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THE PHILIPSBORNITE–SEGNITITE SOLID-SOLUTION SERIES FROM RĘDZINY, EASTERN METAMORPHIC COVER OF THE KARKONOSZE GRANITE (SW POLAND)

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Abstract: Supergene minerals of the philipsbornite–segnitite series, $PbAl_3(AsO_4)(AsO_3OH)(OH)_6$–$PbFe^{3+}_3(AsO_4)(AsO_3OH)(OH)_6$, accompanied by carminite, $PbFe^{3+}_2(AsO_4)_2(OH)_2$, were found in relics of hydrothermal quartz–chlorite–arsenopyrite veins, associated with subordinate polymetallic ores disseminated in contact zones of a dolomitic marble deposit at Rędziny, Western Sudetes, Poland, and recognized by means of electron microprobe and X-ray and electron-back-scattered diffraction (XRD and EBSD). Philipsbornite and segnitite, as the two minerals of the series, exhibit highly variable compositions, especially in terms of the range of $Fe^{3+} \leftrightarrow Al^{3+}$ substitution at the G site, with a distinct gap between the values of 0.52 and 0.89 for the Fe/(Al+Fe) ratio; substitutions at the D and T sites are less important. In this respect, the minerals are almost identical with philipsbornite and segnitite, known from other localities. The gap might be a consequence of the limited miscibility of the end-members, but also might be attributed to crystallization under the changing and distinctly differing activities of Al^{3+} and Fe^{3+}. The unit-cell parameters of philipsbornite, a = 7.1245(13) Å, c = 17.0967(45) Å, make the mineral comparable with philipsbornites from other occurrences. The EBSD analysis confirmed the rhombohedral structure of both minerals and the space group symmetry R-3m. The minerals crystallized in the sequence: philipsbornite → segnitite → carminite, which reflects (*i*) decreasing acidity in the oxidation zone, due to the leaching of sulphate ions and interaction of the solutions with a nearby dolomite lens, and (*ii*) varying activities of Al^{3+}, Fe^{3+} and Pb^{2+} cations, mobilized by the solutions through interaction with the silicate host containing disseminated arsenopyrite and subordinate sulphides, up to complete Pb^{2+} depletion.

Key words: arsenates, oxidation zone, philipsbornite, segnitite, carminite, chemical composition, Rędziny.

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INTRODUCTION

Philipsbornite, $PbAl_3(AsO_4)(AsO_3OH)(OH)_6$, and segnitite, $PbFe^{3+}_3(AsO_4)(AsO_3OH)(OH)_6$, are rare isomorphic arsenates (the space group *R-3m*; Cooper and Hawthorne, 2012), occurring as supergene phases in the oxidation zone of hydrothermal ore deposits. Mills *et al.* (2009), in a discussion of a new mineral-group hierarchy and nomenclature, and Bayliss *et al*. (2010), presenting a new recommended nomenclature of the alunite supergroup, assigned philipsbornite and segnitite to the dussertite group, which is a group within this supergroup, comprising arsenates with medium-sized and large cations.

The chemical compositions of minerals belonging to the alunite supergroup could be presented by the general formula $DG_3(TX_4)_2X'_6$ (Smith *et al*., 1998; Bayliss *et al*., 2010), where the D site in general can be occupied by 12-fold-coordinated tetravalent, trivalent, divalent and monovalent cations, such as Th^{4+}, Ce^{3+}, La^{3+}, Nd^{3+}, Bi^{3+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Hg^{2+}, Na^+, K^+, Rb^+, Ag^+, Tl^+, NH_4^+ and H_3O^+, or remains vacant. The G octahedral position is filled mainly by Al^{3+}, Fe^{3+}, V^{3+} and Cr^{3+}, but also by Sn^{4+}, Ga^{3+}, Cu^{2+}, Zn^{2+} or Mg^{2+}, whereas the tetrahedral T site is occupied mainly by S^{6+}, Cr^{6+}, P^{5+}, As^{5+}, Sb^{5+} and minor Si^{4+} and the X and X' sites by O^{2-}, OH^-, F^- and H_2O. Owing to the compositional complexity and the coexistence of many solid-solution series between minerals representing the alunite supergroup, philipsbornite and segnitite specimens from different localities also may display greatly diversified chemical compositions. Barium is commonly the main substituent at the D site [up to 0.20 Ba atom per formula unit (*apfu*) was noted in philipsbornite from Cínovec

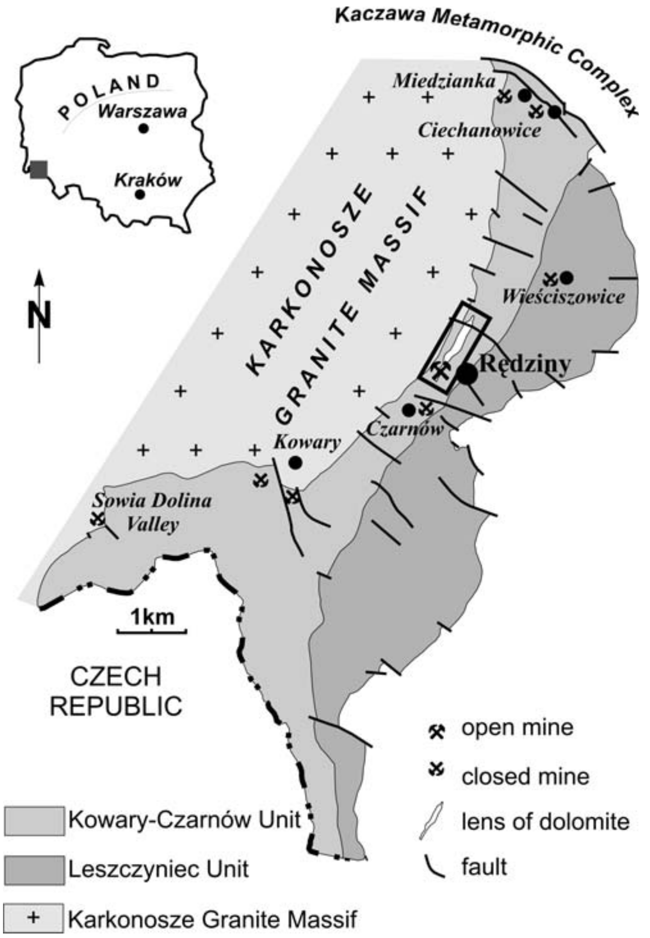

Fig. 1. Geological sketch map of the eastern metamorphic cover of the Karkonosze granite intrusion (after Kozdrój, 2003), supplemented by Pieczka *et al*., 2009).

(Czech Republic); David *et al*. (1990)], Cu and Zn at the G site [up to 0.90 Cu *apfu* found in members of the beudantite–segnitite series from Krupka (Czech Republic) (Sejkora *et al*., 2009), and up to 0.22 Zn *apfu* found in segnitite from Broken Hill (Australia) (Birch *et al*., 1992)], whereas S^{6+} and P^{5+} are the most common substituents for As^{5+} at the T site. The latter substitutions led to the existence of the solid-solution series of philipsbornite with plumbogummite, $PbAl_3(PO_4)(PO_3OH)(OH)_6$, and hidalgoite, $PbAl_3(AsO_4)(SO_4)(OH)_6$, the phosphate and mixed arsenate–sulphate analogues of philipsbornite, respectively; and with kintoreite, $PbFe^{3+}_3(PO_4)(PO_3OH)(OH)_6$, and beudantite, $PbFe^{3+}_3(AsO_4)(SO_4)(OH)_6$, which are the phosphate and mixed arsenate–sulphate analogues of segnitite. Of the solid solutions, the plumbogummite–philipsbornite and beudantite–segnitite have been well documented (e.g., Sejkora *et al*., 1998, 2009). For several samples of the alunite-supergroup minerals, the presence of C^{4+} at the T site was suggested (e.g., Rattray *et al*., 1996). As a result, owing to the difficulties in the determination of the carbonate concentration in specimens of small weight, many analyses of philipsbornite and segnitite may indicate a suboptimal negative charge associated with AsO_4^{3-}, PO_4^{3-} and SO_4^{2-} anions and a relative excess of positive charge from an excess of the D- or G-site cations.

Philipsbornite was described for the first time by Walenta *et al.* (1982) on the basis of a sample from the Dundas ore district (Tasmania, Australia). In the same year, another philipsbornite specimen from the Tsumeb mine (Namibia), was investigated by Schmetzer *et al.* (1982). The first data on segnitite, associated with beudantite, were given by Birch *et al.* (1992) from Broken Hill (New South Wales, Australia). Apart from the type localities, there are only a few well-documented occurrences of the two minerals, commonly associated with the weathering zones of polymetallic, hydrothermal vein-type ore deposits, e.g., the Cínovec, Moldava and Krupka deposits in Krušné hory, the Rovnost mining field at Jáchymov, and the ore deposit at Štěpánov nad Svratkou, all the occurrences in the Czech Republic (David *et al.*, 1990; Sejkora *et al.*,1998, 2001a, b, 2009, 2011). In addition, several other occurrences were noted, e.g., the Sn-In Mangabeira deposit in Central Brazil (Moura *et al.*, 2007) and the Sperkerriegel Quarry in Lower Austria (Kolitsch *et al.*, 2010). The occurrence of both minerals at Rędziny was mentioned briefly by Gołębiowska *et al.* (2008).

The aim of this paper is to discuss in detail the chemical compositions and origin of selected arsenate minerals of the weathering assemblage at Rędziny, representing members of the philipsbornite–segnitite isomorphic series.

GEOLOGICAL SETTING

The village of Rędziny is located in the central part of the Rudawy Janowickie Range, which along with the Lasocki Range forms the eastern metamorphic envelope of the Variscan Karkonosze granite (Fig. 1). Biotite-bearing, porphyritic to equigranular granite, associated with a small volume of two-mica granite and subordinate granophyre granite, are the main granite varieties of 330–310 Ma, forming the Karkonosze pluton (Pin *et al.*, 1987; Duthou *et al.*, 1991; Kusiak *et al.*, 2014). The pluton is considered to be a syn-collisional to magmatic arc intrusion on the margin of a crystalline, continental platform adjacent to oceanic crust, crystallized from relatively reduced, K-rich, calc-alkaline, highly evolved, mostly peraluminous magmas (A/CNK 1.01–1.1) of I type to transitional I–S type (Duthou *et al.*, 1991; Mazur *et al*., 2007; Mikulski, 2007; Słaby and Martin, 2008). The Karkonosze granite is hosted by metamorphic rocks of the Kaczawa Complex in the northeast (phyllites, amphibolites, marbles), the Izera Complex in the northwest (leucogranites, gneisses, mica-schists and hornfelses), the Ješted Unit in the southwest (metasediments and volcanics), the Southern Karkonosze Unit (gneisses, mica-schists, phyllites, metabasites) and the Eastern Karkonosze Unit, all exhibiting differences in lithostratigraphy and metamorphic evolution.

The Eastern Karkonosze Unit of Neoproterozoic–Ordovician age (Mazur and Aleksandrowski, 2001; Kozdrój, 2003; Mazur, 2003), composed of gneisses, mylonites and mica schists and of subordinate marbles, calc-silicate rocks and biotite amphibolites, is divided into the Kowary gneiss series and the Czarnów schist series. The most important ore occurrences in the eastern envelope of the Karkonosze granite within its contact aureole are: a Cu deposit in the Miedzianka–Ciechanowice area (*Kupferberg*) and As-bearing mineralization at Czarnów (both mined to the beginning of the 20th century), and currently the most fully documented ore assemblage recognized in the Rędziny dolomite quarry (e.g., Pieczka *et al*., 2009). All of the aforementioned occurrences are associated with the Czarnów schist series. The so-called Kowary magnetite formation and the polymetallic mineralization in hornfelses of the Sowia Dolina valley (Mochnacka *et al.*, 2007) and of Budniki, near Kowary (Mochnacka *et al.*, 2008), located somewhat to the southwest, already have been associated with the Kowary gneiss series. The origin of all the ore occurrences is related to the strongly fractionated parental magma of the granophyre granite, rich in volatiles and metallic elements that deposited from postmagmatic fluids (Mikulski, 2007).

The quarry at Rędziny is located within the Czarnów schist series, only ca. 200 m from the granite outcrops and ca. 0.5–1 km from the abandoned ore mine at Czarnów, within a large dolomite marble lens (Fig. 1). The dolomite lens, hosted by mylonites, mica-schists and amphibolites and tectonically fragmented during the Karkonosze granite emplacement, is intersected by a NNW–SSE trending schist zone that was conductive to migration of hydrothermal, granite-derived solutions across the lens. Disseminated ores include mainly arsenopyrite, cassiterite and pyrite, accompanied by minor, but numerous, base-metal sulphides, bismuth sulphides and sulphotellurides, Ag(Cu)-Pb-Bi(Sb) sulphosalts, and Sn-bearing sulphides (Parafiniuk and Domańska, 2002; Parafiniuk, 2003; Pieczka *et al.*, 2009; Gołębiowska *et al*., 2012).

Weathering of the primary sulphides resulted in the formation of numerous secondary phases represented, in addition to widespread goethite and hematite, mainly by arsenates, followed by vanadates and phosphates. They include scorodite, pharmacosiderite, yukonite and arseniosiderite as the most common Fe arsenates (Pieczka *et al.*, 1998; Gołębiowska, 2003), and conichalcite, tyrolite and clinotyrolite with subordinate to trace-level mixite, strashimirite, cornwallite, Zn-olivenite and Cu-adamite as Cu-bearing arsenates (Gołębiowska, 1999; Gołębiowska *et al.*, 1998, 2006). Also found are numerous transitional members, representing the mottramite–duftite–conichalcite, and the mimetite–pyromorphite–turneaurite solid-solution series, accompanied by bayldonite, hemimorphite, eulytyne, pingguite and other Bi-tellurates, bismutite, beyerite, bismite, philipsbornite, segnitite, carminite and various minerals of the tsumcorite group (Gołębiowska *et al.*, 2002; Gołębiowska, 2005).

METHODS

The chemical compositions of philipsbornite, segnitite and associated carminite were analyzed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances of the University of Warsaw, using a Cameca SX 100 electron microprobe operating in the wavelength-dispersive spectroscopic (WDS) mode under the following conditions: 15 kV accelerating voltage, 20 nA beam current, 2 µm beam diameter, peak count-time of 20 s and background time of 10 s. Standards, analytical lines, diffracting crystals and mean detection limits (in wt%) were as follows: diopside – Mg (*K*α, TAP, 0.02) and Si – (*K*α, TAP, 0.02), orthoclase – Al (*K*α, TAP, 0.02) and K (*K*α, PET, 0.03), apatite – P (*K*α, PET, 0.03), galena – S (*K*α, PET, 0.03) and Pb (*M*α, PET, 0.23), wollastonite – Ca (*K*α, PET, 0.03), V – metallic V (*K*α, LIF, 0.08), hematite – Fe (Kα, LIF, 0.09), chalcopyrite – Cu (*K*α, LIF, 0.08), sphalerite – Zn (*K*α, LIF, 0.08), GaAs – As (*L*α, TAP, 0.08), barite – Ba (in *L*α, PET, 0.12), and Bi_2Te_3 – Bi (*M*α, PET, 0.09). Fluorine was not analyzed. The raw data were reduced with the PAP routine of Pouchou and Pichoir (1985). The formulae of philipsbornite and segnitite were normalized in relation to 14 O *apfu*, whilst accompanied carminite to 10 O *apfu*, with H_2O in the form of OH groups calculated on the basis of stoichiometry.

X-ray diffraction (XRD) patterns of philipsbornite were collected at room temperature with a Philips APD X'Pert PW2030 diffractometer at the Faculty of Geology, Geophysics and Environmental Protection of AGH–UST under the following conditions: graphite-monochromatized Cu*K*α radiation with λ = 1.5418 Å, accelerating voltage of 35 kV, beam current of 30 mA, registration velocity of 0.02°(2Θ)/1s, registration range of 2–75°(2Θ), quartz as the internal standard. The data were analysed using an X'rayan software (Marciniak *et al.*, 2006) and X-ray standards in the form of ICDD files. Unit-cell refinement and indexing were done using a DHN Powder Diffraction System software (Wolcysz *et al.*, 1983).

Back-scattered electron (BSE) images of polished sections were obtained using a FEI Quanta 200 FEG scanning electron microscope, equipped with a EDS detector. The system operated at 25 kV accelerating voltage in a high-vacuum mode.

Electron back-scattered diffraction (EBSD) measurements on polished thin sections were carried out using a Zeiss Supra 35VP FEG scanning electron microscope equipped with HKL EBSD system at the Center for Advanced Microscopy and Imaging (CAMI), Miami University, Oxford, USA. Uncoated specimens were measured under variable-pressure conditions to limit/eliminate sample charging. A Channel 5 software package was used to display, collect and analyze EBSD data.

RESULTS

Philipsbornite–Segnitite Series

Minerals of the philipsbornite–segnitite series, along with carminite, are rather common accessory supergene phases found in the Rędziny quarry within relics of quartz–chlorite–arsenopyrite veins (N50°49′05.51"; E15°55′24.25"), containing subordinate polymetallic Cu-Ag-Pb-Bi-Sb-As sulphide mineralization (Fig. 2). Philipsbornite, occasionally with carminite, was encountered within phlogopite–clinochlore fillings of small voids in massive arsenopyrite (Fig. 2A), to 3–4 mm across, green to honey-brown in colour. Irregular grains of the mineral reach a maximum of 100 µm in size. Philipsbornite together with segnitite also crystallized in small voids among crystals of arsenopyrite, associated with Cu-Ag-(Bi,Sb,As) sulphosalts and Ag-bearing ga-

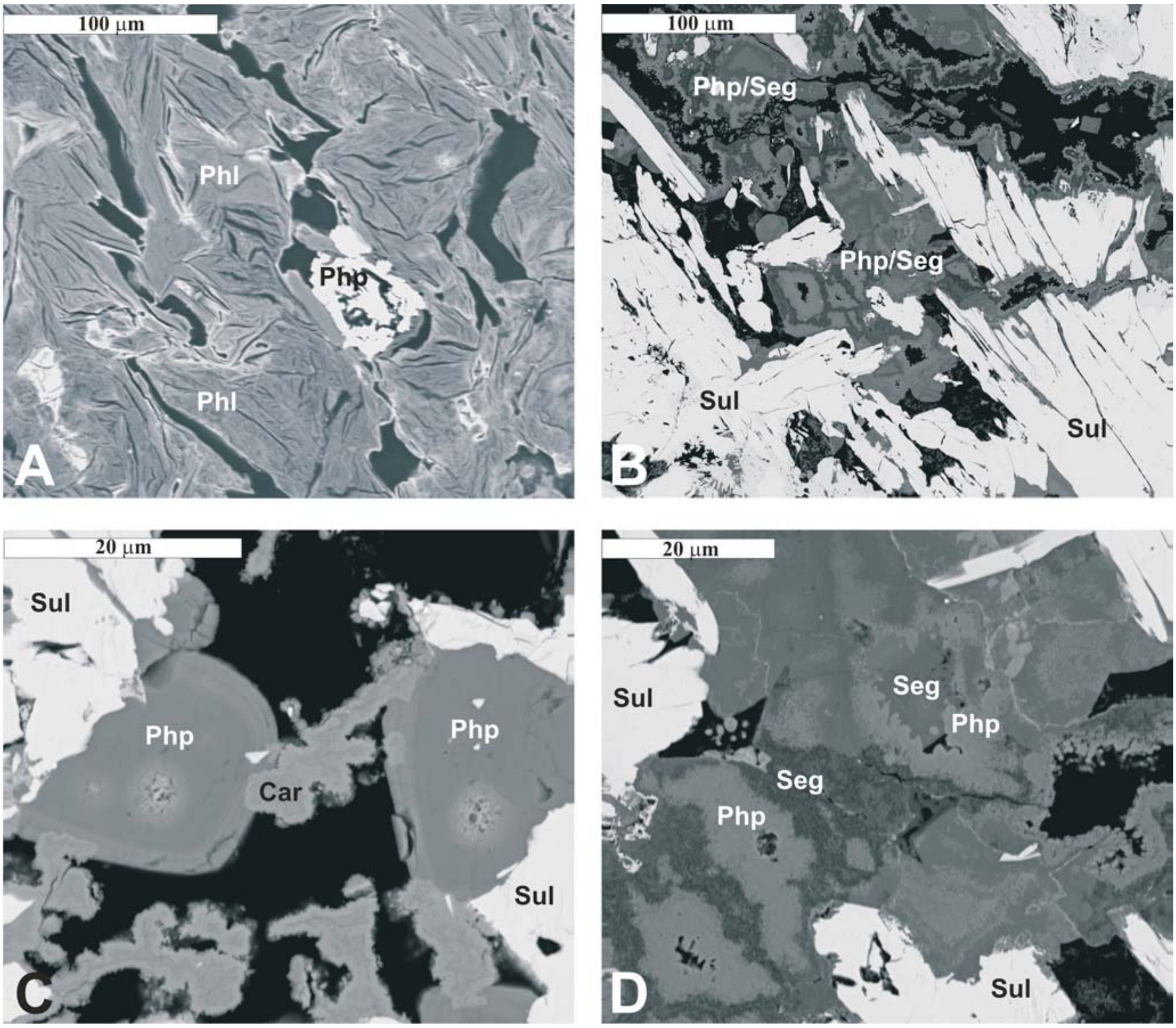

Fig. 2. Back-scattered-electron images of philipsbornite and segnitite. **A.** Philipsbornite within a phlogopite–clinochlore matrix in voids among arsenopyrite crystals. **B.** Intergrowths of philipsbornite with segnitite within Cu-Ag-(Bi,Sb,As)-sulphosalts. **C.** Philipsbornite and carminite crystallized in voids in massive arsenopyrite and Cu-Ag-(Bi,Sb,As) sulphosalts. **D.** Segnitite overgrown philipsbornite among the primary ore minerals. Abbreviations: Php – philipsbornite; Seg – segnitite; Car – carminite; Phl – phlogopite–clinochlore; Sul – Cu-Ag-(Bi,Sb,As) sulphosalts. Black area – epoxy.

lena (Fig. 2B–D). Both minerals co-occur as zoned, two-phase crystals, which are composed of a philipsbornite core and a segnitite rim, overgrown by dendrite carminite, individually not exceeding 20 μm in size, but forming aggregates up to 200 μm across.

The philipsbornite–segnitite members found at Rędziny differ in composition (Fig. 3). The T site is predominantly occupied by As^{5+} (27.87–32.17 wt.% As_2O_5, i.e., 1.81– 1.98 AsO_4^{3-} *pfu*), minor P^{5+} and S^{6+} (up to 2.56 wt.% P_2O_5 and 0.86 wt.% SO_3, i.e., up to 0.23 PO_4^{3-} *pfu* and 0.07 SO_4^{2-} *pfu*, respectively), and traces of Si^{4+} and V^{5+} (to 0.05 wt.% SiO_2 and 0.09 wt.% V_2O_5, i.e., < 0.01 SiO_4^{4-} and VO_4^{3-} *pfu*) (Table 1). The contents of the As^{5+} substituents, mainly P^{5+}, are generally much higher in spots richer in the end-member philipsbornite than segnitite. Occupancy of the G site is dominated by Al^{3+} or Fe^{3+}, typical for philipsbornite and segnitite, with a distinct compositional gap spreading from 0.52 to 0.89 of the Fe/(Fe+Al) value (Fig. 4). The lowest Fe_2O_3 content of philipsbornite, 4.17 wt.% (0.34 Fe *apfu*), corresponds to a member containing 89 mol.% of end-member philipsbornite, $PbAl_3(AsO_4)(AsO_3OH)(OH)_6$, and 11 mol.% of end-member segnitite, $PbFe^{3+}_3(AsO_4)(AsO_3OH)(OH)_6$; one of the highest, 29.40 wt.%, corresponds to almost pure segnitite. Copper and zinc, as the possible G site occupants, have only second-rank importance due to their low concentrations, reaching 0.62 wt.% CuO (0.06 Cu *apfu*) and 1.59 wt.% ZnO (0.14 Zn *apfu*) in segnitite. Lead is always the dominant component at the D site, reaching the content 24.13–32.22 wt.% PbO (0.72–0.95 Pb *apfu*) in philipsbornite and 27.68–32.33 wt.% PbO

Table 1

Representative compositions of minerals of the philipsbornite–segnitite series from Rędziny

wt.%	P1	P2	P3	P4	P5	P6	P7	S1	S2	S3	S4	S5	S6	S7
SO_3	b.d.	b.d.	b.d.	0.08	0.74	0.71	0.86	0.34	0.11	0.12	b.d.	b.d.	b.d.	0.40
P_2O_5	2.56	2.45	2.03	0.79	0.45	0.35	0.41	0.32	0.99	0.31	0.11	b.d.	0.08	0.10
V_2O_5	b.d.	b.d.	0.09	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.08
As_2O_5	32.17	31.87	31.58	30.19	31.44	31.10	30.80	30.75	29.58	30.79	29.71	27.87	29.74	28.67
SiO_4	b.d.	b.d.	0.05	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.04	0.02	0.02	0.03	b.d.
Al_2O_3	20.71	19.21	17.47	17.26	15.32	14.59	13.31	11.19	9.67	2.21	0.22	0.11	0.05	b.d.
Fe_2O_3	4.17	4.96	6.97	8.11	12.25	12.21	14.55	17.82	16.21	27.31	29.82	31.75	30.27	29.40
Bi_2O_3	b.d.	b.d.	b.d.	1.53	5.55	3.47	2.44	2.97	1.91	0.36	b.d.	b.d.	1.08	0.00
CaO	0.15	0.12	0.12	0.29	1.04	0.83	0.59	0.40	0.27	0.14	0.04	0.22	0.08	0.20
CuO	0.33	0.16	0.17	0.11	0.21	0.37	b.d.	b.d.	0.62	b.d.	b.d.	b.d.	b.d.	0.37
ZnO	b.d.	b.d.	b.d.	0.64	b.d.	b.d.	b.d.	b.d.	1.59	0.21	b.d.	0.27	0.10	0.14
BaO	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.13	b.d.	b.d.
PbO	30.26	32.22	30.79	30.19	24.13	26.99	26.84	27.68	29.90	32.05	32.33	31.65	31.21	31.55
K_2O	b.d.	b.d.	b.d.	b.d.	0.03	0.03	0.17	0.03	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
$H_2O_{(calc.)}$	9.80	9.60	9.40	9.47	9.35	9.29	9.15	9.15	9.17	8.55	8.39	8.88	8.42	8.34
Total	100.15	100.59	98.67	98.66	100.51	99.94	99.12	100.65	100.02	102.09	100.64	100.90	101.06	99.25
Number of ions on the basis of $\Sigma O = 14$ *apfu*														
Bi^{3+}	0.000	0.000	0.000	0.045	0.159	0.102	0.072	0.089	0.058	0.011	0.000	0.000	0.035	0.000
Ca^{2+}	0.017	0.015	0.014	0.036	0.124	0.101	0.072	0.049	0.034	0.019	0.005	0.030	0.011	0.027
Ba^{2+}	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.006	0.000	0.000
Pb^{2+}	0.877	0.954	0.933	0.931	0.723	0.825	0.826	0.862	0.957	1.063	1.109	1.074	1.064	1.093
K^+	0.000	0.000	0.000	0.000	0.004	0.004	0.025	0.004	0.000	0.000	0.000	0.000	0.000	0.000
Σ D	0.894	0.969	0.947	1.012	1.010	1.032	0.995	1.004	1.049	1.094	1.114	1.110	1.110	1.120
Al^{3+}	2.628	2.489	2.319	2.330	2.010	1.951	1.794	1.524	1.356	0.322	0.032	0.016	0.007	0.000
Fe^{3+}	0.338	0.410	0.591	0.699	1.027	1.043	1.253	1.550	1.451	2.532	2.859	3.010	2.888	2.847
Cu^{2+}	0.027	0.013	0.014	0.009	0.018	0.032	0.000	0.003	0.055	0.000	0.000	0.000	0.000	0.036
Zn^{2+}	0.000	0.000	0.000	0.054	0.000	0.000	0.000	0.000	0.140	0.019	0.003	0.025	0.009	0.013
Σ G	2.993	2.912	2.924	3.092	3.055	3.026	3.047	3.077	3.002	2.873	2.894	3.051	2.904	2.896
S^{6+}	0.000	0.000	0.000	0.007	0.062	0.060	0.074	0.029	0.010	0.011	0.001	0.000	0.000	0.038
P^{5+}	0.233	0.228	0.194	0.077	0.043	0.034	0.039	0.032	0.099	0.033	0.011	0.001	0.008	0.011
V^{5+}	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007
As5+	1.811	1.832	1.859	1.808	1.830	1.845	1.842	1.859	1.840	1.984	1.979	1.836	1.972	1.929
Si^{4+}	0.000	0.000	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.003	0.003	0.004	0.000
Σ T	2.044	2.060	2.065	1.892	1.935	1.939	1.955	1.920	1.949	2.033	1.994	1.840	1.984	1.985
H^+	7.035	7.039	7.058	7.238	6.942	7.036	6.977	7.059	7.278	7.031	7.134	7.463	7.120	7.162
O^{2-}	14	14	14	14	14	14	14	14	14	14	14	14	14	14
Fe/(Fe+Al)	0.11	0.14	0.20	0.23	0.34	0.35	0.41	0.50	0.52	0.89	0.99	0.99	1.00	1.00

P – philipsbornite; S – segnitite; b.d. – below detection. Σ D (G or T) – totals of cations at structural positions D, G, or T.

(0.86–1.11 Pb *apfu*) in segnitite. In philipsbornite a deficiency in it is supplemented mainly by Bi^{3+} (up to 5.55 wt.% Bi_2O_3; 0.16 Bi *apfu*), Ca^{2+} (up to 1.04 wt.% CaO, 0.12 Ca *apfu*) and K^+ (up to 0.17 wt.% K_2O, 0.03 K *apfu*), whereas in segnitite it is supplemented by Bi^{3+} (up to 2.97 wt.% Bi_2O_3; 0.09 Bi *apfu*), Ca^{2+} (up to 0.40 wt.% CaO, 0.05 Ca *apfu*) and traces of Ba^{2+} (up to 0.13 wt.% BaO).

The presence of philipsbornite in the voids filled by the chlorite–phlogopite aggregates was corroborated by the strongest reflections recorded in an X-ray diffraction pattern of the fillings at [*d*(Å), *I*, (hkl)]: 3.012, 100, (113); 5.823, 55, (101); 3.567, 50, (110); 2.271, 30, (107) and 3.516, 25, (104) (Table 2). No reflections, characteristic of segnitite, were found. The refined unit-cell parameters of philipsbornite from Rędziny, a = 7.1245(13) Å and c = 17.0967(45) Å, presented in the diagram c *versus* a (Fig. 5) plot at the centre of the area characteristic for philipsbornite and hidalgoite, exhibiting very good agreement with other philipsbornite data previously presented in the plot by Sejkora *et al.* (2001a). According to Sejkora *et al.* (1998),

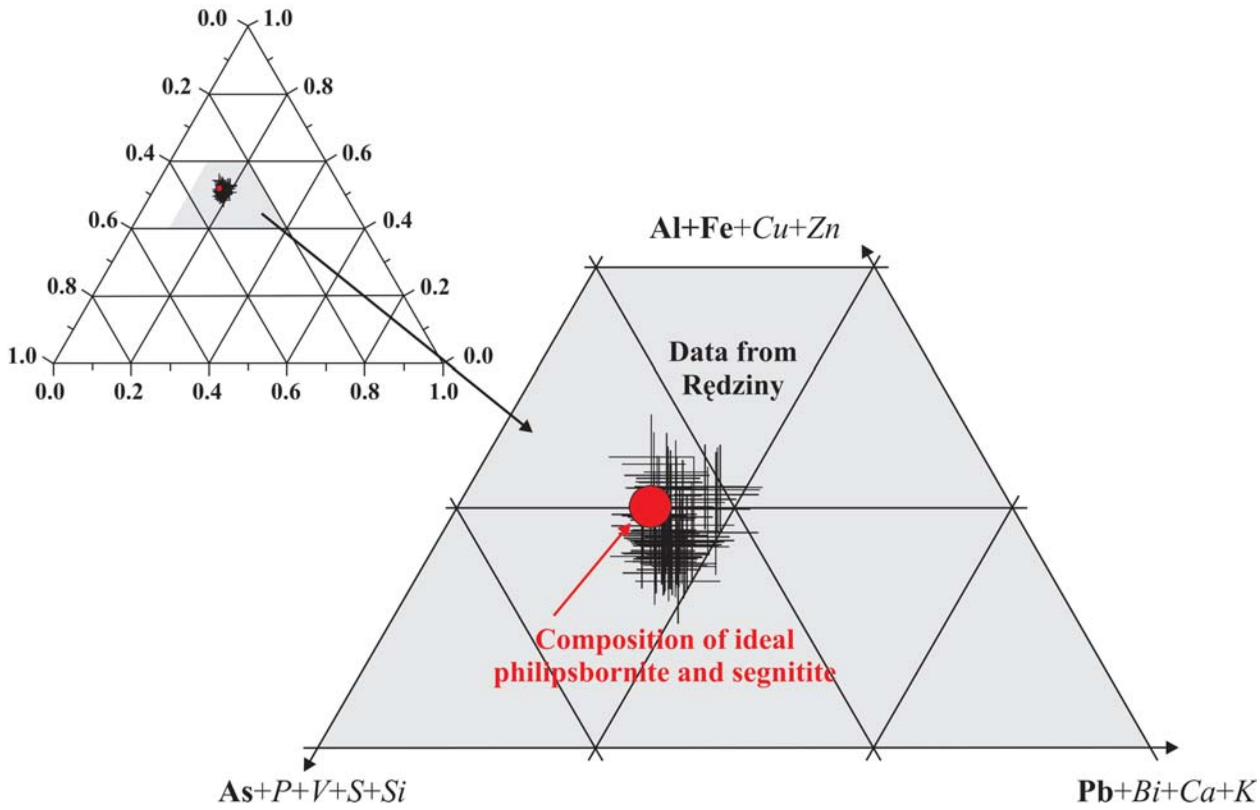

Fig. 3. Compositional plot of the Rędziny philipsbornite and segnitite in As–Pb–(Al, Fe) triangular diagram for Pb-(Al, Fe) arsenates of the dussertite group.

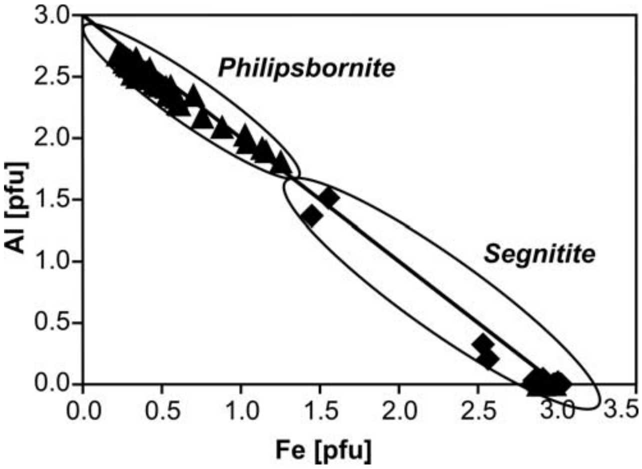

Fig. 4. A compositional gap as a result of limited Al–Fe^{3+} substitution in minerals of the philipsbornite–segnitite series from Rędziny.

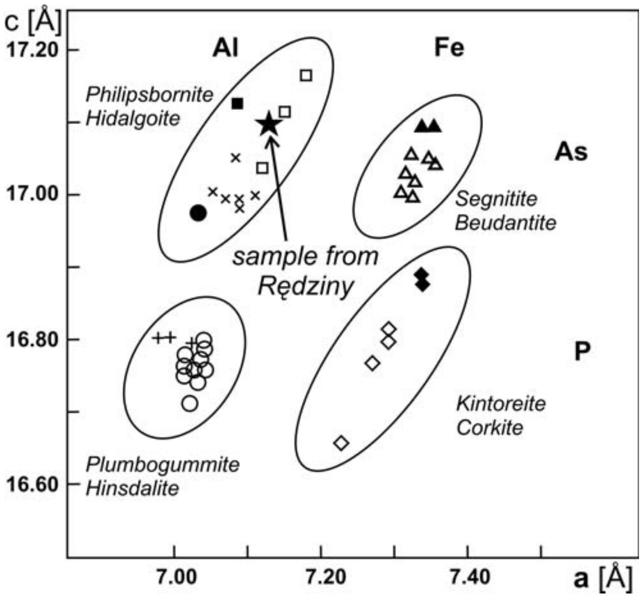

Fig. 5. Philipsbornite from Rędziny in a plot of unit-cell parameters, a *versus* c, for Pb-dominant members of the alunite supergroup. All other data presented are after Sejkora *et al.* (2001a).

this diagram shows that variation in Fe^{3+} and Al^{3+} contents is reflected in the observed changes in values of the a parameter, whereas the substitutions at the position T influence the c parameter.

Philipsbornite and segnitite were also positively identified by EBSD measurements on the zoned crystals present in the voids among arsenopyrite crystals associated with Cu-Ag-(Bi,Sb,As) sulphosalts and Ag-bearing galena. The analyses of the images obtained were matched satisfactorily to the rhombohedral space-group symmetry *R-3m* (no. 166) for both Pb-Al and Pb-Fe^{3+} compounds with mean angular deviations in the range 0.40–0.66°. The raw EBSD images and resulting fits of the modelled structure to the acquired Kikuchi band for the relevant samples are presented in Figure 6.

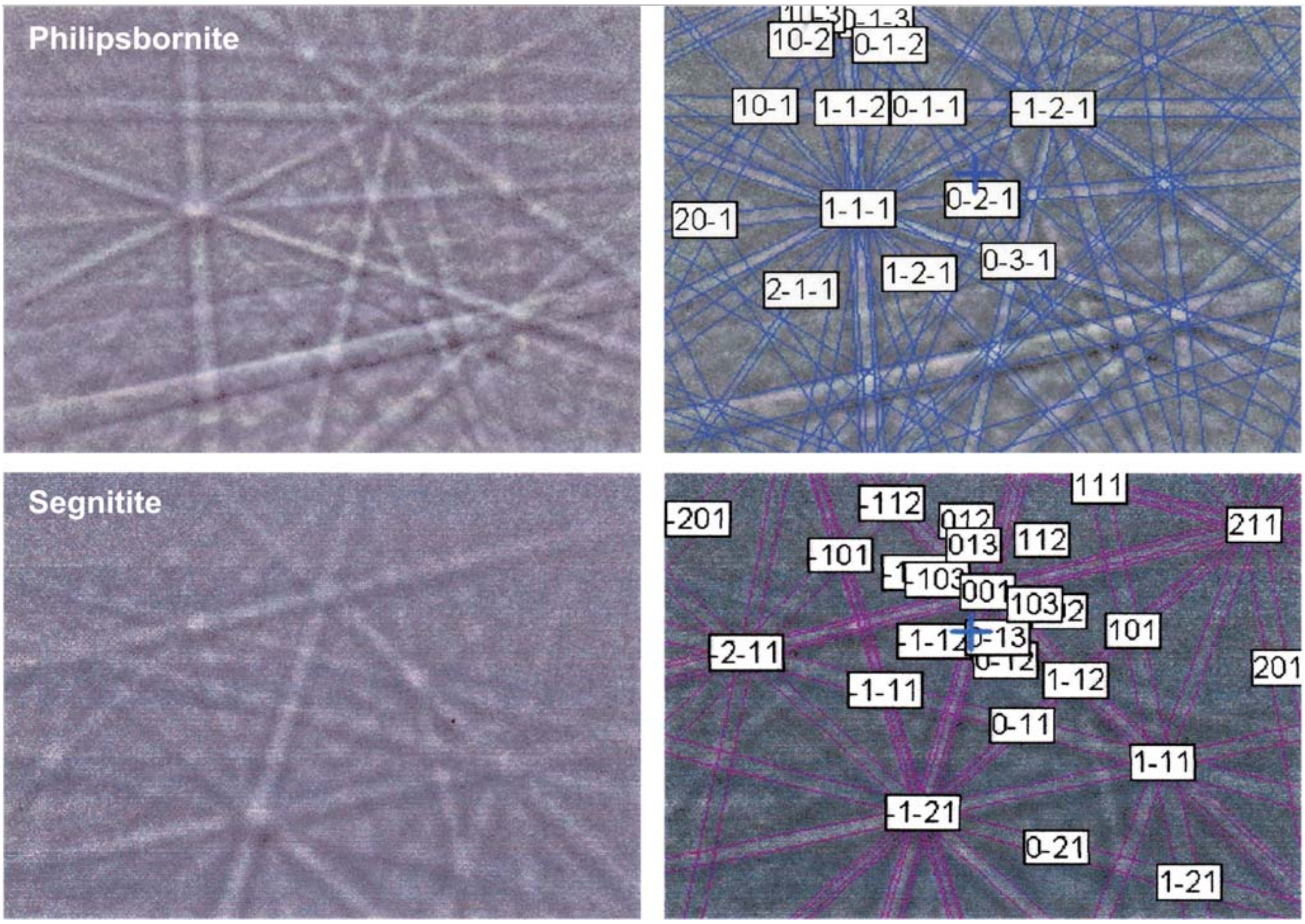

Fig. 6. Electron-back-scattered-diffraction (EBSD; Kikuchi bands) pattern and indexing of philipsbornite and segnitite from Rędziny.

Associated carminite

Carminite, $PbFe^{3+}_2(AsO_4)_2(OH)_2$, an arsenate mineral accompanying members of the philipsbornite–segnitite series at Rędziny, most often forms small, dendrite individuals, grown on and among the crystals of philipsbornite–segnitite (Fig. 2C). Arsenic (33.86–39.52 wt.% As_2O_5; 1.91–2.02 As *apfu*) in the tetrahedral sites is replaced in the same way as in members of the philipsbornite–segnitite series, mainly by traces of P^{5+} (up to 0.38 wt.% P_2O_5; 0.04 P *apfu*), S^{6+} (up to 0.04 wt.% SO_3; < 0.01 S *apfu*) and Si^{4+} (up to 0.03 wt.% SiO_2) (Table 3). Ferric iron is always the dominating component in the [6]-fold-coordinated sites (20.74–26.35 wt.% Fe_2O_3; 1.72–1.98 Fe *apfu*), and its deficiency is supplemented mainly by Al^{3+} (up to 1.06 wt.% Al_2O_3; 0.14 Al *apfu*) and traces of Zn^{2+} (up to 0.09 wt.% ZnO). Similarly as in the members of the philipsbornite–segnitite series, Pb^{2+} is the dominant divalent cation (26.31–35.63 wt.% PbO; 0.71–1.05 Pb *apfu*), with a deficiency supplemented mainly by Ca^{2+} (0.38–2.27 wt.% CaO; 0.05–0.24 Ca *apfu*), Bi^{3+} (up to 1.17 wt.% Bi_2O_3; 0.03 Bi *apfu*), and traces of K^+ (up to 0.04 wt.%; < 0.01 *apfu*).

Carminite was positively identified by X-ray diffraction on the basis of the strongest reflections [*d*(Å), *I*]: 3.225 (100), 2.547 (50), 3.023 (40), 2.723 (30), 2.954 (20).

DISCUSSION

The existence of continuous solid solutions between end-members of the alunite group (a group within the alunite supergroup; Mills *et al.*, 2009; Bayliss *et al.*, 2010), connected with continuous substitution of three-valent Fe^{3+} and Al^{3+} cations at the G site, was well documented, e.g., between alunite and jarosite (Brophy *et al.*, 1962; Scott, 1987) or beaverite and plumbojarosite (Jambor and Dutrizac, 1983). However, a solid solution formed by philipsbornite, $PbAl_3(AsO_4)(AsO_3OH)(OH)_6$, and segnitite, $PbFe^{3+}_3(AsO_4)(AsO_3OH)(OH)_6$, both minerals belonging to the dussertite group, another group in the alunite supergroup, always has been recognized as a series with a compositional gap, due to limitations in $Fe^{3+} \leftrightarrow Al^{3+}$ substitution. Rattray *et al.* (1996) noted such a compositional gap in the solid solution samples coming from Broken Hill in Australia. Sejkora *et al.* (2011) made a similar observation in minerals of the series from Jáchymow in the Czech Republic, in which the highest amount of Fe^{3+} in philipsbornite reached 1.09 *apfu*, corresponding to the content of ~33–34 mol% end-member segnitite. At Rędziny, the upper limit of the Fe^{3+} substitution for Al^{3+} in philipsbornite is much higher and attains compositions already characteristic of the mineral segnitite [~52 mol.% $PbFe^{3+}_3(AsO_4)(AsO_3OH)(OH)_6$]. On the other hand, the Al^{3+} substitution for Fe^{3+} in segnitite

Table 2

X-ray diffraction patterns of philipsbornite from Rędziny

	This study			Schwab *et al.* (1991)		Sejkora *et al.* (1998)	
h k l	**d_{meas}**	**$d_{cal.}$**	**$I/I_{max.}$**	d	$I/I_{max.}$	d	**$I/I_{max.}$**
1 0 1	5.82	5.80	54	5.801	60	5.772	100
0 0 3	5.708	5.705	21	5.690	5	5.698	40
0 1 2	5.046	5.004	10	5.004	5		
1 1 0	3.567	3.562	58	3.564	55		
1 0 4	3.516	3.516	23	3.509	10	3.500	30
0 2 1				3.035	5		
1 1 3	3.023	3.021	100	3.020	100	3.008	90
0 1 5				2.987	5		
2 0 2	2.902	2.902	4	2.903	5	2.882	30
0 0 6	2.848	2.852	23	2.844	10		
0 2 4	2.501	2.502	5	2.501	10	2.498	20
2 1 1	2.309	2.320	5	2.312	15		
2 0 5	2.291	2.291	6	2.289	5		
1 0 7	2.271	2.273	30	2.251	35	2.270	60
1 2 2	2.251	2.250					
1 1 6	2.223	2.223	13	2.223	5	2.227	10
3 0 0	2.061	2.056	5	2.057	5	2.035	10
2 1 4	2.048	2.047	6	2.046	20	2.035	10
0 1 8	2.017	2.021	41	2.015	5		
3 0 3	1.936	1.935	11	1.935	5	1.927	20
1 2 5				1.926	5		
0 2 7, 0 0 9	1.911	1.91	4	1.896	5		
2 2 0	1.781	1.781	10	1.782	10		
2 0 8	1.763	1.758	10	1.755	5		
2 2 3				1.700	5		
1 3 1	1.703	1.703					
2 1 7	1.686	1.687	6	1.685	5		
3 1 2, 1 1 9	1.676	1.678	23	1.674	5		
3 0 6	1.668	1.668	2				
1 3 4	1.588	1.589	5				
4 0 1	1.536	1.536	20				
3 1 5				1.530	5		
0 4 2	1.519	1.518	2				
2 2 6	1.510	1.511	4				
0 2 10	1.495	1.496	6	1.493	5		
4 0 4	1.455	1.451					
0 0 12	1.426	1.426	4	1.422	5		
1 3 7	1.402	1.402	2				
2 1 10	1.379	1.380					
1 4 0	1346	1.346	8				
a	17.0967(45)			17.062		17.14(3)	
c	7.1245(13)			7.127		7.073(7)	

Table 3

Representative compositions of carminite from Rędziny

wt.%	C1	C2	C3	C4	C5	C6	C7
SO_3	b.d.	b.d.	b.d.	b.d.	b.d.	0.04	b.d.
P_2O_5	0.37	0.38	0.31	0.15	0.32	0.19	0.14
As_2O_5	34.98	34.92	34.98	35.31	36.52	34.86	35.15
SiO_2	0.02	0.02	b.d.	b.d.	0.03	0.03	b.d.
Al_2O_3	0.96	1.06	0.93	0.85	1.06	0.71	0.67
Fe_2O_3	21.41	21.15	20.74	21.62	26.35	21.47	22.23
Bi_2O_3	0.22	0.43	0.72	b.d.	b.d.	1.17	b.d.
CaO	0.44	0.40	0.38	0.52	2.27	0.43	0.58
ZnO	b.d.	b.d.	b.d.	b.d.	0.09	b.d.	b.d.
PbO	35.06	35.19	35.09	34.74	26.31	35.63	34.63
K2O	b.d.	b.d.	b.d.	b.d.	0.04	b.d.	b.d.
$H2O_{(calc.)}$	2.78	2.77	2.73	2.79	3.15	2.85	2.85
Total	96.24	96.32	95.88	95.98	96.14	97.38	96.25
Number of ions on the basis of Σ O = 10 apfu							
Bi^{3+}	0.006	0.012	0.020	0.000	0.000	0.033	0.000
Ca^{2+}	0.051	0.046	0.045	0.061	0.243	0.051	0.068
Pb^{2+}	1.030	1.036	1.042	1.021	0.707	1.046	1.014
K^+	0.000	0.000	0.000	0.000	0.004	0.000	0.000
Σ A	1.087	1.094	1.107	1.082	0.954	1.130	1.082
Al^{3+}	0.123	0.137	0.121	0.109	0.124	0.092	0.086
Fe^{3+}	1.758	1.739	1.722	1.775	1.980	1.762	1.819
Zn^{2+}	0.000	0.000	0.000	0.000	0.006	0.000	0.000
Σ B	1.881	1.876	1.843	1.884	2.110	1.854	1.905
S^{6+}	0.000	0.000	0.000	0.000	0.000	0.003	0.000
P^{5+}	0.034	0.035	0.028	0.014	0.027	0.018	0.013
As^{5+}	1.996	1.996	2.018	2.015	1.907	1.988	1.998
Si^{4+}	0.002	0.002	0.000	0.000	0.003	0.004	0.000
Σ T	2.032	2.033	2.046	2.029	1.937	2.013	2.011
H^+	2.021	2.017	2.007	2.029	2.097	2.072	2.064
O^{2-}	10	10	10	10	10	10	10

Ba, Cu and V are below detection (b.d.). Σ A (B or T) – totals of cations at structural positions A, B or T. Low analytical totals are probably results from dendritic form of the carminite crystals.

reaches only 11 mol.%, a value approximately two times smaller than that documented by Rattray *et al.* (1996), but almost identical with observations made by Jansa *et al.* (1998) on segnitite from Cínovec and by Sejkora *et al.* (2011) on the mentioned philipsbornite from Jáchymov. On the basis of these results, the present authors think that the observed gap is a result of the crystallization of both minerals in environments with changing and distinctly different Al^{3+} and Fe^{3+} activities, but also might be a consequence of the limited miscibility of the end-members.

We assumed that the entire Fe is present in the minerals as the trivalent Fe^{3+} cation. However, it should be noted that in the philipsbornite–hidalgonite solid solution (these minerals are distinguished by As > S and S >As, respectively), Cooper and Hawthorne (2012) reported part of the Fe as being divalent, in accordance with the following substitution scheme: $SO_4^{2-} + Fe^{2+} \rightarrow AsO_4^{3-} + (Al/Fe)^{3+}$. According to these authors, if the S content is significantly larger than that of Fe, the substitution of Fe^{3+} for Al^{3+} is negligible and can be excluded. In the philipsbornite–segnitite crystals from Rędziny, we have the opposite case, because the S^{6+}

contents are always small and distinctly lower than those of As^{5+}. Taking this into account, we suppose that most likely the oxidation state of Fe in our samples is trivalent, supporting the simple, isovalent substitution $Fe^{3+} \leftrightarrow Al$, which is typical for minerals of the philipsbornite–segnitite series. The AsO_4^{3-} anion is replaced in part by the lower-charged SO_4^{2-} anion and therefore it must be compensated by additional H^+, occurring in the form of the OH^- group associated with the anion, i.e. $[AsO_3(OH)]^{2-}$. A deficiency in As^{5+} at the tetrahedral T site is completed by P^{5+} and traces of Si^{4+} and V^{5+}, as in the philipsbornite or segnitite of many other occurrences, e.g., Broken Hill (Rattray *et al.*, 1996), Cínovec (David *et al.*, 1990; Jansa *et al.*, 1998), Moldava (Sejkora *et al.*, 1998, 2001a), the Krupka ore deposit (Sejkora *et al.*, 2009) and Jáchymov (Sejkora *et al.*, 2011). Moreover, philipsbornite and segnitite from the localities mentioned often reveal significant differences in chemical composition and are known to form complex solid-solution series within the alunite supergroup, e.g., philipsbornite–plumogummite or beudantite–segnitite (e.g., Moldava; Sejkora *et al.*, 1998, 2001a). Moreover, Sejkora *et al.* (2009) reported a heterovalent substitution between Cu^{2+} and Fe^{3+} at the G site, according to the following substitution scheme $Fe^{3+} + AsO_4^{3-} \leftrightarrow Cu^{2+} + SO_4^{2-}$, and a good correlation of Cu^{2+} and SO_4^{2-} contents. In the case of philips- bornite and segnitite from Rędziny, the contents both of Cu^{2+} as well as SO_4^{2-} are low and such a trend has not been observed.

Environmental features, such as the activities of ions, pH and Eh, and the solubility of compounds give rise to complex phase equilibria forming a succession of precipitated minerals under supergene conditions, including the possible solution of earlier formed compounds. The differentiation of the primary ore assemblage at Rędziny (Pieczka *et al.*, 2009), combined with varying supergene conditions, resulted in the formation of many rare secondary minerals, often representing complex solid-solution series. Members of the philipsbornite–segnitite series were found at one of the deepest exploitation levels of the Rędziny quarry and, additionally, within a zone of weakly altered arsenopyrite with traces of polymetallic mineralization, disseminated within amphibole–chlorite–mica schists. This indicates that the secondary minerals are early alteration products of arsenopyrite and coexisting sulphides. According to the stability field diagram for Cu^{2+} and Pb^{2+} arsenates at 298°C presented by Williams (2005), philipsbornite is stable under conditions of low pH, not exceeding a value of 4. At Rędziny, the occurrence of philipsbornite and segnitite in small voids among arsenopyrite crystals indicates that both minerals could crystallize even in a more acidic environment, in which the oxidation of arsenopyrite and associated sulphides has produced arsenic ($HAsO_4^{2-}$) and sulphuric (SO_4^{2-}) acids. The action of these agents with the aluminosilicate host (chlorite- and mica-group minerals) and with galena and Pb-Bi sulphosalts mobilized the Al^{3+} and Pb^{2+} necessary for the formation of the minerals. When solutions in the Rędziny supergene zone became progressively enriched in Cl at a higher pH, due to SO_4^{2-} leaching and the influence of CO_3^{2-} anion mobilized by reaction of the solutions with the nearby dolomite lens, the precipitation of mimetite and various (Pb,Ca)-(Fe,Cu,Zn) arsenates commenced. This is evidenced particularly in zones more distal with respect to the veins containing arsenopyrite, or in primary ore veins altered completely into arsenates, such as conichalcite, tyrolite, cornwallite, clinoclase, olivenite, bayldonite or duftite (Gołębiowska *et al.*, 1998). The crystallization of carminite after philipsbornite and segnitite may indicate distinct disproportions between the activities of Fe^{3+} cation, common in the Rędziny oxidation zone, and only subordinate Pb^{2+}, which additionally could be easily immobilized in the form of various arsenate, vanadate or phosphate phases. All the Fe-bearing arsenates, including philipsbornite, segnitite and carminite, represent only transitional phases and underwent further alteration into common ferric iron arsenates, and efinally scorodite.

CONCLUSIONS

The Rędziny quarry, located in the contact aureole of the Karkonosze granite, is the next occurrence of philipsbornite, $PbAl_3(AsO_4)(AsO_3OH)(OH)_6$, and segnitite, $PbFe^{3+}_3 AsO_4)(AsO_3OH)(OH)_6$, two rare isomorphic Pb-arsenates in the Bohemian Massif (the first in Poland). The minerals, associated with carminite, $PbFe^{3+}_2(AsO_4)_2(OH)_2$, were found in relics of quartz–chlorite–arsenopyrite veins with subordinate polymetallic Cu-Ag-Pb-Bi-Sb-As mineralization. The philipsbornite and segnitite typically exhibit highly variable chemical compositions, with a distinct compositional gap between values of 0.52 and 0.89 for the Fe/(Fe+Al) ratio, a characteristic rhombohedral structure with a space-group symmetry *R-3m* (no. 166), and unit-cell parameters, a = 7.1245(13) Å and c = 17.0967(45) Å (philipsbornite). The minerals crystallized in the sequence: philipsbornite → segnitite → carminite, which reflects (1) decreasing acidity in the oxidation zone, due to the leaching of sulphate ions and the interaction of acidic solutions with a nearby dolomite lens, and (2) varying activities of Al^{3+}, Fe^{3+} and Pb^{2+} cations mobilized by the solutions through interaction with the silicate host containing disseminated arsenopyrite and subordinate sulphides, up to complete Pb^{2+} depletion.

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