (291.3 ± 6.4) Ma, which corresponds to Carboniferous-Permian transition. The age is contemporaneous to the rhyodacitic and basaltoid volcanism of the Kraków region.

Keywords: K-Ar dating, amphiboles, andesite, Permian, Carboniferous

1. INTRODUCTION

At the north-eastern border of the Upper Silesian Coal Basin, magmatic rocks occur along Myszków-Zawiercie-Kraków zone which is a part of the major, transcontinental, Hamburg-Kraków fault zone (HKFZ) (Żaba, 2000; **Fig. 1**). In this zone, late Palaeozoic magmatism (Jarmołowicz-Szulc, 1984 and 1985; Harańczyk, 1989; Podemski, 2001) comprises large granodiorite intrusions, rhyodacite laccoliths and domes, basaltoid lava extrusions with associated pyroclastic rocks, and small dykes and sills of diabases, andesites, dacites, rhyodacites, rhyolites and minor lamprophyres (Muszyński, 1995 and works cited therein; Czerny and Muszyński, 1997; Lewandowska and Rospondek, 2003).

Among the minor intrusions an example of intermediate rocks is present: an andesite from a complex dyke outcropping in the Dubie quarry located near Krzeszowice, about 20 km north-west of Kraków (**Fig. 1**). The andesitic dyke cuts through Devonian (Givetian) dolomites of the Dębnik brachyanticline. The brachyanticline owes its form to the rhyodacite laccolith, which uplifted and metamorphosed Devonian and early Carboniferous carbonate rocks (Bogacz, 1980; Lewandowska, 1991).

The dyke is up to 3 m wide and can be traced along a distance of about 500 m in the Dubie quarry (**Fig. 2**). Clear zonation, perpendicular to its walls, suggests that the magma passage opened several times. The black andesite builds the central part, while grey-green dacite forms the outer part (Harańczyk and Wala, 1989; Muszyński and Pieczka, 1992). Several centimetres of argilitic rocks are encountered at the interface with the wall rocks, presumably being products of hydrothermal alternation of the volcanic rock (Harańczyk and Chłopecka, 1989). The black andesite is thought to mark the initial stage of the passage opening (Harańczyk, 1982; Harańczyk and Wala, 1989). This variety of andesite reaches about 0.5 m of width.

Geochemically, rocks of the dyke were classified as calc-alkaline andesites and dacites (Muszyński and Pieczka, 1992; Muszyński, 1995, Czerny and Muszyński, 1997) using the classification of Peccarillo and Taylor (1976).

The early Permian age of volcanism of the Kraków area was determined based on the superposition of the volcanic rocks in relation to the palaeontologically dated Karniowice travertine (Lipiarski, 1970). A few geochronological studies of felsic volcanic and plutonic rocks of the region point to the transition between Carboniferous and Permian (Skowroński, 1974; Harańczyk, 1989). In addition, the paleomagnetic data on rhyodacites from Zalas confirm the early Permian age of the felsic rocks (Nawrocki *et al.*, 2005). However, the age of intermediate volcanics has not been determined so far.

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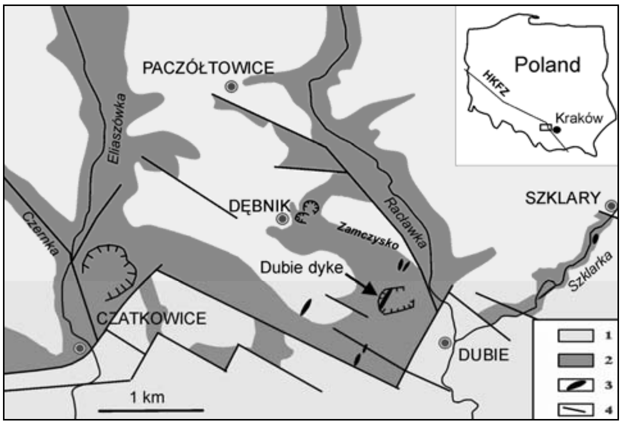

Fig. 1. *Simplified geological map of the area of investigations: 1. Mesozoic sediments; 2. Carboniferous and Devonian limestones and dolomites; 3. Late Paleozoic volcanic rocks; 4. Faults (according to Kozłowski, 1955 and Łaptaś, 1982); HKFZ Hamburg-Kraków fault zone.*

Fig. 2. *The andesitic dyke in Dubie quarry in 2004 (exploitation level is 340 m above sea level).*

This study presents the first dating of andesites of the Kraków region and aims to shed light on chronological constrains of volcanic events.

2. METHODOLOGY

Representative samples were collected from different zones of the dyke in Dubie quarry. For detailed studies the samples from the inner andesitic part of a dyke were selected. Unfortunately, the exploitation progress in the Dubie quarry led to the consumption of a huge part of a dyke in 2005 year, most of contemporary collected samples carry the signs of alteration. Therefore for K-Ar studies the unique sample DW38, from the Jagiellonian University museum collection was chosen. This sample was collected in 70's by A. Wala.

A Nikon Eclipse E600 POL polarising microscope quipped with cathodoluminescence and LUCIA Measurement software for image analyses were used for petrographical observations. Mineralogical investigations were based on the X-ray diffraction analysis using an APD Philips diffractometer with CuK_{α} radiation over an angular range of 4-64°2Θ with X'Pert Philips analytical software. A field-emission scanning electron microscope HITACHI SEM S-4700 coupled with an energy depressive spectrometer (EDS) with a NORAN VANTAGE analytical system and a back-scattered electron image detector were used for chemical composition analyses of separated crystals.

Amphiboles separation.

The sample of black andesite was crushed by hammering, pulverized in a mortar and sieved. Clay minerals were removed by multiple water washing; this procedure was followed by carbonate removal in acetate acetic buffer. Amphiboles were separated from the fraction below 500 µm. The residual heavy minerals were separated in heavy liquid (ρ=3g/cm^3). The light fraction consisted mainly of feldspars and quartz. The heavy fraction was additionally subdivided into three groups using a neodymium magnet. The first group of ferromagnetic minerals was attracted by the magnet from a distance of about 0.8 mm (these were mainly iron-titanium oxides). The second group was attracted by the magnet in the direct contact and these were mainly amphiboles subsequently used in the age determination. The remnant third group of grains consisted of agglomerates of amphiboles, Fe-Ti oxides and plagioclases.

K-Ar age determination.

The monomineral amphibole sample was split into two aliquots: a 100 mg one for potassium determination and 150 mg one for argon analysis. The 100 mg sample was diluted in a mixture of HF and H_2SO_4. The solution was evaporated in a steam bath and once more diluted in HCl (1:1). The potassium content was determined with the use of a spectrophotometer Sherwood 420. During the measurements international standard „Cordoba-muscovite" was used to test the procedure. The analytical error was 0.02 % K_2O.

The isotopic composition of Ar was determined by the extraction method (details in Bonhomme *et al.*, 1975) using an MS20 mass spectrometer. The sample was fused in a Ti-Ta crucible by resistance heating (Durakiewicz, 1995) and the released gas was purified on Ti and Zr-Al getters (**Fig. 3**). The analytical precision was periodically controlled by the measurements of the radiogenic ^{40}Ar content of the international standard GLO. The mean content of six determinations made previously and during the analysis was (24.99 ± 0.48 (2δ)) x 10^{-6}cm^3/g STP being well in the range of the accepted values: (24.85 ± 0.50) (Odin *et al.*, 1982). The overall precision of the K-Ar age determinations which were calculated using the decay constant recommended by Steiger and Jaeger (1977) was better than ±2 %.

3. RESULTS

The Dubie andesite is a porphyritic rock with light plagioclase and black amphibole phenocrysts set in aphanitic black groundmass. The phenocrysts assemblage, apart of plagioclase and amphibole crystals consists of

Fig. 3. *The mass spectrometer and purification line for Ar* (radiogenic Ar) measurements.*

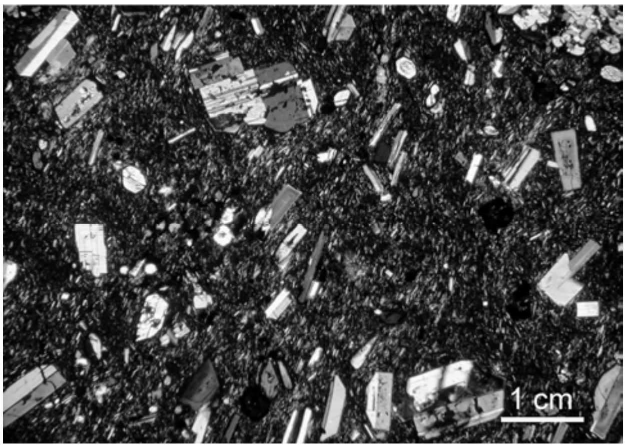

Fig. 4. *Dubie andesite with zoned, twinned plagioclase phenocrysts and smaller amphibole phenocrysts set in a fine crystalline plagioclase matrix (petrographic microscope, crossed polars).*

rare biotite flakes. The idiomorphic and hypidiomorphic plagioclase phenocrysts are abundant and have about 5-8 mm in size, sporadically reaching 2 cm. In plagioclases concentric reverse zoning (labrador - An 50 to 70 %) and polysynthetic twinning are common (**Fig. 4**). Amphibole phenocrysts are represented by idiomorphic prisms up to 0.5 mm in size, they show olive to brown pleochroism and are surrounded by fine opacite reaction rims (**Figs 5** and **6**). The idiomorphic form of amphibole crystals and lack of other than Fe-Ti oxides inclusions indicate that amphiboles were among the first crystallising phases in the Dubie andesite. The rare biotite flakes reach 5 mm in size. The aphanitic matrix is composed of euhedral plagioclase laths (andesine An 35 – 50 %), intergrown in an irregular fashion to form felty texture and volcanic glass altered to clay minerals. Accessory minerals assemblage consists of opaque minerals, represented mainly by iron-titanium oxides and apatite needles.

The amphibole microanalyses recalculations (mean of six) give its formulae as $(Na_{0.44}K_{0.09})Ca_{1.91}(Mg_{2.55}Fe_{2.09}Al_{0.21}Ti_{0.25})[Si_{6.69}Al_{1.31}]O_{22}(OH)_2$. Such a composition straddles the borders among magnesio-hornblende, tschermakite and magnesio-alumino sadanagaite fields, on the diagram showing the compositional variations of the calcium amphiboles (Hawthorne and Oberti, 2006). This identification is in agreement with the X-ray diffraction pattern (**Table 1**), where the amphibole

Table 1. *XRD powder data for DW38 AM sample (separated amphibole fraction) compared to JCPD data.*

Saple DW38 AM				
2Theta	d (Å)	intensity	Magnesio-Hornblende JCPDS21-0149	Ferro-Tschermakite JCPDS43-0665
63.09	1.472	3		1.48
61.62	1.503	8		1.50
61.36	1.509	6		1.51
60.84	1.521	5		1.525
60.08	1.538	5		1.536
59.25	1.558	4		1.555
58.05	1.587	10	1.592	1.581
56.66	1.623	5	1.625	1.622
56.02	1.640	4		1.637
55.49	1.654	14	1.656	1.649
54.46	1.683	2		1.683
54.08	1.694	4		1.695
53.21	1.719	5		1.700
52.13	1.752	1		1.752
50.15	1.817	5		1.811
48.67	1.869	5		1.868
48.01	1.893	7	1.900	1.880
45.98	1.972	2		2.002
44.77	2.022	13	2.025	2.025
44.09	2.051	6	2.054	2.051
41.55	2.171	16	2.172	2.179
40.30	2.235	2		2.227
39.31	2.289	5		2.292
38.59	2.330	11	2.337	2.322
38.32	2.346	19	2.351	2.342
37.59	2.390	7	2.388	2.381
35.07	2.555	16	2.558	2.557
34.39	2.605	17	2.606	2.604
32.90	2.720	39	2.720	2.715
32.59	2.744	27	2.750	2.738
31.81	2.810	13	2.818	2.800
30.29	2.948	17	2.953	2.941
28.5	3.13	100	3.14	3.11
27.6	3.23	5		3.27
27.1	3.29	31	3.29	3.27
26.2	3.40	19	3.40	3.39
23.7	3.75	3	?	?
22.7	3.90	4		3.90
21.8	4.07	5	?	?
21.0	4.22	4	4.23	?
19.5	4.55	8	4.55	4.53
18.6	4.77	2		4.74
18.0	4.93	3		4.92
17.3	5.12	2		5.09
10.4	8.52	60	8.51	8.40
9.6	9.16	6	9.15	9.05

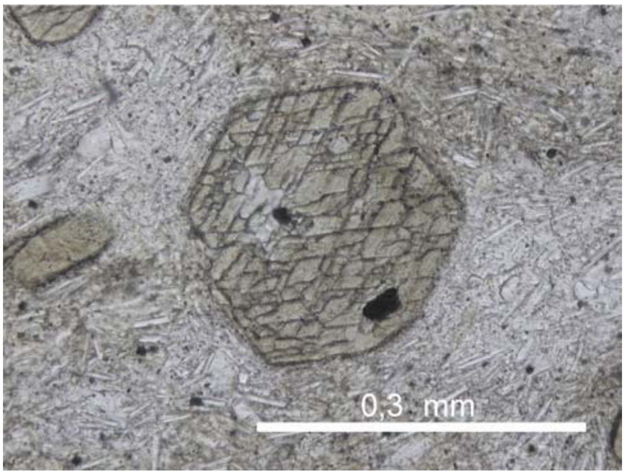

Fig. 5. *Amphibole phenocryst with thin opacite rim from DW38 sample (plane polarised light).*

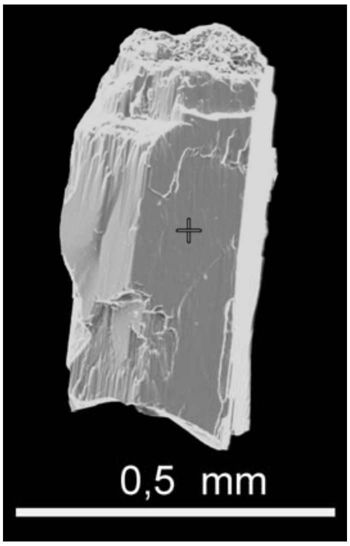

Fig. 6. *SEM image of separated amphibole crystal.*

main reflexes are like those of the reference magnesio-hornblende (JCPDS21-0149) and slightly diverge from those of ferro-tschermakite (JCPDS43-0665). This determination is also consistent with the previous identification of amphibole as magnesio-hornblende (Muszyński and Pieczka, 1992).

Although potassium content in amphibole is minor, ca. 0.44 wt.% K_2O (**Table 2**), its presence allowed the K-Ar age determination. The K_2O content 0.44 wt. % and $^{40}Ar^*$ content 50.1 % correspond to the closing age of amphiboles (291.3 ± 6.4) Ma (**Table 2**).

4. DISCUSSION

The K-Ar amphibole age of (291.3 ± 6.4) Ma of the Dubie andesite, obtained in this study indicates that it is contemporaneous to the other volcanic activities in the Kraków region. Dating of the felsic volcanism of the nearby Myszków area, based on K-Ar biotite and the whole rock analyses (Jarmołowicz-Szulc, 1984 and 1985) gave (301 ± 29) Ma. In the range of the analytical error, it fits the Zalas rhyodacite age of 295 Ma (tracks in biotite) (Skowroński, 1974). The singular Ar-Ar date of basaltic rocks from the region was 305 Ma and concerned the biotite age from the Myszków diabase (Podemski, 2001). Although limited precision of the K-Ar method does not allow to assign the time of andesite formation in chronological order with respect to other rhyodacitoid or basaltoid volcanism of the region, the field observations show that the rhyodacitic laccolith, which formed the Dębnik brachyanticline, had intruded and solidified before the Dubie andesitic dyke formation. This was deduced from the composition of the volcanic breccia uplifted by andesitic magma, which contained rhyodacite fragments in the grain framework (Harańczyk, 1982 and 1989; Harańczyk and Wala, 1989).

Table 2. *The results of K-Ar measurements of amphibole from andesite from Dubie.*

Sample	Mineral	K_2O (%)	$^{40}Ar^*$ (%)	$^{40}Ar^*$ (pmol/g)	Age (Ma)	Error (Ma)
DW38AM	Amphibole	0.44	50.1	200.2	291.3	6.4

$^{40}Ar^*$- radiogenic ^{40}Ar

The almost contemporaneous time of andesitic, rhyodacitic and basaltoid volcanism in the Kraków region is concordant with the observations of contemporary volcanic environments, which show that one volcano can produce magmas from basic to acid compositions within short periods (e.g. Sigurdsson and Sparks, 1981).

The volcanic rocks of the Kraków region carry signs of later, post magmatic alteration processes like K-metasomatosis and feldspatization described from the Zalas rhyodacite (Słaby, 2000; Nawrocki *et al.*, 2005). The mineralogical evidences show that the Dubie complex dyke formation was followed by hydrothermal activity, which resulted in alteration of the dyke rocks and clay minerals formation (Harańczyk and Chłopecka, 1989). Planned K-Ar age measurements on illites from the outer zones of the dyke will probably clarify the timing of postmagmatic processes.

5. CONCLUSION

The K-Ar dating of amphiboles separated from the andesite from the Dubie complex dyke (291.3 ± 6.4) Ma corresponds to Carboniferous-Permian transition. It is contemporaneous to the other Variscan volcanic activity of the Kraków region.

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REFERENCES

Bogacz K, 1980. Budowa geologiczna paleozoiku dębnickiego (Geological structure of Palaeozoic of Dębnik). *Rocznik Polskiego Towarzystwa Geologicznego* 50: 183-208 (in Polish).

Bonhomme MG, Thuizat R, Pinault Y, Clauer N, Wendling R. and Winkler R, 1975. Me´thode de datation potassium – argon. Appareillage et Technique (The potassium – argon dating method). *Notes technique de l'Institut de Ge´ologie, Universite´ Louis Pasteur, Strasbourg* 3: 53 pp.

Durakiewicz T, 1995. Innowacje w aparaturze do wydzielania i oczyszczania argonu (Innovations in the apparatus for argon separation and purifiction). *II Ogólnopolska Sesja Naukowa. Datowanie minerałów i skał*: 38-44 (in Polish).

Czerny J and Muszyński M, 1997. Co-magmatism of the Permian volcanities of the Krzeszowice Area in the light of petrochemical data. *Mineralogia Polonica* 28 (2): 3-25.

Harańczyk C, 1982. Magmatyzm okolic Dubia (The magmatism of the Dubie area). *Przewodnik LIV Zjazdu Polskiego Towarzystwa Geoleologicznego*: 124-127 (in Polish).

Harańczyk C, 1989. Rozwój wulkanizmu krakowskiego (The development of the Kraków area volcanism). *Przewodnik LX Zjazdu Polskiego Towarzystwa Geoleologicznego*: 51-57 (in Polish).

Harańczyk C and Chłopecka A, 1989. Przeobrażenia skał komina andezytowego w Dubiu (The alterations of andesitic chimney in Dubie). *Przegląd Geologiczny* 37: 332-334 (in Polish).

Harańczyk C and Wala A, 1989. Andezytowy komin wulkaniczny w Dubiu (The andesitic volcanic chimney in Dubie). *Przewodnik LX Zjazdu Polskiego Towarzystwa Geologicznego*: 67-71 (in Polish).

Hawthorne FC and Oberti R, 2006. On the classification of amphiboles. *The Canadian Mineralogist, Journal of the Mineralogical Association of Canada* 44: 1-21.

Jarmołowicz-Szulc K, 1984. Datowania metodą K-Ar skał NE obrzeżenie Górnośląskiego Zagłębia Węglowego (K-Ar dating of rocks of the NE edge of the Upper Silesian Coal Basin). *Kwartalnik Geologiczny* 28: 749-750 (in Polish).

Jarmołowicz-Szulc K, 1985. Badania geochronologiczne K- Ar skał magmowych północno-wschodniego obrzeżenia Górnośląskiego Zagłębia Węglowego (K-Ar geochronological studies of the northeastern edge of the Upper Silesian Coal Basin). *Kwartalnik Geologiczny* 29 (2): 343-354 (in Polish).

Kozłowski S, 1955. Intruzje porfirowe w grzbiecie Dębnickim (Porphyritic intrusions of the Dębnik Ridge). *Biuletyn Instytutu Geologicznego* 97: 39-86 (in Polish).

Lewandowska A, 1991. Minerals of the zone of altered Devonian dolomites from Dubie near Kraków (Southern Poland). *Mineralogia Polonica* 22 (2): 29-40.

Lewandowska A, and Rospondek M, 2003. Geochemistry of volcanics of the Zalas area near Kraków, South Poland. *Prace Specjalne Polskiego Towarzystwa Mineralogicznego* 23: 119-121.

Lipiarski I, 1970. The Carboniferous-Permian Boundary in the Eastern Part of the Kraków Silesian Coal Basin. *Biulletin da L'Academie Polonaise des Sciences* 28: 173-178.

Łaptaś A, 1982. Sedymentacja utworów węglanowych dewonu środkowego rejonu Dębnika (Sedimentation of the Middle Devonian carbonates of the Dębnik area). *Studia Geologica Polonica* 75: 59-100.

Muszyński M, 1995. Systematic position of igneous rocks from the northern margin of the Upper Silesian Coal Basin. *Mineralogia Polonica* 26 (1): 33-49.

Muszyński M and Pieczka A, 1992. Hornblende andesites and dacites from Dubie near Krzeszowice. *Mineralogia Polonica* 23 (1): 43-63 (in Polish).

Nawrocki J, Polechońska O, Lewandowska A and Werner T, 2005. On the palaeomagnetic age of the Zalas laccolith (Southern Poland). *Acta Geologica Polonica* 55 (3): 229-236.

Odin GS and 35 Collaborators, 1982. Interlaboratory Standards for Dating Purposes. In: Odin GS, ed., *Numerical Dating in Stratigraphy*. Wiley and Sons, Chichester: 123-149.

Peccarillo A and Taylor SR, 1976. Geochemistry of Eocene calc-alcaline volcanic rocks from the Kastamonu area, Northern Turkey. *Contributions to Mineralogy and Petrology* 58 (1): 63-81.

Podemski M, 2001. Palaeozoic Porphyry Molybdenium-Tungsten Deposit in the Myszków Area, Southern Poland. *Polish Geological Institute Special Papers*, Państwowy Instytut Geologiczny 6: 1-88.

Sigurdsson H and Sparks RSJ, 1981. Petrology of rhyolitic and mixed magma ejecta from 1875 eruption of Aksja, Iceland. *Journal of Petrology* 22: 41-84.

Skowroński A, 1974. Oznaczenie wieku bezwzględnego tzw. porfirów z Zalasu metodą śladów rozszczepienia jąder uranu (Track absolute age of so called Zalas porphyry). *Sprawozdania z Posiedzeń Komisji Nauk PAN Oddział w Krakowie* 17: 236-237 (in Polish).

Słaby E, 2000. Adularia and albite - hydrothermal feldspars from Zalas and Miękinia rocks. *Prace Specjalne Polskiego Towarzystwa Mineralogicznego* 17: 94-96.

Steiger RH and Jaeger E, 1977. Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth and Planetary Science Letters* 36: 259-262.

Żaba J, 2000. Tectono-magmatic activity of the Upper Silesia terrane and Malopolska terrane edge (Southern Poland). *Prace Specjalne Polskiego Towarzystwa Mineralogicznego* 17: 81-83.