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Oxygenic bismuth minerals in the NE part of the Karkonosze pluton (West Sudetes, SW Poland)

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ABSTRACT:

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The study presents fifteen oxygen-bearing secondary minerals of bismuth from the north-eastern part of the Variscan Karkonosze granitoid pluton in the northern zone of the Bohemian massif. The minerals were investigated by optical, electron microprobe, classic chemical, XRD, IR absorption and fluid inclusion methods. The late, very low temperature epithermal solutions most probably caused formation of sillénite, kusachiite, bismoclite, bismutite, beyerite, kettnerite, pucherite, schumacherite, namibite and eulytite. Solutions dominated by supergene (meteoric) waters were the parents for bismite, russellite, koechlinite, ximengite and walpurgite. The paper also contains information on early research on the investigated minerals.

Key words: Karkonosze granitoid pluton; Bismuth minerals; Secondary minerals; Oxidation; Vein; Pegmatite.

FOREWORD

The paper presents an investigation of several oxygen-bearing minerals of bismuth, which were found in the Karkonosze granitoid, collected during field work by AK in 1976–1990. Most of the minerals were not known until the present either from the Polish part of the Karkonosze pluton, or from the area of Poland. The publication is a homage to Professor Andrzej Radwański, who was AK's teacher during his geological studies in both theoretical and field aspects. Moreover, he strongly encouraged AK to publish the results of even his earliest investigations, which, as it happened, concerned the Karkonosze pluton (cf. items listed in Kozłowski *et al.* 2016). Although most of Professor Radwański's scientific activity was pertinent to other fields of geology, he remained strongly interested in mineralogical and petrographic problems, probably due to his earliest studies, including his doctorate (Radwański 1968). AK is glad that in the preparation of this paper he was joined by WM as the co-author, interested like him in further investigations of the Karkonosze pluton (see e.g., Matyszczak 2018).

INTRODUCTION

The systematic scientific investigation of the Karkonosze minerals began with the work of Kaluza (1818). A good review of the Silesian mineralogical publications from the then oldest known till 1832 was given by Glocker (1827, 1832). Partsch (1892–1900), in his extensive list of publications, included a very good section on the Silesian mineralogical literature. A thorough compilation of the studies on minerals known from Silesia was given by Traube (1888); his work was updated almost a hundred years later by Lis and Sylwestrzak (1986). Sachanbiński (2005) and then Kozłowski and Sachanbiński (2007) published new information reviews of the Karkonosze minerals. This formed a good and exhaustive background on the search for minerals not found in the Karkonosze pluton until the present. This publication describes part of the studies performed in this context.

GEOLOGICAL SETTING

The Karkonosze pluton belongs to the northern marginal part of the Bohemian massif (for descriptions of the massif see e.g., Franke and Żelaźniewicz 2002; Mazur *et al.* 2007, 2010; Klomínský *et al.* 2010). The pluton, of which outcrops may be traced over an area c. 70 km long (W-E) and 8 to 20 km wide, was one of the topics of Cloos's studies (1922, 1923, 1925). These works yielded information on the mechanism of the origin of the pluton's parent magma and its intrusion. His conclusions were drawn on the basis of c. 50,000 rock observations from the Lower Silesian granitoid intrusions (*vide* Kemp 1925), in large part from the Karkonosze pluton. They included statements on the complex sources of magma and the direction of its migration, different in various parts of the pluton. The shape of the intrusion was suggested by Schwinner (1928) on the basis of gravimetric measurements to be a kind of harpolith c. 4 km thick. The multiphase intrusion of the Karkonosze pluton was confirmed by Žák and Klomínský (2007) and Žák *et al.* (2013), and to a certain degree by Słaby and Martin (2008).

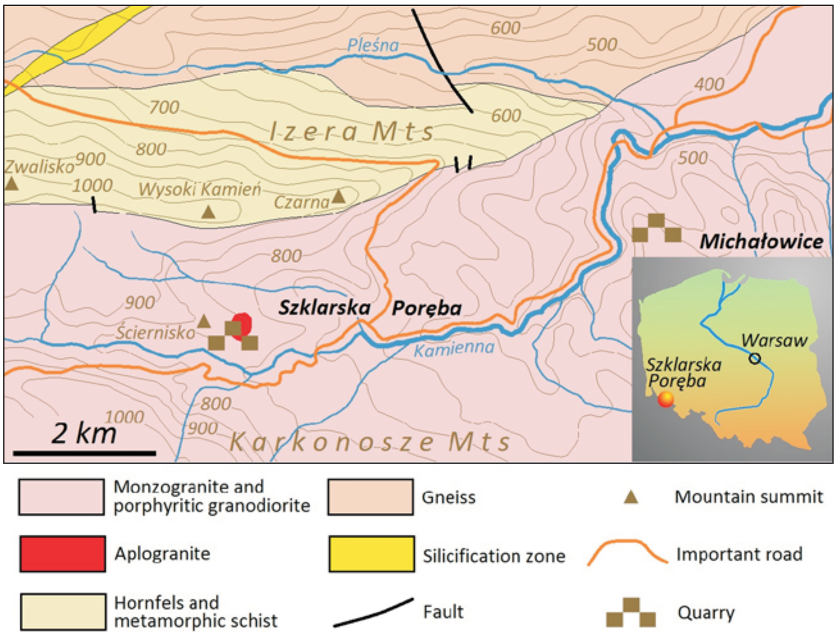
Though recent isotope age measurements gave similar values for the two main granitoid varieties of the Karkonosze pluton, very close to 312 Ma (Kryza *et al.* 2014a, b), this suggests a rather short period of intrusion but does not imply a uniform composition of the parent magma. The pluton consists of a number of mainly granitoid rock types; the early description of the Karkonosze granite was published by Kapf (1790) and later by Manès (1825) with some indications of the lithological differences. Berg (1923) distinguished three main kinds: porphyritic granite occupying the largest part of the pluton outcrops, equigranular granite that formed the highest parts of the Karkonosze Mts, and fine-grained granite with single porphyritic K-feldspars in the northern and eastern parts of the pluton. Borkowska (1966) slightly rearranged this classification, using respectively the names: central, crest and granophyric granites. Since then, more detailed descriptions of the granitoid varieties have appeared (e.g., Chaloupský *et al.* 1989; Klomínský *et al.* 2010), without changing, however, the general scheme. Very careful tectonic, structural, geochemical and petrological features of the whole pluton were presented by Klomínský (1969). The same author with his team published recently a good review of the petrological and mineralogical problems arising from studies of the composite Izera-Karkonosze massif (Klomínský *et al.* 2018).

OUTCROPS STUDIED

The minerals investigated were found in two quarries in the northern zone of the Polish part of the Karkonosze pluton, relatively close to the contact with the Izera metamorphic complex (Text-fig. 1). The quarries are located at Michałowice and at Szklarska Poręba Huta. The quarry at Michałowice, now abandoned, is located in porphyritic (i.e., central) granite. The rock consists of up to c. 1 cm grains of plagioclase, potassium feldspar, quartz and biotite as the dominant phases, with dispersed feldspar crystals up to 8 cm in the largest dimension. The porphyritic grains generally are K-feldspar with albite rims, but commonly their zoning is more complicated, with alteration of several K-feldspar and albite coatings. Granite in this quarry is cut by aplite and quartz veins; it also contains pegmatite nests up to 1 m in size.

The quarry at Szklarska Poręba Huta, currently in operation, is in a large part located in aplite-like granite (called also aplogranite or granophyric granite). This rock is fine- to medium-grained, usually with higher contents of Na_2O and SiO_2 than the neighbouring porphyritic granite. Thus the main minerals of the rock are albite and quartz with subordinate muscovite and relicts of K-feldspar and biotite, the latter usually chloritized. It is probably the result of some differences in the parent magma compositions, and also of post-magmatic albitization and silicification (Kozłowski *et al.* 1975). Post-magmatic processes, mostly hydrothermal, caused the formation of small voids (up to 10 cm in size) lined by albite and quartz with some muscovite or chlorite. Moreover, thin (up to 1 cm) quartz veins with minor albite cut the rock. Aplite-granite contains dispersed ore minerals; they occur also in small voids and in veinlets. Porphyritic granite similar to that from Michałowice is also visible in this quarry.

Ore mineralisation in the rocks of both quarries is of no economic importance, and is of scientific value only. For the Michałowice quarry the list of ore minerals is as follows (in alphabetical order, excluding the minerals formed by supergene alteration): arsenopyrite, bismuthinite, chalcopyrite, covellite, ferberite, fergusonite, gadolinite, galena, hematite, ilmenite, magnetite, molybdenite, native gold, native bismuth, pyrite, rutile, scheelite, siderite, sphalerite, tetrahedrite and thorite (Karwowski *et al.* 1983;



Text-fig. 1. North-eastern section of the Karkonosze pluton with its metamorphic cover; locality map of the Szklarska Poręba Huta and Michałowice quarries (after Berg 1925, 1940, modified)

Kozłowski and Dzierżanowski 2007; Kozłowski and Sachanbiński 2007; Mikulski and Stein 2007, 2011; Kozłowski 2011; Mochnacka *et al.* 2015). The list of the ore non-supergene minerals found in the Szklarska Poręba Huta quarry is much longer: aikinite, arsenopyrite, bismuthinite, canizzarite, cassiterite, chalcopyrite, columbite, cosalite, cuprobismuthite, davidite, emplectite, ferberite, fergusonite, friedrichite, gadolinite, galena, galenobismuthite, gladite, hematite, hingganite-Ce, hingganite-Y, hodrushite, hübnerite, hydroxylbastnaesite, ikunolite, ilmenite, joseite-A, krupkaite, kupčikite, magnetite, marcasite, molybdenite, native silver, native bismuth, niobite, nuffieldite, powellite, pyrite, pyrrhotite, scheelite, sphalerite, stilbite, stolzite, tetrahedrite, thorite, uraninite, wolframite, wulfenite and yttrialite (Karwowski *et al.* 1973; Kozłowski and Karwowski 1975; Kozłowski *et al.* 1975, 2002; Olszyński *et al.* 1976; Pieczka and Gołębiowska 2002; Sachanbiński 2005; Kozłowski and Sachanbiński 2007; Mikulski and Stein 2007, 2011; Mayer *et al.* 2012; Pieczka and Gołębiowska 2012; Mochnacka *et al.* 2015 and references therein).

INVESTIGATION METHODS

The samples were thoroughly checked under a binocular microscope and images of the grains, inferred to be the minerals of interest, were recorded. Next, the grains were separated, if possible with a chip of the mineral on which they had crystallized. The sample, if large enough, was split into two parts, one for electron microprobe analysis and the other for XRD determination. Small samples were first analysed by an electron microprobe and next, after dissolution of the preparation glue in an appropriate organic solvent (acetone, chloroform, or xylene), used in the XRD procedure. ARL and Cameca SX100 electron probe micro-analysers were applied (electron beam accelerating voltage 7–20 keV, beam current 8–12 nA, beam spot diameter 3–8 µm, count time 4–12 sec). Natural sulphide, fluoride, chloride, and synthetic oxide, vanadate and phosphate compounds were the reference materials; the quantitative determinations were made by use of the radiation peaks: Ag*Lα*, As*Lα*, Au*Lα*, Bi*Mα*, Ca*Kα,* Cl*Kα,* Cu*Kα*, F*Kα*, Fe*Kα*, Hg*Mα*, Mn*Kα*, Mo*Kα*, P*Kα*, Pb*Mβ*, S*Kα*, Sb*Lα*, Se*Lα*, Si*Kα*, Te*Kα*, Th*Mβ*, U*Mβ*, V*Kα*, W*Mα*, and Zn*Kα*. The element content calculations were made by the ZAF and MULTI (Trincavelli and Castellano 1999) programs. Carbon dioxide was quantitatively determined by measurements of its volume after carbonate sample (2–20 mg) decomposition in HCl solution. The presence of H_2O and OH^- was checked by the IR absorption method with the use of the Nicolet 6700 spectrometer (radiation source Ever-Glo, beam splitter Ge-coated KBr, DLaTGS-CsI detector); the preparation was a thin film of the mineral mull in nujol onto KBr plate. For the XRD determinations CuK*α* radiation in the X'Pert PRO MPD device was used. Preparations of the mineral powder glued on the glass fibre were mostly made since the amount of the sample was usually very small. Fluid inclusions were investigated by homogenization and freezing immersion methods elaborated for low-temperature inclusions, as described by AK in Matyszkiewicz *et al.* (2016).

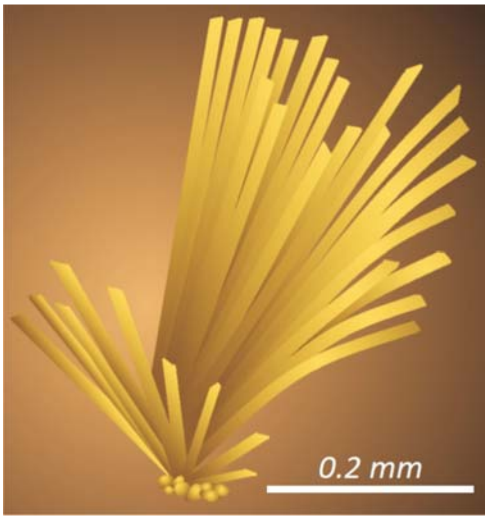
RESULTS

Field work for 15 years in the Karkonosze pluton has resulted in the collection of samples containing a number of interesting minerals, some found in this region for the first time. Studies of the samples revealed a group of fifteen minerals of bismuth, formed under oxidizing conditions, namely bismite, sillénite, kusachiite, russellite, koechlinite, bismoclite, bismutite, beyerite, kettnerite, ximengite, pucherite, walpurgite, schumacherite, namibite and eulytite. Preliminary information on them was published by Kozłowski *et al.* (2016). In this paper the results of more detailed studies are given. The text-figures presenting the minerals were made with the use of computer graphic programs and they clearly show the morphological features and colours of the crystals.

Bismite α-Bi_2O_3[1]

A mineral substance with the supposed composition of bismuth oxide was described by Wallerius (1747); however, the note most probably concerned bismuth carbonate or its mixture with other Bi compounds. The next analytical results for "bismite", given by Lampadius (1801), undoubtedly indicated the presence of Bi carbonate. Suckow (1848) published a true analysis of natural bismuth oxide from Ullersreuth in Thuringia, Germany. The structure of bismite was suggested as orthorhombic by Adolf Erik Nordenskiöld in 1860 (Groth 1906, p. 109). A modern investigation of bismite was published by Frondel (1943a); the structure is pseudoorthorhombic monoclinic (*2/m* prismatic class).

Bismite was found in the quarries at Szklarska Poręba Huta (in 1977) and Michałowice (in 1983). It occurred on quartz in thin veinlets with small grains of bismuthinite, chalcopyrite, arsenopyrite and pyrite. The crystals are laths, sometimes bent, and in two cases arranged in loose fans (Text-fig. 2). More frequently it formed earthy covers or pellets up to 0.5 mm in size. The length of single subhedral crystals also did not exceed this value. Bismite colour was essentially yellow of various, but not very high, intensities, also with brownish, greyish and greenish shades. The crystals were translucent, from nearly completely turbid to almost transparent.



Text-fig. 2. Bismite laths arranged in two fans, an exceptional aggregate; Michałowice

A chemical analysis of bismite from Szklarska Poręba Huta is given in Table 1 as an example. This and another analysis of the specimen from Michałowice recalculated to crystallochemical formulae are respectively: $(Bi_{1.96}Sb_{0.01}As_{0.01}Fe_{0.01}Ag_{0.01})_{\Sigma 2.00}O_3$ and $(Bi_{1.95}Sb_{0.02}As_{0.01}Fe_{0.01}Cu_{0.01})_{\Sigma 2.00}O_3$. Trace amounts (i.e. <0.01 wt. %) of MnO and PbO were found. The chemical identification of the mineral was confirmed by the XRD analysis (Table 2), which was compared to the patterns for bismite published by Frondel (1943a) and Mochnacka *et al.* (2009).

Bismuth ochre in the Szklarska Poręba Huta quarry was first mentioned by Kozłowski *et al.* (1975); it had as one of its components bismite in its earthy form. Mochnacka *et al.* (2015) listed this mineral among others found in this locality. In the eastern outer contact zone of the Karkonosze pluton, bismite was recognised at Rędziny (Parafiniuk 2003) and at Czarnów (Mochnacka *et al.* 2009). Also an occurrence of bismite in the southern Karkonosze pluton contact zone was described by Sejkora and Řídkošil (1997).

[1] Ideal formulae of the minerals are given in the section titles.

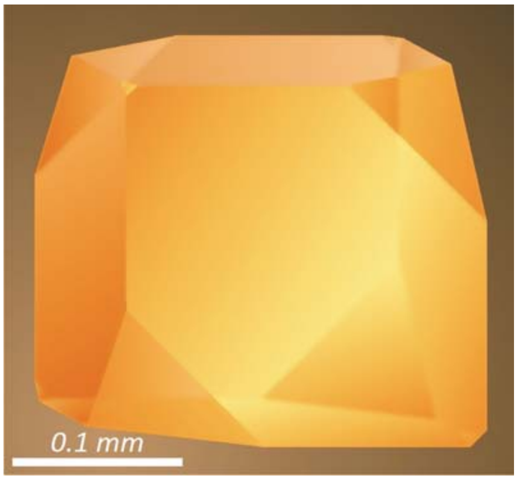
Table 1. Chemical composition in wt. % of the oxygenic bismuth minerals from the Karkonosze pluton. Kusachiite and beyerite specimens from Michałowice, other specimens from Szklarska Poręba Huta; *A* – F, Cl; H_2O calculated, presence confirmed by IR spectra; tr. – traces (0.010-0.001); empty cells – components not detected (<0.001 wt. %)

Component	Bismite	Sillénite	Kusachiite	Russellite	Koechlinite	Bismoclite	Bismutite	Beyerite	Kettnerite	Ximengite	Pucherite	Walpurgite	Schumacherite	Namibite	Eulytite
MoO_3					23.26		tr.								
WO_3				31.69											
UO_3												19.02			
P_2O_5										22.15	0.45	0.45	0.48	0.54	0.64
V_2O_5											27.58	0.31	19.32	12.88	
As_2O_5	0.23		tr.	tr.	tr.	tr.	tr.			1.51	0.36	14.68	0.51	0.35	0.93
SiO_2		2.24													15.23
ThO_2												0.36			
Fe_2O_3	0.20	tr.	tr.	0.82	0.11	tr.	tr.	tr.	tr.	0.53	0.76	0.11	0.27	tr.	0.29
Sb_2O_3	0.30	tr.	0.69	1.07	tr.	tr.	0.29	tr.		tr.	tr.		tr.	tr.	0.66
Bi_2O_3	99.04	97.70	68.74	65.38	76.14	89.36	90.82	74.67	65.04	75.78	70.66	62.27	77.36	70.94	82.16
MnO	tr.		tr.	tr.	tr.					tr.	0.20	tr.	tr.	tr.	tr.
CaO								8.35	15.33						
CuO			29.10		tr.	tr.	tr.	tr.				tr.		12.29	
PbO	tr.			0.98	0.34			2.53	2.52	tr.	tr.	0.30	tr.	tr.	tr.
Ag_2O	0.26	tr.	1.44		tr.		tr.		tr.	tr.	tr.	tr.	tr.	0.18	tr.
F									5.14						
Cl						13.59									
CO_2							8.49	14.18	12.41						
H_2O												2.43	2.04	2.63	
$-O=A_2$						-3.07			-0.48						
Total	100.03	99.94	99.97	99.94	99.85	99.88	99.60	99.73	99.96	99.97	100.01	99.93	99.98	99.81	99.91

Sillénite $Bi_{12}SiO_{20}$

Studies by Sillén (1938) on bismuth trioxides yielded data on their isometric variety determined as γ-Bi_2O_3. After the natural equivalent of this compound was found in an unspecified locality in Durango, Mexico, Frondel (1943a) proposed the name sillénite for this mineral. He also noted the presence of "traces of Si, Al, Cu, Fe, Ca and other elements", detected by the spectral emission method. Further studies of this material indicated the fixed structural positions of certain elements, especially Si (Abrahams *et al.* 1979; Radaev and Simonov 1991). Moreover, investigations of trace elements included in the sillénite structure due to co-doping (Ahmad *et al.* 2011) and their possible non-stoichiometric distribution (Yu 2013) may help to explain the variations in the chemical composition of this mineral.

Sillénite from the Karkonosze pluton was found in a quartz veinlet with bismuthinite, pyrite, molybdenite and chalcopyrite from the Szklarska Poręba Huta quarry (in 1978). It formed single subhedral grains up to 0.5 mm in size in a thin layer of earthy, loose bismite. The colour of transparent crystals was pale orange. One may distinguish crystal faces of the cube and two tetrahedrons, those of the positive tetrahedron were much larger than of the negative



Text-fig. 3. Sillénite crystal drawn on the basis of compilation of 4 subhedral grains of the same habit, each c. 0.3 mm in size; Szklarska Poręba Huta

Table 2. X-ray powder diffraction patterns of the oxygenic bismuth minerals from the Karkonosze pluton. The selection of the most intense reflections of the samples is shown. SP stands for Szklarska Poręba Huta, M stands for Michałowice. Intensity values in italics refer to a 10-grade intensity scale. Numbers in parentheses pertain to the following references: (1) Sejkora and Řídkošil 1997; (2) Kusachi and Henmi 1991; (3) Henmi 1995; (4) Knight 1992; (5) Frondel 1943a; (6) Bannister and Hey 1935; (7) Sahama and Lehtinen 1968; (8) Chandy *et al.* 1969; (9) Hybler and Dušek 2007; (10) Shi 1989; (11) Miyawaki *et al.* 1999; (12) Frondel 1958; (13) Walenta *et al.* 1983; (14) Knorring and Sahama 1981; (15) Parafiniuk 2003

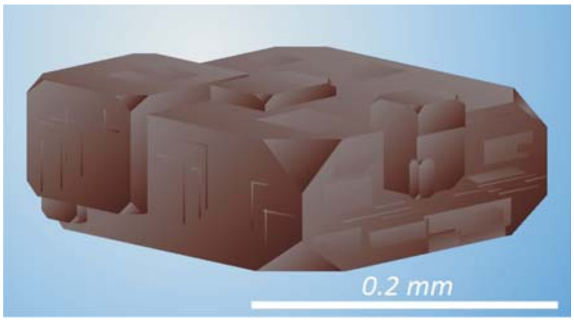
Mineral		d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I	d/n	I
Bismite	SP	3.455	18	3.250	100	3.178	12	2.707	60	2.695	58	2.551	14	2.386	11
	Harrachov (1)	3.454	15	3.252	100	3.183	10	2.709	61	2.696	61	2.554	11	2.391	11
Sillénite	SP	3.570	20	3.200	100	2.920	18	2.695	51	2.260	14	2.151	15	1.985	16
	Fuka (2)	3.573	24	3.197	100	2.917	22	2.701	58	2.260	11	2.155	13	1.983	13
Kusachiite	M	4.250	21	3.190	100	2.915	18	2.695	20	2.402	14	1.950	18	1.728	14
	Fuka (3)	4.260	17	3.191	100	2.913	16	2.695	18	2.404	13	1.947	18	1.728	12
Russellite	SP	3.148	100	2.735	33	2.724	19	2.713	18	1.932	15	1.929	11	1.922	21
	synthetic (4)	3.151	100	2.738	29	2.729	22	2.719	22	1.933	16	1.929	10	1.926	19
Koechlinite	SP	3.129	100	2.730	54	2.679	45	2.470	27	1.931	61	1.914	77	1.642	85
	Schneeberg (5)	3.131	*10*	2.733	*6*	2.683	*5*	2.473	*3*	1.936	*6*	1.918	*8*	1.647	*9*
Bismoclite	SP	3.445	100	2.750	68	2.677	92	2.206	29	1.944	35	1.574	29		
	synthetic (6)	3.440	100	2.751	61	2.675	95	2.204	24	1.945	26	1.573	32		
Bismutite	SP	3.725	33	2.950	100	2.737	40	2.136	27	1.748	23	1.620	29		
	Marropino (7)	3.724	30	2.953	100	2.737	41	2.137	25	1.750	22	1.618	30		
Beyerite	SP	3.350	81	2.850	100	2.673	65	2.146	68	1.908	53	1.890	52		
	Bisundi (8)	3.350	80	2.850	100	2.670	70	2.150	70	1.907	50	1.892	50		
Kettnerite	SP			2.887	100	2.102	73	1.895	82	1.729	87	1.588	91	1.277	64
	Krupka (9)			2.890	100	2.104	70	1.893	80	1.732	90	1.589	90	1.278	60
Ximengite	SP	6.050	66	4.423	87	3.490	84	3.023	100	2.858	71	2.157	53		
	Ximeng (10)	6.052	73	4.420	91	3.493	88	3.024	100	2.854	65	2.157	47		
Pucherite	SP	4.643	56	3.984	51	3.498	100	2.993	47	2.699	93	1.994	42		
	Schneeberg (11)	4.644	55	3.982	55	3.499	100	2.992	45	2.702	100	1.992	45		
Walpurgite	SP	10.010	43	3.269	55	3.123	100	3.053	40	2.728	37	2.379	31		
	Schneeberg (12)	9.900	*4*	3.250	*5*	3.110	*10*	3.050	*5*	2.720	*4*	2.410	*4*		
Schumacherite	SP	6.200	42	4.572	58	3.282	100	3.193	77	3.086	73	1.973	52		
	Schneeberg (13)	6.210	*4*	4.570	*6*	3.280	*10*	3.190	*8*	3.090	*8*	1.976	*5*		
Namibite	SP	5.550	68	3.572	74	3.527	40	3.285	53	3.016	100	2.671	57		
	Khorixas (14)	5.580	70	3.574	75	3.525	40	3.284	50	3.018	100	2.672	60		
Eulytite	SP	4.200	70	3.250	100	2.752	90	2.099	49	2.020	50	1.670	37		
	Rędziny (15)	4.204	57	3.254	67	2.750	100	2.101	66	2.018	72	1.670	58		

one (Text-fig. 3). The morphological features resulted from tetartoidal class *23* of the sillénite structure. The chemical composition (Table 1) most commonly corresponded well to the theoretical formula, in the listed case yielding $Bi_{11.94}Si_{1.02}O_{20}$. However, one of the several analyses of sillénite gave the formula $Bi_{12.03}(Si_{0.61}Bi_{0.39})_{\Sigma 1.00}O_{20}$; it may be connected with the above mentioned non-stoichiometric distribution of the elements in the mineral structure. Fe, Cu and Ag were the common trace elements. The XRD powder patterns of sillénite from Karkonosze (Table 2) were compared to the patterns of this mineral from Durango (Frondel 1943a) and from Fuka, Japan (Kusachi and Henmi 1991).

The present description is the first information on sillénite from the Karkonosze pluton. The mineral is not very common and the list of its known occurrences worldwide contains just about 20 items. In the region adjacent to the Karkonosze pluton one can mention Smrkovec, Czech Republic (Sejkora *et al.* 1993) or the mine Schaar at Johanngeorgenstadt in Saxony, Germany (Gröbner *et al.* 2005).

Kusachiite $CuBi_2O_4$

The copper and bismuth oxide, later named kusachiite, was found in the Fuka mine near Takahashi City, Okayama Prefecture, Honshu Island, Japan (Henmi 1995). The synthetic analogue of this mineral was prepared even earlier (Boivin *et al.* 1973). Kusachiite was formally approved as a new mineral species by the Commission on New Minerals and Mineral Names of International Mineralogical Association in 1994 (Jambor *et al.* 1996).



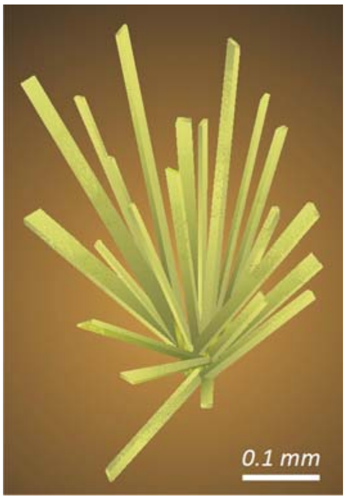
Text-fig. 4. Kusachiite, aggregate of parallel crystals; Michałowice

Kusachiite from the Karkonosze pluton was identified in quartz from a small vein collected in 1985. It was associated with cosalite, chalcopyrite and arsenopyrite. It formed a few grains of parallel growth of several thick platy and short-prismatic *4/mmm* class crystals with faces of tetragonal dipyramid and tetragonal prism (Text-fig. 4). The grains were opaque, dark grey-brown with a reddish-violet tint. Their size was <0.5 mm. Analyses of the chemical composition indicated, in addition to the main components, the presence of Ag and Sb and traces of Fe, Mn and As (Table 1); the formula is $(Cu_{0.96}Ag_{0.04})_{\Sigma 1.00}(Bi_{1.97}Sb_{0.03})_{\Sigma 2.00}O_4$. The results of the XRD determination were compared to the data of kusachiite from Fuka (Table 2). Except for the Fuka mine, the authors did not find any information on other occurrences of kusachiite.

Russellite Bi_2WO_6

Bismuth tungstate or bismuth and tungsten oxide (noted as $Bi_2O_3{\cdot}WO_3$) was collected by Arthur Russell in the Castle-an-Dinas mine near St. Austell in Cornwall, UK (Hey *et al.* 1938); his name was the basis of the mineral's name. A second russellite occurrence was found near the Emerald mine at Poona, Australia (Hodge 1970). Since then the mineral has been recognised at a number of localities, e.g., in the greisen veins of the western Mourne Mts, Northern Ireland (Moles and Tindle 2012).

Russellite in the Szklarska Poręba Huta outcrop, as in its other occurrences, is a product of the alteration of tungsten and bismuth minerals. It was found in 1979 in a small pegmatite nest with wolframite, bismuthinite and pyrite, and in quartz veinlets with wolframite, scheelite, molybdenite, sulfides of iron, copper, bismuth and cassiterite. Russellite occurred mostly on wolframite, partly altered to scheelite. Probably it formed due to the dissolution of scheelite rather than wolframite. Russellite (orthorhombic, pyramidal class *mm2*) had habits of laths, rods, plates or anhedral fine grains; the crystals were up to 0.5 mm, but usually smaller (Text-fig. 5). Crystal aggregates were compact, rarer radial, fan-like or rosette-shaped. The mineral colour was olive green or pale yellow with a green tint. The chemical composition (Table 1) was recalculated to the formula $(Bi_{1.91}Sb_{0.05}Pb_{0.03})_{\Sigma 1.99}(W_{0.93}Fe_{0.07})_{\Sigma 1.00}O_6$; the specimen contained traces of Mn and As. The XRD pattern (Table 2) fits well to the data for synthetic russellite (Knight 1992). The mineral has already been mentioned from the Szklarska Poręba Huta quarry (Mochnacka *et al.* 2015; see also references therein).



Text-fig. 5. Radial aggregate of russellite crystals; Szklarska Poręba Huta

Koechlinite Bi_2MoO_6

The type specimen of this mineral was found in the Daniel mine in Schneeberg, Erzgebirge, Saxony in Germany and it was bought in 1884 from Mr. Kulda by the mineral division of the Vienna Hof-Museum. The specimen was investigated by Schaller (1914, 1916), who named the mineral koechlinite, to honour Rudolf Koechlin, custodian in the Hof-Museum. Up to the present, occurrences of this mineral have been reported moderately frequently; one of them in the Bohemian massif area was noted near Horní Slavkov, Czech Republic, by Beran and Sejkora (2006).

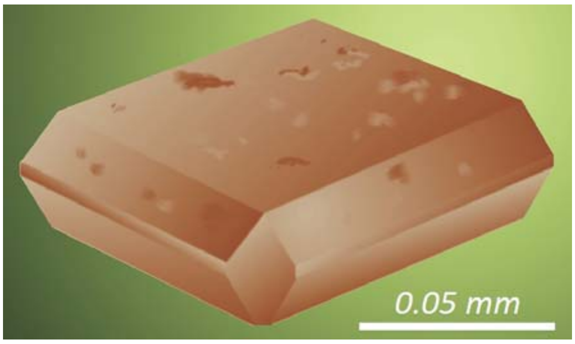
Single crystals of koechlinite were found in 1976 in quartz veinlets bearing sulphides of Mo, Fe, Cu, Bi and cassiterite in the quarry at Szklarska Poręba Huta. This pseudotetragonal orthorhombic (*mm2*)

Text-fig. 6. Parallel growth of koechlinite crystals; Szklarska Poręba Huta

mineral formed needles, laths or prisms terminated by a pyramid, up to 1.5 mm long (Text-fig. 6), and of quite dark green or olive-green colour. Small earthy crusts were also observed. Chemical analysis (Table 1) yielded the formula $(Bi_{1.98}Pb_{0.01})_{\Sigma1.99}(Mo_{0.98}Fe_{0.01})_{\Sigma0.99}O_6$; moreover traces of Cu, Ag, Mn, Sb and As were determined. XRD determination (Table 2) compared to the pattern obtained by Frondel (1943b) from the type specimen confirmed the mineral identification. A note on the presence of koechlinite in the same quarry was also published by Mochnacka *et al.* (2015 and references therein).

Bismoclite BiOCl

The first description of natural bismuth oxychloride in specimens collected in Chile was published by Domeyko (1876, 1879, p. 297). Means (1916) wrote about this type of compound from the Tintic district in Utah, USA. These authors referred it to daubréeite BiO(OH,Cl), however, the specimens' characteristics may suggest a mineral mixture with bismoclite. Mountain (1935) presented undoubted natural BiOCl, i.e., bismoclite, found before 1932 in the neighbourhood of Jackals Water near Steinkopf, Namakawa district, South Africa. Chemical and structural characteristics of bismoclite were given by Bannister and Hey (1935) and by Schaller (1941). Probably bismoclite is not a rare mineral, but its identification may be not trivial. The 31 currently known occurrences were listed by Testa *et al.* (2016).



Text-fig. 7. Tabular crystal of bismoclite; Szklarska Poręba Huta

Bismoclite (ditetragonal dipyramidal class *4/mmm*), found in 1979 in the Szklarska Poręba Huta quarry (for the first time there), forms scales or plates as loose grains up to 0.1 mm (Text-fig. 7) and earthy or compact aggregates. It occurred on quartz of the veinlets with sulphide bismuth minerals. Its colour is pale to moderately intense greyish-brown, the grains are opaque or poorly translucent. The chemical composition (Table 1) gave an almost perfect formula BiOCl, with trace admixtures of Cu, Fe, Sb and As. The XRD data (Table 2) are very close to the pattern of the synthetic equivalent of this mineral (Bannister and Hey 1935).

Bismutite $Bi_2O_2[CO_3]$

Natural bismuth carbonates were known in the 19th century; bismutite was first described by Breithaupt (1841) from the Arme Hilfe mine in Ullersreuth, Thuringia, Germany. A modern description of its structure was published by Grice (2002). The individual forms of Bi carbonates were recognised in the outcrops as the products of supergene processes, e.g., in the Lydenburg district of Transvaal, South Africa, and in South Carolina, USA (Louis 1887). This interest in Bi carbonates continued from the early 20th century (Lindgren and Loughlin 1919) until the present (Sahama and Lehtinen 1968; Leverett *et al.* 2003), in part as to their being indicators of primary Au-Bi mineralisation. Their studies also provided evidence of the development of the ore deposit oxidation zone due to ascending waters and a supergene source of carbon in carbonate ions (Haßler *et al.* 2014). The occurrences of bismutite in the Bohemian massif were briefly described by Sejkora and Řídkošil (1994).

Bismutite in the quarry at Szklarska Poręba Huta occurred in quartz veinlets with sulphides of iron, copper and bismuth, collected in 1978. It forms pseudotetragonal orthorhombic (*mm2* pyramidal

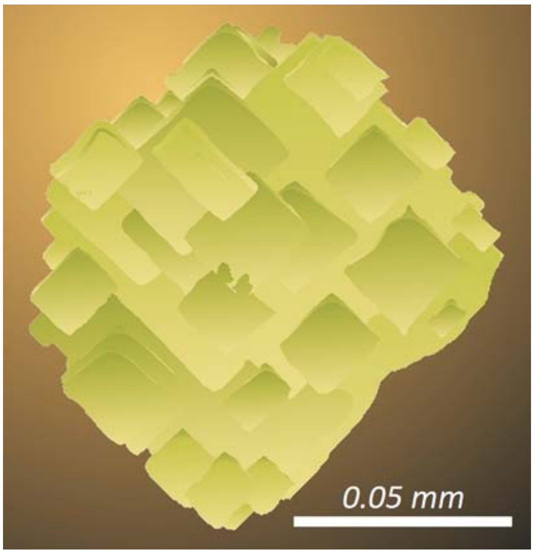
Text-fig. 8. Pseudotetragonal crystals of bismutite with striae on their faces; Szklarska Poręba Huta

class) single subhedral opaque crystals up to 0.6 mm long with striae on the pyramid faces in positions perpendicular to the Z axis (Text-fig. 8). Moreover, small earthy beige grains of very fine crystals were observed. The colour is various shades of brown, occasionally with a greyish or greenish tint. A small amount of antimony was found in the composition of bismutite, thus the formula is $(Bi_{1.98}Sb_{0.01})_{\Sigma 1.99}O_2(CO_3)_{0.98}$; traces of Ag, Cu, Fe, Mo and As were determined. XRD data of the studied mineral agreed well with bismutite from Marropino Mine, Mozambique (Sahama and Lehtinen 1968). This bismuth carbonate was already noted from Szklarska Poręba Huta (Mochnacka *et al.* 2015, and references therein).

Beyerite $CaBi_2O_2[CO_3]_2$

A mineral, which was probably the carbonate later named as beyerite, was described by Arzruni and Thaddeeff (1899) from Schneeberg in Saxony, Germany; the proposed chemical formula was $5Bi_2O_3 \cdot H_2O \cdot CO_2$. No name was given to this mineral at that time. More complete studies on specimens from Schneeberg and from Pala in San Diego County, California, USA, were made by Frondel (1943a). Their results were sufficient to propose a new mineral named beyerite after Adolph Beyer (1743–1805), a mineralogist, who was the mine engineer in Schneeberg and in 1805 found the first natural bismuth carbonate, later determined by Weisbach (1877) as "Bismutosphärit" (= bismutite). Soon Heinrich (1947) described beyerite from pegmatites in three south-central Colorado (USA) localities: School Section, Mica Lode and Meyers Ranch. Chandy *et al.* (1969) characterised beyerite from the Bisundni pegmatite in Rajasthan, India, and made a good comparison of this mineral's XRD data. The structure of the mineral was elucidated by Grice (2002).

In the Karkonosze pluton beyerite was found in quartz veinlets with sulphides of iron, copper and bismuth in the quarries at Szklarska Poręba Huta in 1978 and in pegmatite with uraninite, bismuthinite, chalcopyrite, pyrite and pyrrhotite at Michałowice in 1980. Its crystals (pseudotetragonal orthorhombic, *mmm* bipyramidal class) were single, almost square platy ones up to 0.4 mm in size or forming clusters with parallel individuals (Text-fig. 9). Small crystals (10–15 μm) were frequently subhedral and formed booklet-type aggregates. The colour was green or olive-green in various shades; the crystals were transparent or translucent with a strong lustre. The chemical composition of the specimen from Michałowice (Table 1) yielded the formula $Ca_{0.92}Pb_{0.07}Bi_{1.98}O_2(CO_3)_{1.99}$, with traces of Sb, Cu and Fe. XRD identification (Table 2) was made by comparing with the data published by Frondel (1943a) and Chandy *et al.* (1969). This find of beyerite is the first in the Karkonosze pluton, although it was found at Rędziny, i.e., in the eastern cover of the pluton (Mochnacka *et al.* 2015, and references therein).

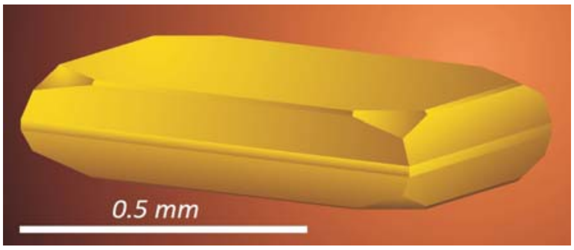


Text-fig. 9. Almost parallel aggregate of many beyerite plates on the positive rhombohedron face of a morion crystal; Michałowice

Kettnerite $CaBiO[CO_3]F$

Kettnerite was found in 1953 in the voids of a quartz veinlet cutting pegmatite K-feldspar in the dump of the Barbora adit near Krupka in Krušné hory, i.e., the Czech Erzgebirge (Žák and Syneček 1956). The name honoured Radim Kettner, the Czech geologist from Charles University in Prague. Other information on kettnerite findings has not been frequent; one may recall a paper on this mineral from a pegmatite near Cordoba, Argentina (Colombo et al. 2002). Kettnerite was found in specimens of quartz from veinlets with bismuthinite, collected in the quarry at Szklarska Poręba Huta in 1979; this is until now the only occurrence of this mineral known from the Karkonosze pluton. It formed grains, in part subhedral short-lath single crystals (orthorhombic, *mmm* bipyramidal class, pseudotetragonal by twinning)

up to 0.7 mm long, and earthy spots on the quartz surface. The crystals were yellow to pale-brown in various shades (Text-fig. 10), usually translucent. The crystallochemical formula was $(Ca_{0.97}Pb_{0.04})_{\Sigma 1.01}Bi_{0.99}O[CO_3]F_{0.96}$ with trace amounts of Ag and Fe (Table 1). The identification of the mineral was confirmed by the XRD pattern (Table 2), close to the data by Hybler and Dušek (2007).

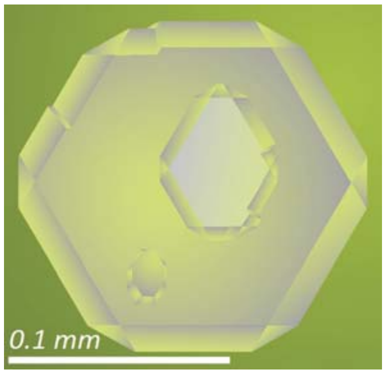


Text-fig. 10. Short-lath-like crystal of kettnerite; Szklarska Poręba Huta

Ximengite $Bi[PO_4]$

This simple bismuth phosphate was discovered by Shi (1989) in the Ximeng region, Junnan province, China. Two other publications on occurrences of this mineral refer to the phosphate-bearing pegmatites in NW Portugal (Leal Gomes 2010) and to hydrothermal veins in Apuan Alps, Italy (Biagnoni *et al.* 2010) as the parent sites of the mineral.

Ximengite from the Szklarska Poręba Huta quarry was found in samples of ore-mineralised pegmatite with sulphides and sulphosalts of bismuth, wolframite, cassiterite, pyrrhotite, pyrite, chalcopyrite, arsenopyrite and monazite, collected in 1983.



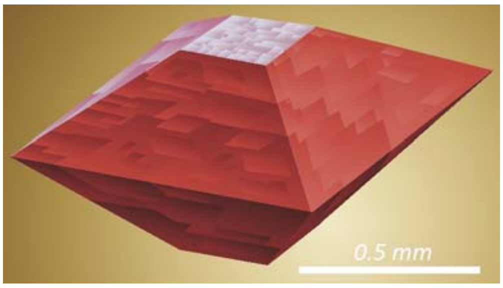
Text-fig. 11. Ximengite, an aggregate of parallel platy crystals; Szklarska Poręba Huta

This mineral (trigonal system, *32* trigonal trapezohedral class) formed small aggregates of anhedral grains and sparse booklet or parallel groups of subhedral to euhedral crystals (Text-fig. 11). The grain size was up to 0.15 mm. The mineral was transparent, colourless or very pale greyish, bluish or greenish with a glassy lustre. The analysis of the composition of the ximengite specimens (Table 1) resulted in the formula $(Bi_{0.99}Fe_{0.02})_{\Sigma 1.01}[(P_{0.95}As_{0.04})_{\Sigma 0.99}O_4]$ with traces of Ag, Sb, Pb and Mn. The XRD pattern (Table 2) corresponded very well to the data for the type specimen from Ximeng (Shi 1989). Up till now the studied samples of ximengite are the only ones known from the Karkonosze pluton.

Pucherite $Bi[VO_4]$

Pucherite, an orthorhombic mineral (Qurashi and Barnes 1952, 1953; Bhattacharya *et al.* 1997), is one of three polymorphs of $BiVO_4$; the others are monoclinic clinobisvanite and tetragonal dreyerite. It was recognised and first investigated by Frenzel (1871), who gave the name derived from the Pucher shaft of the Wolfgang Maassen mine near Schneeberg, Erzgebirge, Germany, where the mineral had been found as a new one. A very good description of pucherite and its localisation in the Wagu mine in the Fukushima prefecture, Japan, was published by Miyawaki *et al.* (1999).

In the Karkonosze pluton pucherite was found in samples of pegmatite with bismuthinite, pyrite and monazite, collected at Szklarska Poręba Huta in 1976. It formed single subhedral to almost euhedral crystals or their loose groups. The crystals (*mmm* bipyramidal class), bipyramidal with a basic dihedron, were up to 2 mm; a blocky scheme of growth could be observed (Text-fig. 12). Their colour was dark red with a dis-



Text-fig. 12. Pucherite, crystal demonstrating blocky growth; Michałowice

tinct brownish tint; they were translucent to almost opaque. Chemically pucherite from Karkonosze differed a little from the theoretical composition; its formula was $(Bi_{0.96}Fe_{0.03}Mn_{0.01})_{\Sigma 1.00}[(V_{0.96}P_{0.02}As_{0.01})_{\Sigma 0.99}O_4]$ with traces of Ag, Sb and Pb (Table 1). Its XRD pattern (Table 2) agreed well with the data from the type locality at Schneeberg (Miyawaki *et al.* 1999). Until now the described specimens are the only known pucherite from the Polish part of the Karkonosze pluton.

Walpurgite $Bi_4(UO_2)O_4[AsO_4]_2{\cdot}2H_2O$

Walpurgite was established as a new mineral in a sample from the Walpurgis vein in the Weisser Hirsch mine at Neustädtel near Schneeberg, Saxony, Germany (Weisbach 1871). Its investigation was continued with modern methods, e.g., by Evans (1950). Walpurgite is a secondary mineral of uraninite-bearing associations (Frondel 1958), formed in supergene conditions (Braithwaite and Knight 1990). Lately its structure was studied by Raman spectroscopy to confirm the molecular state of the bound water (Frost *et al.* 2006b). Geochemical investigations (Göb *et al.* 2013) raised the possibility of including rare earth elements in the walpurgite structure.

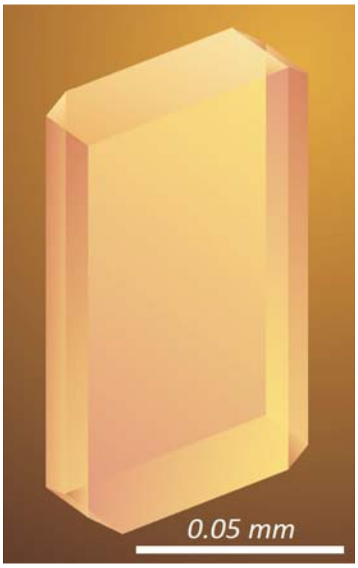
Walpurgite was found in the Czech part of the Karkonosze pluton at Rýžoviště near Harrachov (Sejkora *et al.* 1994) and Medvědín (Plášil *et al.* 2011). Its first occurrence in the Polish part of the pluton was recognised in samples of pegmatite with bismuthinite, grains of uraninite, chalcopyrite, pyrrhotite, pyrite and arsenopyrite, collected at Szklarska Poręba Huta in 1985. It formed separate aggregates of lathy or platy crystals (triclinic, $\bar{I}$ pinacoidal class) up to 2 mm long; they were pale olive-green at the ends with a gradual change to pale beige in the middle (Text-fig. 13). The electron microprobe analysis showed several more elements than in the above theoretical formula, namely: $(Bi_{3.94}Fe_{0.02}Pb_{0.02})_{\Sigma 3.98}[(U_{0.98}Th_{0.02})_{\Sigma 1.00}O_2]O_4[(As_{1.93}P_{0.04}V_{0.02})_{\Sigma 1.99}O_8]{\cdot}2H_2O$ plus Ag, Cu and Mn in trace amounts (Table 1). The identity of the mineral was confirmed by its XRD pattern (Table 2), compared to the values given by Frondel (1958). The occurrence of molecular water was indicated by the IR absorption spectrum at 1605 cm^{-1} (cf. Sejkora *et al.* 1994).

Text-fig. 13. Walpurgite, aggregate of many parallel crystals; Szklarska Poręba Huta

Schumacherite $Bi_3O[VO_4]_2OH$

The new mineral species schumacherite was recognised by Walenta *et al.* (1983) in the ores of the Pucher shaft, Wolfgang Maassen mine, and from the Sauschwart mine dump, Schneeberg area in Erzgebirge, Saxony, Germany. The name is to honour the geologist Friedrich Schumacher from Freiberg, Germany. An additional study of this mineral was made by Krause *et al.* (1993). Later it was found in the São José mine, Brejaúba, Minas Gerais, Brazil (Burns *et al.* 2000) and in the Lodi#1 mine of the Spring Creek area, Last Chance mining district of the Plumas County, California (Dunning and Cooper Jr. 2005); its occurrence in the Kola peninsula is listed (Borisova and Voloshin 2010) without any other information. A literature review suggests, however, that this mineral occurs only rarely.

Schumacherite was found in a sample of quartz from a veinlet bearing sulphides of Fe, Cu, Mo and wolframite, collected in the quarry at Szklarska Poręba Huta in 1977. This was the first find in the



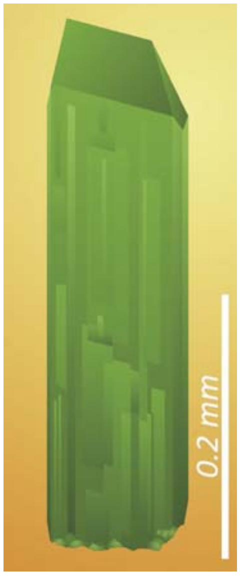
Text-fig. 14. Schumacherite, perfectly euhedral crystal; Szklarska Poręba Huta

Karkonosze pluton. It formed tabular, short-lathy euhedral crystals (triclinic, $\bar{1}$ pinacoidal class) up to c. 0.1 mm long, small solid crusts and single anhedral grains. The colour of the translucent to transparent crystals was yellow with a pale brownish or pinkish tint (Text-fig. 14). The calculated formula was $(Bi_{2.97}Fe_{0.03})_{\Sigma 3.00}O[(V_{0.95}P_{0.03}As_{0.02})_{\Sigma 1.00}O_4]_2OH$ with traces of Ag, Mn, Sb and Pb (Table 1). The XRD pattern (Table 2) was referred to the data published by Walenta *et al.* (1983). The occurrence of the OH^- group was shown by the IR absorption bands at 3260, 3450 and 3560 cm^{-1} (cf. Frost *et al.* 2006a).

Namibite $Cu(BiO)_2[VO_4]OH$

This basic vanadate was discovered in natural samples by Knorring and Sahama (1981). Its name is after the Namib desert in Africa; the sample came from a copper occurrence near Khorixas, NW Namibia. Later it was described from the Pala pegmatite outcrop, San Diego County, California, USA (Foord 1996). Products of the supergene alteration of Bi ore in the Jáchymov deposit, Czech Republic, also included this mineral (Ondruš *et al.* 1997). Dunning and Cooper Jr. (1998) listed twelve occurrences of namibite worldwide and mentioned that this mineral is probably not very rare but rather not identified in the copper-bismuth mineralisation alteration products. Good specimens of namibite were found in the Nagatare mine, Fukuoka Prefecture, Japan (Uehara and Shirose 2013). The structure of the mineral was reinvestigated by Kolitsch and Giester (2000), who also revised its symmetry from the supposed monoclinic to triclinic.

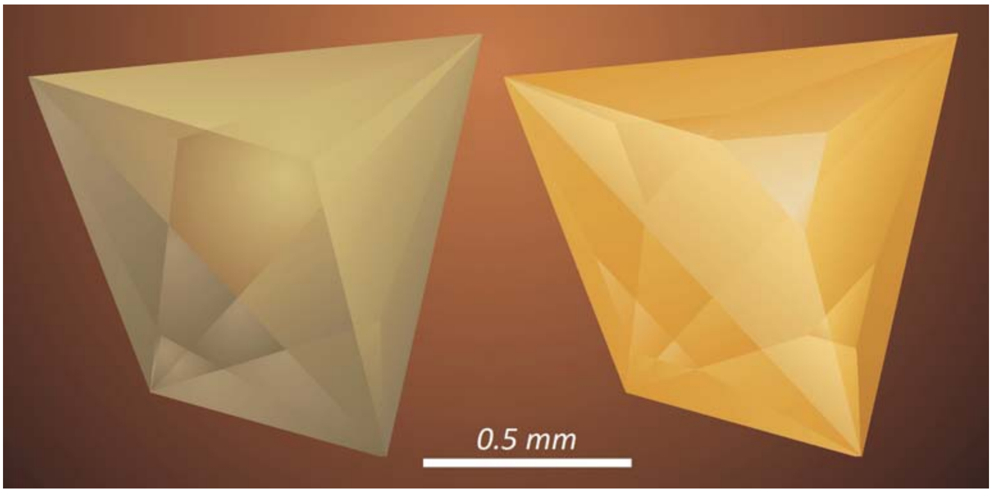
Namibite was found in quartz veinlets with sulphides of Bi, Fe, Cu, Mo, and with wolframite in the quarry at Szklarska Poręba Huta, collected in 1977 (first occurrence in the Karkonosze pluton). The crystals (triclinic, $\bar{1}$ pinacoidal class) to 1 mm long, of the habit of laths or thick plates, formed parallel, radial or bundle aggregates, and small solid crusts. The colour was dark green, the crystals frequently were translucent (Text-fig. 15). The chemical composition (Table 1) yielded the formula $(Cu_{0.99}Ag_{0.01})_{\Sigma 1.00}(BiO)_{2.00}[(V_{0.93}P_{0.05}As_{0.02})_{\Sigma 1.00}O_4]OH$ with traces of Fe, Mn, Sb and Pb. The XRD identification (Table 2) was made on the basis of the Khorixas specimen data (Knorring and Sahama 1981). The presence of the OH^- group was confirmed by the IR absorption bands at 3442 and 3580 cm^{-1} (cf. Ondruš *et al.* 1997; Frost *et al.* 2006a).



Text-fig. 15. Namibite, parallel crystal growth; Szklarska Poręba Huta

Eulytite $Bi_4[SiO_4]_3$

Natural bismuth silicate was recognised in the Neuglücker adit of the Kalbe mine near Schneeberg in Erzgebirge, Germany, by Breithaupt (1827) and described as "Wismuthblende"; later the name "Eulytin" was used (Breithaupt 1832, p. 239). Frenzel (1873a, b) distinguished "Eulytin" from "Agricolit", but Frondel (1943b) wrote about the identity of the two minerals. The name "Kieselwismuth" was also used (Kersten 1833). The structure of eulytite was investigated by Menzer (1931) and then by Segal *et al.*



Text-fig. 16. Eulytite, euhedral crystals; Szklarska Poręba Huta

(1966). Occurrences of eulytite are probably relatively frequent in Bi secondary mineral environments. The exo- and endo-contact zones of the Karkonosze pluton are a good example: eulytite was found e.g., at Rędziny (Parafiniuk 2003), Miedzianka and Ciechanowice (Siuda and Gołębiowska 2011), Szklarska Poręba Huta (Mochnacka *et al.* 2015, and references therein) in Poland, and at Medvědín near Špindlerův Mlýn in the Czech Republic (Plášil *et al.* 2008, 2009).

Eulytite from the Szklarska Poręba Huta quarry was identified in quartz veinlets with bismuthinite, collected in 1978 and 1984. Euhedral crystals up to 2 mm (isometric, hexakistetrahedral class) had faces of trigondodecadedron, sometimes with faces of tetrahedron (Text-fig. 16). The colour of the crystals was grey with a brownish or pale beige tint. The chemical analysis (Table 1) was recalculated to the formula $(Bi_{3.91}Sb_{0.05}Fe_{0.04})_{\Sigma 4.00}[(Si_{0.94}P_{0.03}As_{0.03})_{\Sigma 1.00}O_4]_3$ with trace admixtures of Ag, Mn and Pb. Identification by the XRD method was made by comparing with the pattern of the sample from Rędziny (Parafiniuk 2003).

Fluid inclusions

Post-magmatic hydrothermal solutions of the Karkonosze pluton contained Ca^{2+}, Na^+ and Cl^- as the main ions, and the presence of others such as K^+ and HCO_3^- was low or subordinate. The proportion of Ca^{2+} to Na^+ varied distinctly in hypo- and mesothermal solutions, and in epithermal ones Na^+ became the main cation and the content of Ca^{2+} was very low. The total salt concentration in epithermal solutions did not exceed 5 wt. % as determined by fluid inclusion studies (Kozłowski and Marcinowska 2007).

Moreover, in some pegmatites and quartz veinlets from the studied outcrops, an apparently youngest pale-grey quartz formed very thin (0.1–1.0 mm) laminae on older quartz accumulations. These laminae contained small fluid inclusions, usually <1 to a few micrometres in size. The filling of the inclusions was an aqueous solution with or without a very small contraction gas bubble. A part of the one-phase fillings was in a metastable state, because freezing caused nucleation of a bubble which did not disappear at room temperature. However, some of them returned to the one-phase filling at this temperature. The microscope freezing and heating investigations revealed three types of solutions, differing in their main ions and inclusion homogenisation temperatures (Th): a) essentially Na^+ and Cl^- with total salt concentrations of 4–3 wt. %, Th 88–76°C; b) $Na^+ \geq Ca^{2+}$ with calcium ions always present and with two anions Cl^- and HCO_3^-; total salt concentration was 3.5–2 wt. %, Th 79–46ºC; c) $Na^+ < Ca^{2+}$ and $Cl^- << HCO_3^-$, with total salt concentration 2–0.n wt. %, Th ≥50ºC. Pressure corrections to Th values could not be calculated; their values, however, should be low. The above data were interpreted as characterising respectively: a) post-magmatic epithermal solutions, b) postmagmatic epithermal solutions mixed with descending supergene or formation fluids, c) supergene or formation solutions. The studied oxygenic bismuth minerals in a few cases also contained single fluid inclusions of one of the above-named varieties. Generally, these minerals occurred on the latest quartz laminae or partly in them like in shallow nests, or as very minute grains within this quartz.

FINAL REMARKS

The mineral associations at Szklarska Poręba Huta and Michałowice in the Karkonosze Mts contain numerous primary bismuth minerals such as: aikinite, bismuthinite, canizzarite, cosalite, cuprobismuthite, gladite, hodrushite, ikunolite, joseite-A, friedrichite, krupkaite, kupčikite, native bismuth and nuffieldite (Mochnacka *et al.* 2015 and references therein). All could be altered to the so-called secondary bismuth minerals, including the oxidised types. The term "secondary mineral" may be interpreted as: a) a mineral formed by *in situ* replacement of an earlier mineral; or b) a mineral formed from the substance(s) coming from the dissolved earlier minerals that occurred elsewhere. The oxygenic bismuth minerals, presented in this elaboration, formed by two kinds of alteration – under epithermal and supergene conditions, with distinct overlapping, i.e., mixing of fluids coming from the two sources. Most probably sillénite, kusachiite, bismoclite, bismutite, beyerite, kettnerite, pucherite, schumacherite, namibite and eulytite are of late epithermal origin (epithermal or mixed fluids); in turn, bismite, russellite, koechlinite, ximengite and walpurgite formed due to supergene alteration. Although transitional (mixed) conditions of the origins of the minerals are possible, the condition limits cannot be currently exactly estimated. The conclusions were made on the basis of observations of the position of the listed mineral grains on or in other minerals, mostly quartz, which were of low temperature epithermal formation, as indicated by the presence of gas-liquid inclusions with very small contraction bubbles. It is worth noting that such mixed conditions for the formation of secondary bismuth minerals were also discussed for the Krušne hory deposits in Czech Rapublic (Ondruš *et al.* 1994). Probably thorough studies of samples of post-magmatic mineralization in the Karkonosze pluton may result in the identification of numerous other minerals of so-called secondary origin and a more exact determination of the conditions of their crystallization.

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