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TISCHENDORFITE, $Pd_8Hg_3Se_9$, A NEW MINERAL SPECIES FROM TILKERODE, HARZ MOUNTAINS, GERMANY

Christopher J. STANLEY[§] and Alan J. CRIDDLE

Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, United Kingdom

Hans-Jürgen FÖRSTER[¶]

GeoForschungsZentrum, Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

Andrew C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

ABSTRACT

Tischendorfite, ideally $Pd_8Hg_3Se_9$, is a new mineral species from the Eskaborner Stollen (Eskeborn Adit) at Tilkerode, Harz Mountains, Germany. It occurs as aggregates in a carbonate matrix, together with the associated metallic minerals clausthalite, tiemannite, chrisstanleyite, stibiopalladinite and gold. It is opaque with a metallic luster, has a black streak, is brittle, and the fracture is uneven. In plane-polarized reflected light, tischendorfite has a cream or slightly beige color in association with chrisstanleyite (light buff to slightly gray-green buff), clausthalite (off-white) and tiemannite (gray). It is not pleochroic, and displays a weak bireflectance. It does not possess internal reflections. The anisotropy is weak to moderate, with rotation tints in weak shades of steel blue and greenish brown. Reflectance data and color values are tabulated. Average results of four electron-microprobe analyses are: Pd 39.4, Pt 0.1, Ag 1.0, Cu 0.2, Hg 24.9, Pb 1.4, Se 32.0, total 99.0 wt.%. The empirical formula, $(Pd_{8.05}Pt_{0.01})_{\Sigma 8.06}(Hg_{2.70}Ag_{0.20}Pb_{0.15}Cu_{0.07})_{\Sigma 3.12}Se_{8.82}$, is based on 20 atoms per formula unit. The calculated density is 9.13 g/cm^3 (on the basis of the empirical formula and unit-cell parameters refined from powder data). Tischendorfite is orthorhombic, with *a* 7.219(3), *b* 16.782(7), *c* 6.467(5) Å, *V* 783.6(8) Å^3, *a*:*b*:*c* 0.4302:1:0.3854, and *Z* = 2. The probable space-groups are *Pmmn* (59), $P2_1mn$ (31) or $Pm2_1n$ (31) (diffraction aspect *P**n*). The strongest seven X-ray powder-diffraction lines [*d* in Å(*I*)(*hkl*)] are: 4.819(40)(101), 4.373(40)(130), 2.797(60)(032,122), 2.743(100)(151,231,240), 2.325(40)(052), 2.116(40)(062) and 2.091(100)(261). The mineral's name honors Gerhard Tischendorf, geochemist and mineralogist, in recognition of his contributions to understanding the genesis of selenide mineral deposits.

Keywords: tischendorfite, new mineral species, platinum-group mineral, Pd–Hg selenide, electron-microprobe data, reflectance data, X-ray-diffraction data, Tilkerode, Harz Mountains, Germany.

SOMMAIRE

La tischendorfite, idéalement $Pd_8Hg_3Se_9$, est une nouvelle espèce minérale provenant de Eskaborner Stollen (accès d'Eskeborn) à Tilkerode, montagnes Harz, en Allemagne. Elle se présente en aggrégats dans une matrice de carbonate en association avec les minéraux métalliques clausthalite, tiémannite, chrisstanleyite, stibiopalladinite, et or. Elle est opaque avec un reflet métallique, possède une rayure noire, est fragile, et la fracture est inégale. Observée au microscope polarisant en lumière réfléchie, la tischendorfite est crème ou une couleur légèrement beige en association avec la chrisstanleyite (une couleur de chamois légèrement à gris-vert chamois), la clausthalite (grisâtre blanc) et la tiémannite (gris). Elle ne presente pas de pléochroïsme, mais elle est faiblement biréflectante. Elle ne possède pas de réflexions internes. L'anisotropisme est faible à modéré, avec teintes de rotation aux nuances faibles de bleu acier, et de brun verdâtre. On présente les spectres de réflectivité et les valeurs de couleur. Les analyses obtenues à la microsonde électronique ont donné, en moyenne, Pd 39.4, Pt 0.1, Ag 1.0, Cu 0.2, Hg 24.9, Pb 1.4, Se 32.0, total 99.0% en poids. La formule empirique est $(Pd_{8.05}Pt_{0.01})_{\Sigma 8.06}(Hg_{2.70}Ag_{0.20}Pb_{0.15}Cu_{0.07})_{\Sigma 3.12}Se_{8.82}$ sur une base de 20 atomes par unité de formule. La densité calculée est égale à 9.13 g/cm^3 (sur la base de la formule empirique et des paramètres de la maille élémentaire affinés à partir des données de poudre). La tischendorfite est un minéral orthorhombique, avec *a* 7.219(3), *b* 16.782(7), *c* 6.467(5) Å, *V* 783.6(8) Å^3, *a*:*b*:*c* 0.4302:1:0.3854, *Z* = 2. Les choix de groupe spatial sont *Pmmn*

[§] *E-mail address*: c.stanley@nhm.ac.uk

[¶] *Present address*: Institute of Earth Sciences, University of Potsdam, D-14415 Potsdam, Germany.

(59), $P2_1mn$ (31) ou $Pm2_1n$ (31) (aspect de diffraction $P{*}{*}n$). Les sept raies les plus intenses du spectre de diffraction X [*d* en Å(*I*)(*hkl*)] sont: 4.819(40)(101), 4.373(40)(130), 2.797(60)(032,122), 2.743(100)(151,231,240), 2.325(40)(052), 2.116(40)(062) et 2.091(100)(261). Le nom honore Gerhard Tischendorf, geochimiste et minéralogiste, pour ses contributions à la genèse des gisements de séléniures.

Mots-clés: tischendorfite, nouvelle espèce minérale, minéral du groupe du platine, séléniure de Pd–Hg, données à la microsonde électronique, données de réflectivité, données de diffraction X, Tilkerode, montagnes Harz, Allemagne.

INTRODUCTION

In an investigation of the selenide deposit at Tilkerode in the eastern Harz Mountains, Germany, in 1958, Gerhard Tischendorf noted the presence of two unidentified minerals included in tiemannite in his sample 4154 (Tischendorf 1959, Fig. 25). He reported their optical properties in his thesis. Much later, in 1993 and 1994, both unidentified minerals were analyzed by electron microprobe at the GeoForschungsZentrum, Potsdam, Germany, by one of us (H.-J.F.) and G. Tischendorf. Compositional data obtained then were later confirmed by M. Tarkian of the University of Hamburg, Germany, and by Z. Johan of the BRGM at Orléans, France. Thus, in late 1994, it became apparent that the unidentified minerals discovered in 1958 represented two new species with the formulae $Ag_2Pd_3Se_4$ and $Pd_8Hg_3Se_9$, respectively. However, Paar *et al.* (1998) were the first to formally characterize the mineral $Ag_2Pd_3Se_4$ from a selenide occurrence at Hope's Nose, Torquay, Devon, England (Stanley *et al.* 1990); they named it *chrisstanleyite*. The second new species from Tilkerode, $Pd_8Hg_3Se_9$, which is typically intergrown with chrisstanleyite and other selenide minerals, is the subject of this paper.

The mineral is named *tischendorfite* in honor of Dr. Gerhard Tischendorf (born in 1927 in Vogtland, Germany), formerly at GeoForschungsZentrum, Potsdam, Germany, for his many contributions to mineralogy and geochemistry and, in particular, for his efforts to understand the mechanisms of formation of selenide deposits of the Harz Mountains. It is particularly fitting that the mineral he discovered and described as an unknown species as long ago as 1958 should finally bear his name. The mineral and mineral name were approved by the Commission on New Minerals and Mineral Names (IMA 2001–61). Type material is deposited at the Natural History Museum, London, U.K. as BM 2001,8 and at the GeoForschungsZentrum, Potsdam, Germany. A third polished section is archived at the Mineralogical Institute of the Technische Universität Bergakademie, Freiberg, Germany, under the inventory number 80160. A single-crystal mount and two powder mounts are housed within the Systematic Reference Series of the National Mineral Collection of Canada, Geological Survey of Canada, Ottawa.

OCCURRENCE AND ASSOCIATED MINERALS

Sample 4154 was collected from the Eskaborner Stollen (Eskeborn adit), near Tilkerode, at the 60-m level, 5 m north of the blind shaft IV (Tischendorf 1959, Fig. 2). In addition to chrisstanleyite and tischendorfite, the sample contains tiemannite, clausthalite, stibiopalladinite and native gold in a carbonate matrix (ankerite and calcite). The selenides in sample 4154 are dominated by tiemannite and display a botryoidal development suggestive of possible formation from a gel.

The copper–iron selenide mineral eskebornite, first discovered by Ramdohr (1949), is named for the Eskaborner Berg (in the literature also known as the Eskeborn Hill), on the northwestern flank of which the Eskaborner Stollen (Eskeborn adit) was driven. Tischendorf (1960) conducted the first chemical and X-ray studies on eskebornite.

The occurrence of selenides at Tilkerode is probably the best known and most intensively studied in the Harz Mountains of Germany. It, and the selenide-bearing deposits at Lerbach, Clausthal, Zorge, St. Andreasberg and Trogthal, are recognized as typical of selenide vein deposits of telethermal origin (*e.g.,* Simon *et al.* 1997). At most of these localities, the polymetallic selenide mineralization occurs as small deposits not associated with larger base-metal deposits (Tilkerode, Zorge, Lerbach, Trogthal). However, at Clausthal and St. Andreasberg, the selenide minerals are associated with larger deposits mined primarily for silver, lead, zinc and copper.

In the veins at Tilkerode, which were mined for iron ore from the 18th Century until 1832, selenides were probably discovered prior to 1786, but were not correctly identified as such (Tischendorf 1959, p. 28). Selenide-bearing samples collected during this first episode of mining were studied by optical microscopy by Frebold (1927a, b), Cissarz (1930) and Hesemann (1930). A second period of underground exploration for iron and gold was undertaken between 1951 and 1956, as a result of which the suite of samples that G. Tischendorf later studied for his thesis was collected.

Tischendorf (1959) described the following selenides from Tilkerode: clausthalite PbSe, naumannite Ag_2Se, tiemannite HgSe, eskebornite $CuFeSe_2$, trogtalite $CoSe_2$, hastite $CoSe_2$, freboldite CoSe, bornhardtite

Co_3Se_4, berzelianite Cu_2Se, umangite Cu_3Se_2, klockmannite CuSe, and “allopalladium“, as well as native gold. “Allopalladium“ was later identified as stibiopalladinite Pd_5Sb_2 (Genkin *et al.* 1977). Wallis (1994) succeeded in identifying a number of additional mineral species in the Tilkerode selenide assemblage: kruťaite $CuSe_2$, athabascaite (?) Cu_5Se_4, temagamite Pd_3HgTe_3, eucairite CuAgSe, trüstedtite Ni_3Se_4, penroseite $(Ni,Co,Cu)Se_2$, and geffroyite (?) $(Ag,Cu,Fe)_9(S,Se)_8$.

Physical Properties

Tischendorfite occurs as anhedral to subhedral grains, up to 100 μm in maximum dimension within clusters or aggregates of intermixed selenides a few hundred μm in size. In hand specimen, its color is not known, but it is an opaque mineral with a metallic luster and black streak (as deduced from the powder extracted for X-ray powder-diffraction studies). It is brittle, with an uneven fracture, and has a polishing hardness similar to that of chrisstanleyite, greater than that of tiemannite and clausthalite, but lower than that of stibiopalladinite. It was not possible to measure the VHN owing mainly to its complex intergrowth with other minerals, but also because the grain with the largest area was found to be very thin: this was also the reason why the density could not be measured. The calculated density is 9.13 g/cm^3 (on the basis of the empirical formula and unit-cell parameters refined from powder data).

Optical Properties

The sample containing tischendorfite was prepared for optical investigation and measurement using standard diamond polishing techniques (Stanley & Laflamme 1998).

In plane-polarized reflected light (from an unfiltered quartz-halogen lamp at about 3100 K), tischendorfite has a cream or slightly beige color in association with chrisstanleyite (light buff to slightly gray-green buff), clausthalite (off-white) and tiemannite (gray). Tischendorfite is not pleochroic but is weakly bireflectant. As is to be expected from its quite high reflectance, it has no internal reflections. Digital photomicrographs were taken under the conditions just described using a JVC KY–F7OU 3CCD camera mounted on a Zeiss Axioplan microscope equipped with Synoptics image-capturing software. Figure 1 shows that tischendorfite (T) is somewhat similar in color to chrisstanleyite (C) in some of its orientations, though chrisstanleyite has a lower reflectance and displays greater variation in hue and saturation. A comparison of the optical properties of chrisstanleyite as characterized by Paar *et al.* (1998) with our data for tischendorfite reveals substantial differences in the dispersion of the reflectance and bireflectance of the two minerals. Clausthalite (Cl) is typically off-white and has a higher reflectance; in this assemblage, it contains minute inclusions of an unidentified mineral. Tiemannite (Tie) is gray and the most abundant selenide in this assemblage.

Also present in Figure 1, but in grains too small to be highlighted, is stibiopalladinite. This mineral is quite similar to tischendorfite when viewed in isolation in plane-polarized light, but its lath-like habit, higher reflectance and stronger anisotropy distinguish it from the latter. Tischendorfite is weakly anisotropic, with weak to moderate rotation-tints: from extinction, the sequence observed is from weak shades of steel blue to greenish brown, shades that are only slightly enhanced in oil. None of the grains in the section seems twinned.

Reflectance measurements were made with a Zeiss MPM800 microspectrophotometer relative to a WTiC reflectance standard (Zeiss 314). The objectives used in air and in oil had magnifying powers of ×50, and constant effective numerical apertures were obtained in the two media by adjustment of the aperture diaphragm of

TABLE 1. REFLECTANCE DATA AND COLOR VALUES FOR TISCHENDORFITE

λ nm	R_1	R_2	$^{im}R_1$	$^{im}R_2$
400	38.2	43.3	27.85	33.2
420	42.3	47.6	30.5	35.6
440	44.6	49.6	32.35	37.3
460	46.2	50.85	33.6	38.1
480	47.3	51.7	34.45	38.7
500	48.2	52.4	34.95	39.0
520	48.75	52.75	35.35	39.3
540	49.3	53.1	35.75	39.5
560	49.7	53.1	36.2	39.6
580	49.95	53.2	36.4	39.7
600	49.9	53.4	36.45	40.0
620	49.8	53.3	36.2	39.8
640	49.3	52.9	35.8	39.7
660	48.4	52.45	35.3	39.5
680	47.0	50.7	34.2	38.5
700	43.5	47.0	32.3	37.0
470	46.8	51.3	33.9	38.3
546	49.4	53.1	35.9	39.5
589	49.9	53.25	36.5	39.9
650	48.95	52.55	35.7	39.6
Color Values, A illuminant				
x	0.452	0.450	0.452	0.451
y	0.412	0.411	0.412	0.410
Y%	49.5	53.05	36.0	39.6
λ_d	581	580	581	582
P_e%	6.3	4.0	6.4	3.8
Color Values, C illuminant				
x	0.317	0.314	0.317	0.314
y	0.327	0.324	0.327	0.323
Y%	49.3	52.95	35.8	39.5
λ_d	572	571	572	572
P_e%	4.8	3.2	4.9	2.9

the illuminator. The bandwidth of the grating monochromator was set to 5 nm, and intensity data were collected at an interval of 10 nm from 400 to 700 nm. The weak anisotropy made it difficult to orient the measured grains at their extinction positions, but these were checked photometrically for maxima and minima. Intensity data were collected from five spectral scans at each of the four orthogonal "extinction" positions, and R_1 (lower) and R_2 (higher) data were calculated relative to the intensity values of the WTiC standard. Table 1 includes representative reflectance and color values for tischendorfite. The reflectance curves in air and in oil are given in Figure 2. These data are significantly different from those for chrisstanleyite and the other known palladium selenides, oosterboschite $(Pd,Cu)_7Se_5$ of Johan *et al.* (1970), palladseite $Pd_{17}Se_{15}$ of Davis *et al.* (1977), and verbeekite $PdSe_2$ of Roberts *et al.* (2002).

CHEMICAL COMPOSITION

Chemical analyses were carried out at the Natural History Museum by means of a Cameca SX–50 electron microprobe operated in wavelength-dispersion mode with an accelerating voltage of 15 kV, and a beam current of 20 nA. The counting times on the peak and background varied, according to the count rate of the particular element, from 10 to 100 seconds in order to give detection limits around 0.01 to 0.02 wt.%. ZAF correction was applied through a PAP correction procedure (Pouchou & Pichoir 1985). The following standards were used: synthetic PbSe, HgS and pure elements. Lines measured were Pd$L\alpha$, Pt$L\alpha$, Ag$L\beta$ (to avoid overlap of palladium on the Ag$L\alpha$ line), Cu$K\alpha$, Hg$M\alpha$, Pb$M\alpha$, Se$L\alpha$. The mean analytical results (and ranges based on four analyses of the grain measured for

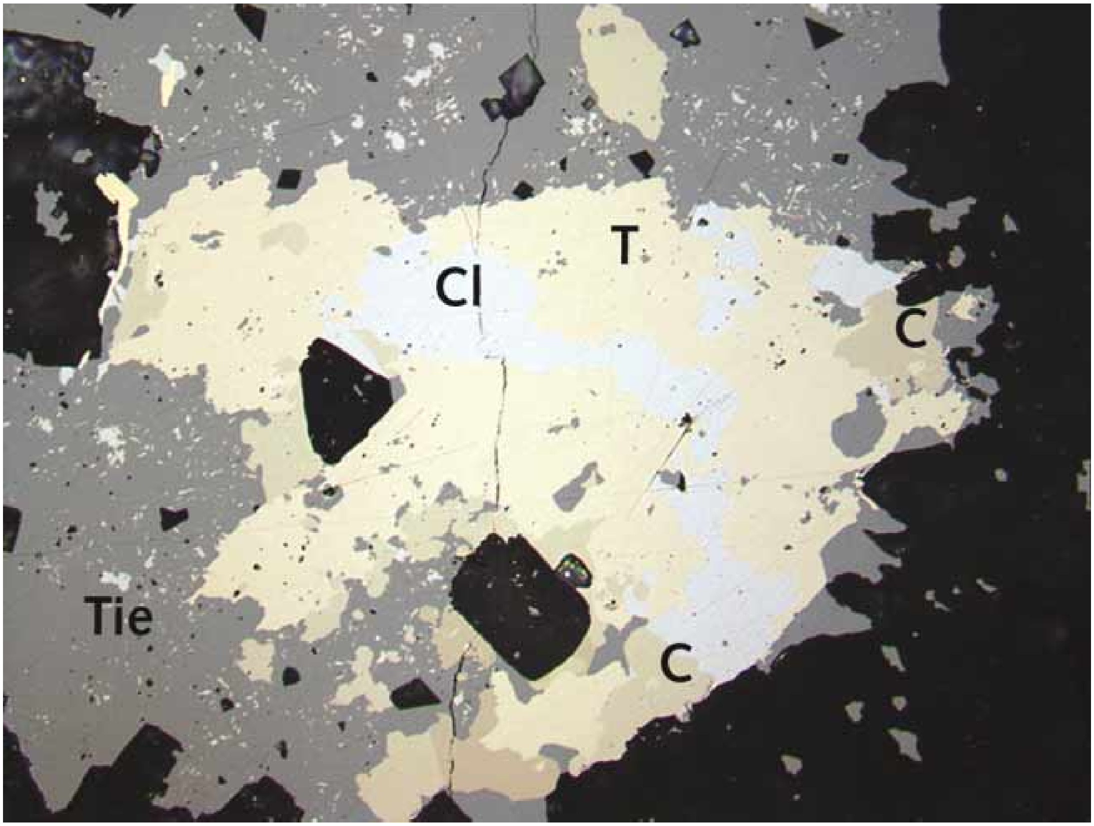

FIG. 1. Reflected light digital image illustrating the largest area of tischendorfite (T, cream) found in section 4154. Grains from this area were used in the reflected-light, electron-microprobe and X-ray-diffraction characterization. The associated minerals are clausthalite (Cl, off-white), tiemannite (Tie, gray), ankerite (black) and chrisstanleyite (C, greenish buff to pale brown). A small grain of stibiopalladinite (pale yellow) also can be seen. Horizontal field: 275 μm.

reflectance and extracted for X-ray studies) are given in Table 2. Results of additional electron-microprobe analyses for tischendorfite, illustrating a greater range in composition, are given in Table 3, together with representative compositions of the associated minerals in Table 4. These additional analyses were conducted using an automated Cameca SX–50 electron microprobe at the GeoForschungsZentrum, Potsdam operating in wavelength-dispersion mode. The operating conditions were as follows: accelerating voltage 20 kV, beam current 40 nA, and beam diameter 1–2 μm. The counting times on the peak were 30 seconds, and for background counts on either side of the peak, 15 seconds. Data reduction was done employing a PAP correction procedure (Pouchou & Pichoir 1985). Primary standards included pure metals for Co, Ag, Pd and Pt, chalcopyrite for Fe, Cu and S, pentlandite for Ni, sphalerite for Zn, cinnabar for Hg, galena for Pb, GaAs for As, Bi_2Se_3 for Bi and Se, Sb_2Te_3 for Te, InSb for Sb, and CdS for Cd. Lines measured were Cu*K*α, Ag*L*β (to avoid overlap of palladium on the Ag*L*α line), Hg*M*α, Pb*M*α, Zn*K*α, Cd*L*α, Fe*K*α, Co*K*α, Ni*K*α, Pd*L*α, Pt*L*α, As*L*α, Sb*L*α, Bi*M*α, S*K*α, Se*L*α, and Te*L*α.

The empirical formula for tischendorfite calculated from the arithmetic mean in Table 2 is $(Pd_{8.05}Pt_{0.01})_{\Sigma 8.06}(Hg_{2.70}Ag_{0.20}Pb_{0.15}Cu_{0.07})_{\Sigma 3.12}Se_{8.82}$, based on 20 atoms per formula unit. The analytical results listed in Table 3 yield $(Pd_{7.82\text{–}8.04}Pt_{0.00\text{–}0.17})_{\Sigma 7.93\text{–}8.05}(Hg_{2.49\text{–}2.85}Ag_{0.07\text{–}0.26}Pb_{0.00\text{–}0.36}Cu_{0.00\text{–}0.09})_{\Sigma 2.95\text{–}3.10}Se_{8.95\text{–}9.03}$. The simplified formula is $Pd_8Hg_3Se_9$, which requires: Pd 39.35, Hg 27.81, Se 32.84, total 100.0 wt.%.

TABLE 2. ELECTRON-MICROPROBE DATA FOR THE GRAIN OF TISCHENDORFITE MEASURED FOR REFLECTANCE AND EXTRACTED FOR X-RAY STUDY

Pd wt.%	39.4	(39.2–39.7)	Hg	24.9	(24.5–25.3)
Pt	0.1	(0.0–0.1)	Pb	1.4	(1.0–1.7)
Ag	1.0	(0.9–1.1)	Se	32.0	(31.9–32.1)
Cu	0.2	(0.2–0.2)			
			Total	99.0	

Average results of four electron-microprobe analyses.

TABLE 3. COMPOSITION OF VARIOUS GRAINS OF TISCHENDORFITE IN SAMPLE 4154

	1	2	3	4	5	6	7	8	9	10	11
Cu	0.07	0.17	0.18	0.13	d.l.	d.l.	0.18	0.21	0.12	0.26	0.24
Ag	0.39	1.32	0.66	0.67	0.69	0.54	0.93	0.33	0.44	0.66	0.37
Hg	26.0	23.7	24.2	24.2	26.4	24.5	24.7	24.8	25.6	23.3	24.4
Pb	1.03	1.81	2.14	1.70	d.l.	2.01	2.23	2.42	1.57	3.18	2.63
Pd	39.9	39.6	39.5	38.4	39.3	39.6	39.5	39.7	39.7	39.4	39.5
Pt	0.11	0.23	0.29	1.55	d.l.	d.l.	d.l.	0.30	d.l.	0.07	d.l.
Sb	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
S	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.
Se	33.0	33.0	33.1	32.9	32.9	33.1	33.2	33.2	32.9	33.2	33.6
Total	100.5	99.8	100.1	99.6	99.5	99.7	100.7	101.0	100.3	100.1	100.7

d.l.: below detection limit. Electron-microprobe data. The data are reported in wt.%.

Among the associated minerals, the data given in Table 4 demonstrate minor incorporation of Hg and Pt in chrisstanleyite, and of Pd and Pt in tiemannite. Stibiopalladinite has a small amount of As substituting for Sb.

X-RAY CRYSTALLOGRAPHY

Single-crystal precession X-ray studies were carried out on a fragment, admixed with clausthalite, that had been dug out of the polished section. This grain had previously been analyzed by electron microprobe and measured for reflectance. The fragment was mounted such that *b** is parallel to the dial axis of the precession camera, but the grain was found to consist of composite grains of tischendorfite,which were unsuitable for crystal-structure analysis. Precession levels collected with both unfiltered and Zr-filtered Mo radiation were *hk*0, *hk*1, 0*kl*, 1*kl*, 101*/\ *b** and 201* /\ *b**. The only systematic absence is *hk*0 with *h* + *k* = 2*n*. The preliminary unit-cell parameters derived from zero-level precession photographs are: *a* 7.25, *b* 16.85 and *c* 6.50 Å. Tischendorfite is orthorhombic; the permissible choices of space group are *Pmmn* (59), $P2_1mn$ (31) or $Pm2_1n$ (31) (diffraction aspect *P**n*).

X-ray powder data (Table 5) were obtained from an area adjacent to that from which the "single-crystal" fragment was dug out; however, owing to the small grain-size, it was not possible to extract tischendorfite without admixed clausthalite. Unit-cell parameters were

TABLE 4. REPRESENTATIVE COMPOSITIONS OF CHRISSTANLEYITE, TIEMANNITE AND STIBIOPALLADINITE IN SAMPLE 4154

	Csl	Csl	Csl	Csl	Csl	Csl	Tmn	Tmn	Tmn	Std
Cu	0.05	0.05	d.l.	0.04	d.l.	0.07	d.l.	d.l.	d.l.	d.l.
Ag	24.5	25.1	24.7	24.3	24.4	24.9	0.37	d.l.	0.12	d.l.
Hg	1.39	0.33	0.50	0.23	1.08	0.35	71.3	71.6	71.8	d.l.
Pb				0.06	d.l.	0.22	d.l.			0.04
Zn				d.l.			d.l.			d.l.
Cd				d.l.			0.10			d.l.
Fe				0.38			d.l.			d.l.
Co				d.l.			0.05			d.l.
Ni				d.l.			d.l.			d.l.
Pd	37.0	37.9	37.7	37.7	37.4	37.5		0.22	0.22	71.0
Pt	0.38	0.22	0.12		0.34	0.00		0.04	0.30	
As				d.l.			d.l.			3.58
Sb	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	d.l.	0.04	d.l.	25.7
Bi							d.l.			
S	0.19	0.19	0.13	d.l.	0.12	0.10	d.l.	d.l.	d.l.	d.l.
Se	36.3	36.4	37.0	37.0	36.5	36.6	28.2	28.8	27.9	0.13
Te							0.02			
Total	99.8	100.2	100.15	99.7	99.8	99.7	100.0	100.7	100.3	100.45

d.l.: below detection limit, blank: not analyzed. Electron-microprobe data, reported in wt.%. Symbols: Csl: chrisstanleyite, Tmn: tiemannite, Std: stibiopalladinite.

refined on 19 powder reflections between 4.819 and 1.700 Å for which unambiguous indexing, based on visual inspection of precession single-crystal photographs, was possible. The refined unit-cell parameters are: *a* 7.219(3), *b* 16.782(7), *c* 6.467(5) Å, *V* 783.6(8) Å^3, *a*:*b*:*c* 0.4302:1:0.3854, *Z* = 2. The PSC (Pearson Symbol Code) is *oP* 40, and the mineral appears to have a unique prototype structure.

CONDITIONS OF FORMATION

All the selenide occurrences from the Harz Mountains share a near-identical temporal sequence of mineral deposition. Initial deposition of ore minerals is characterized predominantly by oxides (hematite, carbonates such as calcite and ankerite), followed by precipitation of locally abundant selenides in a carbonate matrix predominantly made up of ankerite. Widespread crystallization of a limited number of calcite-hosted sulfides (chalcopyrite, pyrite, marcasite) characterizes the final stage of mineral deposition. This systematic order, together with geochemical studies of the country rocks that host the veins, encouraged thermodynamic calculations of various S–Se mineral equilibria. As a result, Tischendorf (1959, 1966, 1968, 1970; see also Tischendorf & Ungethüm 1964) concluded that the high oxygen fugacity of the mineral-forming solutions was the major reason that selenides rather than sulfides formed. Secondly, he proposed that the country rock, carbon-rich graptolitic black shale, was the major source of selenium, sulfur and the accompanying cations (Cu, Fe, Co, Ni, Pd, Hg, Ag, Au and Pb) concentrated in the ore veins. At distances between 0.5 and 3 m from the contact with the selenide-bearing carbonate veins, these black shales are altered, *i.e.*, reddened, bleached and depleted in S, Pb, Cu and Se. A statistically significant difference in the content of platinum metals between fresh and altered black shale could not be established (Tischendorf 1959). The unaltered black shale contains 0.3–1.1 ppm Au, <0.5 ppm Pd, 0.01–0.05 ppm Pt, <0.01–0.02 ppm Rh, and 0.04–0.08 ppm Ru. Altered parts of the rock contain <0.05–0.8 ppm Au, <0.5 ppm Pd, 0.01–0.05 Pt, <0.01–0.02 Rh, and 0.005–0.04 ppm Ru.

Recently, many of the early inferences on the physicochemical environment of selenide-mineral formation were confirmed by the thermodynamic calculations undertaken by Simon & Essene (1996) and Simon *et al.* (1997). The latter proposed a temperature of formation of about 100°C for the telethermal type of selenide deposit. At this temperature, the selenide mineralization, such as in the assemblage containing tischendorfite, would have formed between log $f(\mathrm{Se}_{2(g)}) = -17$, log $f(\mathrm{S}_{2(g)}) = -21$ and log$f(\mathrm{Se}_{2(g)}) = -12$, log $f(\mathrm{S}_{2(g)}) = -19$ [according to the plot of selenium fugacity *versus* sulfur fugacity of Simon *et al.* (1997), assuming that log $f(\mathrm{O}_{2(g)})$ is close to the galena–anglesite buffer, –48.27]. This is within the general trend for the telethermal type of selenide deposit, as defined by Simon *et al.* (1997).

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR TISCHENDORFITE

I_{est}	*d* Å meas.	*d* Å calc.	*hkl*	I_{est}	*d* Å meas.	*d* Å calc.	*hkl*
10	6.563	6.631	110	* 5	2.410	2.408	202
		6.467	001	* 40	2.325	2.329	052
10	5.969	6.034	011	* 10	2.277	2.275	170
* 40	4.819	4.817	101	10	2.247	2.255	301
40	4.373	4.422	130			2.248	071
* 20	3.315	3.316	220	* 40	2.116	2.115	062
* 5	3.236	3.233	002	*100	2.091	2.092	261
* 5	3.166	3.164	141	* 5	1.993	1.995	081
* 20	2.949	2.951	221	* 20	1.955	1.957	252
60	2.797	2.799	032	* 5	1.929	1.926	072
		2.784	122	* 20	1.907	1.908	271
100	2.743	2.754	151	* 20	1.871	1.872	351
		2.746	231	* 20	1.805	1.805	400
		2.736	240	* 10	1.739	1.739	191
* 10	2.562	2.561	042	* 10	1.700	1.698	370

114.6 mm Debye–Scherrer powder camera, Cu radiation, Ni filter (λ Cu*K*α = 1.54178 Å). Intensities estimated visually. Corrected for shrinkage using admixed end-member clausthalite (PbSe) as a standard. All clausthalite lines have been removed from the pattern. Indexed on 19 lines (marked with a *) with *a* 7.219, *b* 16.782, *c* 6.467Å.

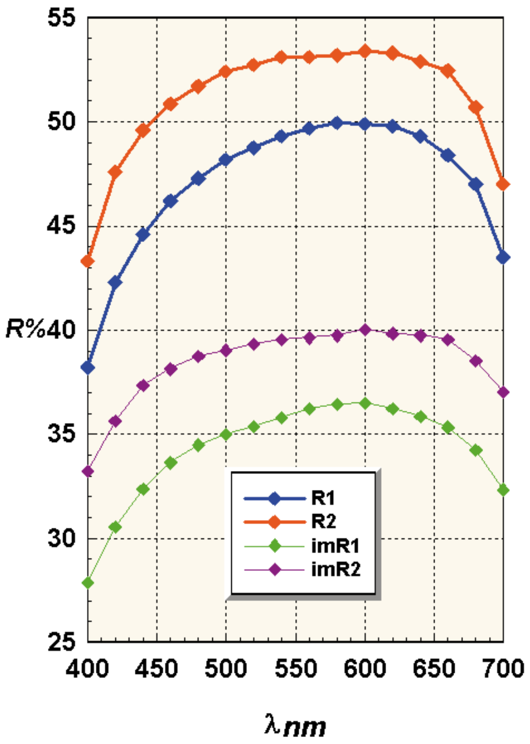

FIG. 2. Reflectance curves for tischendorfite in air and in oil.

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