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Native silver in the eastern part of the Karkonosze granitoid pluton, Lower Silesia, Poland

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ABSTRACT:

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This article describes silver specimens of the size of tenths to a few millimetres, found in small pegmatites and quartz veinlets of the porphyritic granitoid area in 22 sites in the eastern part of the Variscan granitoid Karkonosze pluton, from 20 of which native silver occurrences were previously not known. The sites are scattered on the whole surface of the granitoid. The native silver occurred in wire, rod, platy, dendritic, anhedral granular and euhedral cubic and octahedral habits; in some specimens twins and fenster faces were also found. Associated with native silver small amounts of acanthite crystallized commonly, sometimes apparently formed by sulphur diffusion into silver. Inclusions of native gold, electrum, galena, chalcopyrite and pyrite occurred in the native silver. The parent fluids of the specimens were epithermal, because the homogenization temperature (Th) of inclusions in quartz, calcite and cleavelandite that were the host minerals of the native silver was generally 91–165ºC and for individual samples the Th range was 4–11ºC. The total salinity of the fluid was 2.4–7.2 wt. % with Na and Ca (hydro)carbonates as the main dissolved components and admixtures of K, Mg, Fe, Al, S, Cl and F. The parent granitoid contains Ag in trace amounts (0.034–0.056 ppm) and was probably the source of this element for the crystals of native silver. Migration of Ag was made easier by the presence of fluoride ions in fluids.

Key words: Native silver; Fluid inclusions; Granitoid; Karkonosze pluton.

FOREWORD

The paper presents an investigation of specimens which were collected in the Polish part of the Karkonosze pluton in 1968–2005. The early field work of one of us (AK) in the Karkonosze-Izera Mts. area in the years 1969–1974 was conducted jointly with the late Professor Łukasz Karwowski (at that time M.Sc.). He and AK were graduates of the Faculty of Geology, University of Warsaw, and later became staff members of this institution. The field work of each of them was performed for their separate investigations (like this one), but also for common studies and scientific publications. Though later Professor Karwowski obtained a job in the University of Silesia, he and AK remained really good friends. Thus the news of his death on the 5th of December 2022 was very sad indeed and the Authors would like to dedicate this publication to the memory of him and his scientific achievements.

INTRODUCTION

Since antiquity, silver has been an important raw material in the economic relationships in human communities (cf. e.g., Craddock 2014; Jesus and Dardenız 2015). A similar situation occurred in the Middle Ages, when prospecting for Ag ores and their exploitation was very intensive – the Harz

Mts. and their forefield areas may be a good example (Hautzinger 1877; Liessmann 2010; Klappauf 2014). Early information on the economic and political role of silver in Silesia and on the search for this metal ore was presented by Cureus (1571). A catalogue of Silesian minerals was published by Schvvenckfelt (1600, pp. 364, 365), who wrote "Gigantævs mons propris, accolis der Riesenberg [...] mineræ eius, licet aeris, argenti, auri sint feraces [...]" (Karkonosze Mts. possess in the neighbourhood of Śnieżka Mt. [...] their minerals, [which] probably in copper, silver, gold are fertile [...], op. cit., in the introduction: Silesiae geographica brevis delineatio, unnumbered p. 29 in sequence). Neither in the introduction, nor in the main text, are the locations of Ag ores in the granitoid pluton area named, albeit such ore occurrences are listed from the contact zone of the pluton in both the present-day Czech and Polish parts, e.g., Obří Důl (Riesengrund), Čertův Důl (Teufelsgrund) or Gierczyn (Gieren). Also while Henelius (1613) omitted the pluton area in his description of the Silesian Ag ores (pp. 36, 44, 46), in the late version of this book (Henelius 1704) there is a sentence similar to the Schvvenckfelt's note: "Mons Giganteus fertilis, sed spectro infestus, mons ipse auro, argento, aere gemmis gravidus [...]" (Karkonosze Mts. fertile, though with dangerous ghost[1], the mountain pregnant with gold, silver and copper [...], chapter II p. 154).

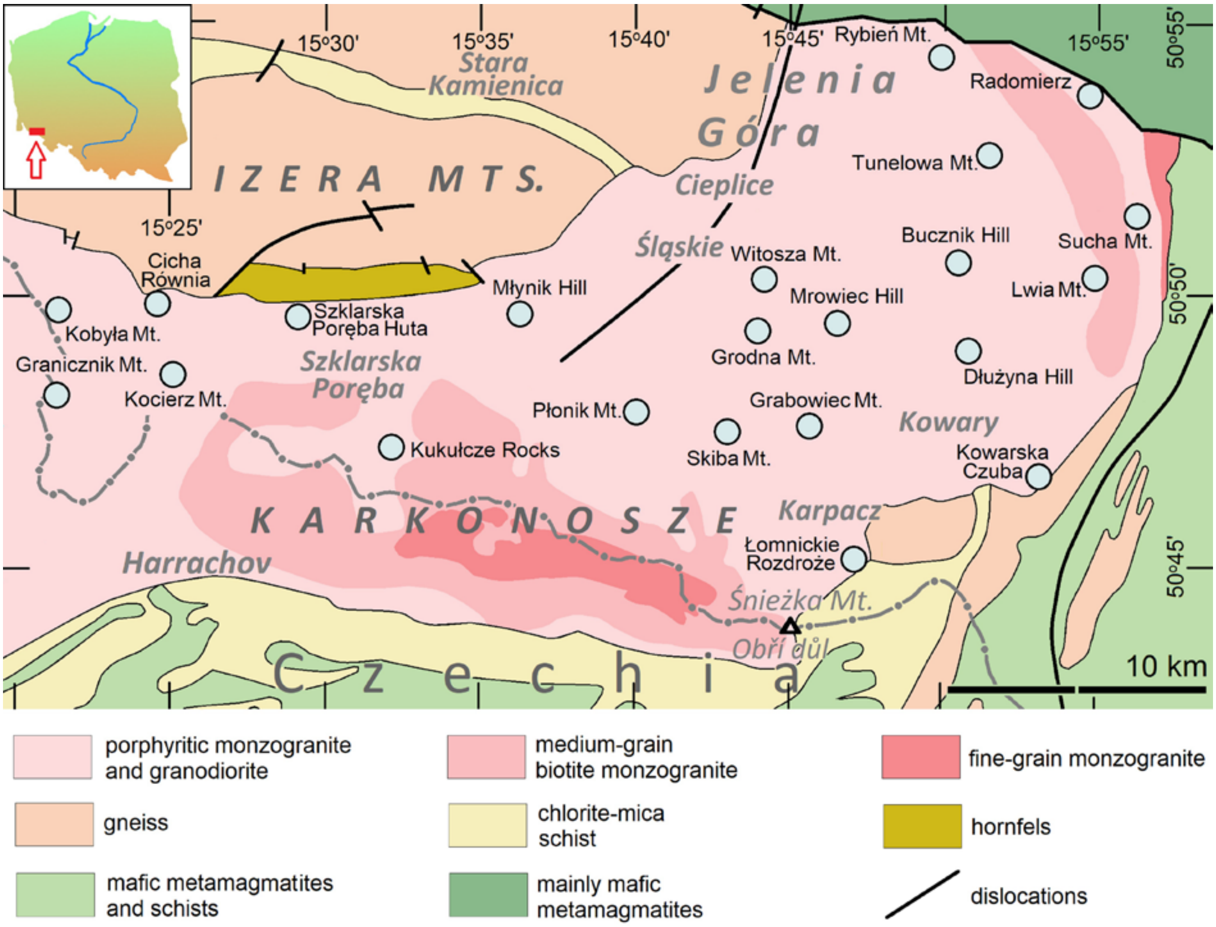
In Lower Silesia, Bruckmann (1727, pp. 211–233; 1730, pp. 769–850) described 19 regions of silver ore exploitation and Fehner (1903) – 12 silver mines, but none in the Karkonosze pluton area. In turn, Kretschmar (1662, chapter 7 – Vom Silber, pp. 22, 23), who listed 14 occurrences of silver from the pluton, named moreover one "between Zacken River (Kamienna) and Queiß River (Kwisa)" which may be related to the Karkonosze granitoid, but also to the area of the Izera gneiss and schist in the northern envelope of the pluton, because at that time the Izera Mts. were also partly included in the Riesengebirge (Karkonosze Mts.). Volkelt (1775, pp. 106–109) described silver ore from 12 separate places in Lower Silesia and additionally the one mentioned by Kretschmar (1662). Volkelt (1775) cited as his source the book by Volkmann (1720), who on pp. 213–217 characterized silver presence in the deposits of the whole Silesia. A contemporary review of mineral occurrences in the Karkonosze pluton and its envelope was published by Mochnacka *et al.* (2015).

[1] In old tales of the Karkonosze area a Mountain Ghost (Rübezahl) saved the underground mineral resources, especially gold and silver ores (Prætorius 1662).

The first undoubted information on Ag mineral occurrences in the eastern part of the Karkonosze pluton was published by Gajda (1960), who found a minute native silver grain (0.5 mm) of platy habit in a pegmatite vein at Biała Dolina, a part of Szklarska Poręba town. The next specimen of native silver found at Szklarska Poręba Huta consisted of three flakes of dimensions of 0.3–0.4 mm (Kozłowski and Sachanbiński 2007, pp. 160, 161). Moreover, the occurrence of this mineral in the granitoid area at Łomnickie Rozdroże was mentioned by Kozłowski *et al.* (2016). This suggested that more finds of Ag minerals in this pluton would depend on very thorough searches of the small-size mineral components of pegmatites and veins. Such investigations resulted in the recognition of 20 Ag minerals of the sulphide, arsenide, selenide, telluride, sulphosalt and chloride groups in 13 locations of this area (Kozłowski and Matyszczak 2022b). The collection of the samples used in the present study was made in the years 1968–2005 and resulted in the finding of 20 previously unknown occurrences of native silver (Text-fig. 1).

GEOLOGICAL SETTING

The Karkonosze pluton is a Variscan granitoid batholith, c. 70 km latitudinally elongated and 8 to 20 km wide from N to S, with its surface forming mountain ridges and intra-montane valleys. Most probably Pallas (1778, p. 5) was the first to classify the pluton rock as granite. The difference between this granite and the neighbouring gneiss was pointed out by Gerhard (1781, p. 47). Rose (1842) recognized varieties of the Karkonosze granitoids: one built of a fine-grained quartz-feldspar-mica groundmass with dispersed several-centimetre long orthoclase phenocrysts, next an equigranular medium-grained one with typical granitoid composition and a very fine-grained granite-type rock with abundant albite, thus an aplitic variety frequently but not always forming veins. These characteristics were completed in petrographic detail by Klockmann (1882) as well as by Müller (1889), who added '*Ganggranit*', i.e., granitoid pegmatites. A review of the important features of the composition of the Karkonosze granitoids and new data on the forms of their occurrence were prepared by Berg (1923). Borkowska (1966) published the exact petrographic description of the pluton rocks and distinguished the central granite (earlier porphyritic granite), the ridge granite (equigranular granite) and the granophyric granite (fine grained granite). The QAPF system (Le Maître *et al.* 2002) applied



Text-fig. 1. Eastern part of the Karkonosze Variscan granitoid pluton and its metamorphic envelope; circles – sampling locations of the native silver specimens. Geological background after Krenz *et al.* (2001), changed. Insert – location in Poland.

to the Karkonosze granitoids indicated that the rock types referred to as central and crest granite are in fact monzogranite and granodiorite (any of them may form parts of the central or crest varieties), whereas the granophyric type is monzogranite only (Text-fig. 1; cf. Krenz *et al.* 2001). The data from melt inclusion investigations in magmatic quartz have provided evidence that the Karkonosze granitoid formed at 990 to 840°C from a melt of tonalitic to granitic composition (Kozłowski 2007). Suggestions were published that the melt formed by mixing or mingling of felsic and mafic components of different origin (Słaby and Martin 2008). Most probably formation of the intrusion was polyphase (Cloos 1924; Žák and Klomínský 2007; Žák *et al.* 2013, 2014; Klomínský 2018). The melt(s) intruded in the late Carboniferous (Pennsylvanian), c. 312–315 Ma ago (Žák *et al.* 2013; Kryza *et al.* 2014a, b; Mikulski *et al.* 2020).

The Karkonosze granitoid pluton belongs to the Lower Silesian NE domain of the Variscan Bohemian massif (Mazur *et al.* 2018). This formed by the accumulation of Neoproterozoic fragments of the Gondwana continent, gneisses of the early Palaeozoic granitoid protoliths, zones of middle Palaeozoic sediments which had accumulated on the continental margins and basin sequences with ophiolite series, as well as Carboniferous granitoid plutons and intramontane basins (Mazur *et al.* 2007). The accretion and accompanying collisions, magmatic intrusion processes and a network of faults of various scales in part formed during the Alpine orogeny resulted in the blocky scheme of the rock series distribution in Lower Silesia (Quenardel *et al.* 1988; Mazur *et al.* 2010). The Karkonosze pluton is a component of this pattern. It is surrounded by an envelope of metamorphic rocks (Text-fig. 1): along the northern contact the envelope includes lower Palaeozoic gneiss, and mica-chlorite and amphibolite schists with hornfels, metamafites with limestone; similar rocks form the eastern and southern outer contact zone with local high-pressure (up to 10 kbar) schists (Oberc 1961; Teisseyre 1971; Borkowska *et al.* 1980; Chaloupský *et al.* 1989; Mazur 2003, 2005; Żelaźniewicz *et al.* 2003; Mazur *et al.* 2007, 2010, 2018 and references therein).

OUTCROPS STUDIED

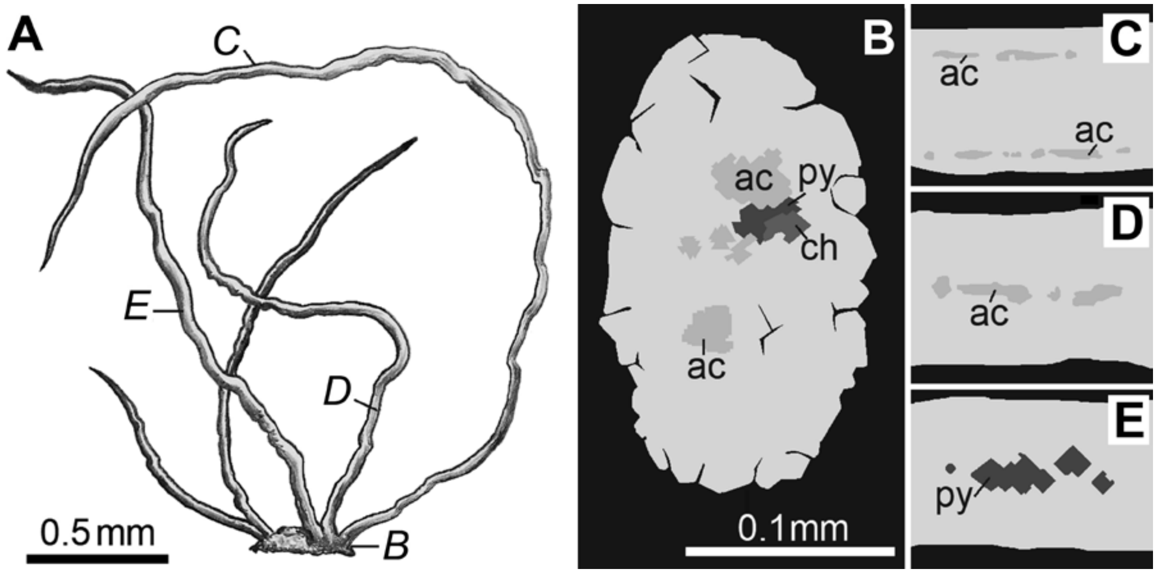
The silver minerals in the eastern part of the Karkonosze pluton were found in pegmatites and quartz veins. Pegmatites of various sizes (few tens of centimetres to rarely several metres) are rather frequent and occur mainly in the porphyritic variety of the batholith granitoid. They are formed by potassium feldspar, quartz, oligoclase, albite, biotite and muscovite arranged in concentric zones, usually with the central miarole in accumulations of more or less isometric habits or in roughly parallel bands when the pegmatite shape is lenticular or of vein-type. Various accessory minerals occur usually in the central parts, but they may also be found dispersed in the whole pegmatite volume (Matyszczak 2018). Commonly the pegmatites are considered as late stage magmatic bodies (e.g., Fersman 1940, pp. 23–32; London 1992, 2008; Thomas *et al.* 2006; Simmons 2008). On the other hand, their textural features may indicate their formation by accumulative metasomatic recrystallization of the parent aplite or granite (Schaller 1925, 1926), as was also found in the Karkonosze pluton (Kozłowski 1978, 2002). The niobium-yttrium-fluorine (NYF) family *sensu* Černý and Ercit (2005, see also Černý *et al.* 2012) is generally accepted as the proper family for the vast majority of the Karkonosze pegmatites (Pieczka *et al.* 2015; Evans *et al.* 2018; Matyszczak 2018). Contemporary investigations indicate that they belong to (i) the euxenite, gadolinite, and allanite-monazite type of rare-elements – rare-earth-elements subclass (Matyszczak 2018), and (ii) the gadolinite-fergusonite type of the miarolitic-rare-earth-elements subclass (Evans *et al.* 2018). The mineralogical characteristics of the Karkonosze pegmatites were published by Pieczka *et al.* (2019; see also Sachanbiński 2021).

The quartz veins in the Karkonosze pluton (Kozłowski 1973, 1978 and references therein) are of variable thickness and extent, but the Ag minerals studied in this research were found in rather small ones – thickness 1–25 cm and visible extent roughly 0.5–3 m. Commonly they were completely filled, mostly by grey quartz of various shades and changing transparency. Feldspars, muscovite and ore minerals were minor components in some. They formed usually in vertical or horizontal fissures, at places with a limited metasomatic replacement of feldspars in the wall granitoid by quartz. Inclined quartz veins were rare.

All the pegmatites from which samples for these investigations were taken occurred in porphyritic granitoid. The localities with native silver (Text-fig. 1) are described in the Appendix.

METHODS

The samples were checked in immersion liquids under a binocular microscope to select the minerals for further investigations. All the collected native silver specimens were analysed by the WDS EPMA method by use of the Cameca SX100 and ARL SEMQ analysers. The preparations were glued on glass, polished and covered by carbon film. The analysis conditions were as follows: electron beam accelerating voltage 7–20 keV, beam current 8–18 nA, diameter of beam spot 3–10 µm, count time 4–15 sec., if necessary 20 sec. The X-ray peaks were used for quantitative analyses: Ag*Lα*, As*Lα*, Au*Lα*, Bi*Mα*, Cd*Kα*, Cl*Kα*, Co*Kα*, Cu*Kα*, F*Kα*, Fe*Kα*, Ge*Kα*, Hg*Mα*, Ni*Kα*, Pb*Mβ*, S*Kα*, Sb*Lα*, Se*Lα*, Sn*Kα*, Te*Kα* and Zn*Kα*, compared to those of the reference substances: synthetic Ag_2S, Ag_2Te, ($Ag_{0.9}Au_{0.1}$), Bi_2S_3, CdS, Co_2S_3, CaF_2, GeSe, HgS, NaCl, Ni, Sb_2S_3, SnO, ZnS and natural $CuFeS_2$ and PbS. The beam parameters for analysis of the minor admixtures in native silver were established by checking of the synthetic reference substances. The detection limits were 0.05–0.01 wt. %. The element contents were calculated by the ZAF and Multi (Trincavelli and Castellano 1999) programs. Trace Ag contents in granitoid were determined by the AAS method (Petrović *et al.* 2001) with use of the Perkin-Elmer PinAAcle 900T spectrometer after chemical extraction from the rock (Hamaguchi and Kuroda 1957, 1959; Marczenko 1968, pp. 524–534). Fluid inclusions in associated minerals were studied by the heating-freezing conventional method (Crawford 1981; Kozłowski 1984; Roedder 1984) and if the inclusion size was very small – by the immersion method with use of the fluids: silicone oil (boiling temp. 315ºC) for heating and ethanol (melting temp. -114.1ºC) for freezing (Karwowski *et al.* 1979). Accuracy of estimation for Th was ±0.5ºC and for Tm ±0.1ºC. Some single inclusions were opened by the microscope hardness tester with diamond indenter or by microscope crushing stage (Roedder 1984, pp. 212–219) and after evaporation of water from the in-



Text-fig. 2. Silver hairs (A) and BSE images of the basis of the hair group (B) and of the fragments of the hairs (C–E); note the inclusions of acanthite (ac), chalcopyrite (ch) and pyrite (py) in native silver (the used abbreviations are shortened to minimize their influence on the image), scale bar 0.1 mm refers to all the BSE images in this figure, Kocierz Mt. Images of the whole specimens here and in the following figures are drawings if not mentioned otherwise.

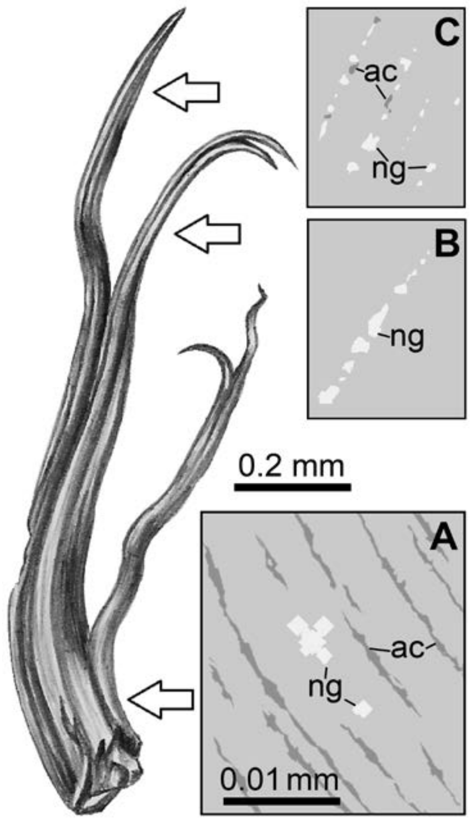
clusion fluid, Cl, F and S were identified in the precipitate by the X-ray scan pictures. It was not possible to make good quality photographs of eu- and subhedral crystals of the investigated 'microminerals', thus very exact drawings were prepared by AK on the basis of binocular observations (see captions to appropriate text-figures).

The investigations were made in the laboratories of University of Warsaw and University of Tübingen.

RESULTS

Native silver specimens

Specimens of native silver found in the Karkonosze pluton are usually represented as single or groups of a few crystals, and their size ranges from tenths of a millimetre to c. 5 mm. In the description below they are arranged in groups according to their crystal habits. One of the typical habits of this mineral is in the shape of hairs or wires. Such sample was found in and on quartz in the vein at Kocierz Mt. (Text-fig. 2A). A flat silver crystals cluster c. 0.4 mm long is the basis of five separate contorted hairs, 1–5 mm in length and c. 0.05 mm thick. Both inside the basic cluster and within the hairs, but not on their surface, grains of sulphide minerals: acanthite, pyrite and chalcopyrite (see BSE images in Text-fig. 2B–E)



Text-fig. 3. Bunch of silver hairs, the inserts show BSE images of parts of the cross-sections perpendicular to (A) and compatible with the bunch elongation (B and C) in the places indicated by the arrows, ac – acanthite, ng – native gold, Cicha Równia.

Occurrence	No.	Ag	Cu	Au	Pb	Hg	Fe	As	Sb	Bi	S	Σ
Bucznik Hill	01	99.85	0.09		0.04	0.01						99.99
	02	99.88	0.06		0.03	0.01						99.98
Cicha Równia	03	99.73	0.18	0.03	0.01					0.01		99.96
	04	99.81	0.08	0.02			0.02					99.93
Dłużyna Hill	05	99.75	0.11		0.03		0.05			0.01		99.95
	06	99.85	0.05		0.01		0.01					99.92
Grabowiec Mt.	07	99.64	0.20		0.05		0.06				0.02	99.97
	08	99.69	0.17		0.05		0.03				0.04	99.98
Granicznik Mt.	09	99.41	0.33		0.05	0.01	0.12					99.92
	10	99.58	0.26		0.02		0.08			0.02		99.96
Grodna Mt.	11	98.83	0.65		0.19	0.05	0.10			0.13		99.95
	12	98.84	0.62		0.17	0.06	0.10			0.14		99.93
Kobyła Mt.	13	98.44	1.30	0.01	0.11	0.01	0.04	0.01	0.01	0.02		99.95
	14	99.79	0.14		0.03		0.02					99.98
	15	99.13	0.73		0.05		0.02			0.01		99.94
	16	99.89	0.09				0.01					99.99
Kocierz Mt.	17	98.88	0.54		0.23	0.02	0.19		0.02	0.01		99.89
Kowarska Czuba Mt.	18	98.77	1.07		0.05		0.04	0.01	0.01	0.02		99.97
	19	99.76	0.12		0.03		0.06			0.01		99.98
Kukułcze Rocks	20	99.76	0.14		0.04		0.01					99.95
	21	99.85	0.10		0.01		0,01			0.01		99.98
Lwia Mt.	22	99.53	0.21		0.12	0.01	0.03			0.02		99.92
	23	99.64	0.17		0.09	0.02	0.02		0.01	0.01		99.96
Łomnickie Rozdroże	24	99.70	0.09	0.01	0.14	0.01	0.03			0.01		99.99
Młynik Hill	25	99.78	0.06		0.09		0.01		0.01			99.95
	26	99.84	0.05		0.08		0.01					99.98
Mrowiec Hill	27	99.02	0.02			0.01	0.02		0.01	0.85		99.93
	28	99.07	0.02			0.01	0.01		0.02	0.83		99.96
Płonik Mt.	29	99.37	0.30		0.16	0.11		0.01	0.01	0.01		99.97
	30	99.51	0.27		0.12	0.07		0.01				99.98
Radomierz	31	99.36	0.31		0.01		0.25		0.01	0.01		99.95
	32	99.83	0.06				0.09					99.98
Rybień Mt.	33	98.90	0.49	0.09	0.11	0.14	0.09	0.03	0.02	0.04		99.91
	34	99.54	0.22		0.03	0.04	0.06	0.01	0.01	0.03		99.94
Skiba Mt.	35	99.30	0.22	0.01	0.03	0.16	0.25			0.01		99.98
	36	99.59	0.14		0.01	0.08	0.10	0.01	0.02	0.01		99.96
Sucha Mt.	37	99.23	0.43		trace	trace	0.28		0.03	0.02		99.99
	38	99.78	0.11		trace		0.09		trace	trace		99.98
	39	99.38	0.27		0.08	0.01	0.19			0.02		99.95
	40	99.48	0.23		0.08		0.17			0.01		99.97
Szklarska Poręba Huta	41	99.04	0.81		0.07	0.02	0.01			0.01		99.96
	42	99.87	0.07		0.03		0.01					99.98
Tunelowa Mt.	43	98.72	0.16		0.18	0.16	0.60		0.08	0.09		99.99
	44	99.01	0.11		0.10	0.09	0.55		0.07	0.05		99.98
Witosza Mt.	45	98.76	0.03		0.88	0.11	0.02		0.02	0.14		99.96
	46	99.00	0.03		0.73	0.07	0.01			0.10		99.94

Table 1. Selected representative analyses of chemical composition of native silver, in wt. %; empty cells – elements below detection limit.

were found. The main admixture elements in native silver are Cu (0.54), Pb (0.23) and Fe (0.19 wt. %) of the same contents in whole specimen within the analytical accuracy ranges (item 17 in Table 1); for acanthite composition see Table 2 items 07–09.

The hairs may form parallel clusters like the bunch from a quartz vein at Cicha Równia (Text-fig. 3), which is 1.7 mm long and almost 0.2 mm thick at its base. At the contact of the hairs very thin and discontinuous acanthite laminae c. 1 μm thick occur with quite high

Mineral/occurrence	No.	Ag	Cu	Au	Fe	Zn	Hg	Pb	Sb	Bi	S	Se	Te	Σ
Acanthite														
Bucznik Hill	01	84.44	0.61		0.43			2.00			12.51	0.60	0.31	99.95
Cicha Równia	02	82.22	0.56	0.47				2.80		0.74	12.55	0.34	0.30	99.98
	03	83.60	0.81	0.46				1.49			13.01	0.28	0.29	99.94
Grabowiec Mt.	04	85.83	0.33		0.23			0.61			12.95			99.95
	05	86.11	0.23		0.16			0.50			12.97			99.97
Grodna Mt.	06	82.56	0.87		0.29		0.58	1.58	0.44	0.50	12.62			99.96
Kocierz Mt.	07	82.74	0.85		0.45		0.49	1.76	0.54		12.78	0.38		99.99
	08	84.08	0.61		0.27		0.56	1.42			12.82	0.22		99.98
	09	84.45	0.41		0.54		0.39	1.17			12.84	0.19		99.99
Łomnickie Rozdroże	10	85.21	0.22		0.28			0.68		0.46	12.76	0.35		99.96
Skiba Mt.	11	82.69	0.59		0.54		0.41	1.17	0.78	0.52	12.69	0.29	0.27	99.95
Rybień Mt.	12	84.28	0.88		0.34		0.39	0.43		0.38	12.74	0.53		99.97
Bornite														
Sucha Mt.	13	0.78	62.36		11.09	0.03		0.12	trace	0.04	25.27	0.19	0.09	99.97
Argentotetrahedrite-(Fe)														
Sucha Mt.	14	34.79	12.26		5.65	0.21			25.07		20.67	1.31		99.96
	15	34.08	13.21		5.82	9.10			25.39		20.93	0.45		99.98

Crystallochemical formulae calculated to 1 anion (items 01–12), to 4 anions (item 13) and to 16 cations (items 14 and 15), apfu.

01: $(Ag_{1.94}Cu_{0.02}Fe_{0.02}Pb_{0.01})_{\Sigma 1.99}(S_{0.97}Se_{0.02}Te_{0.01})_{\Sigma 1.00}$

02: $(Ag_{1.92}Cu_{0.02}Pb_{0.03}Au_{0.01}Bi_{0.01})_{\Sigma 1.99}(S_{0.98}Se_{0.01}Te_{0.01})_{\Sigma 1.00}$

03: $(Ag_{1.94}Cu_{0.03}Pb_{0.02}Au_{0.01})_{\Sigma 2.00}(S_{0.98}Se_{0.01}Te_{0.01})_{\Sigma 1.00}$

04: $(Ag_{1.97}Cu_{0.01}Fe_{0.01}Pb_{0.01})_{\Sigma 2.00}S$

05: $(Ag_{1.97}Cu_{0.01}Fe_{0.01}Pb_{0.01})_{\Sigma 2.00}S$

06: $(Ag_{1.91}Cu_{0.03}Pb_{0.02}Fe_{0.01}Hg_{0.01}Sb_{0.01}Bi_{0.01})_{\Sigma 2.00}(S_{0.98}Se_{0.02})_{\Sigma 1.00}$

07: $(Ag_{1.90}Cu_{0.03}Pb_{0.02}Fe_{0.02}Hg_{0.01}Sb_{0.01})_{\Sigma 1.99}(S_{0.99}Se_{0.01})_{\Sigma 1.00}$

08: $(Ag_{1.94}Cu_{0.02}Pb_{0.02}Fe_{0.01}Hg_{0.01})_{\Sigma 2.00}(S_{0.99}Se_{0.01})_{\Sigma 1.00}$

09: $(Ag_{1.94}Cu_{0.02}Fe_{0.02}Pb_{0.01}Hg_{0.01})_{\Sigma 2.00}(S_{0.99}Se_{0.01})_{\Sigma 1.00}$

10: $(Ag_{1.96}Cu_{0.01}Pb_{0.01}Fe_{0.01}Bi_{0.01})_{\Sigma 2.00}(S_{0.99}Se_{0.01})_{\Sigma 1.00}$

11: $(Ag_{1.91}Cu_{0.02}Fe_{0.02}Sb_{0.02}Pb_{0.01}Hg_{0.01}Bi_{0.01})_{\Sigma 2.00}(S_{0.98}Se_{0.01}Te_{0.01})_{\Sigma 1.00}$

12: $(Ag_{1.93}Cu_{0.03}Fe_{0.02}Pb_{0.01}Hg_{0.01}Bi_{0.01})_{\Sigma 2.01}(S_{0.98}Se_{0.02})_{\Sigma 1.00}$

13: $(Cu_{4.74}Ag_{0.23}Pb_{0.02}Bi_{0.01})_{\Sigma 5.00}(Fe_{0.97}Zn_{0.02})_{0.99}(S_{3.90}Se_{0.08}Te_{0.02})_{\Sigma 4.00}$

14: $Ag_{6.00}(Cu_{3.74}Ag_{0.25})_{\Sigma 3.99}Fe_{1.96}Zn_{0.06}Sb_{3.99}(S_{11.68}Se_{0.32})_{\Sigma 12.00}S_{0.81}$

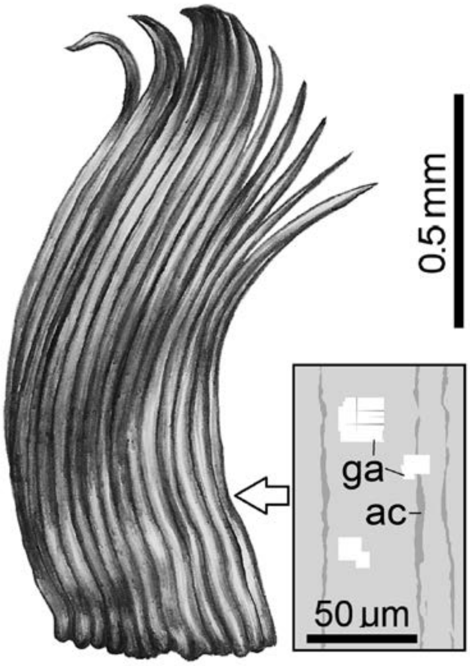
15: $Ag_{6.00}(Cu_{3.97}Ag_{0.03})_{\Sigma 4.00}Fe_{1.99}Zn_{0.03}Sb_{3.98}(S_{11.89}Se_{0.11})_{\Sigma 12.00}S_{0.57}$

Table 2. Chemical composition of sulphide minerals associated with native silver, in wt. %; empty cells – elements below the value that during calculation of the crystallochemical formula gave numbers lower than 0.01 apfu.

contents of minor elements (see Table 2, items 02 and 03); moreover inclusions of native gold 1–5 μm in size were observed (Text-fig. 3A–C). Native gold from the inclusions has admixtures of Ag (up to 1.43 wt. %,) and Cu (0.21–0.24 wt. %; cf. Table 3, items 01–03). Native silver is poor in admixture elements, the main ones are Cu (0.08–0.18) and Au (0.02–0.03 wt. %; cf. items 03 and 04 in Table 1).

Larger bunches of silver hairs have the appearance of curls. An example is one from the quartz veinlet at Łomnickie Rozdroże; its length is 1.6 mm and thickness 0.5 mm (Text-fig. 4). Acanthite laminae up to 5 μm thick between the silver wires also occur, as well as galena inclusions in the form of cubic crystals of an edge up to 20 μm (see insert in Text-fig. 4). Admixture elements in native silver have low and poorly differentiated contents (item 24 in Table 1), the main ones are Cu (0.09) and Pb (0.14 wt. %). The galena inclusions comprise admixtures of Ag (1.9), Cu (0.04), Bi (0.18) and Sb (0.09 in wt. %). Admixtures in acanthite are moderate (Table 2, item 10).

A peculiar aggregate of parallel native silver hairs or wires was found in a thin fissure in a quartz vein at Grabowiec Mt. It has the shape of a short stump, 1 mm high (Text-fig. 5) and of elliptical cross-section, 2×1.3 mm. Probably the wires started to crystallize from one wall of the fissure and reached the other wall, but later the fissure opened more (its present width is c. 5 mm), however the solution in it had already a distinctly lower Ag concentration than during the stump crystallization. On the upper surface of the stump a group of roughly square platy crystals formed. There are two possibilities for their origin: either the ends of thin wires started to recrystallize

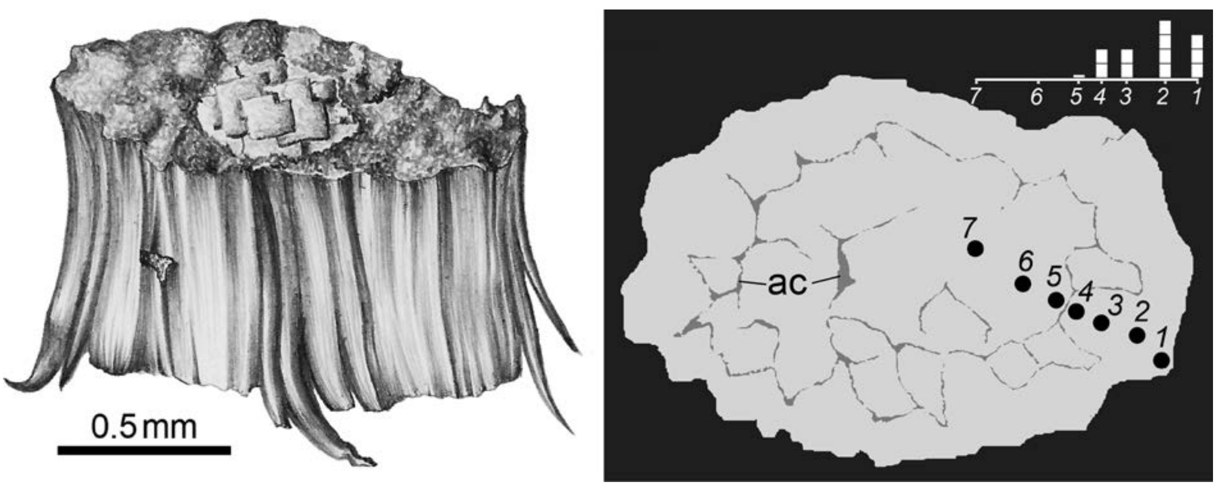


Text-fig. 4. Curl of silver hairs (cf. Kozłowski *et al.* 2016); the insert shows BSE image of a part of the cross-section according to the curl elongation in the place indicated by the arrow, ac – acanthite, ga – galena (one of the crystals with cleavage cracks), Łomnickie Rozdroże.

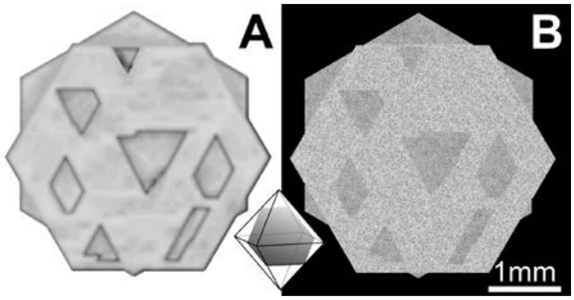
or the last portion of Ag from the mineral-forming solution precipitated in this form. Between groups of wires accumulations of acanthite were found and hence in points 1–7 selected from the stump rim to its central part marked in the BSE image, the occurrence of S in native silver was checked by EPMA. In points 1, 2, 3 and 4, the S contents were 0.03, 0.04, 0.02 and 0.02 wt. %, respectively, but in point 5 – in trace quantities, and in 6 and 7 not detected at all (see diagram in Text-fig. 5). Also in the silver surrounding the ‘S path’ this element was not detected. Other admixture elements occur in rather low contents (items 07 and 08 in Table 1), Cu being the main one (0.17–0.20 wt. %). Acanthite ingrowths are rather poor in the admixture elements (Table 2, items 04 and 05).

Native silver also occurs in the Karkonosze pluton in the shape of platy crystals. A specimen with this habit was found in the pegmatite at Szklarska Poręba Huta. It consists of two crystals of hexagonal habit with the main faces (111) rotated one to another by an angle of 30º; also the twinning plane was in accordance with the (111) face (Text-fig. 6A), as is frequent for native silver (Carpenter and Tamura 1926, p. 172, figs 2 and 3; Neumann 1944, p. 43). The size of the plates in the plane of the (111) face is 3.6 mm, and their thickness is 0.6 mm for the lower and 0.4 mm for the upper one. The lower lamella has c. 0.1 mm thick convexities, generally of triangular and parallelogram shapes. These convexities are not overgrown by the upper lamella. Differences in the two lamellae may be observed after etching their surfaces with an HNO_3 solution (Text-fig. 6B) – the lower lamina is more susceptible to etching. This results from a higher admixture of Cu (0.73–0.81 wt. %) than in the upper one (0.07–0.12 wt. %), the contents of the other admixture elements are low (items 41 and 42 in Table 1).

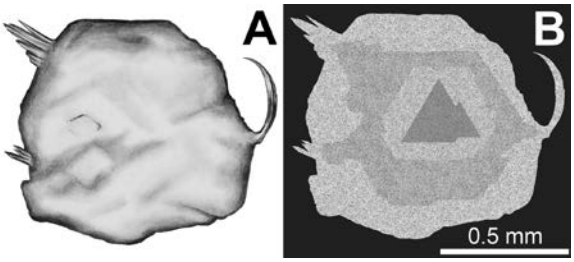
The specimen of native silver from a quartz veinlet at Kobyła Mt. is also a c. 1 mm plate with a thickness of c. 0.3 mm (Text-fig. 7A). The shape is roughly hexagonal with protruding short wires in the



Text-fig. 5. Stump of roughly parallel silver wires with subhedral cubic silver crystals on its upper surface, the BSE image below the drawing shows cross-section parallel to the lower surface of the stump, ac – acanthite, *1-7* – EPMA points for S determination, in the diagram the maximum S amount in the point 2 is 0.04 wt. %, Grabowiec Mt.



Text-fig. 6. Plate of two lamellae of native silver, A – natural appearance with a sketch of the position of the hexagon lamella in the octahedron, B – photomicrograph of finely polished and HNO_3-etched surface of this specimen, Szklarska Poręba Huta.



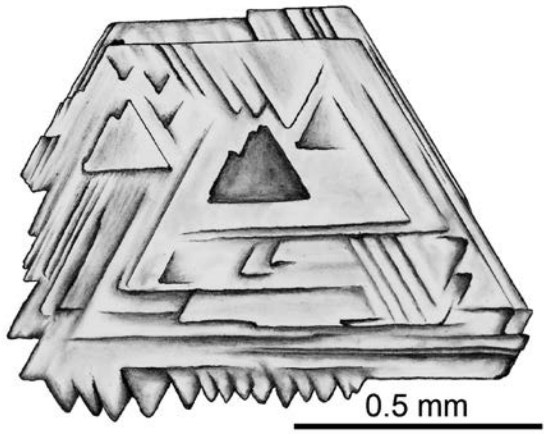
Text-fig. 7. Native silver plate with wires. A – natural appearance, B – photomicrograph of finely polished and HNO_3-etched surface of this specimen with visible variable growth zones, Kobyła Mt.

plate plane. Etching showed four distinct zones (Text-fig. 7B) with a Cu admixture (in wt. %) from the central one to the edge: 1.23–1.30, 0.12–0.14, 0.68–0.73 and 0.09–0.10; other admixture elements have low contents (items 13–16 in Table 1). The wires started to form when the third zone crystallized. The shape of the plate suggests a stationary crystallization environment during the formation of the two inner zones, only with a change of the Cu content (or a change of crystallization parameters like e.g., temperature), and probably later a directional flow of the solution (two outer zones) that caused growth of the wires.

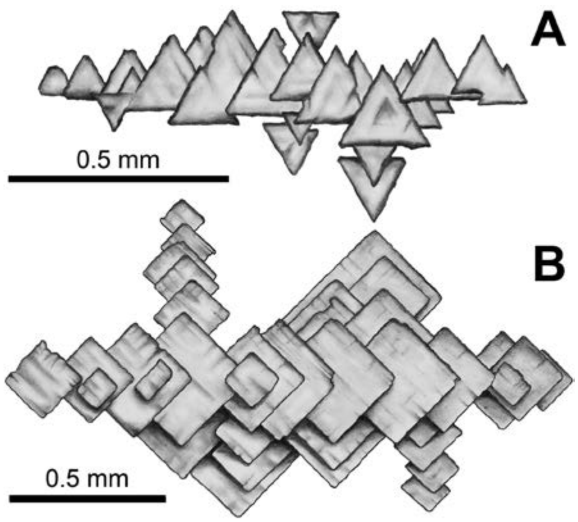
The above described platy specimens of native silver have a relatively simple form. However, the silver plate from the pegmatite at Granicznik Mt. (Text-fig. 8), c. 1.2 mm in length and up to 0.6 mm thick, with the main face (111), has a central pocket and many overgrowths and ‘teeth’ of its opposite face, i.e., with the triangle vertex oriented contrary to the main face. This may suggest rapid changes in the crystallization conditions which caused the appearance of many nuclei or/and a tendency to dendritic growth. The admixture element concentrations in this specimen are poorly variable; the main one is Cu occurring in the ranges 0.26–0.33 wt. % (items 09 and 10 in Table 1).

Moreover, platy native silver crystals can also form true dendritic aggregates. The dendrite found in a quartz-lined nest at Lwia Mt. is a 1.1 mm long group of c. 20 parallel flat triangles (Text-fig. 9A) of various size, from less than 0.1 mm to c. 0.3 mm. No significant differences in the contents of individual admixture elements were recognized; for Cu, the main one, they were from 0.17 to 0.21 wt. % and for Pb, the next important one, from 0.09 to 0.12 wt. % (items 22 and 23 in Table 1).

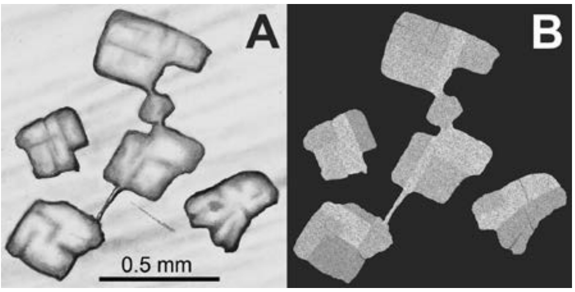
In the pegmatite at Płonik Mt. a group of 35 approximately quadratic silver crystals, 0.05–0.09 mm thick and with edges of 0.1 to 0.5 mm, was also arranged in parallel as a 1.8 mm long dendrite (Text-fig. 9B). Also in this case the contents of the main admixture elements were differentiated in narrow ranges



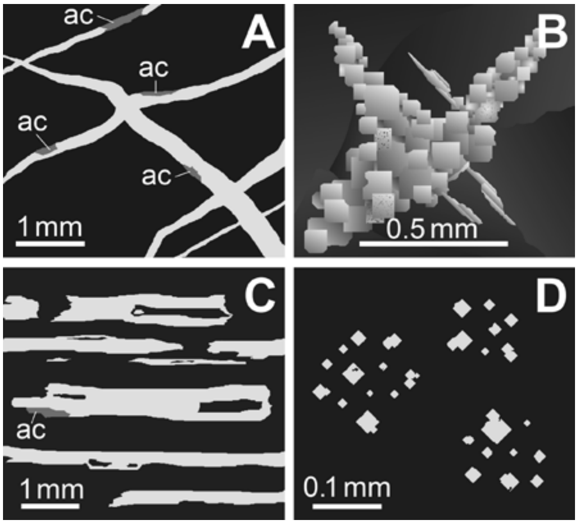
Text-fig. 8. Native silver of the thin plate habit that crystallized under unstable conditions, Granicznik Mt.



Text-fig. 9. Native silver crystals of octahedral habit developed according to the face {111}, Lwia Mt. (A) and crystals of square plate habit with the face {100} as the main one, Płonik Mt. (B).



Text-fig. 10. A group of native silver plates (A) and photomicrograph of the HNO_3-etched surface of this specimen (B), Kowarska Czuba Mt.



Text-fig. 11. Native silver in quartz: A – fillings of fractures, BSE image, Bucznik Mt.; B – dendrite on crossing cracks next healed by quartz, photomicrograph, Dłużyna Hill; C – laths in parallel striae of the prism face, afterward covered by thin layer of quartz, BSE image, Grodna Mt.; D – groups of minute euhedral crystals on positive rhombohedron face of quartz crystal, overgrown by thin quartz layer, BSE image, Młynik Hill (ac – acanthite).

(Cu 0.27–0.30, Pb 0.12–0.16, Hg 0.07–0.11 wt. %, see items 29 and 30 in Table 1).

Six closely neighbouring roughly rectangular plates of native silver (Text-fig. 10A) occurred in a quartz-healed fracture in a quartz vein at Kowarska Czuba Mt. Their size was from 0.15 to 0.45 mm and thickness c. 0.1 mm. Three of the plates have short protruding slats, which is similar to the wires of the specimen from Kobyła Mt. (Text-fig. 7). Etching by an HNO_3 solution revealed different parts of the plates (Text-fig. 10B) with various contents of Cu, the main admixture element: 1.07–0.92, 0.64–0.49 and 0.18–0.12 wt. % from the most etched (the darkest) ones via the intermediate to the least etched (pale) ones. Other admixture elements have lower and less variable contents (items 18 and 19 in Table 1). Most probably, as suggested by the shapes of the plate parts, the crystallization started from the darkest sections and finished with the pale ones.

Small accumulations of native silver were found inside sub- to euhedral quartz, usually the rock crystal variety, which was a late mineral in the investigated pegmatites and veins. Such a crystal from the pegmatite at Bucznik Mt. was strongly cracked and the cracks were healed by quartz. In a small area of crossing cracks (c. 6×7 mm) the fissures were filled by native silver with small spots of acanthite (Text-fig. 11A). The thickness of these fissures was up to 0.35 mm. At the edges of this area native silver was split into fragments surrounded by a quartz filling. Admixture elements are present in native silver in very small amounts: Cu 0.06–0.09, Pb 0.03–0.04, Hg c. 0.01 wt. % (items 01 and 02 in Table 1, for acanthite composition see item 01 in Table 2).

A native silver dendrite, 1.1 mm long, formed by numerous, almost exactly square, crystals (Text-fig. 11B) was found in quartz from a pegmatite at Dłużyna Hill. The square crystals have edges from 0.03 to 0.12 mm. Moreover, three native silver needles, 0.18 to 0.26 mm long, crystallized outside the dendrite in parallel to the diagonals of the squares. The dendrite crystallized approximately along two crossed fractures in quartz, which above the dendrite was younger and not fractured. It is possible that the dendrite origin started from a tiny native silver grain(s) within the fracture which became a nucleus or nuclei and the developing arms of the dendrite followed only roughly the directions of the fractures. The main admixture element contents in native silver were low: Cu 0.05–0.11, Pb 0.01–0.03 wt. % (items 05 and 06 in Table 1).

Also a quartz crystal from pegmatite at Grodna Mt. overgrew inclusions of native silver. This quartz had concave striae parallel to the a_2 axis on the prism face and in several such striae on a surface of c. 9×6 mm laths of native silver crystallized (Text-fig. 11C). The laths were up to 7 mm long and up to c. 1 mm wide. A few grains of acanthite in a paragenesis with native silver were present. The face with silver was covered with a c. 1.5 mm thick layer of transparent quartz. The main admixture elements in the native silver were as follows: Cu 0.62–0.65, Pb 0.17–0.19, Bi 0.14–0.13 and Hg 0.06–0.05 wt. % (items 11 and 12 in Table 1).

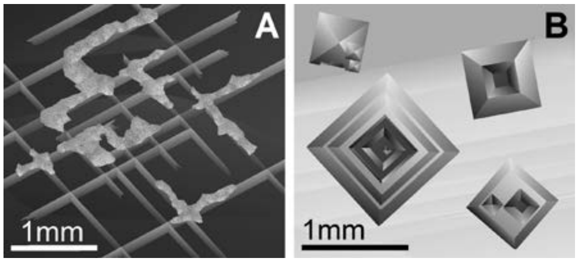
In a quartz veinlet at Młynik Hill on the positive rhombohedron face of quartz, minute (0.01–0.04 mm) euhedral crystals of native silver were identified (Text-fig. 11D). The crystals are octahedral; the same orientation of all crystals is difficult to explain, because the structure of silver does not fit the quartz structure. In this specimen, Pb (0.08–0.09 wt. %) and Cu (0.05–0.06 wt. %) were the dominant admixture elements (items 25 and 26 in Table 1).

Native silver was also found in calcite that crystallized in a void in a milky quartz vein at Tunelowa Mt. The calcite has cleavage cracks that were partly healed and covered by a younger layer of this mineral. In one part of this crystal fine granular native silver precipitated as up to c. 2.5 mm long streaks along such cracks (Text-fig. 12A). This specimen seems to be rich in admixture elements (Fe 0.55–0.60, Pb 0.10–0.18, Cu 0.11–0.16, Hg 0.09–0.16, Bi 0.05–0.09, Sb 0.07–0.08 wt. %; see items 43 and 44 in Table 1).

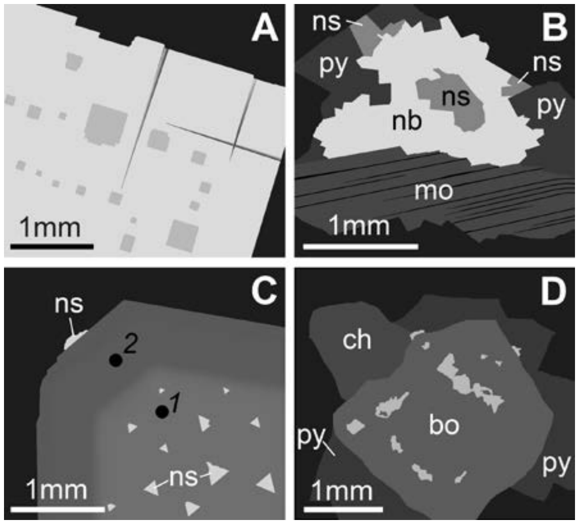
In a pegmatite at Kukułcze Rocks, cleavelandite with native silver inclusions of a generally octahedral habit was collected (Text-fig. 12B). The size of the silver crystals ranged from 0.55 to 1.6 mm. Some crystals are combinations of octahedral and cubic forms; their faces may have fenster shapes sometimes of the two-steps and their bottoms are cube faces. These native silver crystals are rather pure, the main admixture element is Cu (0.10–0.14 wt. %; items 20 and 21 in Table 1).

In the Karkonosze granitoid, native silver was also found in or next to ore mineral crystals. In a pegmatite at Witosza Mt., a few galena grains of several mm in size occurred in quartz. Inside them cubic silver crystals of dimensions 0.1 to 0.6 mm were found (Text-fig. 13A). Galena had substitutions (in wt. %) of Ag (1.03–1.27), Bi (0.24–0.29) and Se (0.07–0.11). The main admixture elements in native silver were Pb (0.73–0.88), Bi (0.10–0.14) and Hg (0.07–0.11) (see items 45 and 46 in Table 1).

A quartz veinlet at Mrowiec Hill contained small clusters of molybdenite, pyrite and native bismuth with grains of native silver 0.2–0.7 mm in size (Text-fig. 13B). These grains formed inclusions only in native bismuth; other ore minerals occurred next to the silver crystals. Native bismuth has a substitution of Ag of c. 0.90 wt. % (item 05 in Table 3) and native silver – c. 0.85 wt. % Bi, but other elements: Fe, Cu Sb and Hg are present in the latter in amounts of 0.01–0.02 wt. % (items 27 and 28 in Table 1). Admixtures of Bi and Ag in sulphides were not de-



Text-fig. 12. A – native silver crystallized along the cleavage fractures in calcite, photomicrograph, Tunelowa Mt.; B – euhedral crystals of native silver with fenster faces in cleavelandite, photomicrograph, Kukułcze Rocks.



Text-fig. 13. Native silver inclusions in ore minerals, BSE images: A – in galena, Witosza Mt.; B – in native bismuth, Mrowiec Hill; C – in argentotetrahedrite-(Fe), *1* and *2* – points of EPMA, Sucha Mt.; D – in bornite, Sucha Mt. (bo – bornite, ch – chalcopyrite, nb – native bismuth, ns – native silver, mo – molybdenite, py – pyrite).

Occurrence and mineral	No.	Au	Ag	Cu	Pb	Sn	Sb	Bi	Zn	Hg	Σ
Cicha Równia											
Native gold	01	98.15	1.43	0.22	0.06	0.01	0.03	0.05	0.01	0.03	99.99
	02	98.33	1.17	0.24	0.09	0.02	0.03	0.04	0.01	0.04	99.97
	03	98.95	0.65	0.21	0.07	0.01	0.02	0.04	0.01	0.02	99.98
Rybień Mt.											
Electrum	04	54.13	43.98	0.94	0.51	0.04	0.09	0.06	0.05	0.18	99.98
Mrowiec Hill											
Native bismuth	05	0.01	0.90	0.37	0.09	0.02	0.24	98.22	0.08	0.03	99.96

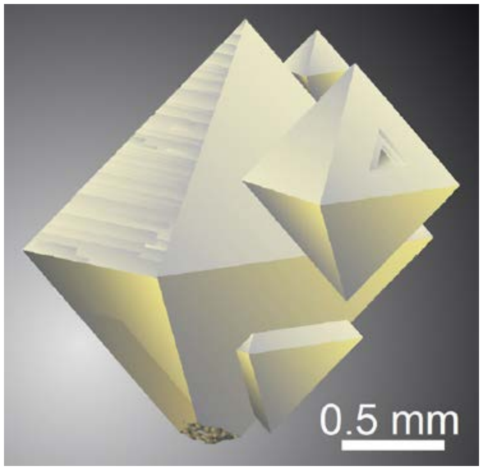
Table 3. Chemical composition of native metals associated with native silver, in wt. %.

tected; this suggests that native silver is in a paragenetic relationship with native bismuth but that the sulphides may be older.

Two samples of sulphide minerals with native silver were found at Sucha Mt. in a grey quartz veinlet. In one sample, native silver occurred as inclusions probably of octahedral habit (their size is 0.05–0.25 mm) in the core of a freibergite series grain (Text-fig. 13C). Native silver in inclusions has rather high Cu and Fe admixtures, very close to the maximum values found there (Cu 0.43 and Fe 0.28 wt. %, see item 37 in Table 1). However, the silver nubble found on the surface of the host mineral is much purer (Cu 0.11, Fe 0.09 wt. %, item 38 in Table 1). The chemical composition of the central part of the grain hosting the native silver inclusions corresponds to argentotetrahedrite-(Fe) – point 1 (Text-fig. 13C), and is an example (item 14 in Table 2). The presence of silver facilitated the formation of separate native silver grains because Ag availability was relatively good, as suggested by the replacement of Cu by Ag in the B-site, though the Cu content in the crystallization space was quite high, since chalcopyrite was present in this mineral association. The chemical composition of the grain rim (example point 2, item 15 in Table 2) is only c. 0.7 wt. % lower than the inner part, however native silver inclusions are absent here. We were, however, not able to recognise the possible change(s) of physical-chemical conditions that caused this variation. However, when argentotetrahedrite-(Fe) crystallization ended, a small grain of native silver formed on its face, but with minor presence of Cu and Fe in its structure.

Moreover, grains of native silver were found in and on bornite (item 13 in Table 2) from the same veinlet, associated with chalcopyrite and pyrite (Text-fig. 13D). The Ag content in this host mineral, measured at 10 points, varied only slightly, from 0.71 to 0.78 wt. %. This value is in the ranges given by Cook *et al.* (2011) as typical for bornite, though Reich *et al.* (2013) suggest contents roughly 10 times lower. Granules of native silver (up to 0.2 mm in size) and their groups occurred in the whole volume of the bornite crystal, as checked in a series of planes formed by gradual grinding and polishing of the sample. In places, native silver inclusions marked the growth zones of the host crystal. In native silver here, the main admixture element was Cu with its narrow content ranging from 0.23–0.27 wt. % (items 39 and 40 in Table 1).

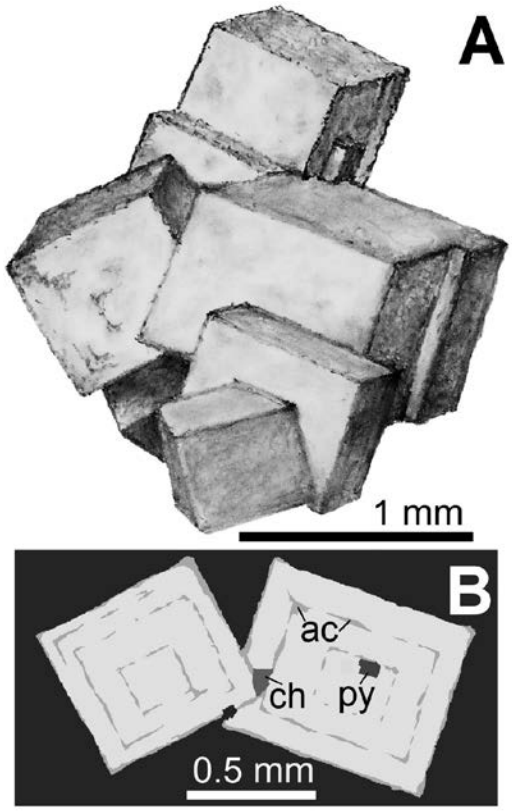
Euhedral free-growth specimens of native silver were found in three locations. A parallel growth of four octahedral crystals, 0.4 to 2.6 mm in size (Text-fig. 14) occurred in a pegmatite in the little quarry



Text-fig. 14. Parallel concrescence of four octahedral crystals of native silver, one crystal with the (111) face of the frame (fenster) type and another with the face formed by lamellae oriented along the [110] edge of the octahedron, Radomierz.

at Radomierz. The largest crystal was located with its vertex in quartz (rock crystal) to a depth of c. 0.3 mm. At first glance the smooth and normal triangular faces of the crystals suggest quiet formation conditions. Nevertheless, one face has a small and shallow fenster of the shape of triangle, another is covered by striae parallel to its edge and on the third face two parts with slightly different intensity of metallic lustre are recognizable. The latter difference was caused by the growth of two crystals which did not change their crystal face shape. In the polished cross-section of the crystal parts combination, the difference between two components became visible after etching with dilute HNO_3. The pale yellowish tint of the specimen faces is caused by a very subtle Ag_2S coating. Admixture elements are scarce, only Fe and Cu exceed 0.01 wt. % – respectively mostly 0.09–0.14 and 0.06–0.17, but in the crystal more susceptible to etching the contents were higher: 0.19–0.25 and 0.20–0.31 wt. % (items 31 and 32 in Table 1).

A 2.5 mm long group of nine native silver crystals (Text-fig. 15A), 0.2–1 mm in size, was found in the pegmatite at Skiba Mt. The crystals are of cubic habit, partly slightly elongated, with finely rough faces. On the faces and especially along their edges black dusty accumulations of acanthite formed; they marked the crystal zoning as well. Streaks of acanthite were observed also inside the crystals between the growth zones (Text-fig. 15B), moreover inclusions of pyrite and chalcopyrite were recognized therein. The admixture element content of native silver was not very high: Cu (0.14–0.22), Fe (0.10–0.25) and Hg



Text-fig. 15. A – group of native silver crystals of cubic habits with fine black precipitates of acanthite; B – same specimen, BSE image of cross-section of the two crystals of the group with visible zoning, Skiba Mt. (ac – acanthite, ch – chalcopyrite, py – pyrite).

(0.08–0.16 wt. %) were the main ones (items 35 and 36 in Table 1).

In a quartz veinlet at Rybień Mt. a specimen of native silver with the habit of two rods in parallel connection was found (Text-fig. 16). The length of the rods was 3.3 mm (c. 0.7 mm in quartz) and the thickness of each c. 0.1 mm; the transverse sections had the shape of hexagons. About the middle of the rods' length they were surrounded by a c. 1 mm calcite rhombohedron. Within the rod close to its end in quartz, a c. 5 µm grain of electrum was identified (lower insert in Text-fig. 16). The composition of electrum was given as item 04 in Table 3; native silver had the following admixtures: Au 0.00–0.09, Cu 0.22–0.49, Fe 0.06–0.09, Pb 0.03–0.11, Hg 0.04–0.14 wt. % (items 33 and 34 in Table 1). In the top parts of the rods, close to their connection surface, inclusions of acanthite, chalcopyrite and pyrite were found, possibly formed due to the migration of Fe, Cu and S along the connection of the rods (see upper insert in Text-fig. 16).

Fluid inclusions

The parent fluids were investigated by the fluid inclusion method in parts of the host minerals in which native silver specimens were included. Certain silver samples had only a fragment overgrown by their host minerals, thus in these cases the crystallization conditions refer only partly to the specimen, namely to its earliest portion. General observations of fluid inclusions were made for 611 inclusions and detailed investigations – for 150. The inclusions were 4–23 µm in size and were selected to be at a distance from other ones to avoid possible cracking on heating or freezing as well as the case that an inclusion had undergone refilling or was a product of the dividing of a larger

Text-fig. 16. Adhesion of two parallel native silver rods partly overgrown by calcite crystal of rhombohedral habit; note the high birefringence effect visible in the calcite crystal. The BSE image inserts show inclusions of Ag-including gold (electrum), found in the lowest part of the silver rods, and acanthite (ac), chalcopyrite (ch) and pyrite (py) inclusions formed along the contact zone (straight strip) of the upper parts of the rods; Rybień Mt.

Occurrence	Th [ºC]	ΣS [wt. %]
Bucznik Hill	150–157	4.6–5.2
Cicha Równia	110–120	3.1–4.2
Dłużyna Hill	97–106	2.7–3.4
Grabowiec Mt.	119–123	4.7–5.0
Graniczmik Mt.	147–153	6.3–6.7
Grodna Mt.	130–134	3.5–3.9
Kobyła Mt.	127–130	3.1–3.2
Kocierz Mt.	117–120	3.0–3.1
Kowarska Czuba Mt.	126–131	3.3–3.7
Kukułcze Rocks (1)	104–111	2.7–3.2
Lwia Mt.	128–135	3.5–4.0
Łomnickie Rozdroże	119–124	4.4–4.6
Młynik Hill	137–142	4.4–5.0
Mrowiec Hill	156–164	5.8–6.4
Płonik Mt.	142–148	3.2–3.7
Radomierz	91–95	5.1–5.6
Rybień Mt.	100–111	3.0–3.9
Rybień Mt. (2)	94–98	2.4–2.6
Skiba Mt.	135–143	4.0–4.8
Sucha Mt.*	157–163	6.9–7.2
Sucha Mt.**	155–165	6.0–6.7
Szklarska Poręba Górna	136–142	4.3–5.0
Tunelowa Mt. (2)	114–118	3.7–4.2
Witosza Mt.	115–122	4.6–5.5

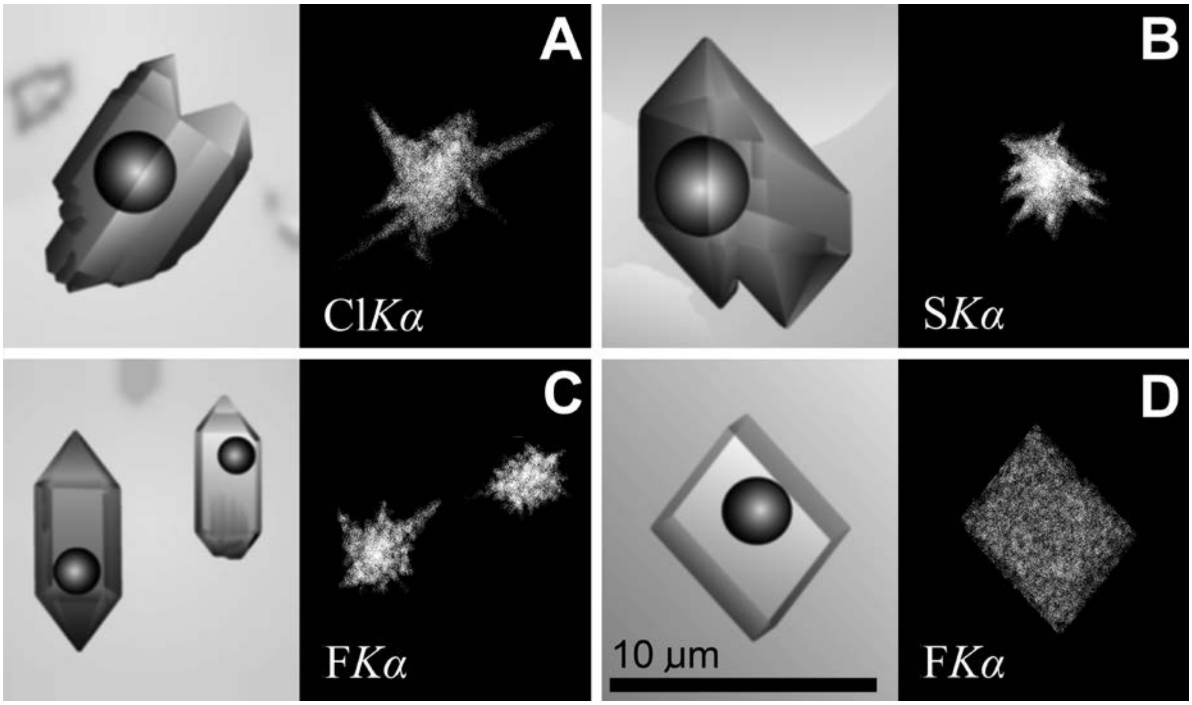
Table 4. Homogenization temperature (Th) and total salinity (ΣS) of fluid inclusions in minerals contacting with native silver. The studied inclusions occurred in quartz except for these in cleavelandite (1) and in calcite (2); * specimen with argentotetrahedrite-(Fe); ** specimen with bornite.

inclusion during recrystallization (Kozłowski and Matyszczak 2022a, pp. 17, 18). The data for 104 inclusions strictly connected with the crystallization of silver are presented in Table 4. Generally, the homogenization temperatures (Th) ranged from 91 to 165ºC. Dividing the data into groups related to the native silver habits and the host minerals, the Th ranges are as follows: fibres or hairs (single or in groups) 110–124ºC, plates (single or in groups) 126–153ºC, various habits in quartz growth or healing zones 97–157ºC, in ore mineral parageneses 115–165ºC, euhedral crystals 91–143ºC. Native silver in calcite and in cleavelandite is related to Th 114–118ºC and 104–111ºC, respectively. Thus the investigated native silver specimens formed at low temperature and the highest Th values were determined in quartz from the associations with ore minerals except for native silver in galena (Th 115–122ºC). Moderate Th (156–164ºC) may be confirmed e.g., in the sample with native bismuth from Mrowiec Hill, in which Bi precipitated in a solid not liquid state (melting temperature of Bi 271.5ºC), as shown by typical twinning seen under the microscope in reflected light.

Native silver crystallized mostly from a solution of Na_2CO_3 and $Ca(HCO_3)_2$ as the main components (0.8–5.5 and 0.3–2.7 wt. % respectively), but it happened rarely that K_2CO_3, NaCl or $CaCl_2$ became significant dissolved salts in the parent fluid (Table 5). Nevertheless, ions of K, Mg, Fe and Al were commonly present as minor or admixture components identified by X-ray scans in the indented inclusions. Also Cl and S occurred in the inclusion fluids frequently (Text-fig. 17A, B). Fluorine was found in all checked inclusions in quartz (Text-fig. 17C), but after indentation of the inclusion in calcite it was not found. However, when the calcite above the inclusion was removed along a cleavage plane by the mi-

Native silver habits and occurrence	Na compound [wt. %]	Ca compound [wt. %]	Proportion
Hairs and their bunches (Th 110–124ºC)			
Cicha Równia	1.8–2.1	1.3–2.1	0.65–1.0
Grabowiec Mt.	2.4–3.3	1.6–1.8	0.51–0.75
Kocierz Mt.	2.5–2.7	0.4–0.5 (1)	0.15–0.20
Łomnickie Rozdroże	3.8–4.0	0.5–0.7 (1)	0.12–0.18
Plates (Th 126–153ºC)			
Granicznik Mt.	5.1–5.5	1.0–1.5	0.19–0.29
Kobyła Mt.	2.7–2.9	0.3–0.5	0.10–0.15
Kowarska Czuba Mt. (2)	2.9–3.0	0.4–0.7	0.19–0.23
Lwia Mt.	2.3–2.9	0.8–1.3	0.29–0.54
Płonik Mt.	2.8–3.1	0.4–0.7	0.14–0.23
Szklarska Poręba Huta	2.8–3.2	1.5–1.8	0.54–0.57
Fissure fillings of various habits (Th 97–15ºC)			
Bucznik Hill	2.2–2.5	2.3–2.7	1.00–1.18
Dłużyna Hill	1.8–2.00	0.9–1.5	0.50–0.79
Tunelowa Mt.	3.3–3.7	0.3–0.5	0.08–0.14
Sub- or euhedral crystals as inclusions (Th 104–142ºC)			
Grodna Mt.	2.6–2.9	0.7–1.1	0.25–0.42
Młynik Hill	3.1–3.5	1.1–1.5	0.36–0.43
Kukułcze Rocks	2.1–2.6	0.5–0.7 (1)	0.22–0.29
Grains in or near ore minerals (Th 115–165ºC)			
Mrowiec Hill	3.7–4.2 (3)	2.1–2.5 (2)	0.54–0.67
Sucha Mt.*	3.0–3.7 (3)	2.7–3.1 (2)	0.78–1.07
Sucha Mt.**	4.8–5.1 (3)	1.9–2.3 (2)	0.38–0.47
Witosza Mt.	2.0–2.3 (3)	2.5–3.3 (2)	1.19–1.50
Euhedral free growth crystals (Th 91–143ºC)			
Radomierz	4.1–4.4	0.8–1.2	0.19–0.29
Rybień Mt.***	0.8–1.0	2.1–2.2	2.20–2.75
Rybień Mt.****	0.3–0.6	1.9–2.1	3.33–7.00
Skiba Mt.	3.5–4.1	0.4–0.7	0.10–0.17

Table 5. Concentrations of two main salts in inclusion fluids and their weight ratio. The Na compound is commonly Na_2CO_3 and it is used as denominator in the ratio, the Ca compound (numerator in the ratio) is $Ca(HCO_3)_2$, however in some inclusions they were replaced due to higher concentrations as follows: $Ca(HCO_3)_2$ by K_2CO_3 (1) or by $CaCl_2$ (2), and Na_2CO_3 by NaCl (3); * specimen with argentotetrahedrite-(Fe); ** specimen with bornite; *** fluid inclusions in quartz; **** fluid inclusions in calcite.

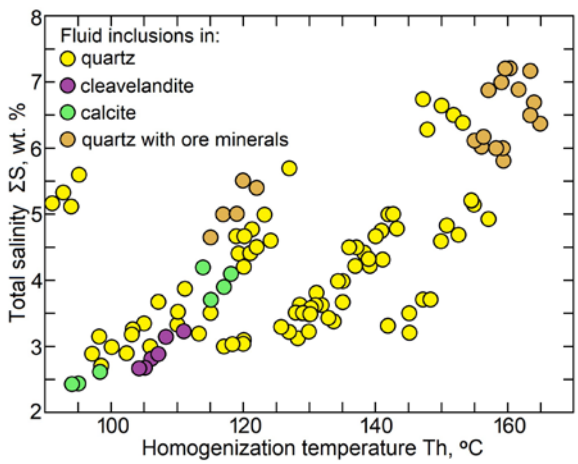


Text-fig. 17. Presence of Cl, S and F in fluid inclusions in host minerals of silver, left – optical microscope images, right – same fields, X-ray scan pictures; A–C inclusions in quartz open by point indentation with inclusion solution leaked and dried on the preparation surface; D – in calcite, a half of the inclusion was removed by crushing and F-bearing precipitate inside this inclusion is visible. Scale bar refers to each image. Sample locations: A – Bucznik Mt., B – Lwia Mt., C – Radomierz, D – Tunelowa Mt.

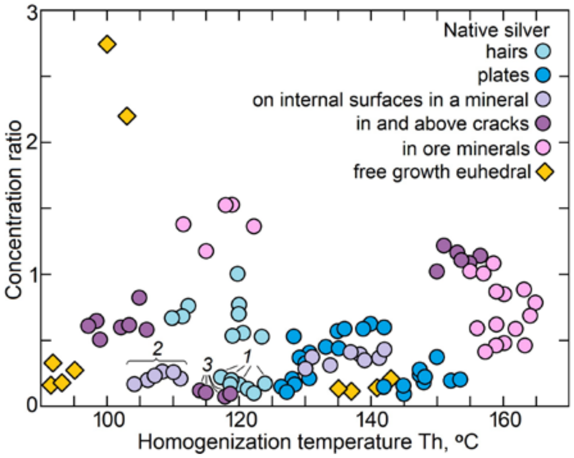
croscope crushing stage, fluorine was detected on the inclusion bottom facet (Text-fig. 17D). Probably on cooling after mineral crystallization fluorine precipitated as calcium fluoride. Carbon dioxide in fluid inclusions was found only in low to very low concentrations.

The relationship of Th and total salinity of the inclusion fluids is not simple. Several spots are arranged only roughly in diagonal paths in the Th *vs* ΣS field (Text-fig. 18), but dispersion of the spots is large. It suggests specific, different conditions of crystallization for various native silver specimens. This suggestion is even more convincing when considering the relationship of Th values and the concentration ratios of the two main compounds dissolved in the inclusion fluids. These two compounds are mostly Na_2CO_3 and $Ca(HCO_3)_2$, but in a number of inclusions they are replaced by the pair K_2CO_3 and $Ca(HCO_3)_2$ or by $CaCl_2$ and NaCl. The ratio was calculated in relation to the Na or K compounds. The plot (Text-fig. 19) presents a scattered arrangement of the calculated ratios and the reasonable explanation of this image is of native silver crystallization in strictly local conditions, different in various parts of the pluton. The plots include 8 inclusions more than in Table 5, which were slightly more distant from silver in the ore mineral parageneses.

The determination of pressure during native silver crystallization was not possible. From the data on the



Text-fig 18. The plot: homogenization temperature vs. total salinity of primary fluid inclusions in host minerals of silver; each circle marks one inclusion.



Text-fig. 19. The plot: homogenization temperature vs. ratio of concentrations of two main compounds dissolved in fluids in the inclusions. Most of the points refers to the $Ca(HCO_3)_2/Na_2CO_3$ value, but in the groups *1* and *2* it is K_2CO_3/Na_2CO_3, and in the group "native silver in ore minerals" – $CaCl_2/NaCl$. Majority of the inclusions was in quartz, but the group *2* – in cleavelandite and the group *3* – in calcite.

hydrothermal environment in the pluton (Kozłowski and Marcinowska 2007) the probable pressure may have been up to c. 0.5 kbar thus the approximate correction added to Th determinations to estimate the temperatures of formation of inclusions should be close to 40ºC.

DISCUSSION

From among c. 1500 samples of post-magmatic mineralization in the Karkonosze pluton, verified by the authors over 50 years starting in 1968, native silver was found in only 23 samples from 22 locations, all in the area of the porphyritic granitoid. These locations are scattered rather uniformly on the pluton's surface; the 'empty' part is in the territory of Jelenia Góra city, where sample collection was not possible. Native silver specimens are very small (tenths of a millimetre to few millimetres) and were found as an individual crystal or a single minute group of crystals at a given occurrence. The kind of distribution, size of 'micromineral' of silver and scanty presence in an outcrop suggest a very local formation process which could develop at various places with a similar and rather low intensity.

Crystallization of native silver occurred at low temperature, apparently below 200ºC, and in most cases below 150ºC, from a parent solution of Na and Ca (hydro)carbonates, but the presence of S (as a sulphate ion?), Cl, F, K, Mg, Al and Fe was common. In some occurrences, the Cl^- ion content was distinctly significant. This fits well to data on present day thermal waters of the Karkonosze pluton – the prevalent anion is hydrocarbonate (see e.g., Fistek and Fistek 2005), but chloride-type waters have also been found, for instance in the Czech part of the pluton close to Albrechtice (Goliáš *et al.* 2014).

The habit and appearance of the native silver specimens are very variable. This suggests a broad range of crystallization conditions. Hairs or wires formed when crystallization was fast, either due to a temperature decrease or a change of composition of the parent fluid. If precipitation was rapid at the beginning, many crystallization nuclei could have appeared to form bunches of wires. Platy crystals formed in thin fissures inside host minerals. If the influx of dissolved Ag was slow and undisturbed, the faces were flat, otherwise convex and concave details of the crystal surfaces appeared. Such inflow disturbances could be caused by healing and repeated opening of the host fissure. Habits and accumulations of native silver crystals included into the host minerals during growth are various, e.g., laths in striae in the mineral face, streaks of various grain shape above healed fractures in the host mineral, dispersed minute grains on flat faces, continuous or spotty accumulations along growth zone(s), etc. Moreover, specimens of almost perfect euhedral habits were collected. They were of octahedral, cubic and rod shape. The nearly ideal shapes suggest virtually undisturbed conditions of crystallization, albeit fenster faces in these crystals were observed; this may suggest a decrease of Ag concentration during the final stage of crystal formation, though other factors cannot be excluded.

Pyrite, chalcopyrite, galena, native gold, electrum and acanthite crystal inclusions were found in native silver. In the considered mineral crystallization environment S, Fe, Cu, Pb and Au occurred, as indicated by the admixture elements in native silver and by the composition of the mineral-forming fluids. Native gold is present in the Karkonosze pluton area and was found in placer deposits (Grodzicki 2005) and pegmatites (Kozłowski 2011), thus its association with silver is normal. Acanthite forms streaks at the border of growth zones and spots inside or at the margins of native silver. Thus this sulphide crystallization most probably occurred together with native silver. The scheme presented of the relationships of acanthite to native silver has one exception, which was found in the specimen from Grabowiec Mt. (Text-fig. 5). In an external wire of this native silver stump, the content of S increased from edge to centre, then slightly decreased to the internal border of the wire where a thin layer of acanthite was found along the border. On the other side of this layer the content of S in silver decreases to trace levels and further to the stump centre S is not detectable, as in other parts of this cross-section of the stump, even close to the outer surface of this silver specimen. But acanthite is present between the wires in the intermediate part of the stump cross-section and disappears in the central part. This suggests the presence of a kind of 'path' used by S to diffuse from the surrounding solution inside the silver and probably the formation of acanthite coatings between the wires could be a result of this diffusion. Four more such cross-sections of the stump parallel to the first one were checked and in three of them similar 'paths' were found – triple in one of them and single in each of the two others. Each 'path' had a different direction but all of them lead from the outer surface towards the centre of the stump, however they end at acanthite accumulations. Early considerations on the migration of sulphide ions in Ag (and both of them jointly) at 300–450ºC in laboratory experiments were published by Beutell (1913, 1916, pp. 470–472). In the specimen studied herein, probably S used for diffusion the zones of structural defects in native silver crystals (cf. Lomaev *et al.* 2014; Bergman and Höijertz 2016). It seems that the changing parameters (decreasing temperature?) stopped this process at some moment (and thus in some point).

Probably a different process caused the presence of acanthite, pyrite and chalcopyrite in the top part of the specimen from Rybień Mt. In this case, sulphides occur at the contact zone of two parallel native silver rods. Probably this zone was the path for migration of Fe, Cu and S inside silver.

The name 'acanthite' was used in this text for the substance Ag_2S. However, if the pressure correction for Th values exceeded c. 30ºC (see above), it could happen in some cases that the acanthite now present precipitated as argentite at temperatures higher than that of the Ag_2S structure inversion (179ºC). However, the diagnosis of acanthite pseudomorphs after argentite is rather not possible, because Ag_2S formed as anhedral grains.

The question of the source of Ag is a basic problem. No significant fracture or structural dislocation that could have been a pathway for fluid flow was found at a reasonable distance from the native silver occurrences. The sites of this mineralization are scattered all over the area of the porphyritic granitoid in the Polish part of the pluton. Moreover, the native silver specimens are very small, true 'microminerals'. These features suggest local sources of Ag. The samples occur in pegmatitic nests and in thin veinlets of very limited length, supporting the above suggestion. The mineral filling of the veinlets crystallized from fluids sucked during fissure opening through minute cracks and intergranular apertures from the surrounding granitoid. After the fissure was filled with fluid, migration of elements from the surrounding rock could continue by diffusion toward the crystallization nuclei in the veinlet. Pegmatites in the Karkonosze pluton formed apparently by recrystallization of the parent granitoid in the presence of early post-magmatic fluids in places of tension and probably multiple cracking caused by cooling (Kozłowski 1978, 2002). This does not exclude formation of the pegmatites from a late-magmatic melt. However, even the pegmatite at Wilcza Poręba in Karpacz that started to form at elevated temperatures of c. 600ºC, as suggested by healed reticular cracks in quartz formed during the high- to low-temperature quartz conversion, did not preserve melt inclusions (Kozłowski 1975). Our current observations may imply that the native silver specimens in the sampled pegmatites could have formed in connection with the process of granitoid recrystallization, which is frequently very intensive (Nowakowski and Kozłowski 1981).

The concentration of Ag was determined in five samples of the porphyritic granitoid. The samples were taken from rocks without a recognizable post-magmatic alteration in the areas where native silver was found. The results do not differ from published data concerning other granitoids (e.g., Hamaguchi and Kuroda 1959; Boyle 1968, p. 47) and were as follows (in ppm): Granicznik Mt. 0.048, Młynik Hill 0.055, Skiba Mt. 0.039, Rybień Mt. 0.056, Sucha Mt. 0.051; average 0.0498 → 0.05. If 1 cm^3 of the granitoid weights c. 2.6 g and the specimen of native silver has c. 2 mg of Ag, this amount of this element should be present in a cube of granitoid of the edge of c. 25 cm. Of course, not the whole amount of Ag would be removed from the granitoid, but even if 10 or 20 % of it migrated to the precipitation nucleus and crystallized, the volume of the rock affected by alteration would be moderate – cubes of the edges of 55 and 44 cm, respectively. The migration of Ag in low-temperature solutions of the hydrothermal type is possible, especially in the presence of the fluoride ion (AgF solubility in water at 50ºC exceeds 200 g/100 ml). Fluorine was detected in fluid inclusions in minerals paragenetic with native silver (see above).

It is also common in parent solutions of other minerals and in geothermal waters of the Karkonosze pluton (Kozłowski and Matyszczak 2022a and references therein). Thus the above considerations and the variable, local conditions of the studied mineral(s) origin support the proposed scheme of formation of native silver in the studied occurrences.

CONCLUSIONS

The occurrences of very small specimens (tenths of millimetres to few millimetres) of native silver are scattered in the whole part of the Karkonosze pluton formed by the porphyritic granitoid and the distance between neighbouring occurrences ranges from 2 to 6 km. They formed from epithermal Na-Ca-(hydro)carbonate solutions of low total salinity (2.7–6.7 wt. %). No traces of significant migration of the solution were observed close to the native silver occurrences. The average content of Ag dispersed in the granitoid is c. 0.05 ppm and in places of rock recrystallization and opening of thin fissures, the local (e.g., intergranular) solution, commonly with minor presence of fluoride anions, caused the mobility of trace Ag from the granitoid. Next, Ag migrated in the solution to the crystallization nuclei and precipitated. Conditions of crystallization were different in various localities and unstable during the formation of native silver crystals, thus their habits are very diverse. These crystals have a number of admixture elements – Cu is common, but the presence of others, such as Pb, Bi, Hg, Fe, etc., varies from place to place very strongly. With native silver paragenetic minerals may appear, such as galena, native bismuth, native gold or electrum, but only acanthite, presumably being sometimes a post-argentite paramorph, is common, frequently as solid inclusions in native silver. A peculiar form of acanthite was found, connected with streaks of S content up to 0.04 wt. % in the adjacent native silver surrounded by this mineral being S-free. This strongly suggests the diffusion of S in Ag from the parent solution towards the place where acanthite could crystallize. Any evidence or suggestion that the studied native silver specimens could form by decomposition of Ag sulphide(s) or sulphosalt(s) was not found. After a thorough consideration of the geological setting, conditions of formation and characteristics of the investigated specimens of native silver, the authors conclude that the samples of native silver are typical trace minerals but not indicators of commercially useful Ag mineralization within the Karkonosze pluton.

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APPENDIX

The descriptions of the individual mineral occurrences, in which the investigated native silver specimens were found, are given below in alphabetical order.

Bucznik Mt. (15º49.436'E, 50º51.105'N): southern slope, slightly inclined rock surface with pegmatite nest with an elliptical cross-section (36×28 cm) and small central void lined by subhedral grey quartz with healed fractures; a few grains of pyrite and chalcopyrite up to 1 mm in size were present.

Cicha Równia Mt. (15º24.909'E, 50º49.766'N): northern slope, block of granitoid up to 1.8 m high. At its eastern edge a vertical veinlet c. 5 cm thick was filled by light-grey quartz with small voids. One of the voids (0.5×1.2×3.2 cm) included few grains (1–3 mm) of pyrite and one of chalcopyrite.

Dłużyna Hill (15º50.937'E, 50º49.705'N): a block of granitoid at the summit with lenticular pegmatite 112 cm long and up to 24 cm thick. In the central part transparent subhedral quartz crystals up to 4 cm long with a few healed fractures occurred; 2 grains of galena, 5 of chalcopyrite and several ones of pyrite (all 0.5–2.5 mm) were found therein.

Grabowiec Mt. (15º43.985'E, 50º48.232'N): northern slope rock inclined wall cut by 7–10 cm thick nearly horizontal vein of dark grey quartz.

Granicznik Mt., Gozdowskie Rocks (15º22.792'E, 50º48.611'N): c. 0.75 km to the south from the mount summit, lenticular pegmatite of the visible section 24×39 cm. In transparent quartz of the central part of the pegmatite two grains of chalcopyrite (c. 1 and 2.5 mm) were found.

Grodna Mt. (15º43.398'E, 50º50.250'N): northern slope orbicular pegmatite (diameter of 63 cm) of typical mineral composition, in subhedral quartz crystals padding the central void needles of tourmaline up to c. 1 cm long and single grains of pyrite, arsenopyrite and tetrahedrite 0.3–1.6 mm in size.

Kobyła Mt. (15º22.635'E, 50º50.083'N): c. 450 m north-north-west from the mountain summit; a vertical veinlet of grey quartz 1–3.4 cm thick in granitoid rocks called Stary Zamek.

Kocierz Mt. (15º26.267'E, 50º48.871'N): c. 100 m to the south from the mount summit a vein of milky quartz c. 12 cm thick with the southern dip of 35º with numerous cracks healed by transparent quartz.

Kowarska Czuba Mt. (15º52.217'E, 50º47.333'N): to the south of the abandoned quarry; outcrop on the western slope of the mount c. 250 m from the summit; a horizontal 20–25 cm thick vein of grey quartz with healed cracks.

Kukułcze Rocks (15º31.916'E, 50º47.463'N): western foot of the rock wall; vein shaped pegmatite of 1.6 m visible length, thickness of 14–17 cm and typical zoning; in central part small voids with subhedral crystals of muscovite, transparent quartz and cleavelandite.

Lwia Mt., Strużnickie Rocks (15º53.739'E, 50º50.807'N): c. 600 m south-west from the mount summit, a block of granitoid with c. 40 cm pegmatite nest of irregular shape. Subhedral translucent quartz crystals up to 4 cm long with pale-amethyst top parts padded the central void.

Łomnickie Rozdroże (15º43.748'E, 50º46.011'N): the Łomnica river bed below the Pląsawa tributary; an apparently vertical 5–8 cm thick veinlet of milky subhedral quartz crystals with transparent vertex parts.

Młynik Hill (15°35.973'E, 50°50.995'N): scarp on the western slope with 7 veinlets (thickness 2–5 cm) of pale grey quartz of a SE dip c. 80º and visible length of 1.6–2.1 m. The veinlets contained dispersed microcline grains (c. 2 mm) and voids with 3–6 mm long rock crystals.

Mrowiec Hill (15º48.186'E, 50º50.283'N): north-eastern slope close to the summit; vertical grey quartz veinlet with a NE–SW strike, the preserved part has a length of 120 cm and thickness of 2–3 cm. Small clusters of molybdenite, pyrite and native bismuth are present.

Płonik Mt. (15º39.805'E, 50º48.319'N): a granitoid block on the northern slope of the mountain at the margin of Przesieka village. The block comprised a 12 cm nest of pale grey translucent quartz.

Radomierz (15º53.784'E, 50º53.547'N): an abandoned small quarry at the SSW periphery of the village on the eastern side of the road to Trzcińsko village. In a pegmatite nest of irregular shape and c. 30 cm in size, the following accessory minerals were recognized: tourmaline, zeolites, calcite, pyrite and molybdenite.

Rybień Mt. (15º49.636'E, 50º54.917'N): rocks c. 400 m to the south from the summit towards Maciejowa village. A veinlet of grey quartz 4–6 mm thick had a void lined by 1–6 mm quartz and calcite crystals.

Skiba Mt. (15º42.652'E, 50º47.947'N): a rock c. 200 m north-east from the hill summit, 0.6 km southwards from Skiba village. The roughly ellipsoid pegmatite of visible dimensions 42×29 cm and with typical main mineral filling had a central nest of subhedral quartz crystals up to 2.5 cm long which lined a 11 cm void.

Sucha Mt. (15º55.254'E, 50º51.738N): foot of the rocks north-west from the summit with a grey quartz veinlet 2–3 cm thick and of c. 90 cm visible length. Clusters (1–2 mm) of ore minerals: freibergite series mineral, bornite, chalcopyrite, pyrite and arsenopyrite occurred in quartz.

Szklarska Poręba Huta (15º29.578'E, 50º49.617'N): blocks of granitoid c. 200 m westwards from the western edge of the quarry, one with an irregular pegmatite of dimensions 27×21 cm and of typical composition, central void with quartz, microcline and cleavelandite.

Tunelowa Mt. (15º51.096'E, 50º52.936'N): western slope milky translucent quartz vein c. 12 cm thick cutting a c. 2.5 m granitoid block. In elongate voids in the vein 0.8–1.3 cm calcite crystals occur.

Witosza Mt. (15º44.229'E, 50º51.116'N): a wall on the SE slope with lenticular typical pegmatite nest, 54 cm long and maximum thickness of 14 cm, with a void, 17×4 cm in size. Small grains (0.5–6 mm) of chlorite, zeolites, marcasite, pyrite, bornite, chalcocite, bismuthinite and galena were found on quartz, microcline and albite in the void.