Palladium minerals from Hope's Nose, Torquay, Devon

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ABSTRACT. Two palladium arsenide-antimonides have been found as small inclusions associated with native gold at Hope's Nose. One of the minerals has been identified as isomertieite; the other is chemically very similar to mertieite-II (Cabri et al., 1975). Electron probe microanalysis gives the formula of the isomertieite as $(Pd_{10.89}Au_{0.08}Cu_{0.03})_{\Sigma 11.00}(Sb_{2.01}As_{1.99})_{\Sigma 4.00}$ and of mertieite II as $(Pd_{7.90}Au_{0.07}Cu_{0.01})_{\Sigma 7.98}(Sb_{2.43}As_{0.59})_{\Sigma 3.02}$. The reflectance spectra of isomertieite in air and in oil at intervals of 10 nm from 400–700 nm are tabulated. The luminance values of the Hope's Nose isomertieite are 55.5% in air and 42.5% in oil. The type specimen of isomertieite from Itabira, Minas Gerais, Brazil, has been re-examined; a new electron probe analysis is given and improved reflectance spectra are tabulated. The latter gives luminance values of 54.3% in air and 41.3% in oil.

TWO palladium minerals have been found as small inclusions in some specimens of native gold from Hope's Nose, near Torquay. The presence of small quantities of gold in the Middle Devonian limestone of this area has been known from around the turn of the present century and the first note of its precise occurrence was given by Professor W. T. Gordon (1922). A few years later Arthur Russell (1929) gave a more detailed account of the arborescent gold sprigs found by him in five distinct calcite veins at Hope's Nose. Russell gives the results of assays of three samples of the gold. The only element accompanying the gold is reported to be silver, 1.89% in a specimen of 'bright rich gold' and 7.47% and 8.41% respectively in two specimens of 'silver-white gold'. He also reported that metals of the platinum group were absent.

In the present investigation we have studied, by electron probe microanalysis and ore microscopy (including spectral reflectance measurements), gold samples deposited by Russell in the British Museum (Natural History) and some small specimens collected much more recently by D. C. N. Smith, R. W. Barstow, and B. V. Cooper. In none of the grains have we found silver concentrations in any way approaching the values quoted by Russell—the maximum figure obtained being near 0.9%, even in grains similar in appearance to those

he described as 'silver-white gold'. However, these latter grains have proved to contain significant concentrations of palladium, over 6% in a number of analyses. Even material similar in appearance to Russell's 'bright rich gold' usually contains about 1% Pd. Although we have not been able to examine the specimens analysed for Russell, which were undoubtedly consumed in the assay, it seems possible that the reported determinations were in error in reporting Ag for Pd, and that this platinum-group metal is present throughout the Hope's Nose gold, primarily in solid solution.

In addition to the presence of palladium in the gold we have observed a number of pale bluish grey inclusions close to, or on the outer surface of a few of the gold dendrites from one of the veins. These inclusions have proved to be palladium arsenide-antimonides and form the subject of this contribution.

Occurrence. The Hope's Nose headland [Grid ref. (SX 637 949)], 3 km east of the centre of Torquay, consists of Lower Devonian grits, shales and slates, and Middle Devonian calcareous shales and limestones. All of these strata, including the thickly bedded limestone platform on the north-eastern shore of the headland in which the gold-bearing calcite veins are found, have been extensively folded, thrusted, and faulted (Lloyd, 1931, pp. 56–7). The high-angle, gold-bearing, veins trend from the low-water mark, 20° W. of N., for a maximum strike length of 25 m, where they are cut off on the landward side by some low cliffs. They vary from 2 to about 30 cm in thickness; some have been slickensided, but brecciation is minor. The wall rock and vein contents are usually iron-stained. Russell (1929) reported five gold-bearing veins over a distance of 38 m to the north of the Torquay sewage outflow; more recently, another, palladium-bearing, gold vein has been found to the south. This almost vertical vein cuts limestone veined by a plexus of pure white, apparently barren, and heavily slickensided, muscovite-bearing calcite veins, which attain a thickness of 3 cm. It was

in specimens from this vein that the palladium arsenide–antimonides were found. These, and specimens from Russell's collection, were examined in hand specimen and polished section.

Mineralogy. The mineral assemblage, at least in hand specimen, appears similar within the six veins. It consists predominantly of clusters and druses of reddish calcite scalenohedra, from 3 to 25 mm in size, the interstices of which are usually filled with buff or creamy coloured fine-grained calcite. The cavities that remain in this otherwise compact material are sometimes partly filled with the ochreous remains of altered dolomite, with fine-grained hematite or, rarely, with pure white aragonite. Dendritic and arborescent gold, revealed by treatment with HCl, is concentrated in the buff calcite and has not been found in the reddish calcite. Gold also occurs, although rarely, in association with the limonitic remains of dolomite, and with the patchily developed, fine-grained, hematite.

The reddish calcite owes its colour to the presence of finely divided hematite which, as well as being distributed throughout the scalenohedra, is concentrated in zones near their outer surfaces. At these surfaces dolomite rhombs about 0.1 mm in size form a discontinuous single layer separating the reddish calcite from the buff. They also form thin 'trains' of crystals within the buff calcite where they are often intimately associated with gold. Similarly, and not uncommonly, the reddish calcite is separated from the buff by a 'shroud' of yellow, presumably ferroan, calcite. This is of variable thickness and is sometimes botryoform enclosing the scalenohedra. Gold-bearing, finely crystalline, hematite occurs in these areas, particularly where thin veinlets (<0.1 mm) of white calcite cut both the reddish and buff calcite. The insoluble residue of one hand specimen after treatment with HCl revealed abundant platy crystals and sheaves of crystals of hematite up to 0.75 mm in size.

The only other materials found in the residue, apart from gold, were crumbly limonitic 'boxworks' of relict dolomite grains. In polished section patches of these grains are found in both the buff and reddish calcite, but only in the former is gold sometimes found. In one polished section the outlines of scalenohedra were seen in the buff calcite which is more usually granular; these presumably represent the first stage of crystallization of this variety of calcite within the drusy cavities formed by the reddish calcite. Quartz was not observed in this investigation although it is known to occur as small euhedral crystals visible in hand specimen (B. V. Cooper, pers. comm.).

The distribution and morphology of the gold was examined in two hand specimens at intervals during the progressive solution of the carbonates
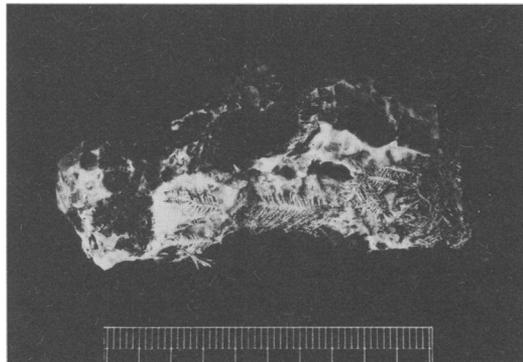

FIG. 1. Specimen of dendritic and arborescent gold from Hope's Nose. The carbonates in this specimen have been partly dissolved with HCl to reveal the gold. The darker areas are reddish calcite and the lighter areas buff calcite. One large division on the scale is 1 cm.

with HCl. Its most common form is as described by Russell (1929)—dendritic, arborescent, and fern-like. Individual planar dendra consist of a central rod from which branches and sub-branches have grown, each at about 60° to the parent branch (fig. 1). The gross morphology of the dendrons appears to have been influenced more by the form of the cavity or druse in the reddish calcite in which they grew than by the crystallization of the buff calcite. They may be straight-linear or curvi-linear, and individual dendra interpenetrate with others. Usually one surface of these planar growths has a much finer mass of dendrites growing from, or attached to it; they do not extend for more than 2–3 mm from the parent dendron. In addition to the main dendra, which Russell (1929) reported as attaining, in one hand specimen, a length of 5 cm, there are abundant small 'clusters' of gold within the buff calcite not apparently attached to the dendritic gold. These are easily overlooked in hand specimen, but are revealed in the insoluble residue after solution of the carbonates, and in polished sections of untreated specimens. While palladium and the palladium arsenide–antimonides are present in the gold of the main dendra, the arsenide–antimonides are much more abundant in these small clusters of minute grains.

Electron probe analysis. Four of the Pd-rich grains have been analysed against pure metal standards, using a Cambridge Scientific Instrument Co. Microscan 9. Grains 1 and 2 are inclusions close to the surface of two gold grains: detailed optical study was not possible (see later) but they could be clearly seen to be anisotropic with the reflecting microscope. The other two grains (3 and 4) are discrete small euhedra on which optical work was possible, and have proved to be isomertieite.
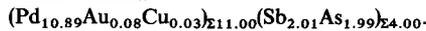
TABLE I. *Electron probe analyses of palladium arsenide–antimonides* (%)

	Grain 1	Grain 2	Mean of 1 and 2	Grain 3	Grain 4	Mean of 3 and 4	Type isomertieite
Pd	70.34	70.06	70.20	74.03	74.12	74.07	72.53
Au	0.84	1.57	1.21	0.54	1.56	1.05	0.37
Cu	0.05	0.07	0.06	0.20	0.07	0.13	1.08
Sb	24.37	24.98	24.68	15.72	15.59	15.65	14.61
As	3.67	3.69	3.68	9.52	9.54	9.53	10.42
Total	99.27	100.37	99.83	100.01	100.88	100.43	99.01

Grains 1 and 2 recalculated to an 11 atom formula

$$(Pd_{7.90}Au_{0.07}Cu_{0.01})_{\Sigma 7.98}(Sb_{2.43}As_{0.59})_{\Sigma 3.02}.$$
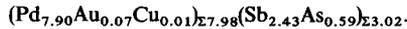
Grains 3 and 4 recalculated to a 15 atom formula

$$(Pd_{10.89}Au_{0.08}Cu_{0.03})_{\Sigma 11.00}(Sb_{2.01}As_{1.99})_{\Sigma 4.00}.$$

Type isomertieite (Itabira, Minas Gerais, Brazil) recalculated to 15 atoms

$$(Pd_{10.66}Cu_{0.27}Au_{0.03})_{\Sigma 10.96}(As_{2.17}Sb_{1.88})_{\Sigma 4.05}.$$

The analyses given in Table I show that grains 1 and 2 are very similar in composition. Plotting the mean of the two analyses (recalculated to atomic units) on a Pd–As–Sb diagram (fig. 2) puts it near the Sb end of the Pd_8As_3–Pd_8Sb_3 join, close to the mineral mertieite-II (the analysis in Cabri et al., 1975, is also shown in fig. 2); the qualitative optical observations do not conflict with this chemical similarity, and analysis 1 and 2 are therefore recalculated (Table I) to the same 11-atom formula associated with mertieite-II.

Hope's Nose Pd-rich grains 3 and 4 have a much higher As/Sb ratio than grains 1 and 2; they plot close to isomertieite (fig. 2) and the optical measure-

ments confirm this identity. Type isomertieite (Clark et al., 1974; the grain in their fig. 1) has been re-analysed and its composition (the mean of 14 spot analyses) is shown for comparison in Table I and fig. 2. Cabri (1980) has noted that isomertieite contains 120 atoms in its unit cell, leading to a probable 15-atom formula. The analyses of the Hope's Nose isomertieite are in very good agreement with the empirical formula $Pd_{11}Sb_2As_2$. Type isomertieite (from Itabira, Minas Gerais, Brazil) departs slightly from an As/Sb ratio of unity and it is worth noting also that it is optically very slightly anisotropic.

The native gold associated with these Pd phases at Hope's Nose also contains Pd in solid solution. Determinations of the Pd content of the zoned gold near the two isomertieite grains gave figures ranging from 0.95% in the 'bright yellow' gold and 5.25% in the pale grey zones. There does not appear to be any marked depletion of Pd in the gold around the inclusions, suggesting that the Pd phases do not form by exsolution of Pd from the gold.

Optical properties in reflected light. In polished section the grain-size of the gold is seen to be extremely variable (fig. 3): the individual crystallites of dendritic gold are appreciably larger—up to 1.5 mm long—than the grains comprising the gold clusters which vary (in plane section) from a few microns to 100 μm in size. In the larger dendra compositional zoning is common (fig. 4), palladian gold appearing pale grey with a slight lilac hue against the yellow purer gold. The boundaries of these zones are, however, not sharply defined (fig. 4) optically, and it is assumed that this reflects a gradual, rather than sharp change in composition.
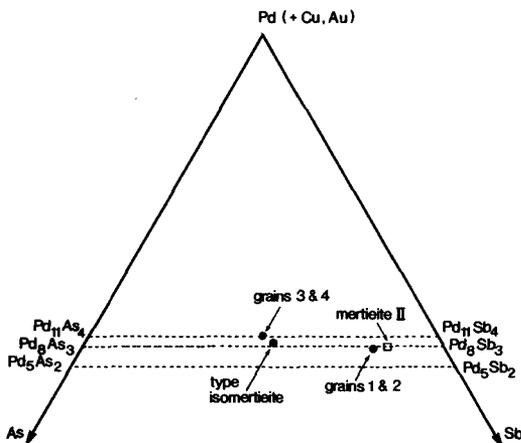

FIG. 2. Isomertieite and mertieite-II compositions plotted on a Pd–Sb–As diagram. The solid circles are the analyses given in Table I. The open square is mertieite II of Cabri et al., 1975
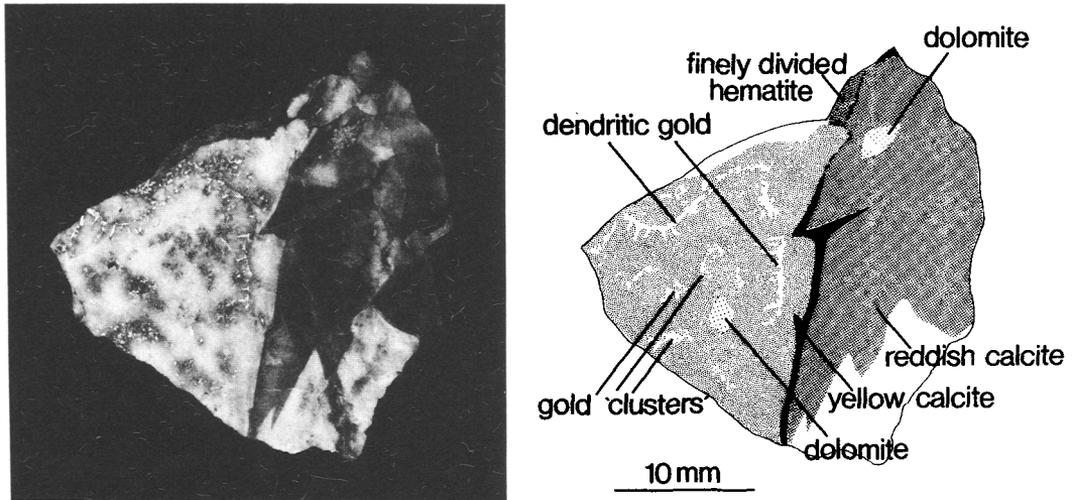
FIG. 3. The distribution of gold, calcite, and dolomite in polished section. The area of reddish calcite was darkened photographically to exaggerate the difference between it and the buff calcite.

Palladian gold is also found in the gold clusters, where it occurs as clearly defined patches within individual grains of gold (fig. 4) and as separate homogeneous grains (up to 30 μm). The outline of these clusters is nebulous, and their distribution is random within the buff calcite. The largest clusters are 2–3 mm across, and consist of dozens of discrete grains which fit like isolated pieces of a jig-saw into the calcite; their margins may be straight, curved, embayed, or carious.

Isomertieite, which appears a bluish grey against the gold, occurs as subhedra and euhedra encrusting the surface of the gold, as euhedra within calcite in embayments in the gold (fig. 4), and rarely as subhedral to anhedral grains within the gold. The largest grains are *c.* 15 μm in cross-section—the same size as the largest grains of mertieite-II with which they are often associated. Mertieite-II differs from isomertieite in being anisotropic, with rotation tints varying from dark blue-grey to dark brown, but in plane polarized light the two minerals cannot be distinguished with confidence as their colour is similar and mertieite-II is neither strongly bireflectant nor pleochroic. All the grains of mertieite-II (which are distributed in the same way as iso-mertieite) are either compound or are twinned; because of this the areas available in any one orientation were too small for the reliable measurement of reflectance.

An intriguing feature of the appearance of iso-mertieite and mertieite-II in these sections is that their colour is markedly different from that of the type specimens: mertieite-II is described

as creamy-yellowish (Desborough *et al.*, 1973) and isomertieite as pale yellow-white (Clark *et al.*, 1974). Grains of isomertieite and mertieite-II from Hope's Nose were isolated in polished section with a 10 μm diameter field diaphragm and re-examined; their colour and the colour of type isomertieite examined under the same optical conditions were the same, not bluish-grey, but a slightly creamy-white. This is discussed further in the following section.

Quantitative optical properties. Reflectance measurements in air and in Zeiss oil, DIN 58.884 ($N_D = 1.515$), were made from 400 to 700 nm at intervals of 10 nm on two grains of isomertieite from Hope's Nose (grains 3 and 4), and on one grain of the type specimen from Itabira, Minas Gerais, Brazil. The equipment used was a Zeiss MPM03 microscope photometer equipped with a motor-driven line-interference filter, bandwidth *c.* 12 nm, controlled by a Hewlett Packard 9830 desk-top computer. The air and oil objectives used were Zeiss × 40, NA 0.85, with the effective aperture angle adjusted to 20°—the minimum practicable angle to obtain sufficient light flux with a measuring field of *c.* 6 μm. A Zeiss 45° plane glass reflector, type UV, was used for all measurements. The specimens and WTiC standard, Zeiss no. 314, were levelled with a modified Lanham superstage. The measurements were made by specimen–standard interchange, with adjustment of the current supply to the Hamamatsu R928, type S-20 photo-cathode and signal strength from it, being made at each wavelength.
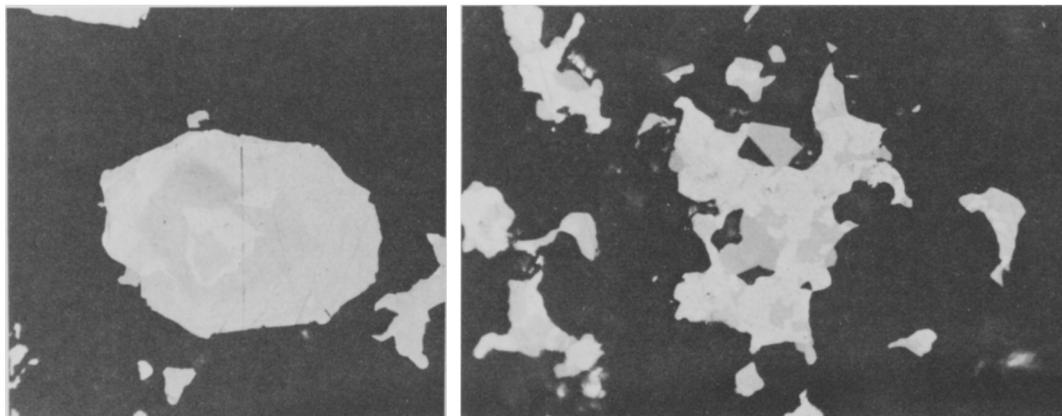
FIG. 4. Reflected light photomicrographs of isomertieite, mertieite-II, gold and palladian gold. (*Left*) Zoned dendritic gold; the large scratched grain (160 μm) across displays compositionally related colour zoning (in black and white, the darker the zone the higher the Pd content). (*Right*) A typical cluster of gold grains displaying angular, rounded, and embayed margins against calcite (black). Gold is white; palladian gold, occurring as patches within the purer gold, is grey; two grains of isomertieite—one, the angular subhedral grain (12 μm across) in the embayment at the top of the central gold grain, and the other, a small euhedral grain north of it, within calcite—are also grey. Mertieite-II and isomertieite (indistinguishable grey) occur in the centre of the grain in a cavity partly filled with calcite.

The type specimen was also measured with Zeiss ×16 objectives NA 0.35(air) and NA 0.4(oil), adjusted to effective aperture angles of about 10°, approximating to the optical conditions under which the original measurements were made (Clark *et al.*, 1974). The reflectances obtained differed by no more than ±0.3% absolute from the results obtained with the ×40 objectives in this investigation, but both sets were consistently 1% higher in air, and 2% higher in oil than the results obtained at the four COM recommended wavelengths by Clark *et al.* in 1974. Their data are, however, the mean values from measurements on six slightly anisotropic grains of isomertieite*: the only isotropic grain, and the one measured in this investigation, was not measured by them as it was smaller, intergrown with arsenopalladinite and hematite, and could not be measured under the same conditions as the other six. The full spectral data presented here may be taken as revised values for isomertieite.

The isomertieite reflectance values for grains 3 and 4 from Hope's Nose are virtually identical in air (Table II) and differ by less than 1% for most of the visible spectrum in oil. Although their spectral curves are indistinguishable in shape from those of the Itabira type specimen (fig. 4) they do differ in being a percent or so higher throughout the spectrum, a difference which may be related to

* Cabri *et al.* (1975) reported that a synthetic compound whose composition was close to that of isomertieite was strongly anisotropic in reflected light.

TABLE II. *Reflectance values for isomertieite*

λ_{nm}	Grain 3		Grain 4		Itabira	
	R	^{im}R	R	^{im}R	R	^{im}R
400	43.3	29.8	43.2	30.8	42.8	29.4
410	43.7	30.3	43.6	31.1	43.0	29.7
420	44.1	30.8	44.1	31.5	43.2	30.0
430	44.7	31.3	44.7	32.0	43.5	30.4
440	45.3	32.0	45.5	32.6	44.05	31.0
450	46.0	32.8	46.3	33.35	44.7	31.6
460	46.8	33.6	47.2	34.2	45.5	32.4
470	47.7	34.5	48.2	35.15	46.4	33.3
480	48.7	35.5	49.15	36.2	47.3	34.3
490	49.7	36.5	50.2	37.3	48.3	35.35
500	50.85	37.6	51.2	38.4	49.4	36.4
510	51.9	38.7	52.2	39.4	50.4	37.5
520	52.95	39.75	53.1	40.3	51.5	38.5
530	53.85	40.7	53.9	41.2	52.45	39.5
540	54.7	41.6	54.75	42.0	53.5	40.4
550	55.5	42.4	55.5	42.8	54.3	41.3
560	56.2	43.15	56.2	43.5	54.95	42.1
570	56.9	43.9	56.85	44.2	55.65	42.7
580	57.5	44.55	57.4	44.8	56.2	43.3
590	58.05	45.15	58.0	45.4	56.8	43.95
600	58.5	45.6	58.55	46.0	57.35	44.55
610	59.0	46.15	59.0	46.5	57.9	45.1
620	59.35	46.6	59.4	46.9	58.4	45.65
630	59.7	46.95	59.75	47.3	58.9	46.05
640	60.0	47.3	60.1	47.6	59.2	46.4
650	60.3	47.6	60.3	47.9	59.45	46.65
660	60.45	47.8	60.5	48.15	59.7	47.0
670	60.6	47.95	60.6	48.3	59.95	47.2
680	60.7	48.05	60.8	48.45	60.2	47.45
690	60.7	48.1	61.0	48.6	60.45	47.7
700	60.7	48.2	61.1	48.75	60.7	47.9

the slight difference in their composition (Table I). We have also plotted (fig. 4) Johan's data for isomertieite (reported in Cabri, 1981, p. 115, and presumably from Lac des Iles, Ontario). These are for air only, but are remarkably similar to the data obtained in this investigation for the type specimen.

The colour of isomertieite. The dispersion of the reflectances from c. 43% at 400 nm to c. 61% at 700 nm in air, and from c. 30% at 400 nm to c. 48% at 700 nm in oil indicates that isomertieite should appear yellowish, or yellowish-white. In practice, as has been noted, this was not the case for the Hope's Nose grains (although it was for Itabira isomertieite adjacent to a whiter arseno-palladinite). A possible explanation of their anomalous blue appearance is to be found in their association with gold and in the phenomenon described in colour terminology as simultaneous contrast. The colour values computed from the

reflectance spectra relative to the CIE illuminant C (6774K) for isomertieite and for gold (Table III) show their hues, or dominant wavelengths (λ_d) are nearly the same at 578 nm and 577 nm respectively; that is, they are yellow. The saturation of this hue, or excitation purity (p_e%), for isomertieite is quite high at c. 11%, which confirms that in isolation the mineral would appear yellowish. However, the excitation purity of gold is much higher at c. 40%. When these factors are allied to the much greater luminance of gold, c. 73%, compared with isomertieite, c. 55%, an explanation emerges. The c. 20% greater luminance of gold means that, although the two minerals have the same hue, isomertieite when adjacent to, or enclosed in gold, will appear much darker, and since the hue of gold is four times as saturated as that of isomertieite, the complement of its colour—blue (c. 475 nm), not yellow—is perceived. The same is true for mertieite-II.
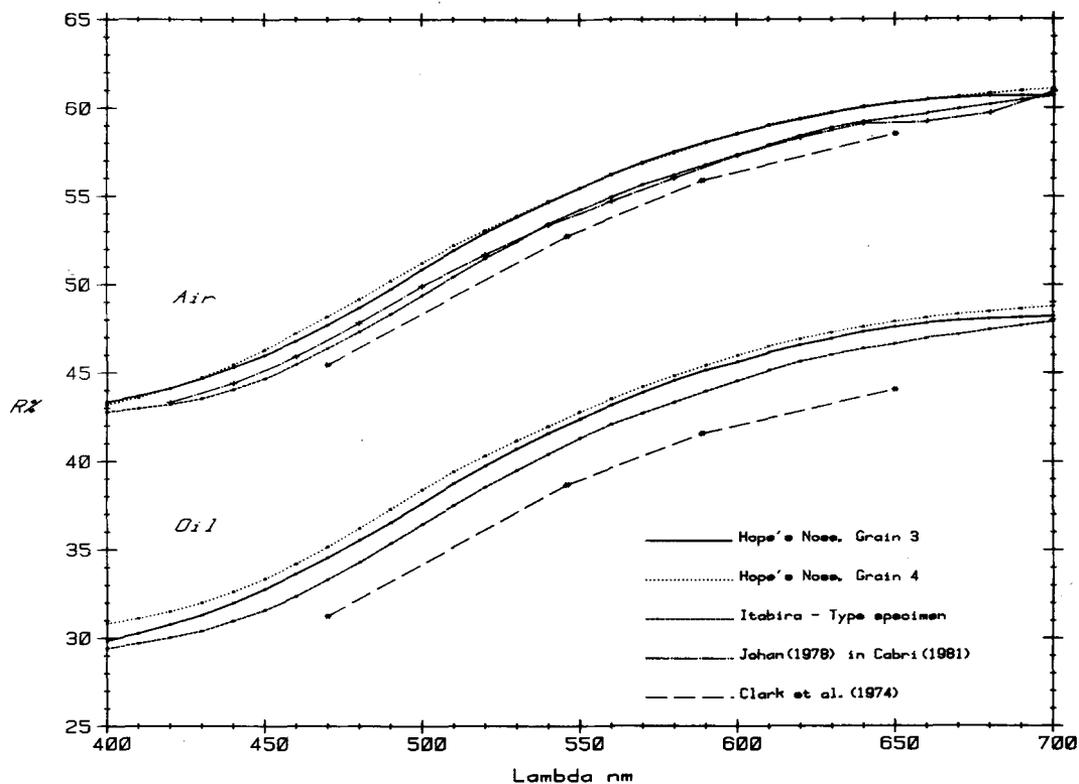

FIG. 5. Air and oil reflectance spectra for isomertieite. Curves from 400–700 nm are shown for the grains measured in this investigation. Johan's data, in air only, from 420–700 nm, are for isomertieite thought to be from Lac des Iles, Ontario, and the 4 COM wavelength data are mean values for six anisotropic grains of the type specimen measured in 1974.

TABLE III. *Colour values relative to CIE illuminant C for isomertieite and gold*

	Air					Oil				
	x	y	$Y\%$	λ_d	$p_e\%$	x	y	$Y\%$	λ_d	$P_e\%$
Grain 3	0.330	0.337	55.5	578	10.8	0.338	0.344	42.5	578	14.8
Grain 4	0.330	0.336	55.6	578	10.5	0.337	0.343	42.9	578	14.3
Itabira	0.331	0.337	54.3	578	11.2	0.339	0.344	41.4	578	15.2
Johan	0.330	0.336	54.2	578	10.6	—	—	—	—	—
Gold	0.384	0.391	72.7	577	39.8	0.396	0.408	63.1	577	47.6

x and y are the chromaticity co-ordinates, $Y\%$ the luminance, λ_d the dominant wavelength, and $p_e\%$ the excitation purity. Johan's data are from Cabri (1981). The gold data are from the Quantitative Data File (QDF) of the International Mineralogical Association—Commission on Ore Microscopy. Card 1.3200, reflectance data of P. R. Simpson *et al.*

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APPENDIX

Specimen preparation. Two specimens collected by Sir Arthur Russell (from the duplicate collection) and one specimen collected by B. V. Cooper were treated with dilute HCl to free the gold from the enclosing calcite. These, and three untreated specimens from B. V. Cooper were mounted in epoxy resin and polished with Engis machines. The abrasive used was diamond, of grain-size 6, 3, 1, and $\frac{1}{4}$-μm, on Hyprocel Pellon laps with a water-soluble lubricant. An attempt to use alumina as the final polishing stage was unsuccessful as the gold surfaces produced, though free of scratches, were left with a fine 'dusting' of black spots which could not be removed with any of the solvents used for cleaning; they were however removed with $\frac{1}{4}$μm diamond, used as the final polishing stage. This grade of diamond was also used to 'buff' the type specimen of isomertieite (BM 1934, 72) before its reflectance spectra were remeasured.