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MINERALOGICAL AND GEOCHEMICAL INVESTIGATION OF MICAS FROM THE GÓRY SOWIE MTS PEGMATITES

A b s t r a c t . Micas from pegmatites of the Góry Sowie Mts were characterized using: microscopic observations, X-ray diffractometry, IR-spectroscopy and chemical analyses. The main stress of this study was put on concentration of main and trace elements in these minerals. Micas are very sensitive indicators of petrogenetic processes. A depletion in F, Rb, Cs, Li, Sn and REE as well as an enrichment in Ba show the high-temperature, post-magmatic crystallization of these minerals. The biotites are enriched in Cr what can confirm metamorphic and metasomatic genesis of the pegmatites.

Key-words: muscovite, biotite, pegmatite, the Góry Sowie Mts, high-temperature crystallization

INTRODUCTION

Micas are the most common sheet silicates on Earth. Their specific structure enables to incorporate a large numbers of main and trace elements of different radii and charges. The concentration of some elements can be a sensitive indicator of physicochemical environment in which a host rock crystallized. Hence, the composition of mica minerals usually bears an important imprint on petrogenetic processes.

The object of this study are dioctahedral and trioctahedral micas from the pegmatites of the Góry Sowie Mts. A special attention was paid to trace and main elements present in the structure of these minerals.

GEOLOGICAL SETTING

The Devonian gneiss formation of the Góry Sowie Mts (Van Breemen et al. 1988), extending among Łagiewniki, Srebrna Góra and Świdnica, is one of major structural elements of the Sudetes. This area was intersected in Tertiary by the Marginal Sudetic

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fault into two fragments: the SW part of the Góry Sowie Mts range proper, and the NE, thrown down part comprising foreland of the Góry Sowie Mts. The region is almost entirely built of the oldest metamorphic formations represented by oligoclase-biotite paragneisses, migmatites (mixed gneisses) and orthogneisses occurring in the SE part of this area. Amphibolites, serpentinites, granulites, pegmatites and quartz veins are less frequent. The pegmatites occur as vein-, lens- or nest-shaped forms within the gneisses. It was suggested that numerous pegmatite small bodies occurring in gneisses and amphibolites are older than the nests and veins intersecting discordantly the structures of their country rocks (Smulikowski 1953). Probably, these pegmatites were formed as a result of partial melting (anatexis) of some rock components during migmatization processes (Kryza 1977; Pieczka 2000). The age of the Góry Sowie Mts pegmatites has been accepted as 370 ± 4 Ma (Van Breemen et al. 1988; *fide* Pieczka 2000).

For the identification and characterization of micas the pegmatites from Jedlinka Górna (GS/2M), Kolce-Walim (GS/3M), Osówka (GS/4M, GS/4B), Sokolec (GS/6M, GS/7M), an area next to Bystrzyckie lake (GS/10B, GS/10M, GS/13M, GS/13B), Zagórze Śląskie (GS/11B), Michałkowa (GS/14M, GS/14B) and Lutomia (GS/1M, GS/1B) were collected (Fig. 1).

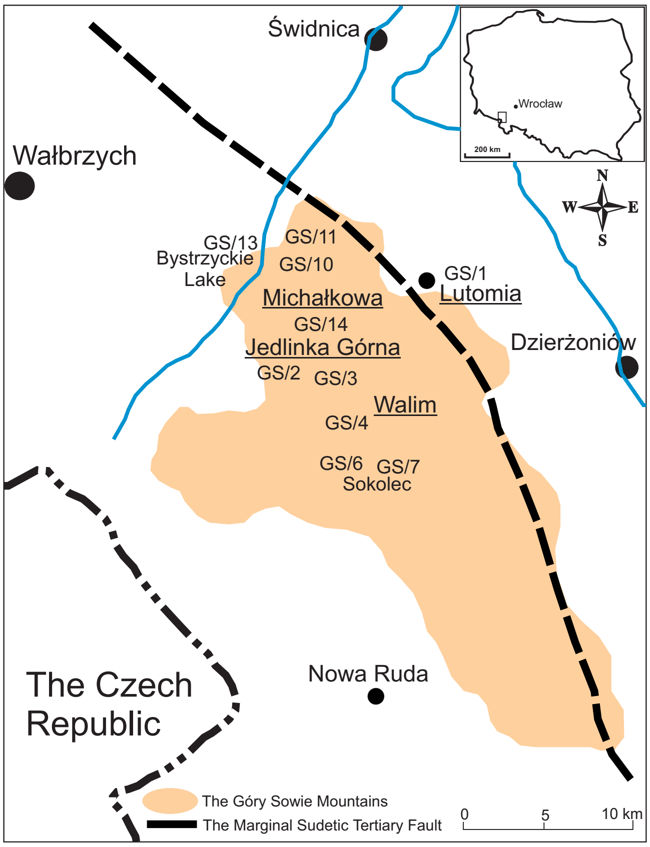

Fig. 1. The sketch map of the Góry Sowie Mts with sampling sites

EXPERIMENTAL METHODS

Micas were analysed using transmitting optical microscopy, chemical analyses, IR spectroscopy and X-ray diffractometry.

Chemical analyses were conducted at the Activation Laboratories Ltd in Ancaster, Ontario (Canada). Main components: SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, and some trace elements: Ba, Sr, Zr, Y, Be, V, Cu, Pb, Zn, Ag, Ni, Cd and Bi were analysed using ICP-AES. The analyses were made with ICP spectrometers (JARRELL ASH model Enviro and PERKIN ELMER model 6000). Over 20 other trace elements, including some REE, were determined using INAA. The irradiations were carried out in a 2 MW Pool Type reactor (neutron flux — 5×10^{11} ncm^{-2} s^{-1}) and further investigations with a Ge ORTEC and CANBERRA detector. Fluorine was analyzed with a Carl Zeiss Jena spectrophotometer. Absorbance was measured using a colorimeter (λ = 532 nm). The formula units of micas were calculated in relation to 22 oxygens.

Infrared spectra for the region 400–3700 cm^{-1} were recorded with a BIO-RAD model FTS-165 spectrophotometer. Monocrystals of mica flakes were pressed in the form of discs with KBr. The special attention was paid to the OH stretching region.

X-ray investigations were carried out on powdered, randomly oriented samples using a Philips X'PERT diffractometer with a graphite monochromator under the following operating conditions: CuKa radiation (λ = 1.53), scanning speed 0.02°(2θ)/1 sec., range 5–75°(2θ).

RESULTS AND DISCUSSION

The Góry Sowie Mts pegmatites are rather enriched in both dioctahedral and trioctahedral micas. The pegmatites, exhibiting non-complex mineral composition, consist mainly of feldspars, quartz, biotite, muscovite, hornblende, chlorite, titanite and opaque minerals. Zircon, apatite, cordierite, epidote, orthite, beryl and garnet occur in traces.

The microscope investigations of thin sections revealed that the muscovites are fresh while some biotites reveal chloritization. Strong, greenish-brown pleochroism of the biotites (GS/1B, GS/7) is probably associated with a considerable amount of Fe in the micas. Orange-brown pleochroism in some biotites (GS/10, GS/11B) is characteristic of micas rich in Ti (Deer et al. 1992).

In the X-ray patterns all basal reflections of dark micas correspond to 1M biotite and $2M_1$ phlogopite (GS/4B, GS/11B, GS/13B, GS/14B). The reflections of biotite--phlogopite solid solution almost completely coincide. In some X-ray patterns (GS/1B, GS/4B, GS/11B) also less intensive chlorite reflections are present (Fig. 2).

Both microscope and X-ray investigations confirm, therefore, the presence of chlorite in biotites samples.

In the IR absorption spectra of the micas there are strong bands of the Si-O and Al-O at 400–1200 cm^{-1}. However, particular attention was paid to the OH-stretching region at 3400–3700 cm^{-1}, because the location of the bands depend on chemical composition of micas (Vedder 1964).

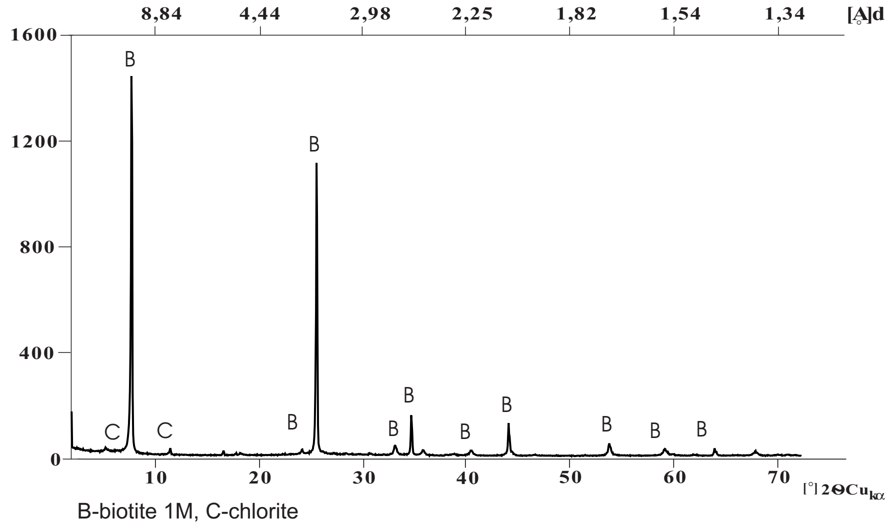

Fig. 2. X-ray pattern of trioctahedral mica from the Zagórze Śląskie pegmatite GS/11

In the IR spectrum of the muscovite from Michałkowa (GS/14M) the band of OH stretching vibrations is located at 3635 cm^{-1} (Fig. 3). The position of this band is caused by higher than average amount of Al at the octahedral sites. The band at 3312 cm^{-1} corresponds to the N-H stretching vibrations, while N-H bending vibrations are responsible for the location of the band at 1427 cm^{-1} (Bastoul et al. 1993). It indicates the presence of some ammonium ions in the muscovite structure, where NH_4^+ ion replaces K^+. The band at 1633 cm^{-1} is connected with the presence of molecular water (Fig. 4). Two weak bands of the biotite (GS/14B) at 1428 and 3267 cm^{-1} are caused by N-H

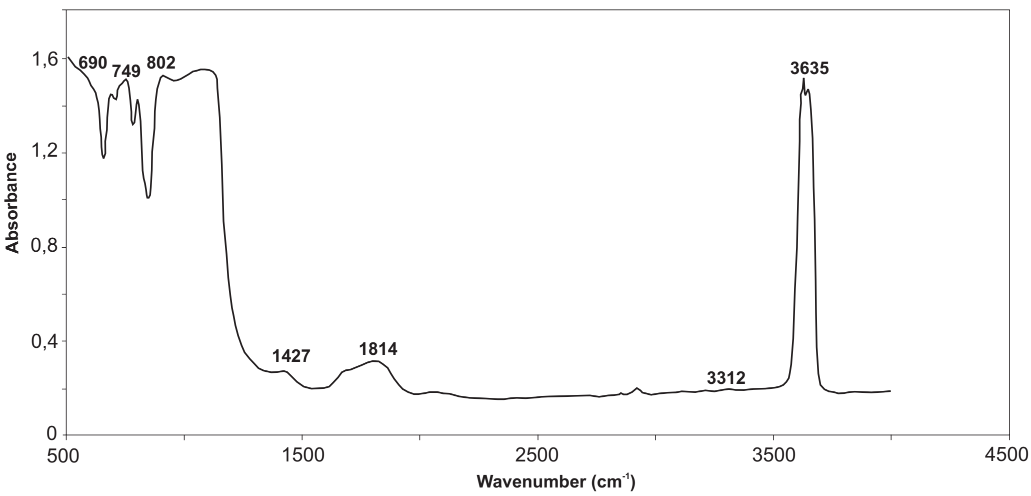

Fig. 3. The IR spectrum of muscovite from the Michałkowa pegmatite GS/14M

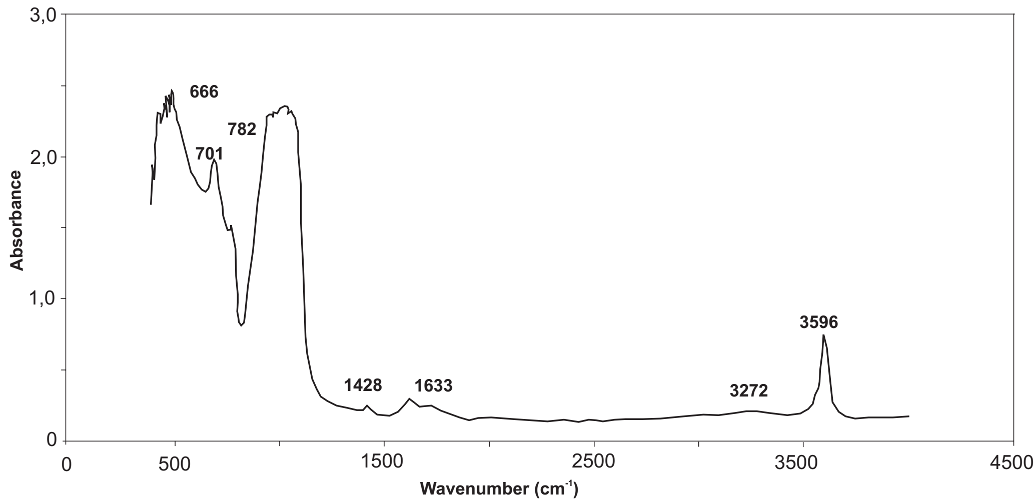

Fig. 4. The IR spectrum of biotite from the Michałkowa pegmatite GS/14B

vibrations. At 3596 cm^{-1} there is a sharp peak associated with OH stretching vibrations (Fig. 4). Location of this band points to the significant content of Fe at octahedral sites, as the higher Mg content of biotite, the higher is the position of the OH stretching band (Vedder 1964).

The main stress of the study put on geochemical analyses of muscovites and biotites from the Góry Sowie Mts pegmatites.

In the **dioctahedral micas** tetrahedral sites are occupied by Si and Al, while in the octahedral positions Al, Fe, Mg, Ti and Mn occur. The muscovite from Lutomia has the most significant amount of Al in the octahedral layer. Relatively high amount of K (1.5–1.7 atoms per formula unit) and traces of Na, Rb, Ba, Ca occur at the interlayer sites (Table 1).

Be accounts on average for 36 ppm in the muscovites from the Góry Sowie Mts pegmatites. Low concentrations of Cr and V are noted in these micas: up to 5 ppm of Cr and 10 ppm of V (Table 3). Similarly the muscovites are depleted of Ni, with the exception of the muscovite from Lutomia (GS/1) which possesses 23 ppm of this element. Co is other element rarely adopted by the muscovites.

Rb and Cs concentration increase with advancing crystallization of magmas. Moreover, Cs rapidly increases in good correlation with Li and F (Černy et al. 1985). An accumulation of these elements in the muscovites investigated is very low: Li content ranges from 9 ppm for GS/6M to 19 ppm for GS/1M, Rb from 96 ppm to 453 ppm, Cs from 4 ppm to 22 ppm and F from 0,08% to 0,19%.

The concentration of Sr in the muscovites ranges from 2 to 19 ppm. On the other hand, the white micas are relatively enriched in Ba, from 28 ppm (GS/14M) up to 1123 (GS/3M), 325 ppm on average. Ba in micas spans from extensive ranges in muscovites of the primitive pegmatites to very low amounts in lepidolite of complex pegmatites (Černy et al. 1985). It follows that the more Cs and Li the less Ba occurs in micas.

TABLE 1

Chemical formulae of the micas from the Góry Sowie Mts

Sample	Mica	Formula
GS/1M Lutomia	muscovite	$(K_{1.770}Na_{0.225}Ca_{0.003})(Al_{3.622}Fe^{3+}{}_{0.213}Mg_{0.139}Ti_{0.025}Mn_{0.002})$ $[Si_{6.098}Al_{1.899}P_{0.003}O_{20}]\ (OH)_2$
GS/2M Jedlinka G.	muscovite	$(K_{1.404}Na_{0.185}Rb_{0.004}Ca_{0.002})(Fe_{0.139}Mg_{0.094}Mn_{0.002})(Al_{2.539}Ti_{0.017})$ $[Al_{2.216}P_{0.002}Si_{5.782}O_{20}](OH)_2$
GS/3M Kolce	muscovite	$(K_{1.487}Na_{0.164}Ca_{0.008}Ba_{0.006}Rb_{0.002})(Fe_{0.172}Mg_{0.148}Mn_{0.003})$ $(Al_{2.278}Ti_{0.034})\ [Al_{2.572}P_{0.001}Si_{5.427}O_{20}](OH)_2$
GS/4M Osówka	muscovite	$(K_{1.481}Na_{0.156}Rb_{0.003}Ba_{0.002}Ca_{0.003})(Fe_{0.209}Mg_{0.161}Mn_{0.004})$ $(Al_{2.249}Ti_{0.03})\ [Al_{2.542}Si_{5.458}O_{20}](OH)_2$
GS/7M Sokolec	muscovite	$(K_{1.518}Na_{0.178}Ca_{0.009}Rb_{0.003}Ba_{0.001})(Fe_{0.134}Mg_{0.117}Mn_{0.003})$ $(Al_{2.36}Ti_{0.037})\ [Al_{2.578}P_{0.002}Si_{5.42}O_{20}](OH)_2$
GS/14M Michałkowa	muscovite	$(K_{1.552}Na_{0.2}Rb_{0.002})(Fe_{0.142}Mg_{0.097}Mn_{0.001})(Al_{2.403}Ti_{0.026})$ $[Al_{2.604}P_{0.004}Si_{5.392}O_{20}]\ (OH)_2$
GS/13B Bystrzyckie lake	biotite	$(K_{1.477}Ca_{0.118}Na_{0.113}Ba_{0.008}Rb_{0.003})(Fe_{2.073}Mg_{1.998}Mn_{0.02}Zn_{0.004})$ $(Al_{0.233}Ti_{0.35}Cr_{0.008}V_{0.06})\ [Al_{2.831}P_{0.02}Si_{5.149}O_{20}]\ (OH)_2$
GS/14B Michałkowa	biotite	$(K_{1.607}Na_{0.068}Ca_{0.012}Rb_{0.004}Ba_{0.005})(Fe_{2.62}Mg_{1.43}Mn_{0.035}Zn_{0.009})$ $(Al_{0.119}Ti_{0.838}\ V_{0.004}Cr_{0.002})\ [Al_{3.132}P_{0.002}Si_{4.866}O_{20}]\ (OH)_2$
GS/1B Lutomia	biotite	Due to the alteration process it was impossible to calculate the formula

The muscovites from Kolce-Walim (GS/3M) and Sokolec (GS/7M) pegmatites can be a good example of it.

Ti content in the muscovite ranges from 0.18 wt.% to 0.41 wt.%. The maximum TiO_2 contents are contained in Mg and Fe biotites, lowest TiO_2 is shown by the most Li-rich micas. It is generally known that TiO_2 content decreases with advancing crystallization. According to Puziewicz (1987) muscovite containing less than 0.30 wt.% of Ti was formed during the post-magmatic stage of crystallization. Hence, muscovites (GS/1M, GS/2M and GS/14M) probably crystallized later than the muscovites (GS/3M, GS/4M, GS/7M) which host a little higher concentration of TiO_2 (Table 2).

Tetrahedral sites of **trioctahedral micas** are mainly filled by Si and Al, P appears in traces. Fe, Mg, Ti, Al and Mn are largely dominant in the octahedral sites, while V, Cr and Zn show typically low concentrations. Interlayer sites are mainly filled with K and minor amounts of Na, Ca, Rb and Ba (Table 1).

Using molecular proportions, the chemical indices of alteration (CIA) (Nesbitt, Young 1982, *fide* Mongelli et al. 1996) were calculated for the biotites to be 70 (GS/1B),

TABLE 2

The content of major elements in the micas from pegmatites of the Góry Sowie Mts

Main elements [wt. %]	GS/1M	GS/1B	GS/2M	GS/3M	GS/4M	GS/7M	GS/13B	GS/14M	GS/14/B
SiO_2	45.23	33.62	47.91	44.88	45.5	44.95	36.34	44.93	33.48
Al_2O_3	34.77	19.07	33.43	34.03	33.89	34.75	18.35	35.4	18.98
TiO_2	0.24	4.02	0.18	0.37	0.33	0.41	3.28	0.28	3.51
Fe_2O_3	2.1	5.17	1.53	1.89	2.31	1.48	19.44	1.54	23.96
FeO		15.59							
MnO	0.01	0.32	0.02	0.025	0.03	0.03	0.16	0.01	0.28
MgO	0.69	8.36	0.52	0.82	0.9	0.65	9.46	0.54	6.6
CaO	0.02	1.72	0.18	0.06	0.02	0.07	0.78	*	0.08
Na_2O	0.86	0.23	0.79	0.7	0.67	0.76	0.41	0.86	0.24
K_2O	10.29	6.3	9.12	9.64	9.68	9.87	8.17	10.14	8.67
P_2O_5	0.03	0.03	0.02	0.01	*	0.02	0.17	0.04	0.02
H_2O^+	5.64	4.31	5.54	6.54	6.6	6.37	2.77	6.31	3.41
F	*	*	*	0.19	0.19	*	*	0.08	0.27
Total	99.90	100.45	99.24	99.15	100.13	99.36	99.34	100.12	99.51

* Not determined.

68 (GS/14B) and 66 (GS/13). The biotite from Lutomia (GS/1B) is slightly or moderately weathered, while the biotite from the Bystrzyckie lake (GS/13) is relatively fresh. It corresponds well to X-ray investigations. X-ray patterns of the biotites from Michałkowa (GS/14B) and the Bystrzyckie lake (GS/13B) have no chlorite reflections.

The biotite (GS/13B) hosts rather high content of Co (Table 3). Cobalt enrichment may be observed in micas formed during interaction of granitic/pegmatitic melt and metamorphic country rock (Tischendorf et al. 2001). The more Cr is present the more V occurs (Zawidzki 1971). The low concentration of Cr in biotite is associated with magmatic genesis of granitoid rocks, while the significant amount of this element shows metamorphic and metasomatic origin of the host rocks (Fröhlich 1960; *fide* Zawidzki 1971). Fairly high concentrations of V and Cr were detected in the biotites, the highest in the biotite (GS/13B): V-356 ppm, Cr-489 ppm.

There is very low content of Be in the biotites (1–3 ppm). Sachanbiński (1971) detected on average 5.5 ppm in biotites from the Góry Sowie Mts pegmatites.

TABLE 3

The content of trace elements in the micas from pegmatites of the Góry Sowie Mts

Trace elements [ppm]	GS/1M	GS/1B	GS/2M	GS/3M	GS/4M	GS/6M	GS/7M	GS/11B	GS/13B	GS/14M	GS/14/B
As	**	3	**	2	16	0.5	12	84	2	6	6
B	*	*	*	*	*	14	*	2	*	*	*
Ba	86	876	64	1123	434	27	217	1350	1350	28	718
Be	5	1	8	4	9	3	7	1	1	2	3
Bi	*	*	**	16	**	1.5	**	0.2	**	**	5
Cd	**	1.9	**	**	**	**	**	0.2	0.4	**	**
Ce	**	14	2	2	1	1	2	14.2	5	**	2
Co	2	28	1	3	4	0.2	2	39.5	62	3	42
Cr	**	120	3.5	4.5	1.5	1	**	134	489	5	138
Cs	7.5	19.5	11	4.5	11.7	22.6	13.5	22	21	9.2	47
Cu	4	**	33	30	144	5.5	16	9.6	130	30	35
Ga	*	*	*	*	*	21.5	*	24.4	*	*	*
Hf	1	1.5	0.5	**	0.5	**	**	0.2	1.1	**	0.8
La	**	5.5	1	1	0.5	**	0.8	6	2	0.5	1.6
Li	19	116	*	*	*	9	*	129	*	*	*
Lu	**	0.5	0.1	0.02	0.2	**	0.1	0.2	0.06	0.03	0.1
Nb	*	*	*	*	*	2	*	4.6	*	*	*
Nd	*	*	**	**	**	0.1	**	10	3	**	1
Ni	23	30	**	**	4	0.5	**	78.4	161	3	57
Pb	*	*	**	11	17	4.5	3	7.2	18	11	59
Rb	453	335	429	223	305	96.5	306	326	344	273	400
S	*	*	10	10	10	30	**	60	180	20	230
Sc	55	83	9.5	32.5	23.5	*	35	*	39	79	54
Sm	**	1.1	0.2	0.2	0.2	**	0.2	3	0.8	0.2	0.4
Sn	*	*	*	*	*	31.4	*	11	*	*	*
Sr	5	14	6	19	9	1	10	2	21	2	4
Ta	4	7	5	2	4.5	0.05	4.4	**	3.6	4.2	9
Th	0.5	1.5	0.5	0.1	0.2	**	0.1	0.5	**	0.6	**
Tl	*	*	*	*	*	0.5	*	2.5	*	*	*
U	**	5	0.5	**	1.5	**	2	1.5	0.6	0.6	1
V	5	312	**	10	9	2	11	232	356	**	233
W	40	**	14	25	12	3	27	1	3	33	4
Y	3	14	2	**	22	0.1	3	16.4	11	1	5
Zn	79	524	53	39	58	14	37	369	326	43	666
Zr	21	33	13	11	18	0.4	1	5	49	5	14

GS/6. GS/11 — semi-quantitative analysis;
* Not determined;
** Not detected.

The relatively high content of Na is observed in the biotite from Lutomia (GS/1B). Chloritized biotite is enriched in Na and depleted of LREE and Th (Mongelli et al. 1996). The biotites are rather depleted of Th and LREE.

Strontium is enriched in late fractions relative to Ca, although the concentrations of both elements decrease. The biotites possess rather low content of Sr.

The biotites host low concentrations of Li, Cs and F which indicate these minerals were formed probably in early stage of post-magmatic crystallization.

Generally, dioctahedral micas show lower content of trace elements than coexisting biotites. Sn and W are the exception of this rule (Neves 1997). Here, W also shows clear preference for the muscovites. This element ranges from 12 ppm to 40 ppm in the muscovites and from 1 ppm to 4 ppm in the biotites.

According to Zawidzki (1971), Cr and V generally show preference for muscovite. Here, the biotites (GS/1B, GS/14B) host more content of these elements than coexisting muscovites (GS/1M, GS/14M).

The K/Rb ratio increases in the sequence biotite-muscovite (Černy et al. 1985). It is consistent with authors' observations (GS/1M = 213, GS/1B = 174, GS/14M = 280 and GS/14B = 180).

Sr and Ba show preference for muscovite (Zawidzki 1971). However these elements, especially Ba, are highly concentrated in the biotites than in the coexisting muscovites from the Góry Sowie Mts pegmatites (Table 3).

Ta-bearing complexes are stable at low temperature (Černy et al. 1985), accordingly the micas of the Góry Sowie Mts pegmatites host only traces of Ta.

Not all detected trace elements were used for mica genesis interpretation. However, it is scientific documentation and can be used by other authors concerned with similar problems. Trace elements: Eu, In, Sb, Se, Tb, Te, Yb were detected, but their concentration is below 1 ppm, therefore they were not included in the Table 3.

CONCLUSIONS

The micas from the Góry Sowie Mts pegmatites host very low concentration of F, Rb, Cs, Li, Sn, REE and Ta. The impoverishment in these elements indicate early post-magmatic crystallization. High-temperature genesis of the micas may also be confirmed by a high content of Ba. The Sr/Ba ratio increases with advancing crystallization. The low Sr/Ba ratio in the biotites (0.01–0.001) also indicates early crystallization of the micas. High concentrations of Cr in the biotites may confirm anatectic genesis of the Góry Sowie Mts pegmatites. Pegmatitic veins occur within metamorphic rocks. The biotites depleted of REE are characteristic of primitive pegmatites. Mineralogical and geochemical investigations of the micas from the Góry Sowie Mts confirm that the minerals represent an early stage of post-magmatic crystallization.

Concentration of Ti in the muscovites confirms the post-magmatic genesis of the host rocks (pegmatite). Relatively simple mineral composition, characteristic of primitive pegmatites, may confirm relatively high-temperature crystallization of the rocks.

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BADANIA MINERALOGICZNE I GEOCHEMICZNE MIK Z PEGMATYTÓW GÓR SOWICH

Streszczenie

Minerały grupy mik pochodzące z pegmatytów Gór Sowich zostały poddane badaniom mikroskopowym, rentgenowskim, spektroskopowym w podczerwieni i chemicznym. Określono zawartości w nich pierwiastków głównych, pobocznych i śladowych. Miki są bardzo czułymi wskaźnikami procesów petrogenetycznych, dlatego też analiza składu chemicznego tych minerałów pozwala przybliżyć warunki fizykochemiczne środowiska powstania skały macierzystej. Zubożenie mik w pierwiastki takie jak F, Rb, Cs, Li, Sn i REE, a wzbogacenie w Ba przemawia za wczesną, wysokotemperaturową krystalizacją pomagmową. Podwyższona koncentracja Cr w biotytach sowiogórskich może być związana z metamorficznym otoczeniem pegmatytów z Gór Sowich.