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MINERALOGICAL CHARACTERISTIC OF ALKALI FELDSPARS FROM THE WESTERN TATRA MTS. (S POLAND)

Abstract. Alkali feldspars were chosen as the most interesting (and most widespread) rock-forming minerals from the Western Tatras pegmatites. They were mainly perthitic microclines (Δr = 0.85—1.0, $T_1 0$ = 0.8662 – 0.9373), orthoclase was subordinate (Tab. 2).

The alkali feldspars differed in the Na/(Na + K) ratio [0.192—0.836] and in the trace element content, especially in the litophyle ones (Tab. 4a, b, b'). The deviation of unit cell parameters, stated in K-feldspars, were probably caused by elevated Ba and Rb contents. Enrichment in Cd and Bi was detected in one sample of grey microcline (SK2; Tab. 4).

The presence of the $Al - O^{-} - Al$ paramagnetic center was detected in all the feldspars from the Western Tatras pegmatites. One sample (SK2) displayed the EPR signal from the additional paramagnetic center of an unknown origin (Fig. 2). Using the PAS method we estimated the size of micropores in feldspars (r = 0.42—0.48; Tab. 5).

Key-words: alkali feldspars, paramagnetic center, EPR, positone annihilation, Tatra Mts.

INTRODUCTION

In the Western Tatras pegmatites feldspars are the most important rock-forming minerals. There were found mainly perthitic K-feldspars and Na-feldspars, acid plagioclases (oligoclases) were subordinate. Those three groups represent simultaneously three generation of feldspars. The pegmatites under consideration belong to the mica-type and they had not the crustal zone developed (in means there are no caverns in the middle, with the „free-growing minerals" of the last period of crystallization), so none of the investigated feldspars formed the automorphic crystals (Gawęda 1993).

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Acid plagioclases are the oldest among the feldspars in question. Their composition range from An_9 to An_{37}, with the predominant between An_{16} and An_{22}. Because of the scantity of the material and the widespread albitization the An content was determined optically using the method of PCP-analysis (Nowakowski 1976). Only sporadically one could separate enough plagioclases for rentgenostructural analysis (samples SP1 and SP6, Tab. 1).

TABLE 1

Optical and X-ray structural parameters of plagioclases

Sample	An opt %	% An rentg.	Si/Al	Θ IR
SP1	11	12	2.614	1.335
SP2	10	9—10	2.61	1.333
SP3	n.d.	1	3.00	1.35
SP5	2	0—1	3.00	1.35
SP6	12—13	13	2.595	n.d.

The next group (and the next generation) of feldspars is represented by alkali feldspars. They were predominantly maximum microclines with the characteristic cross-hatching twinning, orthoclase was found sporadically (Tab. 2). Their optical axes changed from 78° to 81°. Almost all the potassium feldspars were developed in perthites. In several samples the „catastrophic coarsening" of perthites was observed. It led to the full replacement of K-feldspar by Na-feldspar in several cases (Gawęda 1993). However, in some microclines the separation of the pure potassium phase was possible.

Low albites were the youngest generation of feldspars. They occur as individual mineral grains (possible to distinguish microscopically), sometimes they form pseudomorphs after oligoclases and K-feldspars, as well as small albite veins in microclines. They are almost pure albites (An_{0-1} — Tab. 3). Similar results were obtained in optical determination and rentgenostructural and spectroscopic analyses (Tab. 1).

TABLE 2

Optical and X-ray structural parameters of alkali feldspars

Sample	Ab total [%]	Ab s.p. [%]	Δr	A	2V [°]	Θ IR	T_1	$T_1 O$	$T_1 m$
SK1	10	0	1.00	0.680	76	1.10	0.9582	0.9373	0.0209
SK2	13	0	0.975	0.505	—	1.10	0.9052	0.8824	0.0229
SK2'	63	0	0.98	0.480	—	1.10	0.8741	0.8036	0.0705
SK2''	16	0	0.98	0.500	—	1.10	n.d.	n.d.	n.d.
SK3	15	0	0.85	0.560	75	11.00	0.9108	0.8662	0.0446
SK4	14	1	0.913	0.505	81	1.10	0.9424	0.9136	0.0288
SK5	15	0	0.975	0.780	78	1.10	0.9112	0.8667	0.0445
SK6	11	1	0.475	0.225	—	1.00	0.8160	0.7240	0.0920

Ab total — total amount of albite determined in the K-feldspar sample; Ab s.p. — albite included as a solid phase in K-feldspar (as perthites); Δr — triclinity; A — degree of structural order (Sosiedko 1974); 2V — optic axial angle; Θ IR — degree of spectroscopic order (Kuzniecova 1971).

The group of alkali feldspars appeared to be the most interesting for further investigations because of their macroscopical (colour), structural and chemical diversity. Several samples, differing in the colour, Ab content, trace element content and structural features were examined.

TABLE 3

Microprobe compositions of K- and Na-feldspars

	SD (mean)	SP (mean)	SP*
SiO_2	64.84	68.71	68.86
Al_2O_3	18.76	20.70	20.91
K_2O	16.34	0.16	0.18
Na_2O	0.01	10.52	10.23
CaO	—	0.16	—
Total	99.95	100.25	100.18
Si	2.98	2.97	2.98
Al^{IV}	0.02	0.03	0.02
Al^{VI}	1.00	1.036	1.05
K	0.95	0.008	0.01
Na	0.09	0.885	0.86
Ca	—	0.007	—
Al^{IV}/Al^{VI}	0.02	0.03	0.02
Charge	+0.12	–0.015	+0.10

SAMPLES AND METHODS

Samples of feldspars were taken from the various zones of pegmatites with well developed zonality as well as from unzoned small (3—10 cm in width) pegmatitic veins. They were analyzed for major elements (classical „wet" method) and trace elements such as: Rb, Sr, Ba, Li, Fe^{3+}, Fe^{2+}, Mn, Co, Ni, Zn, Pb, Cu, Cr using XRF and AAS methods (University of Silesia, Sosnowiec and Institute of Mining, Katowice). One sample of grey microcline (SK2, Fig. 1) was analysed for REE elements, too. The analyses were carried out by the INAA method for Au, As, Br, Co, Cr, Cs, Hf, Hg, Ir, Mo, Rb, Sb, Sc, Ta, Th, U, W, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu (2MW-Pool Type reactor with g-detectors Ge ORTEC and CANBERRA) as well as by the ICP-method for Cu, Pb, Zn, Ag, Ni, Cd, Bi, V, Be (spectrometers JARRELL ASH Enviro and PERKIN ELMER 6000). Microprobe analyses were carried out for the perthitic microcline by dr. J. Janeczek at the University of New Mexico, Albuquerque (USA). The structural state of K-feldspars was investigated by the DSH method (Laboratory of Mineralogy, University of Silesia). As an additional method the infrared spectroscopy (IR) was used.

EPR investigation were carried out on the spectrometers working in X-frequency (9.2—9.8 GHz): SE (Radiopan) and ESP 300 (Bruker) in the temperature range of 77—300 K (Institute of Chemistry, University of Wrocław). Quantitative EPR measurements were made for 30 mg powder samples at constant experimental parameters: gain, modulation amplitude, modulation frequency, microwave power, phase, etc. The EPR standards were used (Mn^{2+} in MgO and TEMPO free radical). The ^{60}Co isotope was a source of γ-irradiation.

The PAS-method (process of positone annihilation) was carried out using ^{22}Na as the source of positones, with the activity of 4×10^5 Bq (Laboratory of Applied Nuclear Physics, University of Wrocław). The more detailed description of the PAS method can be found in previous works (Sachanbiński et al. 1991).

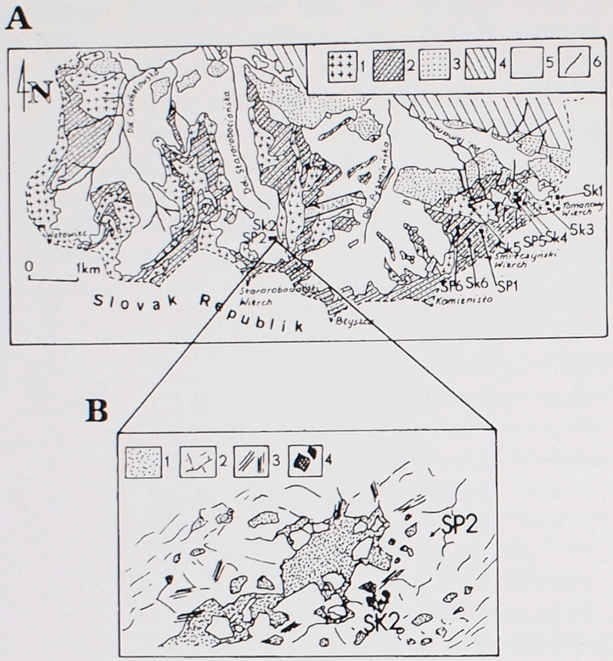

Fig. 1. A. Simplified geological sketch of the Western Tatra Mts. with the sampling points (according to: Geological Map of the Polish Tatra Mts., 1979)
1 — granitoids; 2 — metamorphic rocks; 3 — Triassic sedimentary rocks; 4 — Jurassic carbonate rocks; 5 — Quaternary deposits; 6 — main tectonic lines;
B. Pegmatite from Starorobociańska Rówień with grey K-feldspar (SK2) and the prevalent white albite
1 — quartz; 2 — feldspars (in general); 3 — muscovite; 4 — patches of grey K-feldspar

RESULTS

Classical mineralogical investigations of feldspars

Potassium feldspars from Western Tatras pegmatites show a diversity of the Na/(Na + K) ratio in the samples under consideration. The albitization probably influenced the trace elements content, especially on Rb, Sr, Li and Ba contents. One could observe the negative (but not very strong) correlation between the contents of those four elements and Na/(Na + K) ratio (Tab. 4A, B). The correlation coefficients between Rb, Sr, Ba and Li and the mentioned ratio are as follows: $r_{Rb} = -0.5312$; $r_{Sr} = -0.6258$; $r_{Ba} = -0.5913$; $r_{Li} = -0.4394$. The albitization affected neither the other trace elements content, like: Fe^{+2}, Fe^{+3}, Mn^{+2}, Zn^{+2}, Pb^{+2}, nor the Ba/Rb ratio (Tab. 4B). The alkali feldspars did not display the changes in their trace elements contents and Ba/Rb ratio according to the pegmatite zones from which they were collected as it was suggested by previous authors (Shmakin 1979). The contents of the following trace elements: Ag, Au, As, Be, Bi, Br, Cd, Co, Cr, Cs, Cu, Hf, Hg, Ir, Mo, Ni, Sc, Se, Ta, Th, U, W and REE are rather low (mostly under detection limits) and typical of K-feldspars. Sample SK2 is an exception with higher than typical Cd and Bi contents (respectively 1.7 ppm and 5 ppm, Tab. 4B').

TABLE 4

A. Chemical compositions of the selected samples of alkali feldspars

	SK1	SK2	SK3	SK4	SK5	SK6	SP2	SP4	SP5
SiO_2	66.95	66.13	66.27	68.73	72.79	64.58	66.95	66.93	67.37
TiO_2	0.03	<0.01	0.02	0.03	0.01	0.02	0.01	0.03	0.06
Al_2O_3	17.67	16.92	19.06	18.64	14.10	18.63	17.43	19.69	20.06
Fe_2O_3	0.09	0.08	0.11	0.08	0.11	0.14	0.49	0.08	0.58
FeO	—	—	0.09	0.08	0.40	0.04	0.05	0.09	0.13
MnO	0.001	0.01	0.003	—	0.01	—	0.02	—	0.004
MgO	0.01	0.07	0.02	0.02	0.03	0.02	0.03	0.03	0.12
CaO	0.21	0.1	0.28	0.39	0.10	0.70	2.05	0.73	0.60
Na_2O	2.97	2.01	2.83	7.71	2.33	3.18	8.36	9.16	6.40
K_2O	11.14	12.84	9.88	3.50	9.03	11.19	1.47	2.15	2.97
P_2O_5	0.19	0.36	0.39	0.24	0.20	0.27	0.32	0.22	0.14
H_2O^+	0.15	0.52	0.28	0.38	0.57	0.39	1.35	0.40	0.87
Total	99.41	99.05	99.36	99.77	99.68	99.16	98.53	99.51	99.30

B. Trace elements contents [in ppm] and Na/(Na + K) ratio of selected samples

Li	500	n.d.	600	114	306	50	120	384	260
Ba	570	142	1 220	320	360	475	295	290	670
Rb	70	481	710	150	305	200	55	65	85
Sr	460	31	190	45	30	365	50	30	95
Zn	20	9	20	67	450	515	20	790	170
Pb	80	32	—	60	—	130	60	—	—
Ni	—	2	—	—	—	20	—	—	—
Cu	—	3	—	—	50		—	—	—
Cr	—	15	115	—	—		—	—	—
Na/(Na + K)	0.192	0.123	0.204	0.663	0.436	0.203	0.836	0.792	0.658
Ba/Rb	8.14	0.295	1.718	2.133	1.18	2.375	5.363	4.462	7.882

B'. Sample No SK2 — trace elements [in ppm]

Cd	Ag	Bi	V	Be	Au[ppb]	As	Br	Co	Cs	Hf	Hg	Ir[ppb]	Mo	Zr
1.7	<0.4	5	2	2	20	2	<1	1	3.8	<0.5	<1	<5	<5	11

Sb	Sc	Se	Ta	Th	U	W	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu
0.3	0.2	<3	<1	<0.5	<0.5	<3	0.5	<3	<5	0.1	0.1	<0.5	0.2	<0.05

TABLE 5

Unit cell parameters of representative K- and Na-feldspars

Sample	a_0	b_0	c_0	α	β	γ
SK1	8.53	12.97	7.20	90.34	115.95	90.33
SK2	8.56	12.96	7.22	90.30	115.83	87.70
SK3	8.59	13.02	7.21	90.31	116.00	87.42
SK4	8.59	12.97	7.20	90.39	115.98	87.33
SK5	8.59	12.97	7.21	90.31	115.98	87.42
SK6	8.59	12.99	7.21	90.00	116.09	90.18
SP1	8.14	12.78	7.16	90.40	116.60	90.90
SP2	8.14	12.78	7.16	90.10	116.31	90.00
SP3	8.14	12.79	7.15	94.33	116.57	87.65
SP4	8.16	12.82	7.16	94.45	116.20	88.75
SP5	8.14	12.78	7.16	90.00	116.31	90.00
SP6	8.16	12.80	7.14	90.60	116.20	88.90
SK_{SB}	8.59	12.966	7.22	90.65	115.96	87.65

SKx — alkali feldspar; SPx — plagioclase; SK_{SB} — standard low microcline (Smith and Brown, 1987).

Unit cell parameters for majority of investigated K-feldspars were close to standard ones for maximum microclines (Tab. 5, Smith and Brown 1987). The deviations of b_0 and β could be observed in samples with the elevated content of Ba and Rb. For instance in the sample SK3 with the high triclinity (Δ = 0.85), 2V = 75^0, T_1 = 0.9108, higher than typical is b_0 value (13.02Å) as well as a little higher β value (116°) (Tab. 5).

EPR and PAS investigations

Paramagnetic objects, detected by EPR-method in feldspars, are mainly Fe^{+3}, and Mn^{+2} ions in various positions (Bagmut et al. 1978) and the defect centers caused by radiation. These defects contain paramagnetic forms of nitrogen (mainly NH_3 radical ion, Bagmut et al. 1975) and paramagnetic forms of oxygen (O^- interacting with Al^{+3}, Pb^{+2}, Ti^{+3} etc., Speit and Lehmann 1982). A hole center on oxygen adjacent to two Al^{+3} ions (Al – O^- – Al) is characteristic of various feldspars, e.g. these from Western Tatras pegmatites as well as from Strzegom (Lower Silesia) and Norway. Our EPR investigations proved that for the feldspars from the Western Tatra Mts. the EPR signal intensity was approximately 70% higher than that of the comparatively examines microclines from the Lower Silesia pegmatites and orthoclases from Norway. Moreover, the spectra for the feldspars from the Western Tatra Mts. could be measured at 77 K for the powder samples (Fig. 2) in contrast to the samples investigated as monocrystals at a lower temperature (Speit and Lehmann 1982). The strong signals characteristic of Al – O^- – Al centres were detected in samples SK1, SK2 and SK3. The spectrum had a strongly anisotropic character (Speit and Lehmann 1982; Ikeya 1993) and for the powdered samples we obtained the following experimental spin Hamiltonian parameters: g_{av} = = 2.0150 and hyperfine coupling constant A_{av} = 9.1 (for two equivalent ^{27}Al nuclei with nuclear spin I = 5/2).

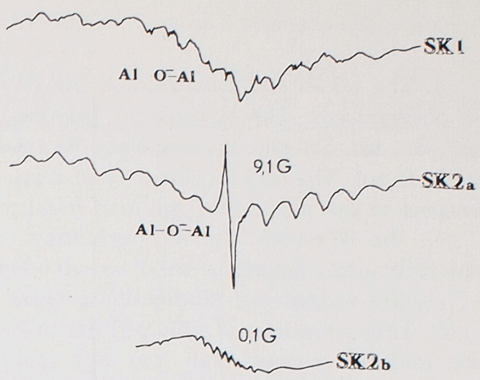

Fig. 2. EPR spectra in pink (SK1) and grey (SK2 a, b) K-feldspars

The radiation nature of the center was confirmed by γ-irradiation of the samples using the ^{60}Co source: after irradiation the intensity of the EPR signal increased without changes of the g and A parameters.

In the grey microcline SK2 the additional signal was detected attributable to the other radiation center characterized by g = 2.0037 and hyperfine coupling constant about 0.1 G (Fig. 2). This center has an unknown nature; it was found only in dark grey microclines from the Western Tatras. The observed g values may be attributed rather to the E-type centers or organic radical silica and silicates (Ikeya 1993). The additional EPR investigation are in progress.

Studies of the positone annihilation (PAS) were carried out, too. Using that method we estimated the size of the micropores („r"). They are smaller than 0.5 nm, which is typical of the most investigated samples (Tab. 6). The biggest micropores (r = 0.48) were found in the pink microcline from Tomanowy Wierch (SK1).

TABLE 6

Size of pores trapping the positonium atoms in feldspars

Sample	Mean pore radius r [nm]
Microcline — Strzegom (Poland)	0.41(2)
Microcline grey — Western Tatra Mts (Poland)	0.42(2)
Microcline pale grey — Western Tatra Mts (Poland)	0.43(2)
Microcline pink — Western Tatra Mts (Poland)	0.48(4)
Microcline — Siedlimowice (Poland)	1.0(2)
Microcline — White Sea	0.47(3)

CONCLUSION

1. The alkali feldspars showed the diversity of features at the different levels of observations. The correlations between the so-called lithophyle trace elements (Li, Ba, Rb, Sr) and the Na/(Na + K) ratio of investigated feldspar samples have been found. The lack of diversity of trace elements contents and Ba/Rb ratios in respect to the pegmatites zonation could result from the following:

— the Western Tatras pegmatites were rather small in size and the microchemical zonation could not develop,

— the widespread albitization process could obliterate the primary diversity.

2. The deviations of unit cell parameters were probably effects of the higher Ba and Rb content (Tab. 4b). For comparison: the pure Ba-feldspar had the b_0 parameter equal to 13.05 Å and β = 115.1° and artificial pure Rb-feldspar had b_0 equal to 12.96 Å and β = 116,14°. Our investigations supported the previous suggestions of Smith and Brown (1987) about the influence of admixtures on the unit cell parameters.

3. The grey microcline (SK2) displayed the enrichment in Cd (1.7 ppm) and Bi (5 ppm). The other feldspars from the investigated pegmatites have these elements contents under the detection limit.

4. The PAS method enabled to determine the size of ultramicropores in the feldspar structure. Their radius ranged from 0.42 to 0.48 nm (Tab. 6). These values are comparable with those of the feldspars from the Strzegom granite and much smaller than those of the feldspars from Siedlimowice.

5. All the feldspars from the Western Tatra Mts. show the presence of the Al – O^- – Al paramagnetic center. In the grey microcline from Starorobociańska Rówień the signal from the additional EPR center of an unknown origin was found.

REFERENCES

BAGMUT N.N., GAVRUSEVICH I. B., MATYASH I.V., 1978: EPR investigations of rare metal containing albites from Precambrian albitites. *Geol. Zhurnal* 4, 130—135.

BAGMUT N.N., BESPALKO N.A., BRIK A. B., MATYASH I.V., FEDOTOV Yu.V., 1975: EPR of NH_3^+radical ion in feldspars. *Geokhimija* 10, 1568—1571.

GAWĘDA A., 1993: Struktura, skład mineralny i geneza pegmatytów polskiej części Tatr Zachodnich. *Arch. Miner.* 49, 2, 113—144.

IKEYA M., 1993: New applications of ESR. World Scientific Publ., 320—336.

KUZNIETSOVA Ł., 1971: Primienienia infrakrasnoy spiektroskopii dla opriedielenia stiepieni uporiadočenosti kali-natrievych polievych špatov. *Min. Sbor.* 25, 1, 18—26.

NOWAKOWSKI A., 1976: Petrologic aspect of pericline twinning in albites of igneous rocks. *Acta Geol. Pol.* 26, 1, 1—56.

SACHANBIŃSKI M., SZUSZKIEWICZ S., SZUSZKIEWICZ M., 1991: Zastosowanie metody anihilacji pozytonów (PAS) w naukach mineralogicznych. *In*: Fizyka minerałów. *Acta Universitatis Vratislaviensis* 1288, *Pr. Geol.-Min.* 23, 227—249. Wyd. Uniw. Wrocławskiego.

SHMAKIN B.M., 1979: Compositional and structural state of K-feldspars from some U.S. pegmatites. *Am. Miner.* 64, 49—56.

SMITH J.V., BROWN W.L., 1987: Feldspar Minerals 1. Springer Verlag, 2nd Edition, Ch. 7.

SOSIEDKO T.A., 1974: Rientgienowskij ekspress-metod opriedielenia stiepieni uporiadočenosti kalievych polievych špatov. *In*: Kristałłochimija i struktura minierałov. Leningrad, 115—117.

SPEIT B., LEHMANN G., 1982: Radiation defects in feldspars. *Phys. Chem. Minerals* 8, 77—82.

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CHARAKTERYSTYKA MINERALOGICZNA SKALENI ALKALICZNYCH Z TATR ZACHODNICH (S POLSKA)

Streszczenie

W pegmatytach Tatr Zachodnich skalenie są nie tylko najpospolitszymi, lecz także najbardziej zróżnicowanymi pod względem cech mineralogicznych minerałami skałotwórczymi. Wyróżniono trzy grupy mineralogiczne, będące równocześnie trzema generacjami skaleni. Są to: 1) najstarsze oligoklazy, 2) skalenie potasowe o budowie pertytowej traktowane tu jako skalenie alkaliczne oraz 3) najmłodsze albity niskotemperaturowe. Szczegółowym badaniom mineralogicznym, w tym EPR-owskim, poddano grupę skaleni potasowych. Są to głównie mikrokliny (Δr = 0,85—1,0; $T_1 0$ = 0,8662—0,9373), ortoklazy występują sporadycznie (Tab. 2).

Skalenie potasowe różnią się także proporcją Na/(Na + K) [0,192—0,836] oraz zawartością pierwiastków śladowych, szczególnie tzw. pierwiastków litofilnych (Sr, Ba, Rb, Li, Tab. 4A, B, B'). Obserwowane odchylenia parametrów komórek elementarnych skaleni potasowych są prawdopodobnie wynikiem podwyższonej zawartości Ba i Rb (pierwiastków o promieniach jonowych większych od K), co potwierdza wcześniejsze sugestie (Smith, Brown 1987). W próbce szarego mikroklinu stwierdzono ponadto podwyższoną zawartość Cd i Bi (SK2; Tab. 4B').

Stosując metodę paramagnetycznego rezonansu jądrowego stwierdzono we wszystkich badanych próbkach skaleni z pegmatytów Tatr Zachodnich obecność centrum typu Al – O^- – Al. W próbce szarego skalenia (SK2; Rys. 2) stwierdzono obecność dodatkowego centrum paramagnetycznego o nieznanym pochodzeniu. Za pomocą metody PAS określono rozmiary mikroporów w badanych próbkach skaleni. Ich średnice r leżą w przedziale 0,42—0,48 (Tab. 5).

OBJAŚNIENIA DO RYSUNKÓW

Rys. 1. A. Uproszczona mapa geologiczna Tatr Zachodnich z punktami opróbowania (wg Mapa Geologiczna Tatr Polskich, 1979): 1 — granitoidy; 2 — skały metamorficzne; 3 — triasowe skały osadowe; 4 — jurajskie skały węglanowe; 5 — utwory czwartorzędowe; 6 — główne linie tektoniczne. B. Pegmatyt ze Starobociańskiej Równi z szarym skaleniem (SK2) i białym albitem (dominującym w tym wystąpieniu): 1 — kwarc; 2 — skalenie (ogólne); 3 — muskowit; 4 — „plamiste" wystąpienia szarego skalenia.

Rys. 2. Widma EPR skalenia różowego (SK1) i szarego (SK2 a, b).