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MUSCOVITES FROM GREISENS OF MARTWY KAMIEŃ NEAR MIRSK (LOWER SILESIA)

A b s t r a c t . Muscovites from quartz-muscovite and quartz-topaz-muscovite greisens and greisenised leucogranite from the Izera Upland were investigated. The white micas of Martwy Kamień have revealed low amounts of most of trace elements, probably due to hydrothermal processes. Enrichment in F, Rb and Cs as well as depletion of Ti, Zn and Cd seem to confirm low-temperature genesis of the white micas.

Key-words: muscovite, greisen, post-magmatic genesis, hydrothermal processes, the Izera Upland

INTRODUCTION

Micas are common sheet silicates, which due to their specific crystalline structure, exhibit an extraordinary ability in incorporation many subordinate and trace elements. Chemical analyses of micas can be helpful in establishing a genesis of these minerals. Some valuable information on the greisen rocks from Martwy Kamień near Mirsk was collected by Kozłowska (1956), Wieser (1956), Heflik (1960, 1964), Pawłowska (1966), Karwowski (1972, 1977), Karwowski and Kozłowski (2002).

Muscovites occurring in these rocks were the object of the study.

GEOLOGICAL SETTING

The Variscan Karkonosze granitoid massif with the metamorphic Izera complex form together the Karkonosze — Izera block (Karwowski, Kozłowski 2002) in the Sudetes Mountains. The area of the Izera Mountains is built mainly of gneisses, granitoids, mica or amphibole schists. The greisens outcrop out in the area of Mirsk

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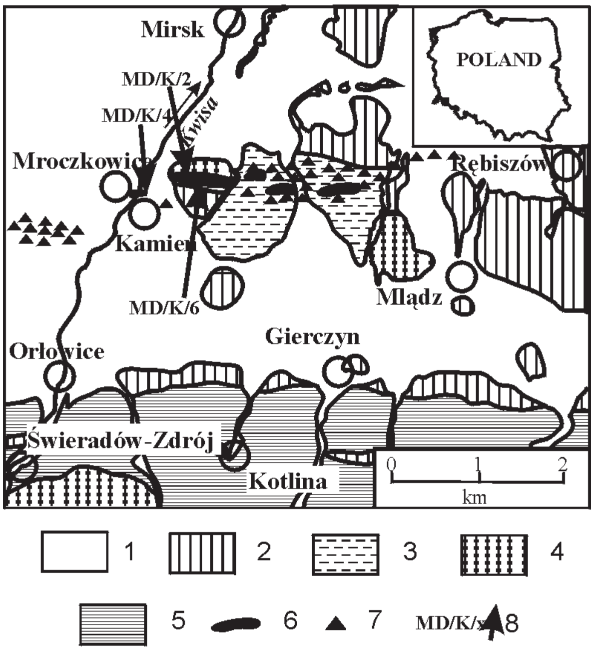
Dale, especially in the bed of the Kwisa River, at the Wyrwak Hill (also known as Martwy Kamień) in the Kamień village near Mirsk, and in the abandoned open-pit kaolin mine near Mlądz (Fig. 1). At the Martwy Kamień Hill the following rock types have been distinguished: leucogranites, leucogneisses, quartz-feldspar-muscovite greisen, quartz-muscovite greisen, quartz-muscovite-topaz greisen, quartz-topaz greisen, irregular muscovite, topaz and tourmaline zones, quartz-tourmaline-muscovite greisen, mica-chlorite schists, amphibolites schists, amphibolites and epidiabases (Karwowski, Kozłowski 2002). The greisens formed from the protholit of the older rocks of granitoid type composition which had passed metamorphic processes. Their genesis is probably connected with post-magmatic activity of the Karkonosze granitoid massif (Karwowski, Kozłowski 2002). Some of the greisen rocks contain relics of Rumburk granitoids, mainly typical blue quartz.

At the Martwy Kamień Hill quartz-mica greisen (K/2), quartz-topaz-mica greisen (K/4) and leucogranite (K/6) were collected for a detailed mica study. The major components of K/2 greisen include quartz and muscovite; fluorite, wolframite, secondary scheelite, apatite and rutile appear among minor minerals. K/4 greisen is mainly built of topaz, quartz and muscovite; apatite, fluorite, zircon, monazite, REE phosphates, ferberite, scheelite and Ti-Nb minerals occur in traces. The rocks' gaps are



1 - Cenozoic
2 - gneisses and granite-gneisses
3 - kaolinitized gneisses
4 - leucogranites
5 - amphibolites, amphibolite schists, mica-chlorite schists
6 - greisens
7 - detached block of greisen
8 - number of sample

Fig. 1. Geological sketch map of part of the Izera Upland (Berg 1925; Berg, Ahrems 1925)

filled with light mica (sericite) and dickite. Among these varieties of greisens the tourmaline zones occur. K/6 leucogranite consists of secondary albite after plagioclase and K-feldspar (chessboard albite), quartz, relicts of K-feldspars and muscovite. Dark mica (biotite) occurs rarely.

METHODS

For the identification and detailed characterisation of the Martwy Kamień micas the following methods were applied: microscopic observations, chemical analyses, infrared spectroscopy, X-ray diffractometry and EPR spectroscopy. The mica samples were taken from the following rock types: K-2 — quartz-mica greisen, K/4 — quartz-topaz-mica greisen and K/6 — partly greisenised leucogranite (Fig. 1).

Microscopic observations were carried out in transmitted light with the Jenapol microscope.

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 determined by ICP-AES. The analyses were made using ICP-spectrometers (a JARRELL ASH model Enviro and a PERKIN ELMER model 6000). Over 20 other trace elements, including some REE, were measured using INAA. The investigations were carried out with 2 MW Pool Type reactor (neutron beam — 5×10^{11}n $cm^{-2}s^{-1}$) and a CANBERRA detector. The formula unit of the muscovites was calculated in relation to 22 oxygens pfu.

Infrared spectra in the region 400–3700 cm^{-1} were obtained using a BIO-RAD FTS 165 spectrometer. Monocrystals of micas flakes were pressed in KBr discs. Special attention was paid to the OH stretching bands.

X-ray investigations were carried out on powdered, randomly oriented samples using a Philips X'PERT diffractometer with a graphite monochromator under the following conditions: CuKα radiation (λ =1.53), scanning speed 0.02°(2θ)/1 sec., recorded range 5–75°(2θ). The X-ray diffraction method was applied to determine mica polytypes.

EPR investigations were conducted at the Physicochemical Analyses and Structural Research Laboratory at the Faculty of Chemistry at the Jagiellonian University. The spectra were obtained with a Bruker ELEXSYS spectrometer under the following conditions: field modulation frequency 100 KHz and temperature 293K. Available parameters are: field modulation amplitude 3.2, time-constant 0.081 s. The spectra were recorded in the range 0–5000 G.

RESULTS AND DISCUSSION

The microscope investigations of thin sections revealed that there are two kinds of muscovites in the greisens: relatively large flakes of primary muscovite and tiny flakes of secondary muscovite which fills spaces among other greisens' originated minerals. Relatively large, frayed muscovite flakes, sometimes exhibiting mechanical deformations, are genetically connected with the gneisses (Karwowski 1972, 1977).

In the X-ray patterns all basal reflections of the muscovites correspond to the $2M_1$ polytype (Fig. 2).

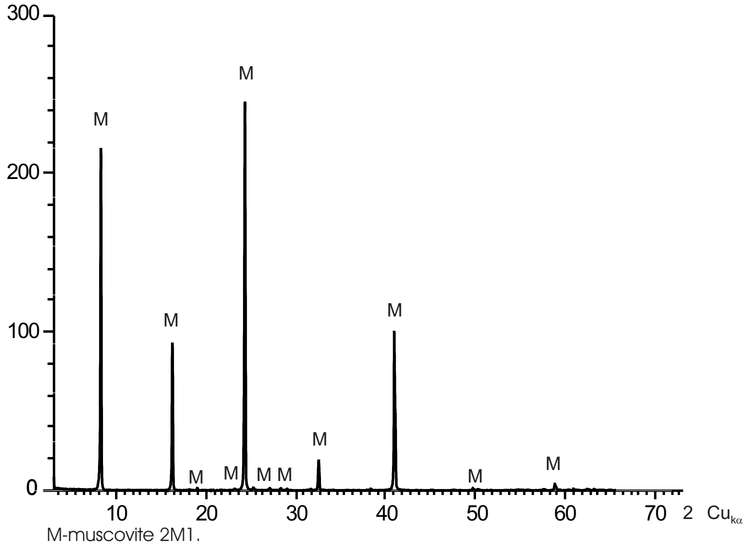


Fig. 2. The X-ray powder diffraction pattern of the muscovite from the K/4 greisen

In the OH stretching region of the absorption spectra of the muscovite from the K/2 greisen there is a wide band at 3655–3627 cm^{-1}. The same band in the muscovite from the K/4 sample occurs at 3646 –3627 cm^{-1} and in the mica from the K/6 greisen at 3647––3627 cm^{-1} (Fig. 3). The position of this band confirms that the OH groups are coordinated with Al-Al cations (Langer 1981, *fide* Mottana et al. 2002). The weak band at 1684 cm^{-1} in the IR spectra of the muscovite from K/6 sample can be caused by N-H bending vibrations (Bastoul et al. 1993). The bands at 1684 cm^{-1} (K/6), 1670 cm^{-1} (K/2) may be associated with H_3O^+ vibrations (Kubisz, Żabiński 1988), however the most characteristic bands of this ion (at 2445 cm^{-1} and 3400 cm^{-1}) have not been recorded.

In the EPR spectra of the K/2, K/4 and K/6 muscovites there are lines associated with octahedral Fe^{3+}. Only the muscovite from K/6 sample shows also characteristic line of Mn^{2+} (Fig. 4), as this mica possesses the highest content of this element (Table 1).

The structural formulae of the muscovites are as follows:

- $(K_{1.52}\,Na_{0.21}\,Rb_{0.01})(Fe_{0.14}\,Mg_{0.02}\,Al_{3.77})[Al_{1.54}\,Si_{6.46}\,O_{20}](F_{0.35}\,OH_{3.65})$
  Muscovite K/2
- $(K_{1.62}\,Na_{0.34}\,Ca_{0.08}\,Rb_{0.01})(Fe_{0.15}\,Mg_{0.04}\,Al_{3.72})[Al_{1.84}\,Si_{6.16}\,O_{20}](F_{0.41}\,OH_{3.59})$
  Muscovite K/4
- $(K_{1.70}\,Na_{0.14}\,Ca_{0.01}\,Rb_{0.01})(Fe_{0.21}\,Mg_{0.03})(Al_{3.65}\,Ti_{0.01})\,[Al_{1.56}\,Si_{6.44}O_{20}](F_{0.27}\,OH_{3.73})$
  Muscovite K/6

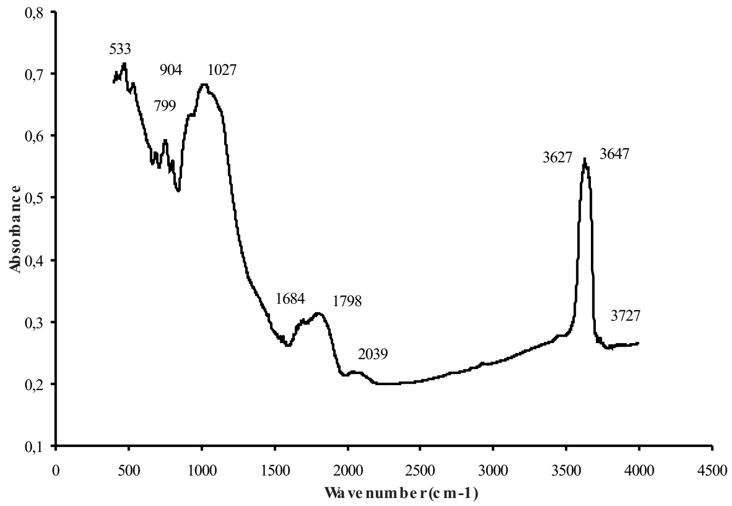


Fig. 3. The IR spectrum of the muscovite from the K/6 greisen

As can be seen, the interlayer sites are occupied by K, Na, Ca and Rb; in the octahedral positions occur Al, Fe, Mg, Ti and Mn, while in the tetrahedral ones there are mainly Si, Al and subordinately P. The relatively low TiO_2 content (Table 1) in the muscovites confirms post-magmatic genesis of the host rocks (Puziewicz 1987). The amount of Ti decreases with the temperature drop. The Na/(Na+K) ratio is 0.07 for K/2, 0.11 for K/4 and 0.04 for K/6 muscovites. Hydrothermal muscovite has the Na/(Na+K)

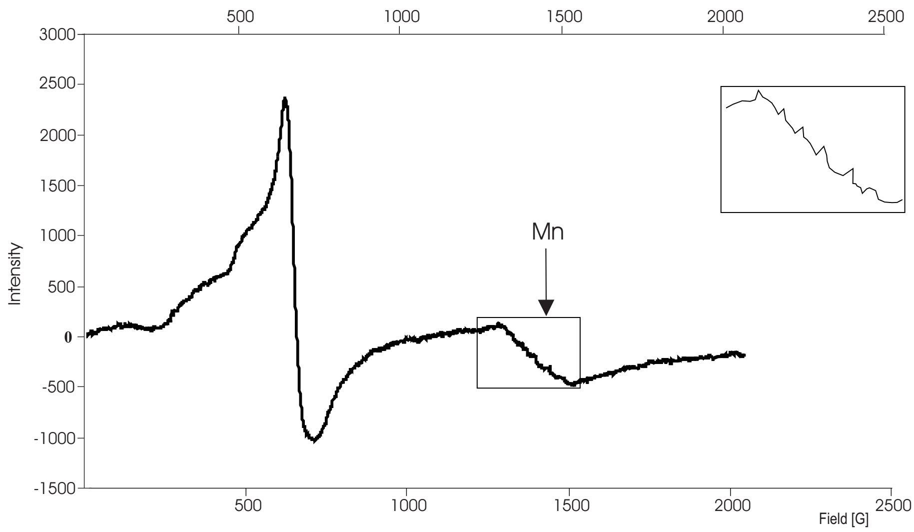


Fig. 4. The EPR spectrum of the muscovite from the K/6 greisen

TABLE 1

Major element composition of the muscovites from Martwy Kamień [wt.%]

Main elements	K/2	K/4	K/6
SiO_2	49.35	46.27	48.73
Al_2O_3	34.41	35.44	33.47
TiO_2	0.045	0.037	0.101
Fe_2O_3	1.42	1.5	2.15
MnO	0.011	0.011	0.031
MgO	0.09	0.19	0.14
CaO	0.02	0.51	0.04
Na_2O	0.82	1.32	0.53
K_2O	9.1	9.52	10.09
P_2O_5	0.07	0.08	0.08
H_2O^+	4.54	5.25	4.51
F	0.83	0.98	0.65
Total	100.71	101.11	100.52

ratio lower than 0.04 while postmagmatic muscovites have this ratio between 0.01 and 0.07 (Bailey 1984). The muscovites from the greisens studied could be formed during different processes. Probably the muscovite from K/6 greisen was formed during hydrothermal processes.

The concentration of Cd and Zn decreases with progressing igneous fractionation (Černy at al. 1985), so depletion of Zn and lack of Cd confirm also post-magmatic genesis of the micas. K is a major element which can be substituted for by Rb and Cs. Both elements accumulate in late fractions of a melt (Černy et al. 1985). The concentrations of Rb in the muscovites studied vary from 0.12 to 0.15 wt%, which is quite significant amount of it. Similarly, the muscovites are rather rich in Cs, as its content reaches 92 ppm in the muscovite (K/4). The enrichment in F in all muscovites can be a proof of hydrothermal activity. The highest concentration of F is in the muscovite (K/4) which is about 0.98 wt% (Table 1). Relatively low Cr and V but high Rb and Cs contents of the muscovites indicate a "metasomatic" replacement (Bailey 1985). Low amounts of Ba in the interlayer sites of micas are characteristic of micas coming from the most fractionated rocks (Černy at al. 1985). The K/4muscovite is relatively enriched in Ca what can be connected with its probable hydrothermal genesis. The muscovites are slightly enriched in Ta (Table 2) and it is known that Ta — bearing complexes are stable at low temperatures (Černy at al. 1985).

Interestingly, the muscovites have low Li content. Depletion of Li may be caused by a far distance of hydrothermal fluids source. If the Karkonosze granitoids are the hydrothermal fluid source, the elements migration is rather distant. However, if it is other source of the fluids — e.g. metamorphic originated one, so it was probably

TABLE 2

Trace element composition of the muscovites from Martwy Kamień

Trace elements [ppm]	K/2	K/4	K/6	Detection limit
Ag	–	–	1	0.5
Au [ppb]	–	7	5	5
As	–	–	–	2
B	63	–	67	2
Ba	44	137	78	3
Be	9	8	7	1
Bi	–	–	–	10
Br	–	–	–	1
Cd	–	–	–	0.5
Ce	–	–	–	3
Co	4	1	2	1
Cr	–	4	–	1
Cs	66	92.5	82.5	0.5
Cu	2	2	1	1
Eu	–	–	–	0.1
Hf	–	–	0.5	0.5
La	1	1	0.7	0.5
Li	8	–	31	1
Lu	–	0.2	0.05	0.05
Mo	–	–	–	5
Nd	–	–	–	5
Ni	7	–	6	1
Pb	5	9	3	5
Rb	1250	1470	1410	20
Sb	1	2	1.5	0.2
Sc	8.5	13	17.5	0.1
Se	–	–	–	3
Sm	0.5	0.5	–	0.1
Sn	210	–	233	1
Sr	11	39	7	2
Ta	8	17	10	1
Tb	–	–	–	0.5
Th	1	5	1	0.5
U	0.5	5	1	0.5
V	–	–	–	5
W	67	1480	68	3
Y	1	4	–	1
Yb	–	1.2	0.5	0.1
Zn	12	10	25	1
Zr	7	21	7	4

– — Under detection limit.

depleted of Li. Besides, greisens were formed in the contact with rocks enriched in micas, which probably had assimilated almost the whole amount of Li.

Hydrothermal fluids were probably enriched in Sn as the micas studied possess relatively high amount of this element (Table 2).

The noticeable high W content in the K/4 muscovite 0.15 wt% is most probably related to contamination with scheelite.

Poor concentration of REE in the micas studied may be connected with scattered mineralization of REE phosphates within fine quartz veins.

CONCLUSIONS

The greisens muscovites exhibit very simple chemical composition. It was expected that the micas coming from rocks, formed by greisenization of gneisses and metasomatic process at 450–300°C and pressure of 800 atm (Karwowski 1972, 1977), would show more chemical diversity. However, the chemical analyses have revealed low concentration of trace elements in micas. Hydrothermal process is the one which can be responsible for depletion of many trace elements in micas (Zawidzki 1973, *fide* Karwowski 1977). On the whole, enrichment in F, Rb and Cs confirms post-magmatic genesis of host rocks, so does the depletion of Ti, Zn and Cd. Naturally, mineral composition of host rocks, especially the presence of topaz and tourmaline, as well as geochemical data of the micas seem to confirm that the micas are of pegmatite-pneumatolytic origin and were later affected by hydrothermal fluids.

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MUSKOWITY ZE SKAŁ GREJZENOWYCH Z KAMIENIA KOŁO MIRSKA (DOLNY ŚLĄSK)

Streszczenie

Muskowity pochodzące ze skał grejzenowych z Kamienia koło Mirska zostały poddane badaniom chemicznym, rentgenowskim, spektroskopowym w podczerwieni oraz elektronowego rezonansu paramagnetycznego. Miki te posiadają stosunkowo ubogi skład chemiczny. Nieznaczne zawartości niektórych pierwiastków śladowych w badanych mikach są prawdopodobnie związane z działalnością procesów hydrotermalnych. Wzbogacenie mik w pierwiastki takie jak F, Rb, Cs, jak również zubożenie przebadanych łyszczyków w Ti, Zn i Cd, wydaje się potwierdzać niskotemperaturową genezę tych minerałów. Na powstanie badanych mik zasadniczy wpływ miały procesy pneumatolityczne i hydrotermalne, co potwierdza także skład mineralny skał macierzystych, zwłaszcza obecność takich minerałów, jak topaz i turmalin.