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A rare mineral-bearing pegmatite from the Szklary serpentinite massif, the Fore-Sudetic Block, SW Poland

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Abstract In the Szklary serpentinite massif, besides serpentinites, amphibolites, rare rodingites and altered gabbros, rather common light-coloured aplites occur. Occurrences of pegmatites are very rare. A small fragment of a pegmatite, basically composed of feldspars, quartz, micas and tourmaline, is exposed only on Mt. Szklana. During detailed mineralogical investigations on it, numerous and sometimes rare or very rare minerals have been identified: chrysoberyl, spessartine, manganocolumbite and manganotantalite, stibiocolumbite, holtite, pyrochlore, beusite, paradocrasite and stibarsen, manganoan apatite and others, occurring in small or very small grains. The pegmatite from Szklary probably represents a product of the crystallization of silicic magma generated from the partial melting of older sediments during high-grade metamorphism. Its structural and textural development (graphic intergrowths), and to some extent its mineral composition make it comparable to some anatectic pegmatites of the gneissic block of the Góry Sowie Mts.

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INTRODUCTION

The Szklary serpentinite massif occurs within the Early Carboniferous Niemcza dislocation zone, adjacent to the Góry Sowie block, in the eastern part of the Fore-Sudetic block (Fig. 1). It consists of serpentinized harzburgites which are considered to be the lowest fragment of an ophiolite suite (*e.g.* Majerowicz & Pin, 1986; Gunia, 1996). In its metamorphic cover gneisses, amphibolites and mylonites dominate, with minor granitoids (Niśkiewicz, 1967), gabbros and rodingites (Heflik & Natkaniec-Nowak, 1986, 1989). In many places the serpentinites are cut by aplites but only rarely by pegmatites. A small fragment of a granitic pegmatite vein is exposed in the N part of Mt. Szklana in an open pit of the abandoned "Marta" mine of silicate nickel ores (Niśkiewicz, 1967). The pegmatite was described as a strongly weathered rock, impregnated with nickel hydrosilicates, and mainly consists of feldspars, quartz, muscovite and tourmaline, its components sometimes developed as crystals some centimetres across. In the last several years, some rare minerals have been described there (Pieczka & Marszałek, 1996; Pieczka *et al.*, 1997a). This paper summarizes the results of mineralogical investigations of the Szklary pegmatite vein.

METHODS

For the identification and characterization of minerals of the pegmatite from the Szklary serpentinite massif, the following methods were employed: chemical analyses (wet and microprobe), microscopic observations in transmitted light and using a JEOL 5200 scanning microscope with an EDS Link Exl. attachment, X-ray diffractometry, and infrared and Mössbauer spectroscopy. The microprobe determinations were carried out at the Institute of Non-Ferrous Metals in Gliwice, the Mössbauer spectroscopic analyses at the Institute of Nuclear Physics at Kraków-Bronowice, and the remainder at the Department of Mineralogy, Petrography and Geochemistry of the University of Mining and Metallurgy in Kraków.

The chemical compositions of some minerals from the pegmatite were determined using wet analyses: the weight method [SiO_2, $H_2O(-)$, $H_2O(+)$], EDTA complexometry (Al_2O_3, Fe_{total} as FeO, CaO, MgO), colorimetry (B_2O_3, F, TiO_2, higher amount of MnO), flame photometry (Na_2O, K_2O) and AAS (Li_2O, MnO, ZnO, also for CaO as the double check), while the true amounts of

FeO and Fe_2O_3 (in garnet and tourmaline) were from the results of Mössbauer spectroscopy. Minerals found in very fine grains, such as holtite, beusite and others, were chemically analysed with a JCXA-733 (JEOL) electron microprobe in the WDS or EDS mode. Microprobe mounts were ground, then polished and coated with graphite. As standards the following phases were used: wollastonite $CaSiO_3$ (Ca), periclase MgO (Mg), GaP (P), quartz SiO_2 (Si), InAs (As), ThO_2 (Th), PbF_2 (Pb), and metallic Fe, Mn, Ti, Al, Nb, Ta, Sb, Zr, Hf and U. The specimen current was 0.02 mA at 20 kV, the beam diameter 1–5 μm. The electron microprobe data were PAP-corrected.

X-ray powder patterns were recorded using a PHILIPS X'PERT diffractometer with a graphite monochromator, $CuK\alpha_1$ radiation (λ_1 = 1.58862 Å), in a range of 3–61°2θ at a scanning speed of 0.02°(2θ)/1s. Quartz served as the internal standard. Mineral phases were identified using computerized JCPDS files, while unit-cell parameters were calculated using the PDS computer program.

IR spectra were recorded with a BIO-RAD model FTS-165 spectrophotometer; samples were prepared in the form of discs with KBr. In the recording of Mössbauer spectra $^{57}Co(Rh)$ was used as a source of γ-radiation. An absorbent was made in the form of a disc with an iron concentration of about 5 mg/cm^2. The resolution of the spectra was done with a computer program that fitted Lorentz curves to the experimental data using the least squares method.

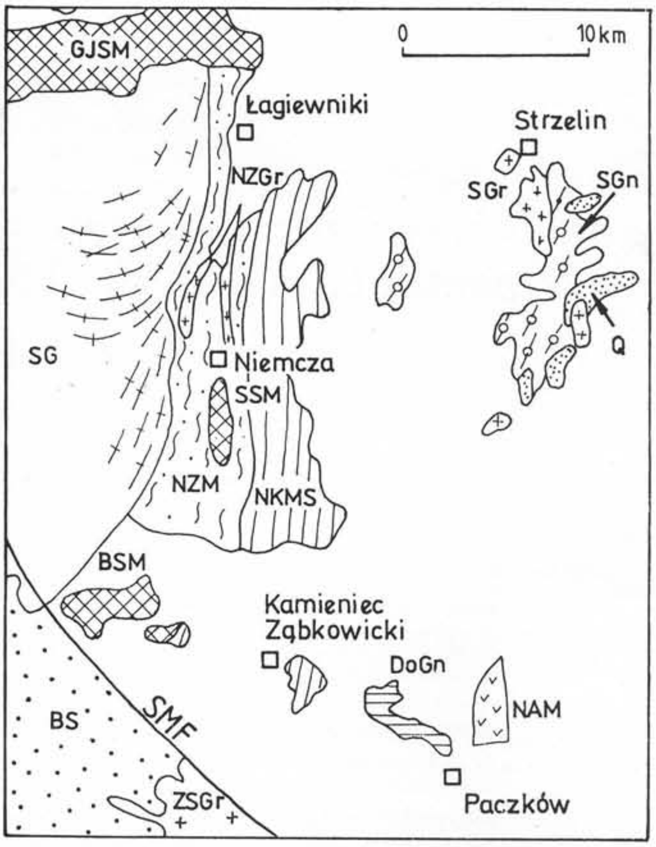


Fig. 1. A simplified geological map of the eastern Fore-Sudetic block with the Niemcza dislocation zone area (Mazur *et al.*, 1997). SSM – the Szklary serpentinite massif; NZGr – the Niemcza zone granitoids: SGn – the Góry Sowie gneisses; GJSM – the Gogołów-Jordanów serpentinite massif, BSM – the Braszowice serpentinite massif; NKMS – the Niemcza-Kamieniec Ząbkowicki mica schists; DoGn – the Doboszowice gneisses; NAM – the Niedźwiedź amphibolite massif; NZM – the Niemcza zone mylonites; SGr – the Strzelin granites; SGn – the Strzelin gneisses; Q – quartzites; ZSGr – the Złoty Stok granitoids, BS – the Bardo structure; SMF – the Sudetic marginal fault.

MODE OF OCCURRENCE

A small fragment of the pegmatite could be seen some years ago in the SW wall of the mentioned open pit on Mt. Szklana, where the vein was hosted by serpentinite. The site, presently covered with serpentinite rubble, is no longer accessible. However, at a distance of approximately 30 m, on the opposite side of the pit, there is a small bench in which another fragment of the pegmatite some 4 m long and almost unaltered is currently exposed; this part of the pegmatite is emplaced in a light aplitic rock. Although the vein between these two sites was mostly mined out during the exploitation of nickel ore, field observations indicate that the pegmatite is less than 1 m thick and strikes NNE–SSW. The contact between the serpentinite and the pegmatite is locally marked with a thin chlorite-vermiculite layer that was more abundant in the non-existing part of the exposure.

THE STRUCTURE OF THE PEGMATITE VEIN

The wall zone

The pegmatite is a poorly zoned, symmetrical vein. The border zone consists of saccharoidal aplite with small flakes of brownish-gold altered biotite.

The wall zone is very thin, only a few centimetres across. In its outermost part, quartz (sometimes red-brownish, coloured by small amounts of Fe-Mn hydroxyl-oxides present in interstices among its grains) forms intergrowths with white plagioclase, and is accompanied by small laths of altered biotite. The primary biotite is altered, basically into Fe-clinochlore with a smaller or larger admixture of vermiculite, and talc. The chlorites and talc may contain some amounts of nickel approximating, respectively, nimite $(Ni,Mg,Fe^{2+})_5Al[(Si_3Al)O_{10}|(OH)_8]$ and willemseite $(Mg,Ni)_3[Si_4O_{10}|(OH)_2]$. Within such aggregates it is possible to observe very rare light blue, acicular crystals, identified in X-ray patterns as magnesioriebeckite, and equally fine crystals of white to light sky-blue apatite, cordierite or titanite. Montmorillonite

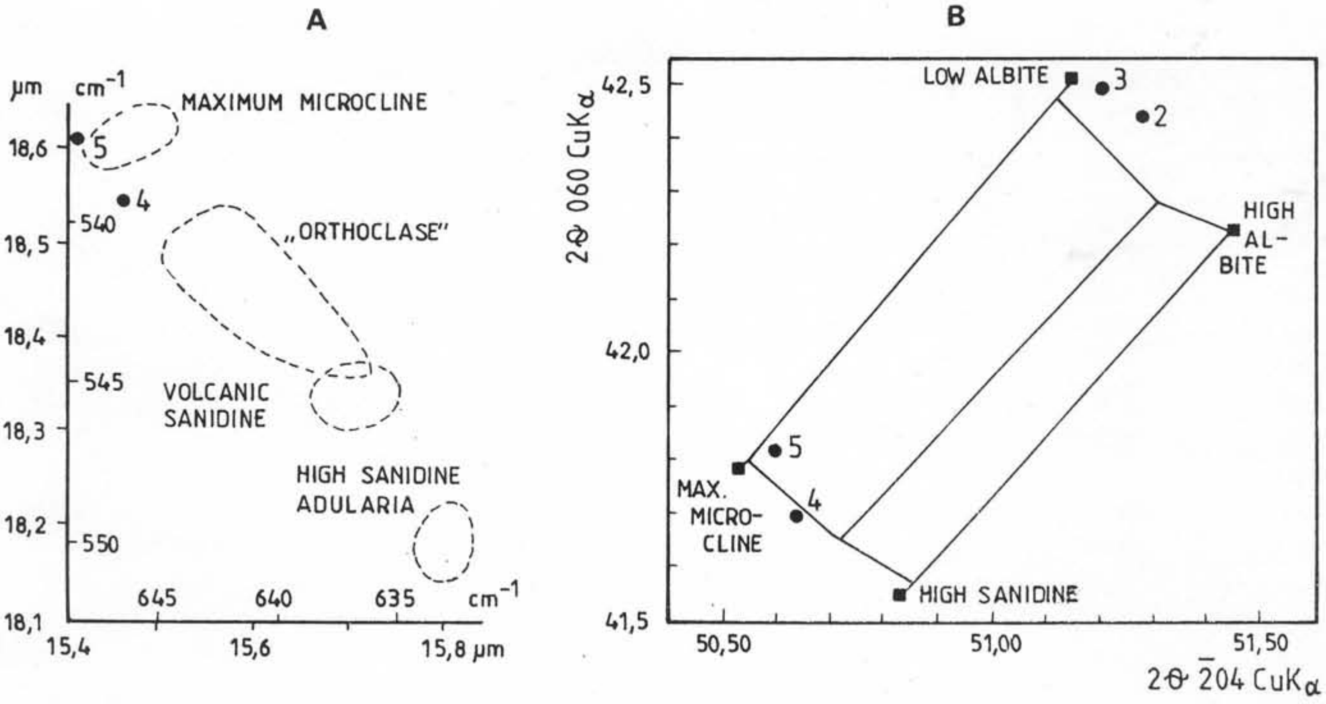


Fig. 2. A characteristic of the feldspar samples: A – the positions of the feldspars from the Szklary pegmatite on the plot of Černý & Chapman (1986); B – the positions of these feldspars on the plot of Wright (1968).

was sporadically noted as a secondary clay mineral. Towards the middle of the vein, the wall zone of the pegmatite consists of graphic intergrowths of white plagioclase $Ab_{92}An_{08}$ (albite) and progressively increasing amounts of orthoclase- and microcline-perthite with quartz, and it grades into a more coarse-crystalline intermediate zone.

The intermediate zone

The intermediate zone is built of graphic, coarse-grained intergrowths of brown-grey to grey K-feldspars (microcline, microcline- and orthoclase-perthites) with quartz, while white, in places translucent, plagioclase $Ab_{86}An_{14}$ (oligoclase) is rare. The triclinity Δ of the K-feldspars (Goldsmith & Laves, 1954) is 81% for dark-grey and 94% for grey, brownish-tinted varieties. On Černý & Chapman's (1986) plot, which characterizes K-feldspars on the positions of selected IR absorption maxima (Fig. 2a), the first of these feldspars is positioned between the fields of *orthoclase* and *microcline max.*, the other in the field of *microcline*. In Wright's (1968) diagram, the white albite characteristic of the wall zone and dark grey K-feldspars are situated approximately on one line between *albite-orthoclase* and *low albite-microcline max.*, while the slightly transparent oligoclase and brown-grey K-feldspars of the intermediate zone correspond to *low albite* and *microcline max.* (Fig. 2b). The content of $K[AlSi_3O_8]$ in the structure of the plagioclase is 0–1%. All these results indicate a highly ordered distribution of silicon and aluminium in the structures of the K-feldspars. In the chemical composition of the dark grey orthoclase-microcline and white albite from the wall zone, and the outer part of the intermediate zone, elevated amounts of MgO, Fe_2O_3 and H_2O_{total} are conspicuous (Table 1); they can show significant admixtures of unidentified Mg-Fe silicates. Considering only these two elements, the feldspars from the inner parts of the vein (slightly transparent oligoclase and brownish-grey microcline) are much purer. The presence of phosphorus noted in all the feldspars is a result of limited $2\ Si^{4+} \Leftrightarrow Al^{3+} + P^{5+}$ substitution, characteristic of rare-element granitic pegmatites (London *et al.*, 1990). The amounts of Na_2O observed in the K-feldspars correspond not only with sodium substitution for potassium, but also with commonly observed perthites. The perthites are of dual genesis; besides exsolution perthites, there are equally common metasomatic ones. The size of the perthites is variable, but they can quite often be observed in hand specimens. No exsolutions of K-feldspar in albites have been observed. The Ba, Sr, Rb and Cs contents in the feldspars have not been determined, but X-ray analyses indicate a possible concentration of barium in late K-feldspars (barium orthoclase). The Li contents are low, usually from several to less than twenty ppm, and are highest in the brownish grey microcline.

In the outer part of the intermediate zone widespread are small accumulations of gold-brownish hydrobiotite with a small admixture of clinochlore, grey-green to gold-brownish in handspecimens, in which the flakes even reach up to 5 cm across. The biotite is significantly depleted in alkalis, particularly in K_2O, at the same time having elevated water contents [$H_2O(-)$ and $H_2O(+)$]. The amounts of Fe and Mg are comparable (Table 1). Present much less frequently than the mica aggregates are: grass-green clinochlore, even occurring as 1–2 cm plates, and bush-like accumulations of small tourmaline crystals, de-

Table 1

The chemical compositions (wt %) of the main minerals from the Szklary pegmatite

Component	Albite	Oligoclase	K-feldspar		Hydrobiotite	Muscovite	Tourmaline		Spesartine
	white	white translucent	dark-grey	brownish grey			wall zone	intermediate zone	
Na_2O	9.03	9.48	1.97	2.32	0.04	0.55	1.58	1.89	0.11
K_2O	0.55	0.81	12.27	11.17	4.55	9.60	0.17	0.25	0.12
CaO	1.70	3.05	0.13	1.53	0.45	0.05	0.14	0.26	1.12
MgO	0.85	0.28	1.63	0.76	14.82	1.61	6.46	3.89	0.18
FeO							4.87	6.76	6.62
Fe_2O_3	0.30	0.29	0.58	0.40	14.42	3.97	1.90	2.71	0.15
MnO	0.00	0.00	0.00	0.00	0.84	<0.01	0.19	0.57	34.15
TiO_2	<0.01	<0.01	<0.01	<0.01	1.02	0.31	0.26	0.22	0.17
ZnO	<0.001	0.001	0.002	0.001	0.04	<0.01	0.057	0.066	0.006
LiO_2	<0.001	0.001	<0.001	0.002	0.05	0.016	0.007	<0.001	0.018
Al_2O_3	20.97	20.71	18.52	18.87	18.95	32.45	33.44	33.71	20.69
B_2O_3							10.62	10.50	
SiO_2	65.68	65.17	63.19	64.77	34.15	45.44	36.56	35.95	36.38
P_2O_5	0.19	0.08	0.37	0.28	<0.01	0.035			0.26
$H_2O(-)$	0.15	0.04	0.28	0.01	1.12	0.76	0.21	0.13	<0.01
$H_2O(+)$	0.40	0.24	0.91	0.19	9.79	5.40	3.30	2.80	<0.01
F						0.04	0.17	0.15	
Total-O=F_2	99.82	100.15	99.85	100.30	100.24	100.23 0.02 100.21	99.93 0.07 99.86	99.76 0.06 99.70	99.97

veloped in plagioclases or biotites.

Muscovite (*$2M_1$* polytype) is a characteristic and rather common component in the intermediate zone, where it forms local accumulations, sometimes of larger crystals, reaching sizes of up to 5 cm. It is usually silvery, sometimes with a gold-yellow tint; both colour types do not differ in their chemical compositions (Table 1). This mineral contains only trace amounts of lithium (less than 0.01 atoms per formula unit, *apfu*), and the observed deficit of alkali ions may be partly supplemented by H_3O^+. Within the muscovite aggregates, it is possible to find single flakes of dark green hydrobiotite.

Tourmaline is equally common in the intermediate zone. It occurs as shining black crystals, well developed and usually idiomorphic, forming prisms of varying size, up to several centimetres long and 1–2 cm thick. In loose pegmatite rubble, the tourmaline crystals are usually fragmented. The tourmalines often contain inclusions of quartz, feldspars, zircon, apatite, or rare opaque minerals, and display distinct pleochroism, ranging from green-grey and bluish (o) to colourless (e) in the crystals from the wall zone and the outermost part of the intermediate zone, and from blue-grey (o) to colourless (e) in those from the more central part of the intermediate zone. Many crystals have a zonal structure, showing variation in the intensity of their pleochroism. The change of shade of the pleochroic colours results from different Fe^{2+}, Fe^{3+} and Ti^{4+} contents (Table 1). The refractive indices are: n_o = 1.667–1.671, n_e = 1.690–1.695, and birefringence Δ is 0.028–0.032. In the wall zone, the tourmalines sometimes co-occur with biotite in the form of thin aggregates, resulting from the incomplete boron metasomatosis of the mica. The chemical composition of the tourmaline varies: magnesium increases in its crystals towards the wall zone of the pegmatite while aluminium and total iron decrease, probably as an effect of the contamination of the silicic pegmatite medium by the surrounding ultrabasic rocks (Table 1). The formula unit calculated on the basis of 31 (O,OH,F) ions for the crystals from the outer part of the intermediate zone (tourmaline collected from the previously accessible pegmatite vein within the serpentinites) is: $(Na_{0.502}K_{0.035}Ca_{0.025}\square_{0.438})(Mg_{1.577}Fe^{2+}{}_{0.667}Fe^{3+}{}_{0.234}Mn_{0.026}Ti_{0.032}Zn_{0.007}Li_{0.005}Al_{0.456})Al_{6.000}B_{3.003}Si_{5.989}O_{27}(OH_{3.606}O_{0.306}F_{0.088})$ and the unit-cell parameters are: a = 15.936(3) Å and c = 7.183(2) Å. The tourmaline crystals from the currently observable, central part of the intermediate zone have the composition: $(Na_{0.616}K_{0.053}Ca_{0.047}\square_{0.284})(Mg_{0.968}Fe^{2+}{}_{0.944}Fe^{3+}{}_{0.341}Mn_{0.081}Ti_{0.008}Zn_{0.007}Li_{0.001}Al_{0.634})Al_{6.000}B_{2.998}Si_{6.003}(OH_{3.116}O_{0.805}F_{0.079})$ and the unit-cell parameters: a = 15.944(3) Å and c = 7.170(2) Å. Both types of tourmaline represent Fe-Al dravites, and their differences are associated with diversified Y cation population.

In the feldspar-quartz-muscovite mass of the intermediate zone, numerous interesting minerals can be sporadically found: spessartine, chrysoberyl, manganotantalite, manganocolumbite and stibiocolumbite, zircon, uraninite, pyrochlore, holtite, beusite, manganoan apatite, Mn-oxides (todorokite, romanechite, hollandite), and also probably paradocrasite and stibarsen.

The quartz core is not observable in the exposed fragment of the pegmatite; it is possible it did not develop at all.

THE RARE MINERALS OF THE PEGMATITE

Of the rare minerals, only spessartine and chryzoberyl form relatively large crystals some millimetres in size, to a maximum of 1 cm across.

The grains of spessartine are mostly anhedral, but dodecahedral and trapezohedral faces may also be observed. Spessartine is light, usually orange-yellowish to orange-reddish, sometimes its grains are covered by brownish manganese hydroxyl-oxides. Its unit-cell parameter is 11.6033–11.6067 Å, only slightly lower than the value of 11.615–11.617 Å characteristic for the spessartine end-member. The crystals of spessartine contain numerous inclusions of quartz and sericite, less frequent manganocolumbite, and in grains which neighbour manganoan apatite, inclusions of this mineral. The chemical composition of spessartine is presented in Table 1. The formula unit calculated on the basis of 12 oxygens is: $(Mn_{2.37}Fe^{2+}{}_{0.45}Ca_{0.10}Mg_{0.02})Al_{2.00}[(Si_{2.98}Fe^{3+}{}_{0.01}Ti_{0.01})O_{12}]$ which corresponds to $Sp_{81}Alm_{15}Gros_3Py_1$ (alkalis and P_2O_5, most probably attributable to traces of other mineral phases, have been omitted from the formula).

Very rare chrysoberyl ($Al_2[BeO_4]$) occurs mostly in muscovite aggregates as idiomorphic, coarse-tabular, orthorhombic crystals, displaying bipiramidal {111} as well as pinacoidal {100} and {010} faces, sometimes in the form of characteristic double twins. The mineral is transparent or at least translucent, with a greenish or yellow-green colour. Its unit-cell parameters are: a = 5.480 Å, b = 9.415 Å, c = 4.429 Å.

Zircon occurs as single crystals, or parallel or radial aggregates. Its grains are most often enclosed in quartz or feldspar, and also within tourmaline. In the latter case, zircon affects the optical properties of the tourmaline and distinct pleochroic halos appear around its grains. The crystals of zircon display characteristic prismatic habit with elongation from 5:1 to more than 10:1 and rather weakly developed pyramidal terminations, straw grey colour and strong vitreous lustre. The largest grains are up to 1–2 mm long. The microprobe analyses (Table 2) showed elevated amounts of hafnium, uranium and thorium, and the mean chemical composition of the zircon is $(Zr_{0.95}Hf_{0.03}U_{0.02}Th_{0.001})[SiO_4]$. It is possible to find rare zircons with higher amounts of hafnium, even about 0.10 *apfu*. In the zircon crystals, there are local microzones rich in fine (up to 3 μm) inclusions of uraninite, and slightly longer (up to 5 μm) inclusions of probable paradocrasite $Sb_2(Sb,As)_2$ and stibarsen SbAs (or other antimony and arsenic oxides). In the case of uraninite, the lead content (Table 2) is typical for this mineral. The antimony-arsenic inclusions (Table 2) were tentatively identified from their stoichiometric ratios, differing only slightly from the theoretical values.

Manganocolumbites-manganotantalites $(Mn,Fe)(Nb,Ta)_2O_6$ are the most common Nb-Ta minerals and often occur in quartz grains neighbouring spessartine, less frequently in spessartine itself, feldspars or beusite. The grains are very fragile, thin and lath-like, with orthorhombic symmetry, characterized by steel-black colour and metallic lustre. They most often reach 1 mm in length, although some specimens up to 3–4 mm long and 1 mm wide have also been noted. Microprobe analysis results for over 20 crystals of manganocolumbite- manganotantalite were quoted in Pieczka *et al.* (1997a). A projection of these results in the (Fe,Mn)-tantalite – (Fe,Mn)-columbite quadrilateral (Fig. 3) shows the chemical evolution of the mineral. The horizontal branch with a Ta/(Ta+Nb) ratio of less than 0.1 is distinctly elongated between Mn/(Mn+Fe) values of 0.70–0.90. In one case the latter ratio is 0.95. It can be interpreted as an indicator of pegmatitic melt evolution due to the precipitation of Fe-bearing minerals,

Table 2

The chemical compositions (wt %) of zircon, uraninite, paradocrasite, stibarsen and holtite

Component	Zircon	Uraninite	Paradocrasite	Stibarsen	Holtite
	n=14	n=2	n=2	n=1	n=10
MgO					1.43
Fe_2O_3					0.20
TiO_2					1.56
Al_2O_3					47.38
B_2O_3					5.39
SiO_2	31.49				20.23
ZrO_2	61.55				
HfO_2	3.54				
ThO_2	0.17				
UO_2	3.25				
Sb_2O_3			84.49*	68.01*	12.94
As_2O_5		0.05	15.51*	31.99*	5.04
Ta_2O_5					5.14
Nb_2O_5					0.69
U_3O_8		94.85			
PbO		5.03			
Cs_2O		0.07			
Total	100.00	100.00	100.00	100.00	100.00

* – as metallic Sb and As

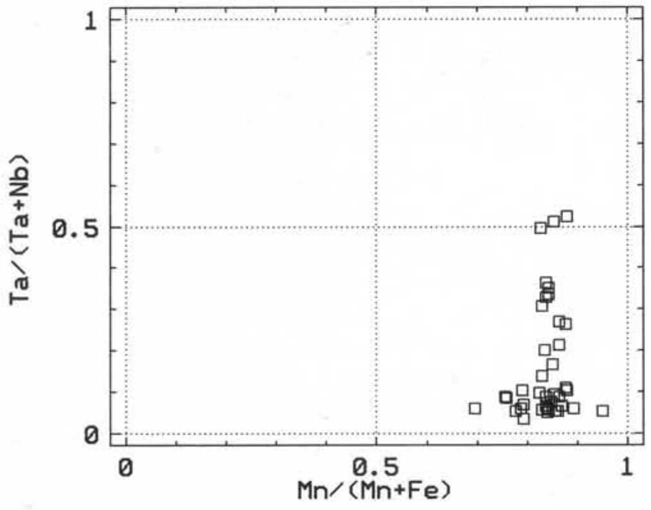


Fig. 3. Compositional trends of the manganocolumbite-manganotantalite crystals from the Szklary pegmatite in the (Fe,Mn)-tantalite - (Fe,Mn)-columbite quadrilateral.

whereas the Ta/(Ta+Nb) ratio remains almost constant because columbite-tantalite had just begun precipitation. The vertical branch is characterized by an almost constant Mn/(Mn+Fe) ratio of about 0.82–0.85 and changes from 0.10 to more than 0.50 in the Ta/(Ta+Nb) ratio. The scatter of the Ta/(Ta+Nb) values and, simultanously, Mn/(Mn+Fe) buffering during columbite-tantalite crystallization is considered to be characteristic of the initial Mn/(Mn+Fe) ratio of the melt. This behaviour of Ta/(Ta+Nb) and Mn/(Mn+Fe) relations is related to the evolution of the pegmatite-forming melts, but there may have been resetting by postmagmatic processes (Raimbault, 1998). The position of the Ta/(Ta+Nb) asymptote for the columbites-tantalites from Szklary along with the relatively low values of the Mn/(Mn+Fe) ratio may indicate a muscovite subunit of the pegmatite, as for the lepidolite subunit rather higher values of this ratio are characteristic. In the manganocolumbites- manganotantalites of the Szklary pegmatite, the visible compositional trend may rather be associated with late Ta-enrichment as it is within the Puklice pegmatite (Czech Republic) described by Novák & Diviš (1996). As a result of this, the increase in Ta/(Ta+Nb) values was recorded in the thin, outer rim of the zoned crystals.

Out of 20 columbite crystals which were chemically analysed, only in one case was stibiocolumbite $Sb(Nb,Ta)O_4$ found, in the form of fine, dendritic grains, overgrowing a crystal of manganocolumbite. The size of the grains is approximately 25x5 μm and their chemical composition is variable (Pieczka *et al.*, 1997a). The stibiocolumbite reveals a small deficit of antimony, supplemented by bivalent ions and a small excess of niobium and tantalum. In a few cases, small (below 1 wt %) admixtures of scandium were observed in the stibiocolumbite.

Holtite $(Si_{2.25}Sb_{0.75})B[Al_{6.00}(Al_{0.43}Ta_{0.27}\square_{0.30})O_{15}(O,OH)_{2.25})$ is a very rare mineral related to dumortierite and Szklary is the third location from which it has been reported in the world. Earlier, it was described from Greenbushes, Australia (Pryce, 1968) and the Kola Peninsula, Russia (Voloshin *et al.*, 1976), both occurrences associated with intrusions of granitic rocks into older metamorphic complexes of greenstones, amphibolites and gneisses. In Australia, holtite co-occurs with quartz, microcline, tourmaline, tantalite and stibiotantalite, while in Russia, also with plagioclase, muscovite, spodumene, amblygonite, pollucite, lepidolite, microlite, simpsonite and zircon. In Szklary, holtite was only found in one fragment of the pegmatite, where it occurs as a thin (*c.* 1 mm) vein, sometimes as radial aggregates of strongly elongated fibres, straw-yellowish in colour and with silky lustre. Its crystals are few tenths of a millimetre long and 2–5 μm thick. The holtite from Szklary is characterized by the refractive indices: n_α = 1.740–1.747, n_β and $n_\gamma \cong 1.76$, the unit-cell parameters (the *Pnma* space group): a = 4.7023(6) Å, b = 11.9030(15) Å, c = 20.3982(25) Å, and the unit-cell volume V is 1141.7(4) Å^3. Its chemical composition presented in Table 2 corresponds to the formula unit: $(Si_{2.18}Sb_{0.56}As_{0.26})B[(Al_{6.03}Mg_{0.23}Ti_{0.13}Ta_{0.15}Nb_{0.03}As_{0.02}Fe^{3+}_{0.02}\square_{0.39})(O_{17.44}\square_{0.56})]$.

In addition to the mentioned Nb-Ta phases, a few grains of pyrochlore have also been found. They are up to 0.5 mm long, show vitreous-greasy lustre, intensive green-yellow to yellow-orange colour and contain *c.* 3.5% SiO_2, 30.2% Ta_2O_5, 3.8% Nb_2O_5, 4.0% TiO_2, 3.5% CaO, 1.4% FeO, 15.0% UO_2, 1.0–20.0% Bi_2O_3, 1.3% As_2O_3, 9–11.0% Sb_2O_3, 3–5% BaO, 1–4% PbO, 1.5% ThO_2 and traces of W and F.

Of the phosphate minerals, only beusite and different varieties of apatite have been identified so far.

Beusite $(Mn,Fe,Ca,Mg)_3[PO_4]_2$ is the rare manganese end-member of the graftonite-beusite series, described from granitic pegmatites of Argentina (Hurlbut & Aristarain, 1968), Finland (Lahti, 1981), Namibia (Fransolet *et al.*, 1986), the Northwest Territories, Canada (Wise & Černý, 1990), the Czech Republic (Staněk, 1991), and recently of Ontario and Winnipeg, Canada (Černý *et al.*, 1998), and Sweden (Smeds *et al.*, 1998). The occurrence of an Mn-rich graftonite-like mineral was also earlier reported from the Turkestan Mountains (Beus, 1950) and Queensland, Australia (Brooks & Shipway, 1960).

In the Szklary pegmatite, beusite occurs within feldspars and quartz, sometimes accompanied by tourmaline, most often as fine, anhedral grains reaching up to 1 cm in size, some of them partly leached. Brownish to brownish black with strong vitreous lustre, it contains sporadic inclusions of apatite. The chemical composition of the beusite from Szklary is presented in Table 3, and the formula unit calculated on the basis of 8 O^{2-} ions is $(Mn_{1.83}Ca_{0.46}Fe^{2+}_{0.44}Mg_{0.16})[P_{1.02}O_4]_2$. The beusite is homogeneous, as the values of the Mn/(Mn+Fe) ratio change in the very narrow range of 0.79–0.82. It is monoclinic with the space group $P2_1/c$, and its unit-cell parameters are: a = 8.793(2) Å, b = 11.574(2) Å, c = 6.165(1) Å, β = 99.20(2)°, while the unit-cell volume V is 621.6(2) Å^3. In nature, graftonite-beusite commonly occurs intergrown with members of the triphylite-lithiophilite series or with sarcopside. Such intergrowths represent exsolutions from a high-temperature, (Ca,Li)-rich graftonite-like parent phase, but in the beusite from Szklary such intergrowths have not been found. This fact corresponds well with the geological setting of the Szklary pegmatite, as the surrounding rocks of the Niemcza zone are Li-poor and no lithium minerals have been found so far. Occurrences of beusite-graftonite of a similar character have recently been noted from Ontario and Winnipeg, Canada (Černý *et al.*, 1998). The stabilization of graftonite-beusite members is facilitated by the relatively low activities of F, Na and Li.

Manganoan apatite occurs as accumulations of anhedral grains or as euhedral prismatic crystals, up to 2 cm long, brown-green, grey-green to bottle-green with vitreous lustre, enclosed in quartz, most often in the immediate vicinity of spessartine. The chemical composition of this mineral is presented in Table 3, and its formula unit calculated on the basis of five bivalent cations is $(Ca_{3.91}Mn_{1.06}Fe^{2+}_{0.02}Mg_{<0.01})[(PO_4)_{2.96}/(OH,F)_{1.11}]$. The Mn/ (Mn+Ca+Fe+Mg) ratio is in the range 0.20–0.23, indicating that the manganoan apatite crystals are also homogeneous. The unit-cell parameters of the mineral are: a = 9.347(2) Å and c = 6.740(2) Å, significantly lower than those characteristic for typical fluoroapatites. The amount of manganese higher than 1 *apfu* is reflected in the lower unit-cell parameters as a result of replacement of Ca^{2+} ions by considerably smaller Mn^{2+} ions.

The list of minerals of this pegmatite is completed by manganese oxides-hydroxides occurring as small accumulations of dark-brown todorokite $NaMn_8O_{16}$, romanechite $BaMn_9O_{16}(OH)_4$, hollandite $BaMn_8O_{16}$, or pyrolusite MnO_2 (or other manganese oxides of a similar composition) intergrown with white hydroxyl-chlorapatite or hydroxyl-carbonate apatite, secondary clay minerals (montmorillonite), sometimes accompanied by sidorenkite $Na_3Mn[PO_4|CO_3]$, and rarer goethite.

Table 3

The chemical compositions (wt %) of the phosphate minerals (beusite and Mn-apatite)

Component	Beusite	Mn-apatite
	n=11	n=11
CaO	7.57	41.62
MgO	2.13	0.07
FeO	9.32	0.32
MnO	38.15	14.32
Li_2O	<0.01	
P_2O_5	42.83	39.88
$H_2O(-)$		n.d.
$H_2O(+)$		n.d.
F		n.d.
Total	100.00	96.21

n.d. – not detected

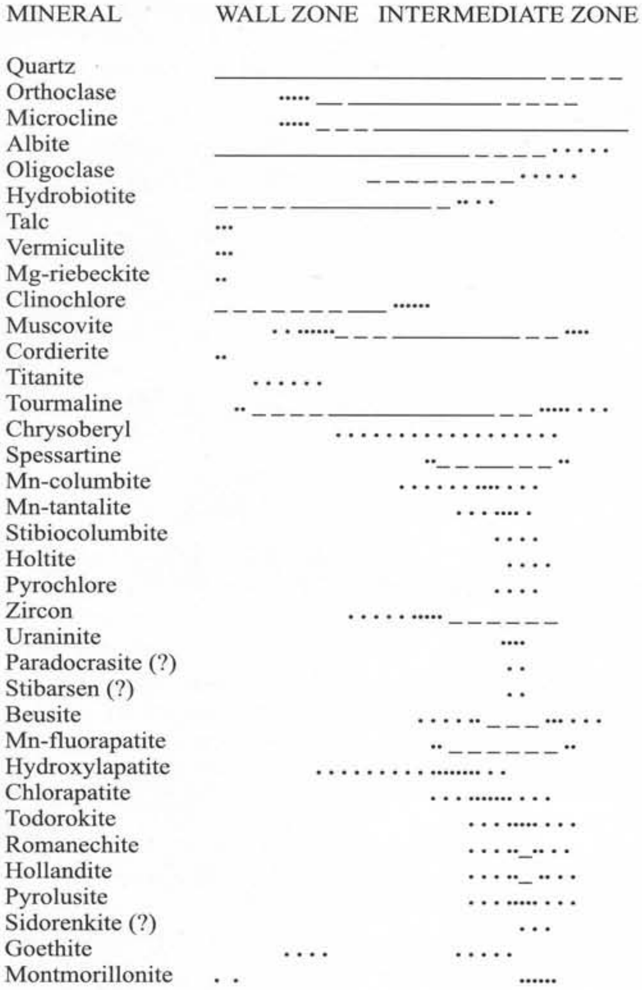
CONCLUSIONS

The pegmatite from Szklary represents the beryl-columbite-phosphate subtype of the rare-element pegmatite class. It is completely different to other Polish granitoid pegmatites (from the Karkonosze–Izera block, Strzegom and Strzelin massifs and the Tatra Mts) in terms of both its structural development (graphic intergrowths within the whole body of the pegmatite) and unique mineral composition (Table 4). Of particular interest are its local concentrations of numerous rare elements, among others B, Be, Zr, Hf, As, Sb, Nb, Ta, Bi, U, Sc and also Mn, Ti, P, Ba and Cl, which are so high that some of these elements form their own, sometimes rare mineral phases. At the same time, the absence of Li, W and Sn minerals in the pegmatite is conspicuous. The carbonate content is very low: they occur as late-formed hydroxyl-carbonate apatite and – possibly – traces of sidorenkite, while common carbonate minerals have not been found so far. In the last stages of fractionation, the very low activity of Li combined with high and very high activities of Ca and Mn, respectively, stabilized beusite as a homogeneous phase and prevented the crystallization of primary phosphate minerals, such as triphylite-litiophilite or sarcopside. The environment of the late stages of the pegmatite differentiation was extremely enriched in manganese and, as a result, Mn oxides formed (*e.g.* todorokite, romanechite, hollandite). The presence of rare elements distinctly differs the Szklary pegmatite from the aplites, in which such elements were not found (Muszyński & Natkaniec-Nowak, 1992).

The genesis of rare-element pegmatites can be related to granitoid intrusions and the late stages of their differentiation, in which the residual magma is strongly saturated with water and other vapours, or to the high-grade metamorphism and anatectic generation of granitic magmas enriched in rare elements (*e.g.* Slack & Stevens, 1994). Pegmatites of this class are usually associated with S-type granitoids. According to Dziedzic (1985, 1987), the rocks of the Niemcza zone are quartzites, metasiliceous graphitic rocks, metapsammites and metamudstones that underwent low-pressure and high-temperature metamorphism under andalusite-cordierite facies conditions. Those rocks enclose small, concordant intrusions of granitoids, the age of which was determined as 338±4 Ma using U-Pb dating of zircons (Oliver *et al.*, 1993). Lorenc (1998) suggests that the granitoids represent magmas generated from diversified sources. Within the Niemcza granitoids there are no larger pegmatitic bodies. Small pegmatite nests can be seen in Przedborowa, Brodziszów and Kośmin, within monzodiorites or granodiorites, while fragments of a larger body are visible in the granodiorites of the old quarry on Strach Hill. All of these lack graphic intergrowths typical for the Szklary pegmatite, and their mineral compositions are simple (hornblende, biotite, plagioclase, pyrite, chabasite in Przedborowa; quartz, alkali feldspars, biotite, muscovite, sericite in Brodziszów; alkali feldspars, quartz, biotite, magnetite, titanite, muscovite, sericite and epidote on Strach Hill). These features are basically different from those characteristic for the Szklary pegmatite, and suggest the lack of a direct genetic link between the Szklary pegmatite and the pegmatites within the Niemcza granitoid intrusions. It is rather possible that this pegmatite is a product of the crystallization of silicic magma generated from the partial melting of some components of the primary sediments during high-grade metamorphism. Based on the microprobe analyses of uraninite inclusions in the zircon from Szklary, the age of the uraninite was estimated at *c.* 400 Ma, applying the approach of Kucha *et al.* (1986). This approach follows the Holmes & Laves (1927) method used in standard non-isotope U-Th-Pb dating. Kucha *et al.* (1986) did not discuss the relative error of the method, but concluded that the results obtained with an electron microprobe concur with K-Ar and Rb-Sr dating results. It is a tentative approach, as such dating should be based on the amounts of U and Pb isotopes, and not on the total contents of these elements. The age obtained here indicates that the pegmatite in question may be older than the Niemcza granitoids. Its structural and textural development (vein form and graphic intergrowths) and also partly its mineral composition make the Szklary pegmatite comparable in some respects to the anatectic pegmatites of the gneissic block of the Góry Sowie. Some of them, particularly larger pegmatitic bodies from the vicinities of Różana, Bielawa and Michałkowa, also reveal graphic intergrowths of quartz and alkali feldspars, the presence of black tourmaline (schorl), almandine-spessartine garnet (Pieczka *et al.*, 1997b), beryl, phosphate minerals: triplite, sarcopside, huréaulite, vivianite (*vide* Lis & Sylwestrzak, 1986), and less frequent columbite (*ibidem*). The age of the Góry Sowie pegmatites has been accepted as 370 ± 4 Ma (Van Breemen *et al.*, 1988). This value is slightly lower than that obtained here for the uraninite from Szklary. U-Pb isotope dating should rather lower the age of the latter, and in this case the rare-element pegmatite from Szklary and at least a part of the pegmatites cutting the migmatitic gneisess of the Góry Sowie might be regarded as having originated from the same source.

Table 4

A list of the minerals of the rare-element pegmatite from Szklary



____ - very frequent,
_ _ _ - frequent,
.... - rare,
. . . . - very rare,
(?) - tentatively identified.

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