A new mineral, chrisstanleyite, Ag₂Pd₃Se₄, from Hope's Nose, Torquay, Devon, England

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ABSTRACT

Chrisstanleyite, Ag₂Pd₃Se₄, is a new mineral from gold-bearing carbonate veins in Middle Devonian limestones at Hope's Nose, Torquay, Devon, England. It is associated with palladian and argentian gold, fischesserite, clausthalite, eucairite, tiemannite, umangite, a Pd arsenide-antimonide (possibly mertieite II), cerussite, calcite and bromian chlorargyrite. Also present in the assemblage is a phase similar to oosterboschite, and two unknown minerals with the compositions, PdSe2 and HgPd2Se3. Chrisstanleyite occurs as composite grains of anhedral crystals ranging from a few µm to several hundred µm in size. It is opaque, has a metallic lustre and a black streak, VHN100 ranges from 371-421, mean 395 kp/mm² (15 indentations), roughly approximating to a Mohs hardness of 5. $D_{calc} =$ 8.308 g/cm³ for the ideal formula with Z = 2. In plane-polarised reflected light, the mineral is very slightly pleochroic from very light buff to slightly grey-green buff; is weakly bireflectant and has no internal reflections. Bireflectance is weak to moderate (higher in oil). Anisotropy is moderate and rotation tints vary from rose-brown to grey-green to pale bluish grey to dark steel-blue. Polysynthetic twinning is characteristic of the mineral. Reflectance spectra and colour values are tabulated. Very little variation was noted in eleven electron-microprobe analyses on five grains, the mean is: Ag 25.3, Cu 0.17, Pd 37.5, Se 36.4, total 99.37 wt.%. The empirical formula (on the basis of ΣM + Se = 9) is $(Ag_{2.01}Cu_{0.02})_{\Sigma 2.03}$ Pd_{3.02}Se_{3.95}, ideally Ag₂Pd₃Se₄. Chrisstanleyite is monoclinic, *a* 6.350(6), *b* 10.387(4), c 5.683(3) Å, β 114.90(5)°, space group $P2_1/m$ (11) or $P2_1(4)$. The five strongest X-ray powder-diffraction lines [d in Å (I)(hkl)] are: 2.742 (100) (-121), 2.688 (80) (-221), 2.367 (50) (140), 1.956 (100) (-321,150) and 1.829 (30) (-321, 042). The name is in honour of Dr Chris J. Stanley of The Natural History Museum in London. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

Keywords: chrisstanleyite, new mineral, palladium-silver selenide, gold, selenide minerals, X-ray data, electron-microprobe data, reflectance data, Hope's Nose, Devon, England.

Introduction

AT the end of 1995 one of the authors (WHP) obtained a few black fragments with traces of visible gold and possibly fischesserite from Hope's Nose, Torquay, Devon, U.K. The polished section prepared from these fragments included sufficient of a new mineral for its characterization to be completed. The mineral is named in honour of Dr Chris J. Stanley (b.1954), Associate Keeper

and Deputy Head of the Department of Mineralogy at The Natural History Museum in London [known formerly as the British Museum (Natural History)] for his contributions to ore mineralogy.

The holotype is preserved in the mineral collections (polished section collection) of the Institut für Mineralogie, University, Salzburg, Austria (catalogue number II/A 1070). Cotype samples (four polished sections: E.1534; E.1527;

E.1538 and E.1537) are registered as BM 1997,59 at The Natural History Museum in London.

Hope's Nose is designated a Site of Special Scientific Interest by English Nature. Specimens may be collected from this locality solely for the purpose of scientific investigation, and only when prior approval has been obtained from the Department. In truth, the site has been so seriously vandalised by gold collector/dealers, illegally using drills and explosives, that little remains for scientific investigation, let alone personal gain.

Historical background

Hope's Nose is a steeply sloping headland, bounded by low cliffs, on the northern side of Tor Bay at 58°28'N, 3°28'W. Evidence of mineralisation was first recorded at the locality by Professor W.T. Gordon (1922) who, whilst leading a party of students on a geological field trip, noticed some sprigs of native gold in the weathered surfaces of calcite veins on the foreshore. He was followed by Sir Arthur Russell (1929) who discovered five of the goldbearing calcite veins cutting across the flat-lying limestones, of Devonian age, which form the shallow cliffs, on the south-eastern foreshore of the promontory, near the open sewage outflow for Torquay. Assay of these very beautiful 'arborescent' or dendritic gold specimens revealed Ag at between 1.89 and 8.41 wt.% (the higher the silver content, the more silvery the native gold appeared), but PGE's were not found. Apparently, gold at Torquay did not excite much interest for the next fifty years or more, as it was next recorded by Clark and Criddle (1982) who found little argentian gold, but plentiful palladian gold (up to 5.25 wt.% Pd) mixed with relatively pure native gold. In addition, they found the palladium arsenide-antimonide, isomertieite which was the first PGM to be confirmed from the UK. This, and an anisotropic mineral with the same composition (which was probably mertiete II but was too small for confirmation by X-ray) were the only minerals noted by them. Gold, richer in Pd (up to 16 wt.%), was reported by Scrivener et al. (1982), but it was not until 1990 that selenide mineralisation was reported from one of these calcite veins (Stanley et al., 1990). In a vein, which they designated the 'selenide vein' (and drew in a sketch map in their paper), they found, in addition to native gold, chalcopyrite and isomertieite, a remarkable assemblage of selenide minerals: tiemannite HgSe, trüstedite Ni₃Se₄, penroseite (Ni,Co,Cu)Se₂, tyrellite (Cu,Co,Ni)₃Se₄, umangite Cu₃Se₂, klockmannite CuSe, fischesserite Ag₃AuSe₂, eucairite CuAgSe, naumannite Ag₂Se and clausthalite PbSe. Cerussite, malachite, aragonite and goethite accompanied the selenides.

Proof that gold, palladium and selenium mineralisation in south Devon is not restricted to Hope's Nose was supplied by Leake et al. (1991). In South Hams, the area to the west of Hope's Nose, between the Dartmoor granite and the south Devon coast, their geochemical drainage survey proved that gold is widespread. From the superheavy concentrate fractions (from panned samples), they hand-picked precious metal grains for microchemical mapping with the electron-microprobe. In some of these grains the gold and palladian gold was strongly zoned; in others, the zonation was of native gold, potarite (PdHg) and native platinum (so far, not encountered at Hope's Nose) and, in Ag-enriched grains of gold, they found minute inclusions of selenide minerals. These inclusions, though too small to be positively identified with the electron-microprobe, included selenides of Hg (tiemannite?), Pb (clausthalite?) and Bi (guanajuatite?): other selenides, about which they were less sure, were those of Pd-Hg, Bi-Pd and Cu.

Chrisstanleyite, occurrence and association

One of the high-angled calcite veins transecting the almost flat-lying shelf of limestones of the Middle Devonian, Torquay limestone group, and which is about 50 m NE of the 'selenide vein' (of Stanley et al., 1990), is the source of the chrisstanleyite. Trending WNW, the vein is about 4-6 cm wide, and the mineralisation was found 10 cm below the outcrop of the calcite. It formed a pocket or lens 10 cm long by 0.07 cm deep by 4 cm wide in which the minerals were distinctly zoned. The sequence from top to bottom was dendritic or fern-like native gold, with small amounts of Ag, followed by palladian gold, then by the selenide mineralisation (S. Weiss, pers. comm.). For the sake of future identification we have called the vein the 'fischesserite vein (after its most abundant selenide).

The selenide assemblage is found as inclusions up to 1 cm in size or as fine 'networks' which have followed cleavage or grain boundaries in calcite. The complete, chrisstanleyite-bearing assemblage, consists of native gold (argentian and palladian), fischesserite, clausthalite, a

mineral which is similar to oosterboschite (Pd,Cu)₇Se₅ (uk3), and two hitherto unknown compounds, PdSe₂ (uk2) and Pd₂HgSe₃ (uk1). Tiny inclusions of tiemannite, eucairite and umangite have been observed in the gold and in uk1. Other constituents include an optically anisotropic palladium arsenide-antimonide, possibly merticite II Pd₈(Sb,As)₃ - associated with the gold (cf. Clark and Criddle, 1982) - and cerussite and bromian chlorargyrite Ag(Cl,Br), associated with the selenides. Back-scattered electron images of the textural relationships of chrisstanleyite with other minerals in the assemblage in the 'fischesserite vein' are shown in Figs. 1-4: typical monominerallic inclusions in cerussite (Fig. 1 and 4); random intergrowths and inclusions in gold-silver alloys, bordered by fischesserite (Fig. 2), or clausthalite, or both; and inclusions in fischesserite in association with gold and bromian chlorargyrite (Fig. 3). Occasionally, chrisstanleyite contains inclusions of clausthalite (Fig. 1).

Electron-microprobe analyses

Seven grains of chrisstanleyite in two polished sections were analysed at the Institute of Geology and Palaeontology (University of Salzburg) using a JEOL Superprobe JXA-8600 with an ELX-Link system, and operated at 25kV and 30nA. The raw data were processed with the LINK ZAF-4 program. Natural Cu_9S_5 (digenite) (Cu-K α), natural Cu₃Se₂ (umangite) (Se- $L\alpha$), synthetic Pd (Pd-L α) and synthetic Ag (Ag-L β) standards were used. The results (Table 1) reveal only minor differences between the analyses. The average composition derived from these 26 analyses corresponds to (Ag_{2.01}Cu_{0.02})_{\$\Sigma2.03}Pd_{3.02}Se_{3.95} or, ideally, Ag₂Pd₃Se₄, on the basis of 9 atoms $(\Sigma M+Se)$ and Z=2. The ideal formula requires Pd 37.52, Ag 25.36, Se 37.12, total 100.00 wt.%.

The gold alloys directly associated with chrisstanleyite include: (1) a gold-silver alloy without palladium as anhedral grains in cerussite and calcite; (2) palladian-argentian-gold randomly intergrown with fischesserite; and (3) fine-grained gold with only traces of Ag, also in fischesserite.

The composition of dendritic and fern-like gold ranges (in atomic %) from $Au_{0.994}Ag_{0.003}Pd_{0.003}$ to $Au_{0.731}Ag_{0.004}Pd_{0.228}$. Typically, along their axes, the dendrites consist of a gold-rich core surrounded by palladian gold, though a very irregular distribution of the different alloys is not

uncommon. The Pd content (wt.%) varies between 0.2 and 13.9% with most of the analyses clustering in the 5.7-7.2% range. The distribution in atomic percentage of composition of the alloys in this study are shown in the Au-Ag-Pd ternary diagram (Fig. 5).

Appearance and physical properties

Chrisstanleyite occurs as composite grains of anhedral crystals ranging from a few to several hundred µm in size. Its colour (as seen with a hand lens on polished material) is a silvery metallic grey. It is opaque, has a metallic lustre, a black streak and, as is shown by the slight fracturing of the VHN indentations, is slightly brittle. The VHN₁₀₀ measured from 15 indentations is in the range 371-421, mean 395 kp/mm, which corresponds to a Mohs hardness of about 5 (calculation after Young and Millman, 1964). The indentations, which were made with a Leitz Miniload 2 Hardness tester were all perfectly formed but slightly fractured. It was not possible to measure the density of the mineral, but that calculated for the ideal formula and Z = 2 is 8.308 g/cm^3 .

Optical properties

Specimens were polished using standard diamond polishing procedures. In plane-polarised reflected light the specular reflectance of chrisstanlevite (at a colour temperature of approximately 3200K), is higher than that of fischesserite and lower than the gold and gold alloys with which it is associated. It is weakly to moderately bireflectant (this is more noticeable when immersed in oil), and very slightly pleochroic from a very light buff to a slightly grey-green buff. It does not possess internal reflections. Between crossed polars its anisotropy is moderate (enhanced in oil) and its sequence of rotation tints (from extinction) is: rose-brown, grey-green, pale bluish grey and dark steel-blue. A most characteristic feature of the mineral is its fine polysynthetic and parquet-like twinning - a feature it shares with oosterboschite (cf. Picot and Johan, 1982). The anisotropic rotation tints of chrisstanleyite are, however, much more colourful than the bluish to brownish grey tints, typical of the latter.

The reflectance spectra of chrisstanleyite were measured using a Zeiss MPM800 microscopespectrophotometer system relative to the spectra from a WTiC reflectance standard (Zeiss 314).



FIGS. 1–4: Back-scattered electron images of typical textures of chrisstanleyite and its associated minerals. Fig. 1. (top left) Inclusions of chrisstanleyite (chr) and gold (go) in cerussite (ce). The tiny white spots in the chrisstanleyite on the left are inclusions of clausthalite (cl). Fig. 2. (top right) Inclusions of chrisstanleyite and fischesserite (fi) in gold intergrown with clausthalite and cerussite. Fig. 3. (bottom left) Chrisstanleyite associated with chlorargyrite (chl) and fine-grained gold in fischesserite. Fig. 4. (bottom right) Inclusions of chrisstanleyite in cerussite. A large gold grain contains three unknown phases (uk1–3), uk3 is compositionally similar to oosterboschite.

Although relatively large areas of chrisstanleyite were exposed in the polished section, obtaining an optically continuous area of crystals of sufficient size for measurement was made difficult by the ubiquitous twins. It proved necessary to measure with high power objectives (\times 50, NA 0.8, air, 1.0 oil), the effective numerical apertures of which were adjusted to 0.3, and with the diameter of the measuring field set at 8 μ m. Immersion measurements were made in Zeiss oil, $N_D = 0.515$ (Table 2). The spectra collected are compared with published data for the two other known

CHRISSTANLEYITE, A NEW AG-PD SELENIDE

Sample	$\mathbf{N^1}$	Pd	Ag	Cu	Se	Total
sec 1, gr1	3	37.43	25.18	0.17	36.33	99.11
gr2	4	37.50	25.23	0.19	36.39	99.30
gr3	4	37.68	25.42	0.17	36.35	99.62
gr4	4	37.80	24.97	0.13	35.99	98.89
gr5	5	37.60	24.76	0.22	36.45	99.03
gr6	5	37.83	24.87	0.23	37.08	100.01
sec2. gr1	1	37.67	25.23	0.13	36.12	99.15
average:	26	37.64	25.09	0.18	36.39	99.30
sd ²		0.20	0.18	0.02	0.30	
minimum		37.01	24.71	0.08	35.85	
maximum			38.05	25.30	0.25	37.21

TABLE I. Electron-incrodrope analyses of christianev	TABLE 1.	Electron-micro	brobe analyses	of chi	risstanlev	ite
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 N^1 = number of analyses, sd^2 = standard deviation

selenides of palladium, oosterboschite (Pd,Cu)₇Se₅ (Picot and Johan, 1982) and palladseite $Pd_{17}Se_{15}$ (Criddle and Stanley, 1993), in Fig. 6.

It will be seen that the spectra of chrisstanleyite 'bracket' those of the isotropic palladseite, whilst those of oosterboschite (data only for air) show it to be about as bireflectant as chrisstanleyite, but between 2 and 3% higher reflecting and with a somewhat different dispersion. These differences are further quantified in the colour values relative to the CIE Illuminant A and C (A is the colour temperature nearest that of the tungsten-halogen



TABLE 2. Reflectance percentages for chrisstanleyite



FIG. 5. Au-Ag-Pd ternary diagram (atomic %) for the gold alloys in the fischesserite vein.

λnm	R _I	R_2	$^{im}R_{I}$	$^{im}R_2$
470	39.7	47.2	26.2	34.4
546	43.1	48.8	29.3	35.15
589	44.3	49.4	30.4	35.55
650	44.4	49.2	31.0	35.6
400	35.6	43.3	22.8	30.7
420	36.8	44.2	23.6	31.8
440	37.8	45.3	24.45	32.9
460	39.1	46.7	25.65	34.0
480	40.0	47.5	26.5	34.6
500	41.1	48.0	27.5	34.9
520	42.1	48.5	28.3	34.9
540	42.9	48.7	29.1	35.05
560	43.5	49.1	29.7	35.3
580	44.1	49.3	30.2	35.5
600	44.45	49.5	30.6	35.55
620	44.6	49.5	30.7	35.6
640	44.5	49.3	30.9	35.6
660	44.4	49.2	31.0	35.8
680	44.2	49.1	31.1	35.8
700	44.0	49.0	31.2	35.9



FIG. 6. Reflectance spectra for chrisstanleyite (C), palladseite (P) and oosterboschite(O).

why the excitation purity (Pe%) or saturation of oosterboschite is lower than that of chrisstanleyite – quite simply the mid-spectrum fall in reflectance in oosterboschite means that the saturation of its hue is reduced as compared with that of chrisstanleyite. The colour values also confirm the qualitative observation that chrisstanleyite is weakly to moderately bireflectant and weakly pleochroic. Tabulated reflectance data characteristic of chrisstanleyite are given in Table 2.

X-ray powder and single-crystal study

A single fragment, dug out of the polished section, was mounted and studied by singlecrystal precession methods employing Zr-filtered Mo radiation. The fragment was orientated with a^* parallel to the dial axis and the reciprocal lattice levels collected were: $h01 \rightarrow h21$, hk0, hk1, $011^* \land a^*$, $021^* \land a^*$, $031^* \land a^*$ and $032^* \land a^*$. The fragment is composed of two individual crystals (in roughly 60:40 ratio) and is not suitable

CHRISSTANLEYITE, A NEW AG-PD SELENIDE

1 0054 W	Chrisstanleyite				Oosterboschite		
A = 2856 K	R_I	R_2	$^{im}R_{I}$	$^{im}R_2$	R_I	R_2	
	0.4566	0.4516	0.4602	0.4511	0.4534	0.4497	
У	0.4210	0.4102	0.4132	0.4096	0.4111	0.4108	
Y%	43.6	49.1	29.8	35.3	46.1	51.5	
λ_d	585	583	585	584	584	579	
$P_e\%$	9.3	4.6	12.8	3.9	6.5	3.8	
C = 6774 K							
x	0.3217	0.3155	0.3262	0.3148	0.3177	0.3138	
V	0.3294	0.3235	0.3340	0.3225	0.3266	0.3237	
Y%	43.1	48.9	29.4	35.2	45.9	51.4	
2a	576	574	576	574	573	569	
$P_e\%$	6.2	3.4	9.1	2.9	4.8	3.0	

TABLE 3. Colour values relative to CIE (1931) illuminants

TABLE 4. X-ray powder diffraction data for chrisstanleyite

	Iest	$d \text{\AA}_{\text{meas.}}$	dÅ _{calc.}	hkl		I _{est.}	dÅ _{meas.}	dÅ _{cale.}	hkl
	5	5.18	5.155	001	*	10	1.990	1.992	221
	5	4.62	4.617	011				1.958	321
	10	4.534	4.532	111		100	1.956	1.958	312
	10	3.621	3.659	021				1.954	150
	10	3.621	3.616	Ī21	*	20	1.918	1.917	Ī42
			2.880	200	*	3	1.861	1.860	2 03
	50b	2.868	2.874	031	*	3	1.846	1.847	ī13
			2.853	ī31				1.831	231
*	100	2.742	2.740	Ī21		30	1.829	1.831	<u>2</u> 13
*	80	2.688	2.687	Ž 21				1.829	042
	3	2.582	2.577	002	*	10	1.807	1.808	<u>2</u> 42
*	20	2.521	2.519	2 02	*	5	1.766	1.765	ī23
	10	2.496	2.501	012	*	3	1.749	1.751	223
	10	2.496	2.492	Ī22	*	10	1.731	1.731	060
*	3	2.448	2.448	<u>2</u> 12	*	3	1.719	1.718	003
*	50	2.367	2.367	140				1.641	061
*	10	2.328	2.326	<u>2</u> 31		10	1.639	1.639	341
	10	2.309	2.309	022		10	1.639	1.638	<u>2</u> 33
	10	2.309	2.308	Ī41				1.637	Ī61
*	5	2.265	2.266	2 22					
	10	2.068	2.067	032					

114.6 mm Debye-Scherrer powder camera, Co radiation, Fe filter (λ Co-K α = 1.79021 Å) b = broad line, intensities visually estimated

Not corrected for shrinkage and no internal standard

Pattern run at CANMET by Mr P Carrière

Minor clausthalite lines have been estimated from the pattern

Indexed with a = 6.350, b = 10.387 and c = 5.683 Å, $\beta = 114.90^{\circ}$

for crystal-structure analysis. Chrisstanleyite is monoclinic with space-group choices $P2_1/m$ (11) or $P2_1(4)$ and the diffraction aspect is $P2_1/*$. The only systematic absence is 0k0 with k = 2n. The refined unit-cell parameters: $a \ 6.350(6)$, $b \ 10.387(4)$, $c \ 5.683(3)$ Å, $\beta 114.90(5)^\circ$, $V \ 340.0(4)$ Å³, and a:b:c = 0.6113:1:0.5471 are based on 17 reflections, between 2.742 and 1.719 Å, in the Xray powder pattern for which unambiguous indexing was possible.

All possible reflections down to 1.61 Å were visually examined on single-crystal precession films. Fully indexed 114.6 mm Debye-Scherrer camera X-ray powder data are presented in Table 4. Three lines which are ascribable to clausthalite contamination have been omitted. Two other reflections at 1.846 and 1.766 Å have had their visual intensities decreased because of probable overlap with clausthalite. The data are unique and do not bear resemblance to any mineral or inorganic compound listed in the PDF file up to and including Set 45.

It has been suggested, however, that chrisstanleyite is structurally derivative of synthetic $K_2Ni_3S_4$ and related compounds (Y.Moelo, pers.comm.). $K_2Ni_3S_4$ has a 5.723, b 10.040 and c 26.059 (equal to 6.515×4) Å. A replacement of K by Ag would contract c from 6.52 to 5.68 Å. The substitution of Ni by Pd and S by Se would increase a and b (orthohexagonal cell) from 5.72/10.04 to 6.35/10.39 Å (Y. Moelo, pers.comm.). Confirmation of this suggestion would only be possible from a crystal-structure analysis — for which better material would be needed.

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