ARGENTIAN-PENTLANDITE-BEARING ASSEMBLAGES IN METAMORPHIC ROCKS OF THE KTB PILOT HOLE, OBERPFALZ, GERMANY

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ABSTRACT

Different assemblages of argentian pentlandite occur in intermediate-grade metamorphic rocks from the pilot hole of the German Continental Deep Drilling Program (KTB). Assemblage 1 consists of small inclusions in chalcopyrite within quartz veins. Argentian pentlandite is also intergrown with chalcopyrite, pyrrhotite, pentlandite and pyrite (assemblage 2) or cobaltian pentlandite, chalcopyrite, pyrrhotite and sphalerite or chalcopyrite and galena (assemblage 3); assemblages 2 and 3 occur in paragneissic rocks. The Ag content of argentian pentlandite ranges from 10.3 to 12.6 wt.%. The exsolution origin of argentian pentlandite from chalcopyrite, as well as inversion twins and negative $\delta^{34}S$ values, of $-6.7‰$ in chalcopyrite from assemblage 1, point to mineralization during retrograde metamorphism at conditions of elevated pressure and temperature. Pressures of 2–3 kbar and temperatures of about 400°C are in agreement with the modeling of the retrograde P–T–t path for the KTB rocks. Temperature and sulfur fugacity estimates based on sphalerite and chlorite compositions suggest conditions of formation in assemblages 2 and 3 at or slightly below 260°C and at a value of $a(S_2)$ less than 10^{-13}. Bulk-rock $\delta^{34}S$ values of $-11‰$ are consistent with sulfur from a sedimentary source. Argentian pentlandite and associated sulfides are attributed to hydrothermal mineralization in which sulfur and the metals are derived from sedimentary host-rocks.

Keywords: argentian pentlandite, pentlandite, pyrrhotite, pyrite, chalcopyrite, sphalerite, chlorite, temperature, mineral chemistry, sulfur fugacity, KTB pilot hole, Oberpfalz, Germany.

SOMMAIRE

Nous avons découvert divers assemblages de minéraux contenant la pentlandite argentifère dans une suite de roches métamorphiques dans le trou de forage exploratoire KTB du programme allemand de forages profonds dans la croûte continentale. L'assemblage 1 est fait de petites inclusions de pentlandite argentifère dans la chalcopyrite incluse dans des veines de quartz. La pentlandite argentifère se présente aussi en intercroissances avec chalcopyrite, pyrrhotite, pentlandite et pyrite (assemblage 2), ou avec pentlandite cobaltifère, chalcopyrite, pyrrhotite et sphalérite, ou bien avec chalcopyrite et galène (assemblage 3). On trouve les assemblages 2 et 3 dans des roches paragneissiques. La teneur en Ag de la pentlandite argentifère varie de 10.3 à 12.6% (par poids). Une origine de celle-ci par exsolution à partir de la chalcopyrite, aussi bien que la présence de macles d'inversion et les valeurs négatives de $\delta^{34}S$ ($-6.7‰$) dans la chalcopyrite de l'assemblage 1, font penser que cette minéralisation a eu lieu lors d'un métamorphisme rétrograde à conditions de pression et de température élevées. Un intervalle de pression entre 2 et 3 kilobars et une température d'environ 400°C concordent avec un modèle d'évolution du tracé P–T–t pour les roches hôtes. La température et la fugacité du soufre, estimées à partir de la composition de la sphalérite et de la chlorite, font penser que les assemblages 2 et 3 se seraient formés à environ 260°C ou légèrement plus bas, et à une fugacité de soufre inférieure à 10^{-13}. Les valeurs de $\delta^{34}S$ des roches totales, $-11‰$, étayent l'hypothèse voulant que la source du soufre soit sédimentaire. La pentlandite argentifère et les sulfures associés témoignent d'une minéralisation hydrothermale au cours de laquelle le soufre et les métaux ont été dérivés des roches hôtes sédimentaires.

(Traduit par la Rédaction)

Mots-clés: pentlandite argentifère, pentlandite, pyrrhotite, pyrite, chalcopyrite, sphalérite, chlorite, température, composition des minéraux, fugacité du soufre, trou de forage exploratoire KTB, Oberpfalz, Allemagne.

INTRODUCTION

Argentian pentlandite was first described by Shishkin *et al.* (1971) and Vuorelainen *et al.* (1972) from Russian and Finnish sulfide deposits. Subsequent reports on the occurrence, composition, structure and phase relations of argentian pentlandite were published by Scott & Gasparrini (1973), Hall & Stewart (1973), Karpenkov *et al.* (1973), Mandziuk & Scott

(1977), Groves & Hall (1978), Mposkos (1983), Kozlovskiy *et al.* (1988) and Benvenuti (1991). These investigations have shown that argentian pentlandite is not simply a member of an isomorphous solid-solution series with pentlandite, but a distinct mineral species, $(Fe,Ni)_{8+x}Ag_{1-x}S_8$. It is commonly in close association with chalcopyrite, either as small blebs or exsolution-induced bodies or in direct contact with chalcopyrite, with or without pentlandite and pyrrhotite (Mandziuk
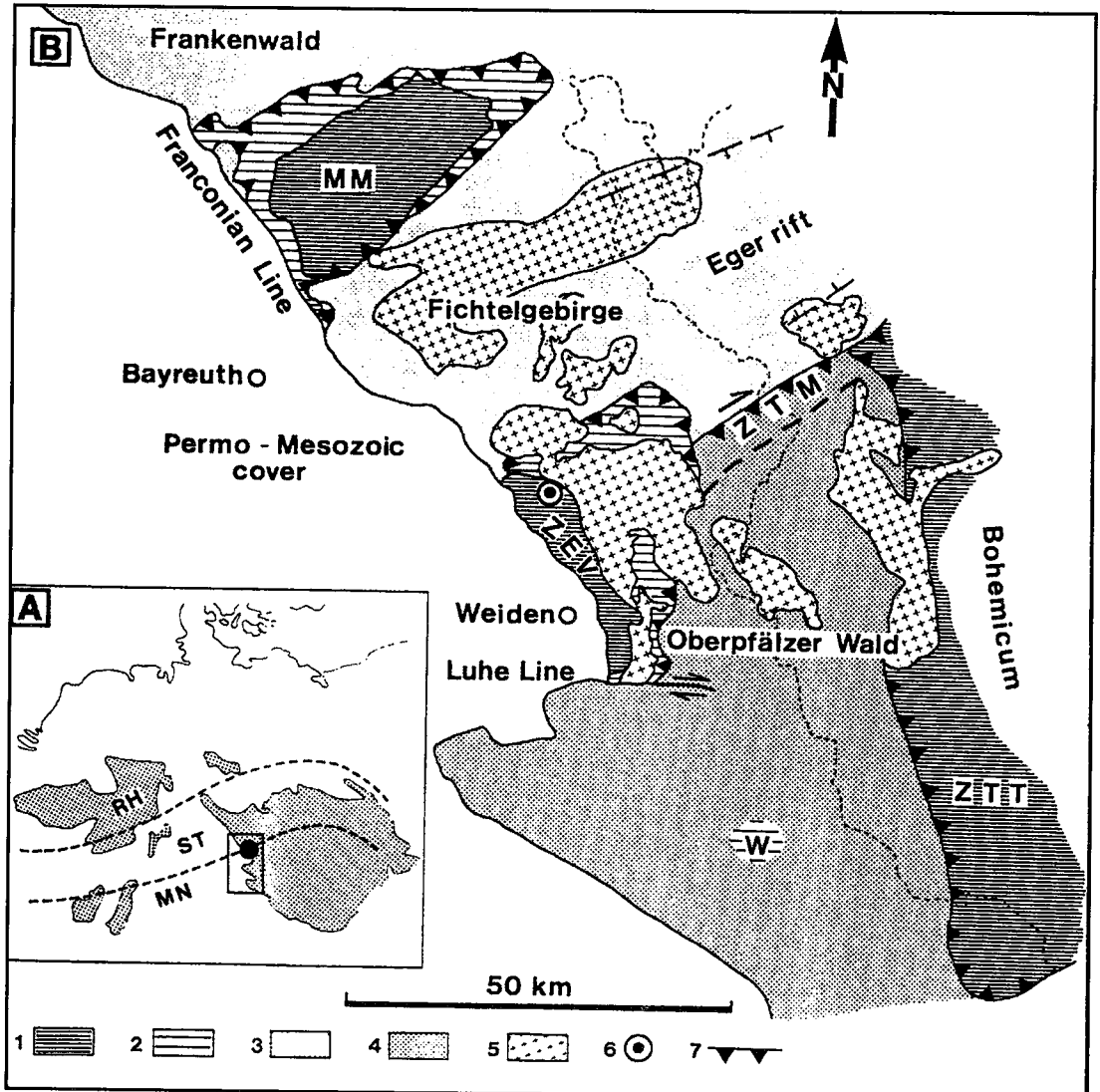

FIG. 1. Geological sketch-map of the western rim of the Bohemian Massif in northeastern Bavaria. A. Variscan basement outcrops in mid-Europe. RH: Rhenohercynian Zone, ST: Saxothuringian Zone, MN: Moldanubian Zone. B. Geological map with tectonomorphic units. 1: crystalline nappe complexes, 2: basal units of the nappe complexes, MM: Münchberg nappe complex, ZEV: Zone of Erbendorf-Vohenstrauβ, ZTT: Zone of Tepla-Taus, 3: Saxothuringian; 4: Moldanubian of the Oberpfälzer Wald; 5: late- to post-tectonic granites; 6: KTB drilling site. 7: overthrust; ZTM: Zone of Tirschenreuth-Mähring; W: Winklarn (Weber 1990).

& Scott 1977). Groves & Hall (1978) described an occurrence in which pyrrhotite and pentlandite are replaced by argentian pentlandite in association with galena, galenobismutite ($PbBi_2S_4$), native bismuth and parkerite ($Ni_3Bi_2S_2$).

Natural argentian pentlandite ranges in Fe/Ni atomic ratio from 1.34 to 2.57, and in metal/sulfur ratio from 1.096 to 1.173. The crystal structure determined by Hall & Stewart (1973) is face-centered, space group $Fm3m$. Hall & Stewart (1973) demonstrated that the octahedrally coordinated sites in argentian pentlandite are occupied exclusively by Ag atoms. Groves & Hall (1978) suggested that Fe and Ni occupy specific tetrahedrally coordinated sites; the structure of argentian pentlandite may thus be based on the primitive space-group $P43m$.

Experimental investigations of Mandziuk & Scott (1977) showed that argentian pentlandite is a stable phase in the system Ag–Fe–Ni–S below 455°C. The authors confirmed that the breakdown temperature of Fe-rich argentian pentlandite undersaturated in Ag (less than 1 atom per formula unit) is slightly lower than for Ag-saturated argentian pentlandite.

In magmatic Cu–Ni deposits, argentian pentlandite is restricted to Cu-rich zones. Experimental investigations of Mandziuk & Scott (1977) have shown that subsequent subsolidus reactions between Ag-bearing intermediate solid-solution (*Iss*), chalcopyrite and Fe–Ni sulfides below 455°C can produce argentian pentlandite either at grain boundaries or as exsolved bodies in *Iss* or chalcopyrite. Both textures occur in natural argentian pentlandite. However, Groves & Hall (1978) and Benvenuti (1991) assumed that argentian pentlandite could also be formed by replacement processes.

Argentian pentlandite occurs in various mineral assemblages and lithologic units of the pilot hole of the German Continental Deep Drilling Program. Argentian pentlandite was formed not only during retrograde metamorphism at conditions of elevated pressure and temperature, but also under hydrothermal conditions; it is not of magmatic origin.

GEOLOGICAL SETTING

The 4000-m pilot hole of the German Continental Deep Drilling Program (Emmermann *et al.* 1991) is located at the western margin of the Bohemian Massif, in the Zone of Erbendorf-Vohenstrauss (ZEV, Oberpfalz region, Fig. 1). This area is interpreted to be a suture zone between the Moldanubian and Saxothuringian units of the mid-European Variscan fold belt (Franke 1989). The ZEV, a section of the metamorphic basement, is mainly composed of paragneiss and metabasic rocks (amphibolite, metagabbro and meta-ultramafic rocks). The paragneissic rocks are derived from greywacke (Wimmenauer 1991), and the metabasic rocks are essentially derived from an intru-

sive complex of basaltic composition (Schalkwijk 1991). The basic rocks are suggested to be Ordovician in age on the basis of Rb–Sr, U–Pb and Sm–Nd isotopic systems (von Drach & Köhler 1990, von Quadt 1990). Paragneissic and metabasic rocks underwent intermediate-grade metamorphism (675°C and 7 kbar, Reinhardt *et al.* 1989) at about 380 Ma (Teufel 1988). An earlier high-pressure, granulite-facies metamorphism is sporadically documented in the metabasic rocks. Relict parageneses imply pressures up to 12 kbar (Röhr *et al.* 1990, Schalkwijk 1991). Locally, there is a greenschist-facies overprint. Deformation in the brittle field resulted in the formation of cataclasites, which are partially graphitized.

The lithostratigraphy of the KTB pilot hole is shown in Figure 2, and can be subdivided into four characteristic units (Röhr *et al.* 1990): (1) 0–460 m:
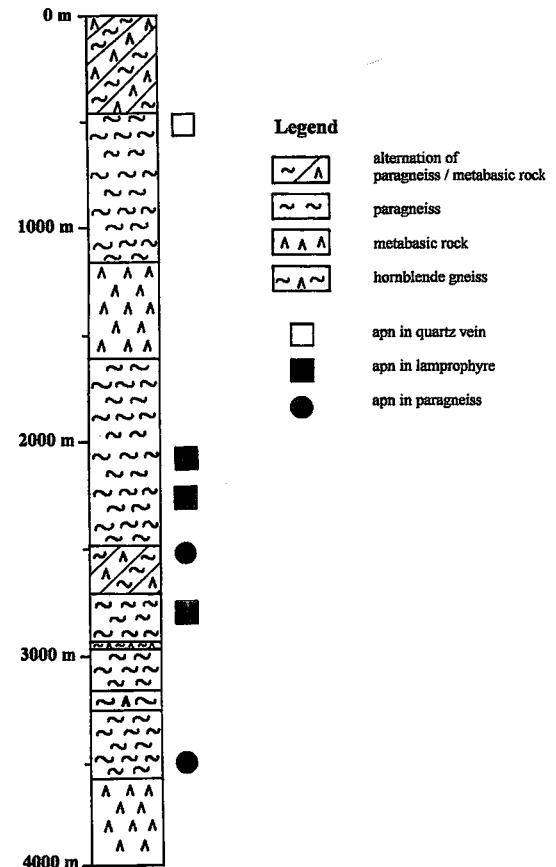

FIG. 2. Lithological profile of the KTB pilot hole, with occurrences of argentian pentlandite (apn).

garnet amphibolite with calc-silicate layers, muscovite–biotite gneiss, biotite–hornblende gneiss and minor marble; (2) 460–1160 m, 1610–2470 m and 2690–3575 m: monotonous garnet-bearing biotite gneiss with kyanite or sillimanite (or both), intersected by dikes of Late Variscan lamprophyre and aplite; (3) 1160–1610 m and 3575–4000 m: amphibolite, metagabbro and minor meta-ultramafic rocks, and (4) 2470–2690 m: biotite–hornblende gneiss with

common interlayering of amphibolite, calc-silicate rocks and sillimanite–biotite gneiss. This sequence resembles unit (1).

Argentian pentlandite in the KTB pilot hole occurs in quartz veins at a depth of 509.77 m and, furthermore, in paragneiss at a depth of 2533.21 and 3546.78 m, as well as in lamprophyre dikes that cut the paragneiss at 2046.52, 2083.62, 2244 and 2811.68 m depth (Fig. 2).
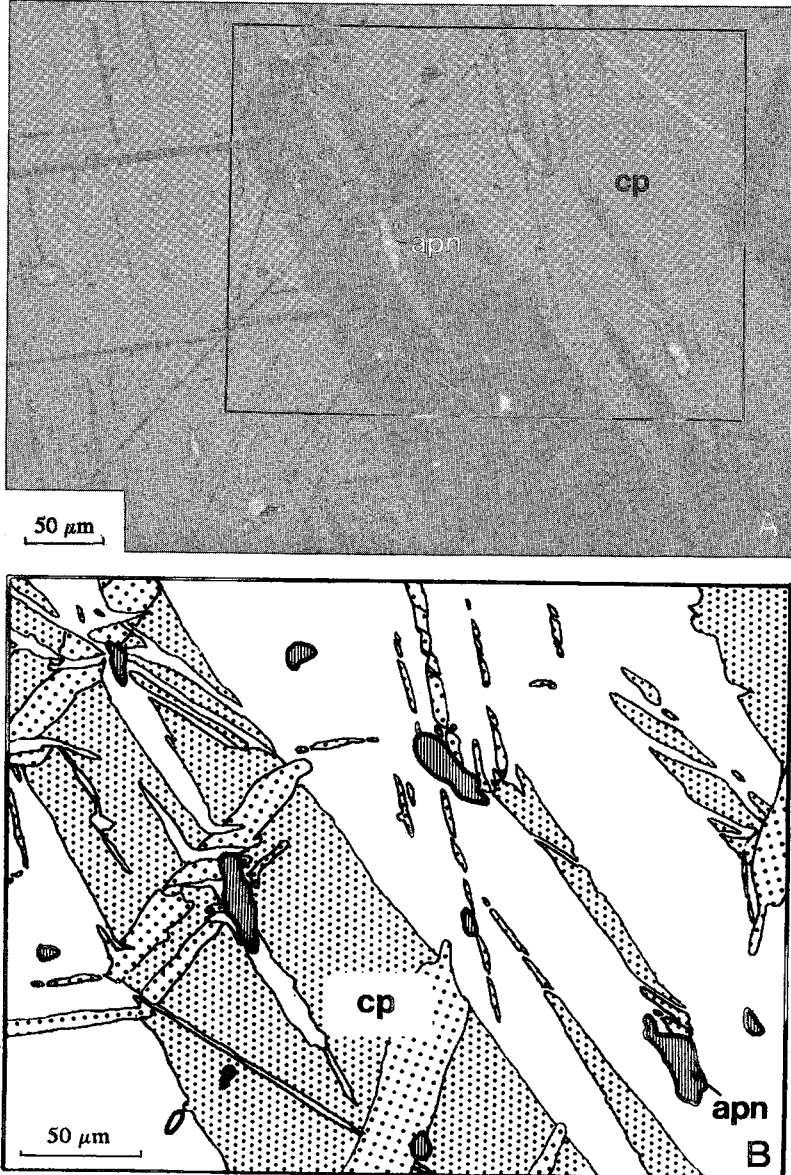

FIG. 3. A. Argentian pentlandite (apn) occurs as small patches in chalcopyrite (cp) with inversion-twin lamellae. Assemblage 1, 509.77 m, oil immersion, parallel polars. B. Detailed sketch of the marked area in A.

TEXTURAL RELATIONSHIPS

The occurrences of argentian pentlandite in different lithologies of the KTB pilot hole can be related to different stages of hydrothermal mineralization (Friedrich *et al.* 1991, Kontny 1994). One type is preserved in quartz veins (assemblage 1). A second type is characterized by dispersed sulfide mineralization including pyrite, pyrrhotite, chalcopyrite, pentlandite, sphalerite, galena and argentian pentlandite in paragneiss (assemblages 2 and 3) and in fine-grained, unmetamorphosed lamprophyre. The textural features of argentian pentlandite in the three associations as seen in reflected light microscopy are described below.

Argentian pentlandite of *assemblage 1* occurs as small (3–10 μm) reddish brown patches or strings in chalcopyrite in a deformed quartz vein at a depth of
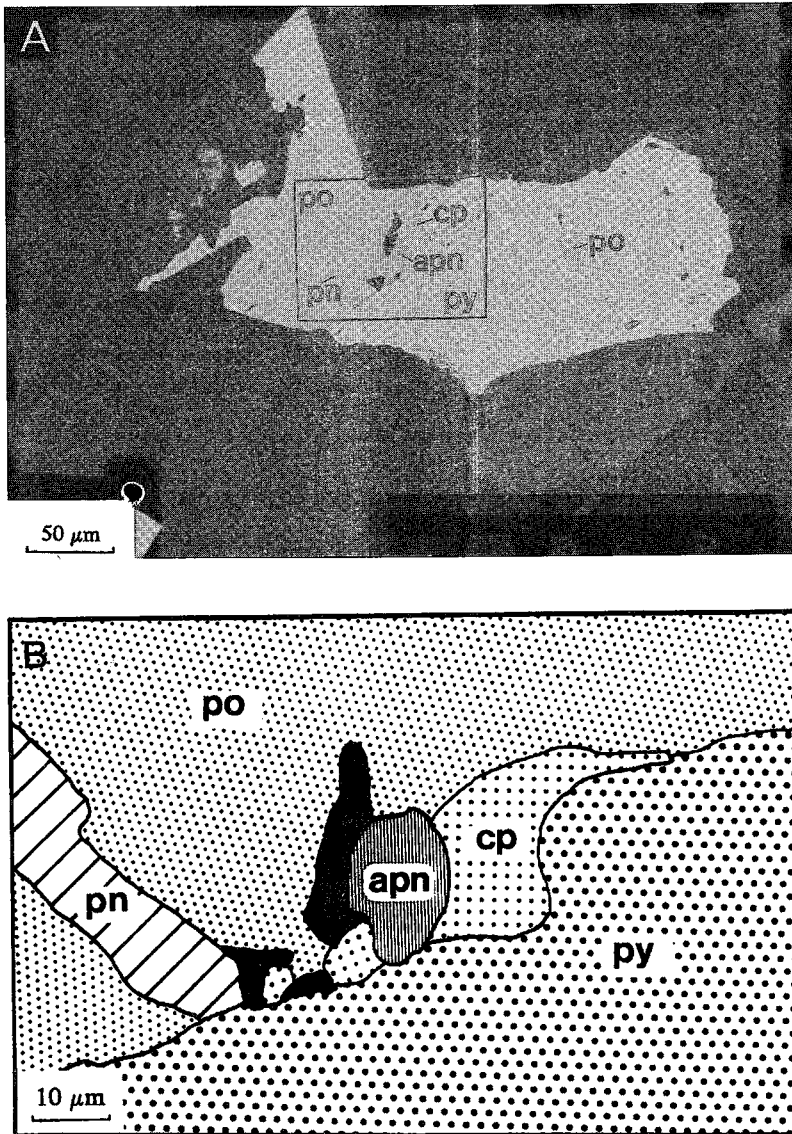

FIG. 4. A. Pyrite (py) and pyrrhotite (po) with flamelike pentlandite (pn) intergrown with argentian pentlandite (apn) and chalcopyrite (cp). Assemblage 2, 2533.21 m, oil immersion, plane-polarized light. B. Detailed sketch of the marked area in A to characterize intergrowth relations.

509.77 m. The characteristic feature of the chalco-
pyrite is the development of twin lamellae. The inclu-
sions of argentian pentlandite are mainly oriented
along the twin lamellae (Figs. 3A, B), suggesting that
they may have exsolved from chalcopyrite.

Assemblage 2 occurs in biotite–hornblende gneiss
at a depth of 2533.21 m. Here, argentian pentlandite is
intergrown with chalcopyrite and occurs in close asso-
ciation with pyrrhotite and pyrite (Figs. 4A, B). The
pyrrhotite contains flame-like lamellae of pentlandite,
which are not in direct contact with argentian pent-
landite, and the pyrite contains inclusions of, and is

intergrown with, pyrrhotite. Textural relationships
indicate that pyrite is younger than pyrrhotite.

Assemblage 3, consisting of argentian pentlandite,
cobaltian pentlandite, chalcopyrite, pyrrhotite and
sphalerite, occurs in biotite–sillimanite gneiss at a
depth of 3546.78 m (Figs. 5A, B). Argentian pent-
landite is intimately intergrown with cobaltian
pentlandite. Pyrite occurs as inclusions in pyrrhotite.
The sulfide aggregates are aligned along the cleavage
planes of biotite, which has been altered to chlorite.
The textural features imply a genetic relationship
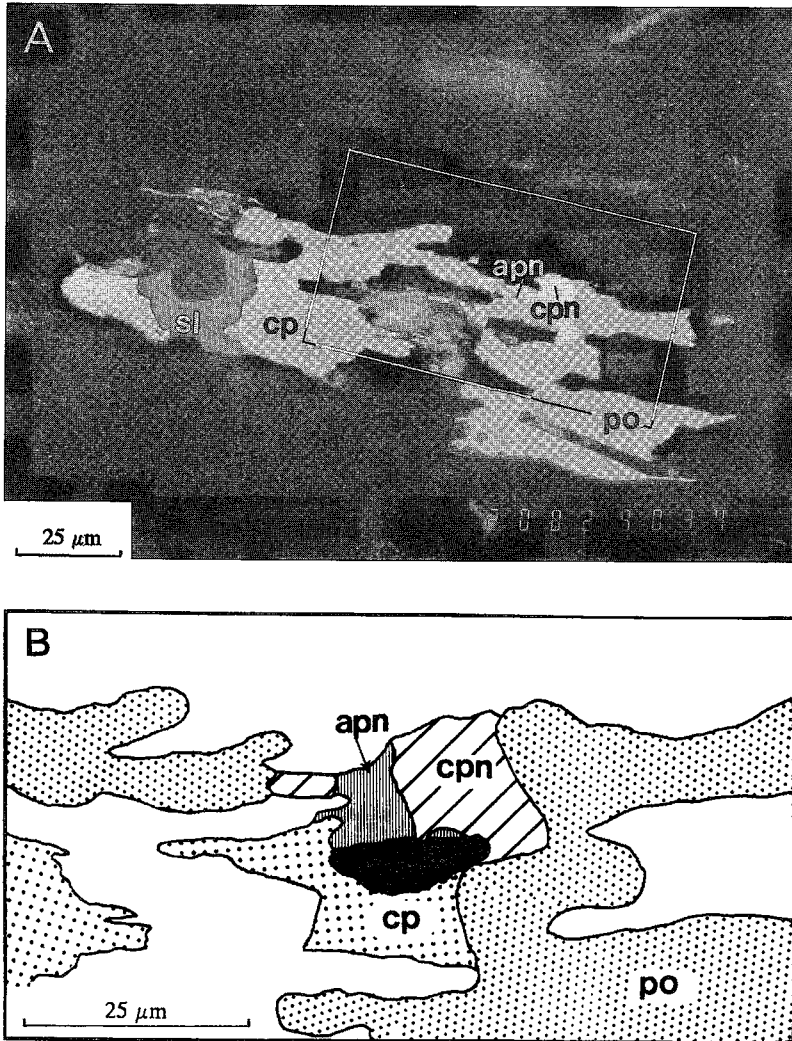between the formation of chlorite and the sulfides.

FIG. 5. A. Complex aggregate of the sulfides chalcopyrite (cp), pyrrhotite (po), cobaltian
pentlandite (cpn), argentian pentlandite (apn), and sphalerite (sl). Assemblage 3,
3546.78 m, oil immersion, plane-polarized light. B. Detailed sketch of the marked
area in A.

At a depth of 3537.83 m, argentian pentlandite is intergrown with chalcopyrite and galena (biotite–sillimanite gneiss). In this sample, pyrite is the dominant Fe-bearing sulfide. Chalcopyrite and galena also occur in fractures of pyrite, whereas pyrrhotite is absent.

In lamprophyres, argentian pentlandite is invariably associated with chalcopyrite, and in places with pyrrhotite and pentlandite or galena. These grains of argentian pentlandite are too small for investigations by electron microprobe.

MINERAL CHEMISTRY

The chemical composition of argentian pentlandite and associated chalcopyrite, pentlandite, pyrrhotite and pyrite was determined by electron-microprobe analysis (ARL–SEMQ, 20 kV, 10 nA sample current, 10 s counting time) using the following standards: pyrite (Fe, S), niccolite (Ni), chalcopyrite (Cu) and pure metals (Co, Ag). ZAF corrections were made using a modified version of program MAGIC IV (Colby 1968).

Results of the analyses are summarized in Table 1. The stoichiometry of argentian pentlandite was calculated on the basis of eight atoms of sulfur and is compared with published information in Table 2. The Ag content of the KTB material ranges from 10.28 to 12.6 wt.% and amounts to less than 1 atom of Ag per formula unit (0.82–0.91) This Ag deficiency is not a common feature in natural argentian pentlandite, but was described previously by Vuorelainen *et al.* (1972) and by Friedrich *et al.* (1989). The Fe/Ni atomic ratio varies from 1.75 to 1.9 and lies within the range determined for other examples of argentian pentlandite, *e.g.*, 1.34 to 2.57 (Mandziuk & Scott 1977). However, the Fe/Ni ratio is typically higher than for stoichiometric argentian pentlandite (1.67). The metal/sulfur ratio ranges between 1.102 and 1.148, in agreement with published data (1.096–1.173).

TABLE 1. RESULTS OF ELECTRON–MICROPROBE ANALYSES OF SELECTED MINERALS
FROM ARGENTIAN–PENTLANDITE–BEARING ASSEMBLAGES,
KTB PILOT HOLE, OBERPFALZ, GERMANY

		n	Fe	Ni	Co	Cu wt.%	Ag	S	total	Fe/Ni	M/S at.%
Assemblage 1											
apn[*]	x	8	35.86	19.86	--	1.39	11.94	31.20	100.20	1.90	1.15
	s.d.		1.22	1.02	--	0.16	0.09	0.33			
cp	x	6	30.99	0.08	0.03	34.24	--	35.00	100.34		1.04
	s.d.		0.29	0.08	0.01	0.24	--	0.20			
Assemblage 2											
apn	x	5	34.48	20.76	0.03	0.43	12.60	31.71	100.01	1.75	1.11
	s.d.		0.09	0.04	0.01	0.03	0.05	0.05			
pn	x	2	29.88	35.43	0.12	--	--	33.53	98.96	0.89	1.09
	s.d.		0.07	0.14	0.03	--	--	0.13			
po	x	4	59.15	1.16	0.05	--	--	39.55	99.95		0.88
	s.d.		0.19	0.05	0.01	--	--	0.01			
py	x	4	47.09	0.15	0.09	--	--	51.93	99.42		0.52
	s.d.		0.30	0.07	0.02	--	--	0.22			
cp	x	2	29.93	0.04	0.04	33.86	--	35.51	99.58		1.00
	s.d.		0.97	0.08	0.01	0.15	--	0.94			
Assemblage 3											
apn	x	3	33.11	19.32	3.12	0.65	10.28	31.55	98.03	1.86	1.10
	s.d.		0.63	0.23	0.82	0.02	0.50	0.16			
cpn	x	3	20.79	23.42	20.65	0.04	--	33.53	98.39	0.93	1.07
	s.d.		0.18	0.61	0.10	0.01	--	0.08			
po	x	3	59.25	0.66	0.23	0.05	--	38.99	99.13		0.88
	s.d.		0.03	0.03	0.02	0.04	--	0.10			
cp	x	3	30.89	0.07	0.07	33.14	0.03	35.32	99.49		0.98
	s.d.		0.16	0.04	0.02	0.56	0.03	0.20			

M/S: metal/sulfur ratio; symbols: apn argentian pentlandite, cp chalcopyrite, cpn cobaltian pentlandite, pn pentlandite, po pyrrhotite, py pyrite, n number of analyses, x average, s.d. standard deviation, — below limit of detection, * specimen re-analyzed by B. Griffin, Nedlands, Perth, Western Australia.

$Fe_{5.30}Ni_{2.79}Cu_{0.18}Ag_{0.91}S_8$	KTB pilot hole/Oberpfalz (assemblage 1)
$Fe_{4.97}Ni_{2.86}Ag_{0.94}S_8$	KTB pilot hole/Oberpfalz (assemblage 2)
$Fe_{4.94}Ni_{2.66}Co_{0.32}Ag_{0.82}S_8$	KTB pilot hole/Oberpfalz (assemblage 3)
$Fe_{4.92}Ni_{2.64}(Co,Cu)_{0.15}Ag_{0.83}S_8$	Schönmatt, Germany (Friedrich et al. 1989)
$Fe_{4.78}Ni_{3.07}Ag_{1.00}S_8$	Bottino, Italy (Benvenuti 1991)
$Fe_{4.72}Ni_{2.83}Ag_{1.03}S_8$	Kola, USSR (Kozlovskiy et al. 1988)
$(Fe,Co,Cu)_{4.92}Ni_{3.03}Ag_{1.03}S_8$	Koronuda, Greece (Mposkos 1983)
$(Fe,Co,Cu)_{5.28}Ni_{2.63}Ag_{1.00}S_8$	Koronuda, Greece (Mposkos 1983)
$Fe_{5.18}Ni_{2.79}Ag_{1.00}S_8$	Windarra (Groves & Hall 1978)
$Fe_{5.24}Ni_{2.81}Ag_{1.01}S_8$	Windarra (Groves & Hall 1978)
$Fe_{5.62}Ni_{1.87}Ag_{1.53}S_8$	Kamaishi Mine, Japan (Mariko et al. 1973)
$Fe_{4.83}Ni_{3.17}Ag_{0.99}S_8$	Bird River, Man. (Hall & Stewart 1973)
$Fe_{4.93}Ni_{3.28}Ag_{1.03}S_8$	Bird River, Man. (Scott & Gasparrini 1973)
$Fe_{5.62}Ni_{2.62}Ag_{1.03}S_8$	Sudbury (Karpenkov et al. 1973)
$Fe_{5.41}Ni_{2.82}Ag_{0.81}S_8$	Finnish deposits (Vuorelainen et al. 1972)
$Fe_{5.55}Ni_{2.57}Ag_{1.10}S_8$	Talnakh, GUS (Shishkin et al. 1971)
$Fe_{4.51}Ni_{3.37}Ag_{1.09}S_8$	Khovuaksa, GUS (Shishkin et al. 1971)

Assemblage 1

Argentian pentlandite occurring as inclusions in chalcopyrite contains 11.9 wt.% Ag. The Cu content, 1.39 wt.%, does not seem to be incorporated into the structure of argentian pentlandite. Rather, it probably is an artifact of the microprobe sampling region below the surface of the grain. A very strong negative correlation was detected between the Cu content and the size of the argentian pentlandite grains.

Assemblage 2

Argentian pentlandite intergrown with chalcopyrite, pyrrhotite and pyrite, has a higher Fe/Ni (1.75) and a lower metal/sulfur atomic ratio (1.107) than stoichiometric argentian pentlandite (1.67 and 1.125), and contains 12.6 wt.% Ag. The Fe/Ni ratio of pentlandite (0.89) corresponds to pentlandite in association with pyrrhotite, or pyrrhotite and pyrite, as documented by Harris & Nickel (1972) and Misra & Fleet (1973). Pyrrhotite has a metal/sulfur ratio of 0.876 and a high Ni content (1.2 wt.%). Petrographic examinations of a polished sample coated with a magnetic colloid have shown that almost all pyrrhotite is ferrimagnetic. The magnetic character and the Fe_{eq} content of 46.67 at.% (Fe_{eq}= Fe + Ni + Co) suggest that pyrrhotite is of the monoclinic $4C$ modification (Keyssner 1992).

Assemblage 3

Argentian pentlandite, intimately intergrown with cobaltian pentlandite, has an Ag content of 10.3 wt.%, the lowest value of all three assemblages. In this paragenesis, argentian pentlandite is characterized by an extraordinary high Co content, 3.12 wt.%. This might also be an analytical artifact as appears to be the case for Cu, but elevated Co contents in the associated chalcopyrite and pyrrhotite (0.07 and 0.23 wt.%, Table 1) and the occurrence of cobaltian pentlandite imply a strong relation between chemical composition and paragenesis. The pyrrhotite contains 46.94 at.% Fe_{eq} and has antiferromagnetic properties (Keyssner 1992). The present borehole temperature at a depth of 3500 m is about 110°C (Zoth 1990). This temperature is in good agreement with that necessary for the formation of hexagonal pyrrhotite with an NC supercell (Nakazawa & Morimoto 1971, Kissin & Scott 1982).

DISCUSSION

Known phase-equilibria in the systems Ag–Fe–Ni–S and Fe–Ni(–Co)–S, as well as the composition of associated sphalerite and chlorite, allow constraints to be placed on the environment of deposition of hydrothermal sulfide (–chlorite) assemblages containing argentian pentlandite. In the system Ag–Fe–Ni–S, the assemblage argentian pentlandite + pentlandite + monosulfide solid-solution (= pyrrhotite) + Ag appears to be stable at defined sulfur activities (stability field of pyrrhotite) and temperatures below 455°C (Mandziuk & Scott 1977; see Fig. 6).

Argentian pentlandite is commonly interpreted to be an exsolution product of chalcopyrite (Shishkin et al. 1971, Vuorelainen et al. 1972, Scott & Gasparrini 1973, Mandziuk & Scott 1977, Groves & Hall 1978). Argentian pentlandite in assemblage 1 at 509.77 m occurs as inclusions in chalcopyrite characterized by inversion twins, also pointing to an origin by exsolution. Twin lamellae in chalcopyrite with a metal/sulfur ratio greater than 1 form at the cubic-tetragonal transition, which occurs below approximately 550°C (Yund & Kullerud 1966). Although the inversion temperature of chalcopyrite is known to be a function of composition and pressure (Yund & Kullerud 1966), the twin lamellae along (102) have also been produced by compression at a confining pressure of 3 kbar and a temperature of 400°C (Hennig-Michaeli & Couderc 1989) without involvement of any phase transformation. Therefore, the observed twin-lamellae in chalcopyrite could have formed during the retrograde deformation of the KTB rocks under conditions of moderate pressure and temperature. This is also consistent with an exsolution origin of argentian pentlandite below 455°C.

Unfortunately, the fluid inclusions of the argentian-pentlandite-bearing quartz vein were found to be too small for study. However, in the rocks of the KTB, an alkaline palaeofluid system with low salinity is described by Reutel (1992); it shows temperatures in excess of 400°C at pressures of about 2 kbar. This fluid system could be responsible for the formation of argentian pentlandite of assemblage 1.
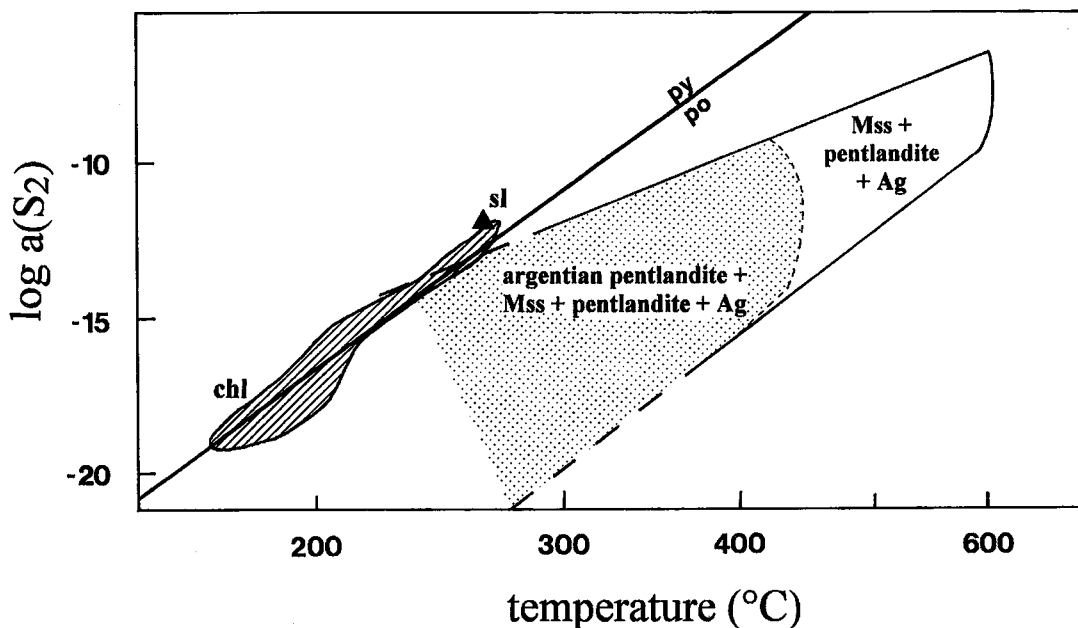
FIG. 6. Temperature – sulfur fugacity diagram with sulfidation curve for the pyrite–pyrrhotite buffer from Scott & Barnes (1971) and extrapolated field of stability of argentian pentlandite to lower temperatures in the system Ag–Fe–Ni–S, modified from Mandziuk & Scott (1977). Striped field: chlorite (chl) from assemblages 2 and 3, triangle: sphalerite (sl) from assemblage 3.

The sulfides associated with argentian pentlandite of assemblage 2 and 3 are oriented parallel to the metamorphic foliation, and are mostly associated with phyllosilicates and titanite. Chlorite, which is inter-grown with the assemblage-3 argentian-pentlandite-bearing sulfides, is a product of alteration of biotite and can be classified as magnesian chamosite (Fe^{2+} dominates Mg^{2+}; Bailey 1980). In association with assemblage 2, two varieties of chlorite can be distin-guished: Mg-rich chlorite that formed from alteration of hornblende and Fe-rich chlorite showing textural features consistent with hydrothermal formation. Both types of chlorite can be classified as magnesian chamosite. Applying the "six-component solid-solution model" of Walshe (1986), temperatures of chlorite formation are calculated to be 160°–260°C in assemblage 3 and 185°–250°C in assemblage 2. These calculations are based on a pressure of 1 kbar. This pressure is in accordance with results of Borchardt & Emmermann (1989), who found that the formation of alteration minerals in the KTB pilot hole took place at pressures of less than 1.5 kbar.

Sulfur activities have been calculated assuming quartz – chlorite – pyrite equilibrium following Walshe (1986). The log $a(S_2)$ values range from 10^{-18} to 10^{-14} in assemblage 2 and from 10^{-20} to 10^{-13} in

assemblage 3. In the sulfur fugacity – temperature diagram (Fig. 6), all chlorite data plot very close to the pyrite–pyrrhotite buffer. This could explain the common occurrence of pyrrhotite and pyrite in the samples, as well as the sudden changes in proportion of pyrite and pyrrhotite over a few meters.

Sphalerite associated with argentian pentlandite of assemblage 3, which is intergrown with chlorite, contains 12 mole % FeS. The log activity of sulfur calculated from FeS content in sphalerite (Scott 1973) and a temperature of about 260°C determined from the associated chlorite is about 10^{-12}. This value of $a(S_2)$ is higher than those obtained from the chlorite data. A possible reason for this deviation is loss of FeS in sphalerite that is not enclosed in pyrite. Therefore, the FeS content determined in sphalerite may be too low, and the calculated activity of sulfur correspond-ingly too high. However, the values of sulfur activity indicate that chlorite and sphalerite have formed within the stability field of pyrite (Fig. 6).

According to the solid-solution fields determined by Kaneda et al. (1986), the chemical composition of cobaltian pentlandite intergrown with assemblage-3 argentian pentlandite points to a temperature of forma-tion of less than 200°C. Thus it is assumed that at least cobaltian pentlandite and sphalerite have been

deposited under hydrothermal conditions at a temperature of 200°–260°C and a low fugacity of sulfur, less than 10^{-13}. These data are close to the extrapolated upper stability-limit of argentian pentlandite (Fig. 6), which cross-cuts the pyrite–pyrrhotite equilibrium at about 260°C [log $a(S_2)$ 10^{-14}] and seems to reflect the environment of deposition in which argentian pentlandite of the KTB pilot hole has equilibrated. Thus the temperature of final equilibration of argentian pentlandite must have been about or slightly below 260°C. This corresponds to the experimental data from Mandziuk & Scott (1977), which imply that reaction rates in the solid state of the system Ag–Fe–Ni–S decrease significantly in the range between 200° and 300°C.

Argentian pentlandite of assemblage 3 in association with chalcopyrite, pyrrhotite, pentlandite and sphalerite has also been described from paragneissic rocks in the Black Forest, Germany (Friedrich et al. 1989) and the Kola deep drilling, Russia (Genkin et al. 1984, Kozlovskiy et al. 1988). In the latter case, argentian pentlandite occurs in carbonate–quartz veinlets in metabasic rocks containing chlorite, epidote, pyrite and pyrrhotite; the assemblage is interpreted to result from hydrothermal mineralization in zones of retrograde metamorphism. Kozlovskiy et al. (1988) assumed that the presence of argentian pentlandite points to an epigenetic origin of hydrothermal sulfide mineralization. The temperature of formation estimated from the distribution coefficient of cobalt in the pyrrhotite–pyrite intergrowth ranges from 180 to 323°C (Bezmen et al. 1975). This is in good agreement with the postulated temperature of formation of the hydrothermal sulfide mineralization in the KTB pilot hole, as estimated from sulfide and chlorite thermometry (200–260°C). Values of $\delta^{34}S$ determined for the KTB rocks containing sulfide assemblages 2 and 3 are depleted (–11.48 and –10.95‰), and are different from data on argentian pentlandite mineralization in the Kola deep drill-hole, which are in the range of –1 to +2‰. This may reflect the different host-rock lithology of argentian-pentlandite-bearing mineralization in the Kola deep drill-hole (metabasite) and in the KTB pilot hole (mainly paragneiss). The negative sulfur isotope ratios of the argentian-pentlandite-bearing rocks in the KTB pilot hole are consistent with an origin of sulfur from a sedimentary source. Thus remobilization is assumed to be responsible for the formation of sulfides, with sulfur derived from a sedimentary host-rock.

SUMMARY
AND CONCLUSIONS

Petrographic and electron-microprobe studies of different argentian-pentlandite-bearing assemblages occurring in the KTB pilot hole show a variation in composition of the argentian pentlandite with para-

genesis. The Ag content of argentian pentlandite ranges from 10.3 to 12.6 wt.%, the Fe content from 33.1 to 35.9 wt.%, and the Ni content from 19.3 to 20.8 wt.%.

Two mechanisms are proposed for the formation of argentian pentlandite: (1) textural features of argentian pentlandite from assemblage 1, occurring as inclusions in inversion-twinned chalcopyrite in a quartz vein, are consistent with an origin by exsolution. This type of mineralization has probably been formed by remobilization from the host rock during the retrograde deformation of the KTB rocks. Negative $\delta^{34}S$ ratios of chalcopyrite (–6.74‰) point to a mobilization of sulfur from metasedimentary rocks (Berner et al. 1991). The normal retrograde P–T path inferred by Reutel (1992), giving conditions of 2–3 kbar and about 400°C, is considered realistic. (2) Subsolidus reactions between Ag-bearing chalcopyrite and Fe–Ni sulfides are proposed for the formation of argentian pentlandite of assemblage 2, which is intimately intergrown with chalcopyrite, pyrite and pyrrhotite. The same process probably is responsible for the presence of argentian pentlandite of assemblage 3, in which it is in close association with cobaltian pentlandite, chalcopyrite, pyrrhotite and sphalerite. Textural relationships, as well as estimates of temperature and sulfur activity based on the chemical composition of associated chlorite, point to formation of argentian-pentlandite-bearing sulfide–chlorite assemblages under hydrothermal conditions. The conditions of final equilibration are assumed to be about 260°C or slightly lower, at pressures of about 1–2 kbar and at log $a(S_2)$ less than 10^{-13}. Negative $\delta^{34}S$ values (–11.48 and –10.95‰) are consistent with those from hydrothermal environments, and further suggest that sulfur and metals were remobilized from sedimentary host-rocks.

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