N. Jb. Miner. Mh.	Jg. 1996, H. 7	313–320	Stuttgart, Juli 1996

Fettelite, a new Hg–sulfosalt mineral from Odenwald

By **Naiding Wang**, Heidelberg, and **Andres Paniagua**, Oviedo, Spain

With 1 figure and 3 tables in the text

WANG, N. & PANIAGUA, A.: Fettelite, a new Hg–sulfosalt mineral from Odenwald. – N. Jb. Miner. Mh. **1996**, H. 7, 313–320; Stuttgart 1996.

Abstract: Fettelite, $Ag_{24}HgAs_5S_{20}$, is a new Hg-bearing species found in hydrothermal veins cutting basic intrusives of Variscan age at the Nieder-Beerbach mine near Darmstadt, Odenwald. This low-temperature mineral occurs within calcite–quartz–prehnite veins in close association with native silver, proustite, pearceite, safflorite, xanthoconite, polybasite, cinnabar, sphalerite, chalcopyrite, pyrite, and other minerals. Fettelite has a mica-like appearance. It occurs as individual hexagonal flakes or as clusters of subparallel growth or rosette-like groups, with flake dimensions up to 0.2 mm across and mostly 5–10 μm in thickness. It has a reddish color, is brittle with perfect {0001} cleavage. Fracture is irregular and luster is submetallic to adamantine. Measured Vicker's hardness is 1.58 which corresponds to Mohs hardness of 3¾. The calculated density for the idealized formula is 6.29 g/cm³. Under reflected light, fettelite is grey in color, with weak but still perceptible anisotropism. The internal reflection is red. Reflectance values measured at 420–700 nm range between 9.2–14.4 (oil) and 22.5–31.3 (air), respectively. The empirical formula from microprobe analysis (based on 24 Ag atoms) is: $Ag_{24}HgCu_{0.04}Fe_{0.03}Tl_{0.02}Pb_{0.01}Sb_{0.07}As_{5.01}S_{20.07}$, ideally $Ag_{24}HgAs_5S_{20}$. Fettelite is trigonal, with a_h = 15.00 Å and c_h = 15.46 Å, and crystallizes in one of the six possible space groups P312, P321, P31m, P3m1, P$\bar{3}$1m, P$\bar{3}$m1. The five strongest powder lines are 3.091 (10)(005), 1.878 (8)(440), 3.175 (6)(401), 2.998 (4)(402), 2.755(3)(043). The name honours Mr. M. FETTEL, an experienced field worker in the area, who found the mineral.

Key words: Fettelite, New Ag–Hg–As–S mineral from Odenwald, chemical analysis, X-ray, powder and single crystal data, reflectance data.

Introduction

A number of closely spaced occurrences of silver mineralization are known in the northwestern part of the "crystalline Odenwald", SW Germany, where Variscan-age intrusives of gabbro-diorite rocks containing amphibolite inclusions are exposed (FETTEL 1982, NICKEL & FETTEL 1985). One of the occurrences, the Nieder-Beerbach mine 10 km south of Darmstadt, was discovered in 1977. Here hydrothermal veins are structurally controlled by Tertiary shear zones cross cutting the basic intrusives. The ladder-like veins, averaging 5–10 cm in thickness, contain mainly calcite, quartz, barite, and in lower lev-

0028-3649/96/1996-0313 $ 2.00

els also prehnite as gangue minerals. The ore minerals comprise a remarkably large number of native elements, sulfides and sulfosalts, including native silver, copper, arsenic, argentite, acanthite, pearceite, proustite, xanthoconite, safflorite, löllingite, polybasite, trechmannite, smithite, cinnabar, galena, sphalerite, chalcopyrite, and pyrrhotite (FETTEL 1985, BELENDORFF 1986). Unique to the area is the unusual enrichment of Hg, as revealed by high Hg contents in native silver and by the presence of the mineral cinnabar.

Mr. M. FETTEL, an experienced worker in the field geology of the area, found in 1992 a reddish colored, mica-like mineral in close association with proustite, pearceite, xanthoconite and safflorite and sent it to us for investigation. This mineral, after being identified as a new Hg-bearing species, was named fettelite in honour of him in recognition of the unusual finding and of his contribution to the geology of the Odenwald. The mineral and the proposed name were approved by the Commission on New Minerals and Mineral Names in February, 1995. A major, representative part of the type material is deposited at the Institute of Mineralogy, University of Heidelberg for future reference.

Physical and optical properties

As one of the latest in the paragenetic sequence, fettelite occurs in clusters of hexagonal flakes with dimensions up to 0.2 mm across and mostly 5 – 10 μm thick. In other specimens it also occurs as somewhat larger, subparallel aggregates of more compact hexagonal tablets, with thickness of the individual grains reaching 0.05 mm. The color is dark violet to scarlet and appears wine red if split in thin fragments. The streak is dark vermillion. The crystals are brittle with perfect {0001} cleavage and an irregular fracture. The luster is submetallic to adamantine. The Vicker's microhardness measured from 20 indentations under 20 g load is 158 (range 138 – 174) which corresponds to a calculated Mohs hardness of 3¾. No data at higher loads were obtained due to the minute size of the crystals available in the polished section.

Under the reflecting microscope, the color of the opaque material is grey with a greenish tint, the latter only perceptible if in contact with other Ag–As sulfosalts. This greenish hue appears similar to that observed in acanthite, tenanntite or pearceite. The bireflectance is weak, being noticeable in oil, but nearly inperceptible in air.

The anisotropism, generally weak and masked by strong red internal reflections, shows bright greenish grey to dark bluish grey tints which could be better observed when sections are nearly perpendicular to the basal plane and when the nicols are slightly off the extinction position. In the wave length range 546 – 650 nm, the anisotropic effect is noticeably enhanced.

Reflectance values in air and in oil (nD = 1.515, DIN 58.884 at 20 °C) were measured in the range 420 – 700 nm against a SiC standard (Zeiss No. 133)

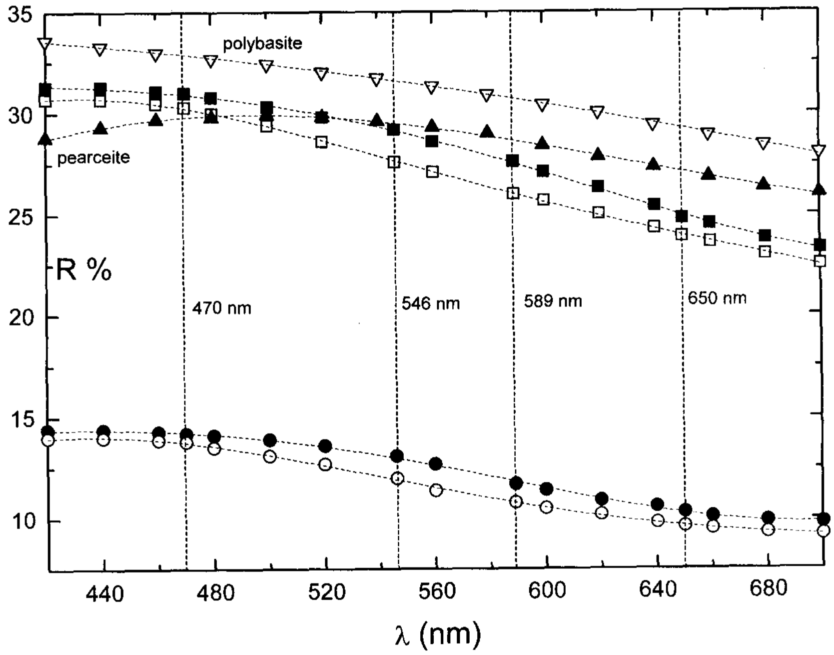

Fig. 1. Graphical representation of the reflectance of fettelite compared with that of polybasite and pearceite. Solid and open squares are the maximum and minimum reflectance in air, respectively. Solid and open circles are the maximum and minimum reflectance in oil. Upward pointing solid triangles: reflectance of pearceite. Downward pointing open triangles: reflectance of polybasite. Data for the latter two minerals after Picot & Johan (1982).

using a Zeiss microscope photometer (Table 1, Fig. 1). The results are close to those reported for the mineral pearceite and slightly lower than those for polybasite (data for pearceite and polybasite taken from Picot & Johan 1982).

Chemical compositions

The chemical composition of this new species was determined with a CAMECA SX 50 microprobe by means of wave length dispersive spectrometry. Conditions selected for the analysis were an accelerating voltage of 20 kV and beam current of 10 nA; counting times were 20 seconds on the peak and background. The beam diameter was adjusted throughout the investigation of this mineral to the optimal value 10 μm in order to minimize the beam damage to the beam-sensitive surface. Raw counts were corrected with the Cameca supplied software PAP.

Table 1. Measured reflectance data of fettelite compared with that of pearceite and polybasite. Measurement conditions: plane polarized light, normal incidence, monochromator, standard SiC, objectives 40 air/oil. half-field prism illuminator, obliquity corrected through $(R \perp + R//)/2$. Data for pearceite and polybasite after Picot & Johan (1982).

λnm	R%$_{max}$ air	R%$_{min}$ air	R%$_{max}$ oil	R%$_{min}$ oil	R% pearceite	R% polibasite
420	31.3	30.7	14.4	14.0	28.8	33.6
440	31.3	30.7	14.4	14.0	29.3	33.3
460	31.1	30.5	14.3	13.9	29.7	33.0
470	**31.0**	**30.3**	**14.2**	**13.8**	–	–
480	30.8	30.0	14.1	13.5	29.8	32.7
500	30.3	29.4	13.9	13.1	29.9	32.4
520	29.8	28.6	13.6	12.7	29.8	32.0
540	–	–	–	–	29.6	31.7
546	**29.2**	**27.6**	**13.1**	**12.0**	–	–
560	28.6	27.1	12.7	11.4	29.3	31.3
580	–	–	–	–	29.0	30.9
589	**27.6**	**26.0**	**11.7**	**10.8**	–	–
600	27.1	25.7	11.4	10.5	28.4	30.4
620	26.3	25.0	10.9	10.2	27.8	30.0
640	25.4	24.3	10.6	9.8	27.3	29.4
650	**24.8**	**23.9**	**10.3**	**9.6**	–	–
660	24.5	23.6	10.1	9.5	26.8	28.9
680	23.8	23.0	9.9	9.3	26.3	28.4
700	23.3	22.5	9.8	9.2	26.0	28.0

For the various elements detected in this mineral, the following characteristic wave lengths and synthetic standards (in brackets) were used:

As: Lα (NiAs), Cu: Kα ($CuFeS_2$), S: Kα (Ag_2S), Fe: Kα ($CuFeS_2$), Ag: Lα (Ag_2S), Tl: Lα ($TlSbS_2$), Sb: Lα ($TlSbS_2$), Hg: Lα (HgTe), Pb: Mα (PbS).

Five fettelite grains were selected for analysis. Despite limitations imposed by the beam sensitivity of this mineral, the overall results were satisfactorily constant, indicating the homogeneity of the analyzed material. A total of 28 analyses on five crystals gave a mean composition (and ranges in brackets) of: As 9.80 (9.19–10.33), Cu 0.07, S 16.79 (16.18–17.25), Fe 0.04, Ag 67.55 (66.53–68.44), Tl 0.13, Sb 0.23, Hg 5.21 (5.12–5.38), Pb 0.07, total 99.88 wt.% (Table 2). The empirical formula, based on 24 Ag atoms is $Ag_{24}Hg_{1.0}Cu_{0.04}Fe_{0.03}Tl_{0.02}Pb_{0.01}Sb_{0.07}As_{5.01}S_{20.07}$. This can be idealized or simplified to $Ag_{24}HgAs_5S_{20}$ by eliminating the traces of Cu, Fe, Tl, Pb and Sb which are considered as inessential elements. The low and variable analytical values of these minor elements should be interpreted with care due to possible alterations induced by beam damage under approaching of the detection limit.

Table 2. Chemical composition of fettelite from 28 microprobe analysis.

Crystal	1		2		3		4		5		average	
number of anal.	8		8		5		3		4		(28 anal.)	
	mean	std. dv.	mean	std. dv.	mean	std. dv.	mean	std. dv	mean	std. dv	mean	std. dv.
As wt.%	9.19	0.46	10.33	0.66	10.02	0.45	9.43	0.36	9.99	0.31	9.80	0.66
Cu wt.%	0.06	0.06	0.08	0.09	0.07	0.05	0.07	0.12	0.07	0.07	0.07	0.08
S wt.%	17.01	0.68	17.25	0.72	16.37	0.20	16.18	0.50	16.41	0.23	16.79	0.66
Fe wt.%	0.03	0.05	0.04	0.04	0.03	0.03	0.04	0.07	0.04	0.04	0.04	0.04
Ag wt.%	68.01	1.32	66.53	1.39	67.45	0.59	68.01	0.19	68.44	0.59	67.55	1.09
Tl wt.%	0.06	0.11	0.16	0.25	0.17	0.24	0.23	0.13	0.07	0.15	0.13	0.16
Sb wt.%	0.18	0.07	0.22	0.11	0.26	0.29	0.17	0.15	0.36	0.19	0.23	0.17
Hg wt.%	5.23	0.45	5.22	0.59	5.12	0.41	5.38	0.31	5.13	0.36	5.21	0.51
Pb wt.%	0.02	0.04	0.05	0.09	0.16	0.15	0.08	0.09	0.09	0.14	0.07	0.09
Total wt.%	99.77	0.50	99.88	0.40	99.65	0.48	99.60	0.56	100.61	0.45	99.88	0.46
wt.%/mol.wt.												
Ag	0.6305	0.0122	0.6168	0.0129	0.6253	0.0054	0.6305	0.0017	0.6345	0.0055	0.6262	0.01
Hg	0.0261	0.0023	0.0260	0.0030	0.0255	0.0020	0.0268	0.0015	0.0256	0.0018	0.0260	0.00
As	0.1226	0.0062	0.1379	0.0088	0.1337	0.0060	0.1258	0.0047	0.1333	0.0041	0.1308	0.01
S	0.5304	0.0212	0.5380	0.0224	0.5106	0.0063	0.5047	0.0157	0.5118	0.0071	0.5236	0.02
At.p.f.u.*												
Ag	24.00	0.00	24.00	0.00	24.00	0.00	24.00	0.00	24.00	0.00	24.00	0.00
Hg	0.99	0.10	1.01	0.13	0.98	0.08	1.02	0.06	0.97	0.07	1.00	0.10
As	4.67	0.30	5.37	0.43	5.13	0.23	4.79	0.19	5.04	0.17	5.01	0.40
S	20.19	1.11	20.93	1.16	19.60	0.28	19.21	0.65	19.36	0.33	20.07	1.04

* Per formula unit calculated on the basis of 24 Ag atoms.

X-ray crystallography

Minute flakes split from the crystal aggregate were investigated by the precession method, using molybdenum radiation. The excellent {0001} basal cleavage permitted the splitting of fragments down to thicknesses as small as a few microns. All test fragments, independent of size or thickness or growth state, yielded the same diffraction patterns.

With the direction normal to the flake taken as the c-axis, the hk0 pattern of two 10-micron thick crystal fragments yields a hexagonal subcell of $a_s = 3.75$ Å and a hexagonal unit cell with a_h four times as large (15.00 Å). A complete rotation of the crystal plate parallel to the c-axis yielded 3 identical patterns spaced 120 degrees apart that contain only a symmetry center. Halfway inbetween are three more identical patterns having 2 mm plane symmetry. The crystal is, therefore, trigonal with a hexagonal lattice (diff. symm. $\bar{3}$m). The lattice parameters, refined from powder data, are $a_h = 15.00$ Å and $c_h = 15.46$ Å. The observed systematic absence of the 0kl (h0l) reflections, $k(h) = 2n+1$, appears to be related to the superstructure and unrelated to space group extinction involving glide operations. Six space groups are consistent with extinction conditions limiting certain reflections: P312, P321, P3m1, P31m, P$\bar{3}$m1, P$\bar{3}$1m.

Despite the firm evidence in favour of a trigonal symmetry, repeated long exposures of the hk0 layer of the investigated crystals indicate a slight inconsistency in the intensity of two equivalent superstructural reflections. As a result of this inconsistency, the hk0 pattern appears orthorhombic. At the present stage, however, no other supporting criteria are available which favours the orthorhombic alternative with the resulting C-centered lattice. The possibility of polysynthetic twinning of an orthorhombic crystal, dimensionally hexagonal should be similarly ruled out, since otherwise an apparent symmetry plane normal to the c-axis would have been generated in the diffraction patterns.

The powder pattern, prepared from a few cleavage fragments hand picked under the microscope, was indexed with the aid of the observed reflections on the single crystal pattern. Notable in the pattern is the most intense (005) reflection which appears unique in sulfosalts. The refined powder data are listed in Table 3. The hexagonal unit cell contains 3 formula units of $Ag_{24}HgAs_5S_{20}$, yielding a calculated density of 6.29 g/cm^3, which is closely comparable to that of stephanite (Ag_5SbS_4).

Discussion

On the basis of the analyzed formula $Ag_{24}HgAs_5S_{20}$, two conceivable alternatives for the valence state of Hg in fettelite can be expected. In the first case, Hg is monovalent and structurally indistinguishable from the dominant Ag component. This assumption would lead to a simplified, stephanite type formula $(Ag,Hg)_5AsS_4$ for fettelite and would support the still unconfirmed exist-

Table 3. X-ray powder diffraction data for fettelite.

$d_{obs.}$	$d_{cal.}$	I_{est}	h k l
7.69	7.731	1	0 0 2
5.97	5.989	1	2 0 1
4.98	4.974	1	0 2 2
3.243	3.248	2	4 0 0
3.175	3.179	6	4 0 1
3.091	3.093	10	0 0 5
2.998	2.995	4	4 0 2
2.925	2.927	1	3 2 1
2.755	2.748	3	0 4 3
2.667	2.662	1	4 1 2
2.497	2.500 2.487	2	3 3 0 0 4 4
2.471	2.468	2	3 3 1
2.426	2.425	1	4 2 1
2.245	2.250 2.240	1	3 3 3 4 0 5
2.076	2.073	2	4 2 4
1.878	1.875	8	4 4 0
1.825	1.827 1.822	1	4 0 7 4 4 2
1.664	1.664 1.661	1	5 4 0 4 0 8
1.613	1.615	2	0 8 1
1.553	1.551	1	3 1 9

CuKα radiation, 57.3 mm camera.

ence of a complete $Ag_5(Sb,As)S_4$ solid solution. However, the completely different powder patterns of stephanite and fettelite, the unusually strong (005) reflection in fettelite, and the lack of basal cleavage in stephanite all argue against a possible structural analogy of the two species. The hexagonal subcell of fettelite similarly does not appear to fit into a highly distorted pseudo-hexagonal cell of the orthorhombic species stephanite (Ribar & Nowacki 1970). Analysis aimed at the paragenetical relations of fettelite indicates the existence of an independent Ag_5AsS_4 phase in the polished section, where stephanite is also present. Isolation of this phase for detailed study was not possible due to its extremely small grain size.

The second alternative involving divalent Hg^{2+} ordered with respect to Ag^{1+} requires, for charge balance, $\frac{1}{5}$ of the 15 As^{3+} atoms in the unit cell to be reduced to As^{2+}. The resulting ordered structure will certainly differ from stephanite, and from the still insufficiently defined Hg-free Ag_5AsS_4 phase detected in coexistence with both.

Other paragenetical features observed were used to estimate the formation conditions of the new mineral. Inversion twinning found in acanthite coexisting with fettelite indicates, for example, formation temperatures above 176 °C (HANSEN & ANDERKO 1958). The coexistence of xanthoconite with proustite suggests a stability temperature close to 192 °C (HALL 1966). Both data, together with growth occurring in open spaces along the veins, suggest the new mineral formed in a low temperature, (close to 200 °C) hydrothermal environment, under possibly hydrostatic pressures.

References

BELENDORFF, K. (1986): Eine Paragenese seltener Minerale aus Nieder-Beerbach, Odenwald: Lautit, Kutinait, Paxit. – N. Jb. Miner. Mh. **1986,** 511–518.

FETTEL, M. (1982): Silver and associated minerals in the Northwestern Odenwald/Germany. – In: AMSTUTZ, G. C., EL GORESY, A., FRENZEL, G., KLUTH, C., MOH, G., WAUSCHKUHN, A. & ZIMMERMANN, R. A. (eds.): Ore minerals, the state of the art. – Springer Verlag, pp. 573–581.

– (1985): Silber, Arsen und Lautit aus dem Odenwald. – Lapis **10,** 35–39.

HALL, H. T. (1966): The system Ag–Sb–S, Ag–As–S and Ag–Bi–S: phase relations and mineralogical significance. – Ph. D. Dissertation, Brown University, USA.

HANSEN, M. & ANDERKO, K. (1958): Constitution of binary alloys. – McGraw-Hill, New York.

NICKEL, E. & FETTEL, M. (1985): Odenwald. Sammlung geolog. Führer, Band **65.** – Gebr. Borntraeger, Berlin/Stuttgart.

PICOT, P. & JOHAN, Z. (1982): Atlas of ore minerals. – B.R.G.M. – Elsevier.

RIBAR, B. & NOWACKI, W. (1970): Die Kristallstruktur von Stephanit ($SbS_3/S/Ag_5^{III}$). – Acta Crystallogr. **26,** 201–207.

Received: March 19, 1996; accepted (revised version): July 5, 1996.

Authors' addresses:

Dr. N. WANG, Mineralogisches Institut der Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany.

Dr. A. PANIAGUA, Departmento de Geologia, Universidad de Oviedo, c/ Arias de Velasko s/n, E33005 Oviedo, Spain.