UDC 549.328

ON FORMS OF SILVER IN GALENA FROM SOME LEAD–ZINC DEPOSITS OF THE DALNEGORSK DISTRICT, PRIMOR'YE

Oksana L. Sveshnikova
Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, min@fmm.ru

Galenas with silver and antimony admixtures from 7 lead-zinc mainly hydrothermal deposits of Dalnegorsk district of Primorsky Territory were investigated. A special technique of chemical phase analysis has been used for determination of silver forms in galena. It was established that the amount of isomorphic silver in galena changes from 0.003 % to 0.01 %. The ratio of isomorphic silver in total silver in galena is insignificant and rarely accedes 10 % of its total in the mineral. The basic part of silver in galena, about 90 rel %, is related to inclusions of various silver minerals (visible or invisible). Sulfide mineral form dominates among inclusions (sulphosalts + Ag_2S), which share is 62 % to 87 % from total silver in the mineral. Much less silver is related to inclusions of native silver and intermetallic compounds, and very little with inclusions of silver-containing cogwhell. The epitaxial intergrowth with galena was established for invisible inclusions of argnetite and native silver using methods of electronic microsclpy.
3 tables, 4 figures and 18 references.

Galena from base-metal and lead-zinc deposits almost always contains an admixture of silver, which amount changes from 0 to some percents. Silver in galena is considered in numerous publications, but many unresolved questions in this problem continue till now.

Currently, existence of two forms of silver in galena is generally accepted: isomorphic and mineral as inclusions of silver minerals. Publications quite often mention invisible (dispersed) silver in galena (Patalakha, Gavrilov, 1971), which should include total amount of silver, isomorphic and related to invisible inclusions of silver minerals.

The conception of isomorphic replacements in natural galena is based on experimental researches. Van Hook (1960) and Hutta and Wright (1964) have shown that Ag_2S dissolves in PbS with formation of solid solutions. The limit of isomorphic replacement in natural galena is 0.6 mol % at 800° C and 0.2 mol % at room temperature. P. Ramdor (1960) has supposed that in conditions close to hydrothermal mineralogenesis solubility of Ag_2S does not exceed 0.1 mol % for high-temperature ore and 0.01 mol % for low-temperature ore.

Studies of the system $PbS-AgSbS_2$ have shown that the heterovalent isomorphism in galena under the scheme $2Pb^{2+}$ by $Ag^{1+} + Sb^{3+}$ is possible. Works Wernick (1960) and Nenasheva (1975) established the existence of solid solutions in the high-temperature part of the system $AgSbS_2$ — PbS. At temperature below 400° C, in data of Nenasheva S.N., continuos series of solid solutions disintegrate into some phases and limited solid solutions. The revealed phases are $Ag_3PbSb_3S_7$ and $AgPbSbS_3$. The last corresponds to a rare mineral — freieslebenite.

Researchers, as a rule, use a complex of methods at the study of silver admixtures in natural galenas. Currently, various kinds of spectral micromethods and electronic microscopy methods are determining among them. In addition, at solution of separate problems, recalculations of chemical analysis data with application of mathematical processing methods are used (Nesterova, 1958; Godovikov, 1966), as well as measurement of lattice cell parameters and some physical characteristics of galena to study correlations between them and silver content in a mineral (Ryabev *et al.*, 1969; Dobrovolskaya *et al.*, 1973).

For the solution of ore-dressing related problems, we used the technique of chemical phase analysis of silver in galena, developed in the Satpaev Institute of Geological Sciences of the Academy of Sciences of the Kazakh SSR (Timerbulatova, Antipin, 1973). This technique enables to determine simultaneously total silver in galena, amount of isomorphic silver and silver in inclusions, separately for diverse mineral forms of inclusions. Ag_2S and silver sulphosalts are determined jointly; native silver and intermetallic compounds of silver (dyscrasite) and separately — silver-containing cogwhell remaining in insoluble residue. The essence of analysis is selective extraction of silver minerals from galena basing on their unequal stability in relation to some dissolvents.

Seven deposits were subject to study: four hydrothermal and three skarn deposits. Galena from hydrothermal deposits was regularly studied and galena from skarn was presented by individual samples.

The list of deposits and brief data on their mineral composition are shown in Table 1.

Table 1. Mineral composition of deposits

Deposit - type	*Deposit*	*Ore minerals*		*Non-ore minerals (main and minor)*	*Visible inclusions of silver minerals in galena*	*Notes*
		Main	*Minor and rare (are italic)*			
Hydro-thermal	Yuzhnoye	Pyrrhotite, sphalerite, galena, magnetite, jamesonite (on upper levels)	Arsenopyrite, *cassiterite*, chalcopyrite, *boulangerite, menegenit, stannite*, Ag-containing tetrahedrite, *dyscrasite, native antimony, pyrargyrite, miargyrite, owyheeite, argentite*, *native silver, diaphorite (?)*	Mangan-siderite, quartz, calcite, rhodochrosite, actinolite	**Frequent in galena on upper levels:** pyrargyrite (predominates), owyheeite, miar-gyrite, Ag-containing tetrahedrite, native Ag, dyscrasite, argentite. **Rare in galenas on lover horizons:** pyrar-gyrite, dyscrasite, native Ag, argentite.	
	Maiminovskoye	Sphalerite, galena, chalcopyrite	Arsenopyrite, pyrite, chalcopyrite, Ag-containing tetrahedrite, *pyrrhotite, polybasite*	Quartz, carbonate, chlorite	**Rare:** pyrargyrite, polybasite, steph-anite, native Ag. **More frequent**: Ag-containing tetrahedrite	
	Augustovskoye	Pyrite, marcasite, sphalerite, galena, pyrrhotite	Arsenopyrite, chalcopyrite, magnetite, stannite, *boulangerite*, *bournonite*	Quartz, dolomite, rhodochrosite, calcite	**Rare:** pyrargyrite, native Ag, Ag-containing tetrahedrite	
	Zayavochnoye	Pyrite, pyrrhotite, marcasite, sphalerite, galena	Chalcopyrite, arsenopyrite, *stannite*	Quartz, carbonate	**Rather rare:** Ag-containing tetrahedrite	For separate samples only composition of ore bodies is characterized
Skarn	Vostochny Partizan — Borisovskoye ore body (hydrothermal)	Sphalerite, galena, chalcopyrite	Arsenopyrite Ag-containing tetrahedrite, bournonite	Calcite, laumontite	**Rare:** Ag-containing tetrahedrite, native Ag	Borisovskoye ore body represents sandstone zone , broken by thick network of frac-tures filled with hydrothermal sulfide
	Verkhneye	Galena, sphalerite	Chalcopyrite	Calcite, hedenbergite	Not observed in the investigated sample	Sample B-465 is presented by crys-tals of late galena from pocket-like segregations of calcite in massive galena-sphalerite ore
	Nikolaevskoye	Sphalerite, galena	Chalcopyrite, pyrrhotite, arsenopyrite	Hedenbergite, calcite, quartz	Were not observed	

Results of chemical phase analysis of galena are indicated in Table 2. The Table shows that the investigated galenas considerably differ in total contents of silver in them. The values oscillate in the range of 0.054 to 0.900 mass %. Minimum values are characteristic for galenas from skarn (an. 21-23), maximum — for galena from jamesonite-sphalerite-galena ore developed on upper levels of the Yuzhnoye Deposit (an. 1). According to the data of spectral analysis (quantitative and semi-quantitative) not resulted in this article, all galenas are also characterized by increased contents of antimony.

The analysis of the data resulted in Table 2 gives the main conclusion: the part of isomorphic silver is insignificant and usually makes some percents, rarely above 10 % (an. 19, 21. and 23), from total silver in all investigated galenas. Respectively, the basic amount of silver, about 90 rel %, is related to inclusions of various silver minerals.

As to absolute values of isomorphic silver contents in galena, they are different not only

Table 2 Results of chevical phase analysis of galena (mass %)

##	Deposit type	Deposit	Sample		Location	Total Ag	Isomorphic Ag		Sulfide Ag: Ag2S+sulphosalt		Native Ag and intermetallic compounds		Ag-containing cogwhill	
							abs. %	rel. %	abs. %	rel. %	abs. %	rel. %	abs. %	rel. %
1	Hydro-thermal	Yuzhnoye	52		Level +870m Adit 203	0,900	0,006	0,67	0,740	82,22	0,061	6,78	0,006	0,67
2			83		Level +830m adit 204	0,430	0,005	1,16	0,351	81,63	0,034	7,91	0,007	1,63
3			510		Level +690m adit 205	0,240	0,010	4,17	0,160	66,67	0,056	23,33	0,004	1,67
4			540	Below level +620	Well 505	0,200	0,010	5,00	0,154	77,00	0,024	12,00	0,022	1,00
5			28		Well 488	0,195	0,009	4,62	0,134	68,72	0,023	11,80	0,007	3,59
6			715		Well 511-bis	0,190	0,011	5,79	0,141	73,68	0,033	17,37	0,004	2,11
7			538		Well 508	0,189	0,012	6,35	0,129	68,25	0,033	17,46	0,051	2,70
8			548		Well 501	0,185	0,014	7,63	0,115	62,16	0,030	16,22	0,005	2,76
9			21		Well 84	0,140	0,005	3,57	0,090	64,30	0,040	28,57	Not detected	
10		Maimini-vskoye	614		Well 63	0,165	0,003	1,82	0,120	72,73	0,014	8,49	0,011	6,67
11			570		Well 65	0,160	0,003	1,90	0,100	62,50	0,032	20,00	0,014	8,75
12			872		Well 136	0,110	0,010	9,09	0,074	67,27	0,021	19,09	Traces	Traces
13			803		Well 161	0,096	0,005	5,26	0,069	71,88	0,016	16,57	0,005	5,26
14			854		Well 131	0,059	0,006	10,17	0,045	76,27	0,008	13,56	Traces	Traces
15		Augusto-vskoye	28-a		Well 37	0,460	0,022	4,78	0,400	86,96	0,024	5,22	Traces	Traces
16			288		Site 32	0,400	0,007	1,75	0,320	80,00	0,045	11,25	0,010	2,50
17			993		Adit 2	0,250	Traces	Traces	0,200	80,00	0,024	9,60	Traces	Traces
18			13		Well 35	0,177	0,007	3,95	0,140	79,10	0,010	5,63	0,007	3,95
19		Zayavo-chnoye	829		Well 87a	0,089	0,010	11,23	0,060	69,76	0,011	12,36	0,005	5,62
20	Skarn	Verkhneye	465		Level -162m	0,300	0,010	3,33	0,250	83,33	0,013	4,33	0,005	1,67
21		Vostochny Partizan	75		Level +215m Capital adit	0,054	0,007	12,96	0,040	74,07	0,010	18,52	Traces	Traces
22		Nikola-yevskoye	936		Well 924	0,070	0,005	7,17	0,048	68,57	0,012	17,14	Traces	Traces
23			907		Well 923	0,060	0,007	11,67	0,038	63,33	0,011	18,33	Traces	Traces

Analyses were made by A.I. Antipina in the chemical laboratory of Satpaev Institute of Geological Sciences of Academy of Sciences of the Kazakh SSR in 1990.
Average relative error of the method is 10 %..

for galenas from different deposits, but also within the limits of one deposit. The most vivid example in this respect is the Augustovskoye deposit, where one of galenas shows traces of isomorphic admixture of silver (an. 17), while in another one (an. 15) the silver content riches 0.022 mass %, which is abnormally high value in the studied galenas.

If to exclude extreme values, the amount of isomorphic admixture of silver in 90 % of investigated samples changes in the range of 0.003 to 0.01 mass %. It is difficult to interpret any dependence of the total contents of silver on the amount of isomorphic admixture basing on available data. We shall only notice that galenas with the highest silver contents of 0.900 mass % (an. 1); 0.430 mass % (an. 2) and 0.400 mass % (an. 16) are characterized by very low values of isomorphic admixture: 0.006, 0.005 and 0.007 mass % respectively.

The silver isomorphism in investigated galenas is related to formation of solid solutions in the system $AgSbS_2-PbS$. Their existence is manifested by regular relation of silver with antimony, established by various analytical methods, and presence of freieslebenite $AgPbSbS_3$ in galena from the Yuzhnoye deposit as submicroscopic inclusions reminding products of solid solution decomposition (Fig. 1), which will be discussed below in more detail, and finally by the data of X-ray studies of galena samples with known amount of isomorphic

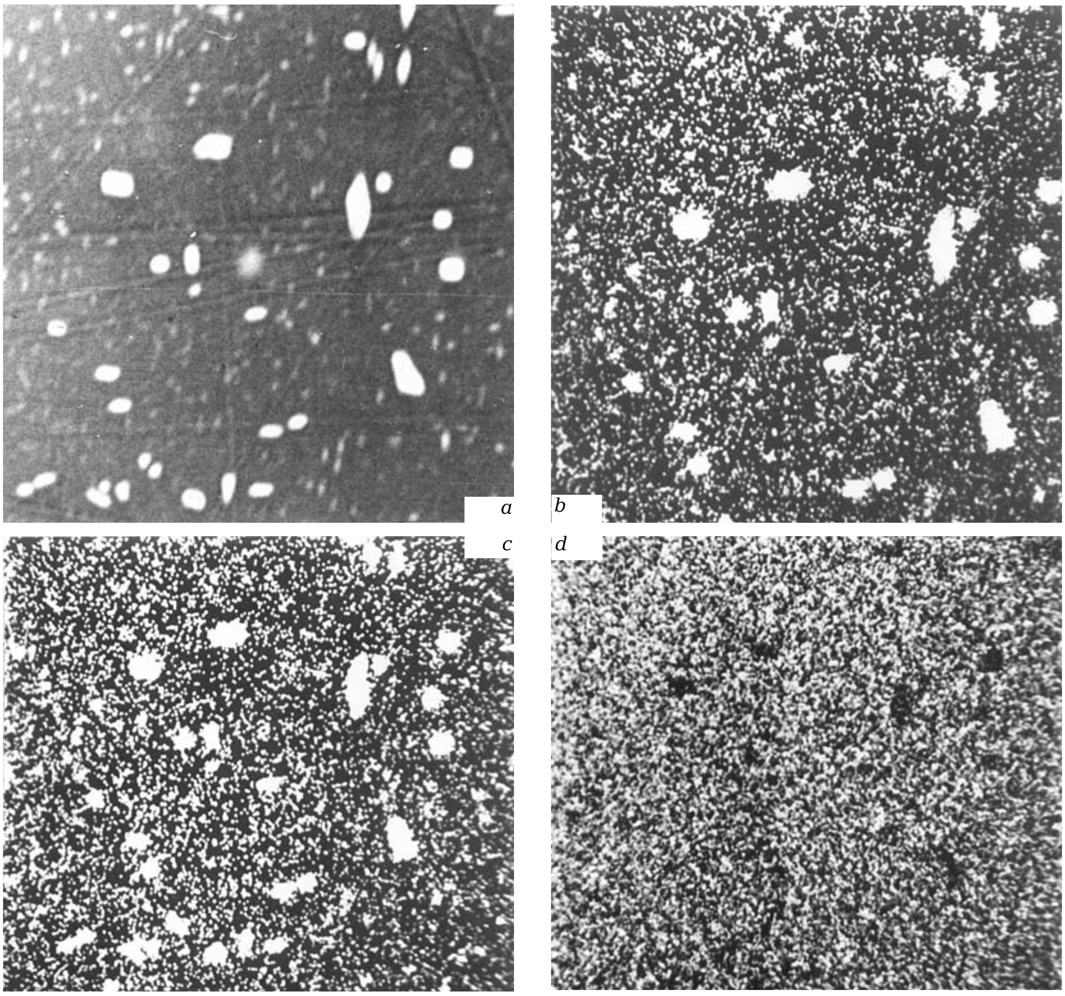

FIG. 1. Freieslebenite inclusions in galena. Yuzhnoye deposit. Surface of galena in the microanalyser: in absorbed electrons (a), in characteristic X-ray radiation: AgLa1 (b), SbLa1 (c), PbLa (d). Scanning site 100 x 100 microns

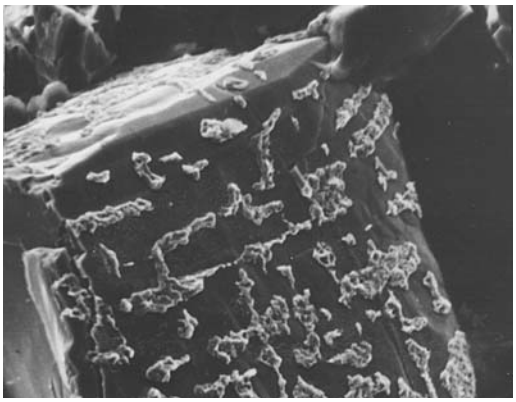

FIG. 2. Dendrites of native silver, epitactically growing up on a plane of galena. Vostochny Partizan deposit. SEM image. x 5000. Photo by R.V. Boyarskaya

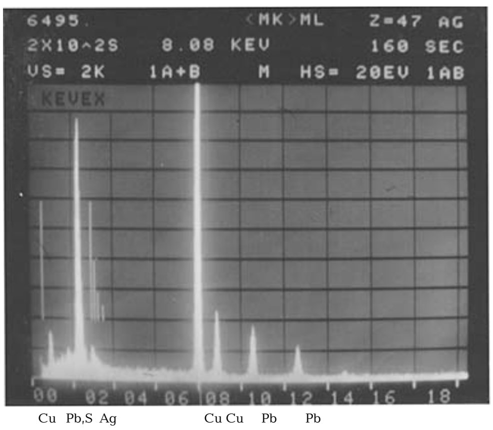

FIG. 3. Energy dispersion spectrum of native silver composition growing up on galena. (Cu peaks in the spectrum result from preparation).

Table 3. Parameter of lattice cell of cell of galena with different contents of total and isomorphic silver

##	Sample	Total Ag mass %	Isomorphic Ag, mass %	a_o, Å
1	993	0,250	-	5,933
2	570	0,160	0,003	5,932
3	614	0,165	0,003	5,932
4	854	0,059	0,006	5,932
5	288	0,400	0,007	5,931
6	829	0,089	0,010	5,931
7	28-a	0,460	0,022	5,929

Conditions:
DRON-3; regime: 40kv-15ma. Internal standard — metal silicon. Accuracy of determination — ±0.001Å.

silver. The work was executed by O.V. Kuzmina in the X-ray laboratory of IGEM of the Russian Academy of Sciences.

Table 3 shows the designed values of a_0 in lattice cell of galenas with diverse contents of total and isomorphic silver. As follows from the Table, the a_0 parameter in galena decreases from 5.933Å to 5.929Å (accuracy ±0.001) in accordance with the increase of isomorphic admixture of silver in it from 0 mass % to 0.022 mass %.

As mentioned above, the mineral form of silver in galena is dominant in the investigated deposits. About 90 % of silver from its total amount in galena are related to inclusions of various silver minerals. Among inclusions, sulfide minerals (Ag_2S + silver sulphosalts) sharply predominate. Their share is from 62 (an. 8) to 87 (an. 15) rel % of silver in galena. Much less silver is related to inclusions of native silver and intermetallic compounds (dyscrasite) and very little with the admixture of silver-containing cogwhell presented in all investigated samples by silver-containing tetrahedrite.

The share of this or that mineral form of inclusions in total silver in galena oscillates even within one deposit; this is related to features of mineral composition of deposits. So, in the Yuzhnoye deposit, the observed decrease with depth of the sulfide silver share (from 82.2 rel % to 62.16 rel %) with simultaneous increase of native silver (fom 6.7 rel % to 28.57 rel %) is related to general change of ore composition, in particular, with disappearance of silver — sulphosalt association of minerals on deep levels. Cogwhell, forming visible accumulations on some plots of ore bodies, is more abundant in the Maiminovskoye deposit than in other deposits. Cogwhell occurs in galena not only as fine inclusions, but also as streaks and replacement rims, which is probably the reason for a significant increase of the share of related to it silver in some samples of galena (an. 10 — 6.67 rel %; an. 11 — 8.75 rel %).

Rare inclusions of silver minerals interpreted in investigated galenas by optical methods cannot explain, in our opinion, all amount of silver related to inclusions, which follows from the data of chemical analysis. A part of this silver, we assume, is unconditionally related to submicroscopic (invisible) inclusions, which sizes lay outside of resolving power of optical microscope. A.P. Pronin with co-authors (1971), who studied silver in galena from the Zyryanovskoye base-metal deposit, earlier came to a similar conclusion. Their data allow to make some assumptions on the silver amount related to invisible inclusions, having received it as a difference of contents of invisible and isomorphic silver. So, the contents of invisible silver determined using the quantitative spectral microanalysis in galenas from late carbonate – quartz – sulfides veins of the Zyryanovskoye deposit oscillate between 0.013 and 0.290 mass % (average of 144 determinations is 0.117 mass %), while the contents of isomorphic silver determined by the selective solution does not exceed 0.079 mass %.

For the purpose to reveal invisible inclusions in investigated galenas, the IGEM laboratory has conducted studies of their surface in backscattered electrons on microprobe MS «Cameca» and also with application of transmission and scanning electron microscopes. Invisible inclusions were only detected in three samples of galena.

So, in «curvistriated» (broken down) galena from jamesonite-sphalerite-galena ore of the Yuzhnoye deposit, submicroscopic inclusions of freieslebenite from parts of micron to 3-5 microns were observed by the microprobe. The most fine grains are dot impregnations, larger have oval, sometimes lanceolate form. The composition of mineral was determined in one of coarse grains and its recalculation well fitted to the formula of freieslebenite: Ag — 21.97 mass %; Pb — 40.29 mass %; Sb — 23.21 mass %; S — 18.23 mass % (analyst Malov V.S.). The microanalyser image of freieslebenite grain surface is given on Fig. 1. The described segregations of freieslebenite can be a product of solid solution decay in the system $AgSbS_2$-PbS and increase of their grains (as well as decay itself) is the consequence of dynamometamorphism. L.N. Indolev (1974) paid attention to a similar fact at studying of

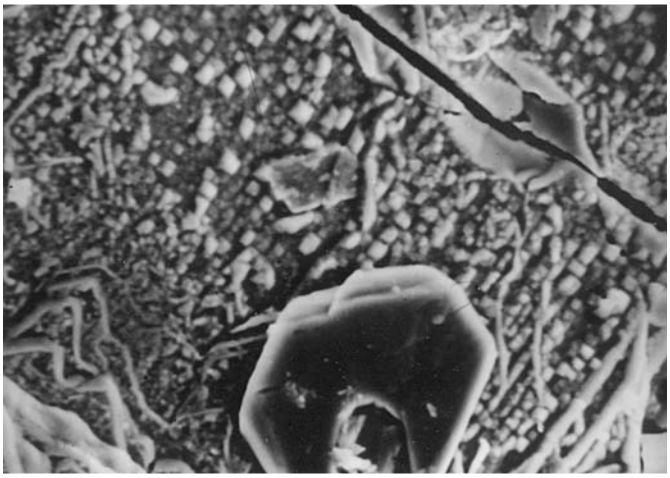

FIG. 4. Cubic crystals of argentite epitactically growing up on a plane of galena. Verkhneye deposit. SEM image. x5000. Photo by R.V. Boyarskaya

lead-zinc deposits of Yakutia. The association of decay products as miargyrite to plots of strained galena was also registered by M.G.Dobrovolskaya *et al.* (1973).

Presence of freieslebenite as a solid solution decay product is a rare phenomenon. In publications (Indolev, 1974; Czamanske and Hall, 1976; Sharp and Buseck, 1993) similar inclusions in galena are usually presented by diaphorite ($Ag_3Pb_2Sb_3S_8$), though some researches (Nenasheva, 1975; Hoda and Chang, 1975) have established existence of solid solution between galena and freieslebenite.

Dendrites of native silver, epitactically growing up on the plane of galena in two perpendicular directions were detected with the help of electronic microscopy in galena from the Vostochny Partizan deposit (Fig. 2, Fig. 3).

Epitactic intergrowths with Ag_2S are characteristic for galena from the Verkhneye deposit. In Fig. 4, cubic crystals representing a pseudomorph of acanthite after argentite are well visible. Diagnostic of acanthite was made on the basis of calculation of microdiffraction data of R.V. Boyarskaya.

Epitactic form of inclusions, in the opinion of some researchers (Frank-Kamenetsky, 1964; Badalov and Povarenykh, 1967), is rather widely distributed in minerals. In galena a significant part of silver mineral inclusions could have the epitactic nature owing to geometrical similarity of their structures to the structure of galena. Epitactic inclusions, as specifies V.A. Frank-Kamenetsky, can originate at different conditions, including, at disintegration of solid solutions.

The nature of silver inclusions in galena can be rather diverse and it is not restricted to the discussed examples. So, P. Costagliola *et al.* (2003) in recent studies using EPR-spectroscopy have revealed the presence of initial native silver (Ag^0) in silver-containing galena from the Tuscan ore region (Italy). This silver forms pairs and clusters, which can associate with pairs of metal gold or silver-gold hetero-nuclear pairs.

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