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GADOLINITE FROM THE MICHAŁOWICE QUARRY, KARKONOSZE MASSIF, SW POLAND

Abstract: Gadolinite crystal 16 mm long was collected from a pegmatite in the quarry at Michałowice, in the northern part of the Karkonosze Variscan granitoid massif. The studied mineral is metamictic gadolinite-Y with only 0.14 vacancies, 0.32 (OH) and 0.04 F pfu. The content of total REE is 1.64 apfu and relatively high content of boron reaches 0.21 apfu. Homogenization studies of fluid inclusions in quartz coeval with gadolinite yielded temperatures 327-347°C; tentative determinations of pressure during the gadolinite crystallization gave values 1-1.2 kbar. The parent solutions were aqueous with ca. 15% NaCl, 3% KCl and 3% CaCl₂; carbon dioxide was present.

Key words: gadolinite, pegmatite, fluid inclusions, temperature, pressure, Karkonosze

INTRODUCTION

Karkonosze Variscan granitoid massif, located in the north-eastern marginal part of the Bohemian massif (Mazur et al. 2007), contains numerous pegmatites consisting mainly of microcline, albite, quartz, biotite, muscovite, chlorite and hematite. The detailed list of the Karkonosze pegmatite minerals may be found in the paper published by Kozłowski and Sachanbiński (2007).

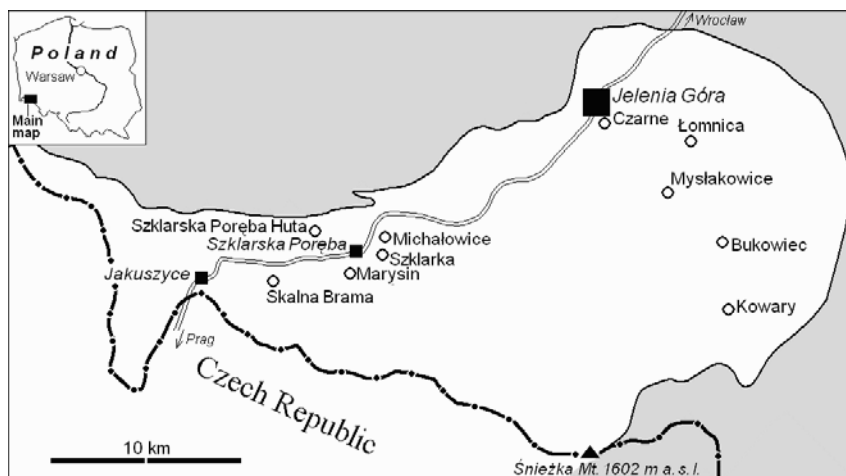


Fig. 1. Locations of the gadolinite-bearing pegmatites, marked as circles, in the Polish part of the Karkonosze granitoid massif.

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As the minor components, the pegmatites contain numerous minerals, the rare earth ones inclusively (*op. cit.*). Gadolinite apparently occurs relatively frequently (Fig. 1) and was noted from pegmatites found at Marysin in Szklarska Poręba, in the quarry at Szklarska Poręba Huta, in the rocks of Skalna Brama, in the Szklarka Creek valley, moreover at Czarna, Bukowiec, Łomnica, Mysłakowice, Kowary and Michałowice (*see* Kozłowski and Sachanbiński 2007, and the references quoted there).

THE SAMPLE

The investigated crystal of gadolinite was collected in 1977 in the granite quarry at Michałowice from a typical pegmatite nest ca. 55 by 43 cm in size. The crystal was euhedral, rich in faces (Fig. 2), and its largest dimension was 16 mm. Its colour was black, with tar lustre. The crystal formed between and on quartz, microcline and albite; in its lower part, hidden between the named minerals, large grain of magnetite closely contacted with gadolinite (Fig. 3).

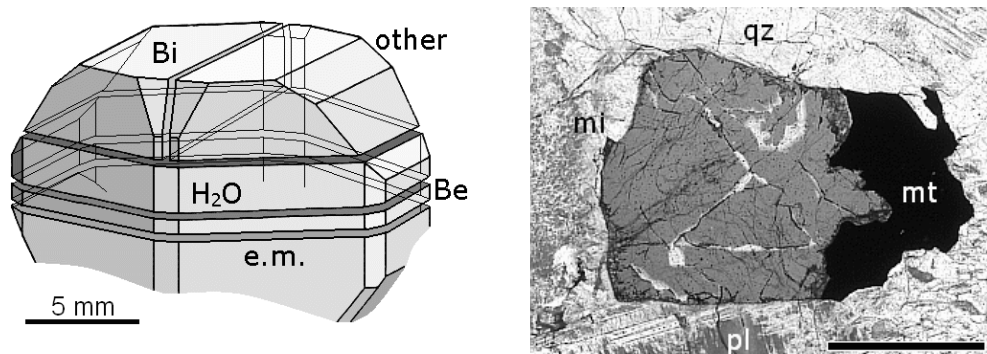


Fig. 2 (*left*). Habit of the studied gadolinite crystal, the parts cut off for various determinations are shown: e. m. – electron microprobe determinations, Be – beryllium determinations, H₂O – water determinations, Bi – bismuth determinations, other – other investigations.

Fig. 3 (*right*). Gadolinite (gray) in the preparation used for the electron microprobe investigations; mt – magnetite, qz – quartz, mi – microcline, pl – plagioclase (albite), scale bar 5 mm.

METHODS OF INVESTIGATIONS

Most of the elements, except for those named below, have been analysed in thin section by means of a Cameca SX 100 electron microprobe (in the Inter-Institutional Laboratory of Microanalysis of Minerals and Synthetic Substances, Faculty of Geology, Warsaw). The analytical procedure for most of elements was as follows: an accelerating voltage of 20 kV and a beam current 10 or 20 nA, natural and artificial standards.

The gadolinite slices for the special methods of the component determinations were cut off from the crystal (Fig. 2) by the tungsten wire micro-saw.

Beryllium was determined quantitatively by the colorimetric methods. The slice was divided into 7 pieces (samples), each piece was powdered, mixed with the Na₂CO₃ flux, fused and dissolved with HCl. Four samples were analyzed for the Be content by the colorimetric alberton method in weakly acid solution, and the three samples – by the colorimetric beryllon III method in alkaline solution. The average BeO content was 10.21 wt. %.

The slice for the water determinations was split in 3 parts, washed by alcohol, dried at 105°C, powdered with K₂CrO₄ and fused in miniature Penfield tubes to determine the water content by weight. The average H₂O+ content was 0.62 wt. %.

Bismuth was determined by spectral emission method, the DFS-13 spectrograph with the 1200 lines/mm diffraction grid was used. The spectrum was recorded in the 2nd order, for the determination the longer-wave component of the Bi 3067.712 Å line was applied (with the detection limit 1 ppm). The powdered sample was mixed with the buffer: graphite 95%, Na₂CO₃ 4.97% and Sb₂O₃ 0.03% as internal standard. Natural epidote, with the same buffer and Bi₂O₃ sp. pure added, was used as the analytical standard. The average value of 7 determinations was 312 ppm Bi.

X-ray diffraction method was applied to check the structural properties of gadolinite. The fluid inclusions were investigated by the conventional heating-freezing microscope stage method.

RESULTS

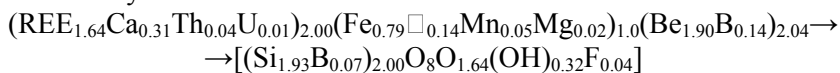
The chemical investigations of the studied mineral yielded the gadolinite-Y composition (Table 1).

Table 1. Chemical composition and crystallochemical formula of gadolinite from the Michałowice quarry

Component	Wt. %	Component	At. pfu	Component	Wt. %	Component	At. pfu
SiO ₂	24.88	Si ⁴⁺	1.93	Dy ₂ O ₃	1.08	Dy ³⁺	0.03
B ₂ O ₃	1.61	B ³⁺	0.07	Ho ₂ O ₃	0.17	Ho ³⁺	0.004
			0.14	Er ₂ O ₃	1.34	Er ³⁺	0.03
BeO	10.21	Be ²⁺	1.90	Yb ₂ O ₃	3.31	Yb ³⁺	0.08
ThO ₂	2.53	Th ⁴⁺	0.04	Lu ₂ O ₃	0.55	Lu ³⁺	0.006
UO ₂	0.56	U ⁴⁺	0.01	CaO	3.72	Ca ²⁺	0.31
Y ₂ O ₃	26.80	Y ³⁺	1.11	MgO	0.15	Mg ²⁺	0.02
La ₂ O ₃	0.87	La ³⁺	0.02	MnO	0.70	Mn ²⁺	0.05
Ce ₂ O ₃	4.38	Ce ³⁺	0.24	FeO	12.22	Fe ²⁺	0.79
Pr ₂ O ₃	0.74	Pr ³⁺	0.02	H ₂ O+	0.62	OH ⁻	0.32
Nd ₂ O ₃	2.27	Nd ³⁺	0.06	F	0.15	F ⁻	0.04
Sm ₂ O ₃	0.53	Sm ³⁺	0.01	Subtotal	100.21	<i>Note:</i> total Fe as bivalent iron; Bi content 0.03 wt. %.	
Gd ₂ O ₃	0.89	Gd ³⁺	0.02	- O = 2F	0.06		
Tb ₂ O ₃	0.08	Tb ³⁺	0.004	Total	100.15		

The heavy horizontal lines in the column with the atoms pfu values separate the groups of elements occurring in the same crystallochemical sites. Other elements than these listed in the Table were below the detection limit.

The calculated crystallochemical formula:



indicates typical gadolinite-Y composition with small shift toward the hingganite field, shown by the 0.14 vacancies, 0.32 (OH) and 0.04 F pfu (Pezzotta et al. 1999). The high content of boron in part replaces beryllium, suggesting the admixture of the homilite end member. However, the content of boron is in excess with respect to the beryllium deficit, but silicon is lacking to the full 2 atoms pfu as well. Thus, we suppose the partial replacement of silicon by boron. The spectrum of the rare earth elements present in the studied gadolinite is rich, only few of them were under the detection limit (Table 1). Ce, Yb and Nd are the most abundant rare earth elements. Thorium distinctly prevails over uranium, but contents of the two elements are low. Calcium occupies only 15% of the large-cation sites.

Bismuth content (312 ppm), though generally low, is rather high when compared with concentrations of this element in the other gadolinite specimens, varying from 12 to 262 ppm (Gurney, Ahrens 1969). This element most probably replaces rare earth elements in the gadolinite structure. On the other hand, the structure was completely metamictised.

The investigated aqueous fluid inclusions in quartz coeval with the gadolinite yielded homogenization temperatures 327-347°C; tentative determinations of pressure during the gadolinite crystallization on the basis of the carbon dioxide inclusion investigations gave values 1-1.2 kbar. The parent solutions were aqueous with ca. 15% NaCl, 3% KCl and 3% CaCl₂ dissolved. Thus, the correction caused by the influence of pressure, which should be added to the homogenization temperatures, is ca. 80 to 90°C.

Acknowledgments: The research work was financially supported by the Warsaw University, Faculty of Geology grant No. BW 1761/14.

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