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PLATINUM AND PALLADIUM MINERALS FROM TWO PGE-RICH LOCALITIES IN THE SHETLAND OPHIOLITE COMPLEX

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ABSTRACT

The mineralogy of Pt- and Pd-bearing platinum-group minerals (PGM), which form a varied assemblage previously undescribed from other ophiolite complexes, is recorded from two localities in the Shetland ophiolite, Scotland. In order of abundance the minerals include sperrylite, mertieite or stibiopalladinite, Pt–Pd–Cu–Au alloys, hongshiite, genkinite and potarite. All six platinum-group elements (PGE) form major components of minerals in the Shetland ophiolite complex. The different PGM occur in association with each other. Textural evidence indicates that Ru- and Os-bearing PGM formed early and were followed by Ir, Pd-, Rh- and, finally, Pt-bearing PGM. The concentration of all six PGE could be magmatic, but much of the PGE mineralogy, except for laurite in the center of chromite grains, has been modified by subsequent processes. During PGM formation, the environment became more antimony- and arsenic-rich, which finally led to the formation of low-temperature alteration minerals.

Keywords: platinum-group minerals, Shetland, ophiolite, sperrylite, mertieite, stibiopalladinite, hongshiite, genkinite, potarite, Scotland.

SOMMAIRE

Les minéraux du groupe du platine enrichis en Pt et Pd, découverts à deux endroits dans le massif ophiolitique de Shetland, en Ecosse, définissent un assemblage varié jamais décrit auparavant dans de tels massifs. Dans l'ordre de leur abondance, ce sont sperrylite, mertieite ou stibiopalladinite, alliages de Pt–Pd–Cu–Au, hongshiite, genkinite et potarite. Les six éléments du groupe du platine constituent des composants majeurs de ces minéraux dans le massif de Shetland. Ils sont associés. Les textures indiquent que les minéraux porteurs de Ru et de Os ont été formés à un stade précoce, et ont été suivis par des minéraux porteurs de Ir, Pd et Rh, et, à la toute fin, Pt. La concentration des six éléments pourrait être magmatique, mais la grande partie des assemblages de minéraux observés aurait été modifiée par des processus tardifs, sauf dans le cas de la laurite piégée au centre des cristaux de chromite. Au cours de la formation de ces minéraux, le milieu s'est enrichi en antimoine et en arsenic, ce qui a éventuellement mené à la formation de minéraux d'altération stables à basses températures.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, Shetland, ophiolite, sperrylite, mertieite, stibiopalladinite, hongshiite, genkinite, potarite, Écosse.

INTRODUCTION

Traditionally, the PGM considered typical of ophiolite complexes are Os-, Ir- and Ru-bearing (Constantinides *et al.* 1979, Talkington 1981, Prichard *et al.* 1981, Legendre 1982, Augé 1985) and are associated with chromitites. Pt and Pd compounds may be more common; for example, sperrylite has been described from northern Tibet (Yu & Chou 1979), and one sperrylite grain has been tentatively identified from the Josephine peridotite (Stockman & Hlava 1984). Chang *et al.* (1973) have reported the presence of sperrylite and stibiopalladinite in ophiolites in northwestern China. Recently, a much more diverse assemblage of PGM, including Pt- and Pd-bearing minerals (Neary *et al.* 1984, Prichard *et al.* 1984, 1986, Gunn *et al.* 1985) has been discovered in the Shetland ophiolite complex. These PGM are reminiscent of those found in stratiform complexes such as the Bushveld and Stillwater.

The Shetland mafic and ultramafic complex, which lies in the northeast of Scotland, on the islands of Unst and Fetlar, was first described as an ophiolite complex by Garson & Plant (1973) and subsequently by Flinn *et al.* (1979), Gass *et al.* (1962) and Prichard (1985). The complex is of Caledonian origin and corresponds to the lower part of a typical ophiolite suite. The PGE are concentrated within the mantle sequence. They occur in chromite-rich samples located in two separate lenses of dunite within harzburgite at Cliff and Harold's Grave (Gass *et al.* 1982). The first aim of this paper is to describe these Pt- and Pd-bearing minerals, all of which are unusual in an ophiolite complex. The mineralogy of the Os-, Ir-, Ru- and Rh-bearing PGM from Cliff and Harold's Grave are described elsewhere (Tarkian & Prichard 1987). Secondly, the relative sequence of formation of the PGM is examined, and their genesis discussed.

THE PGM ASSEMBLAGE AT CLIFF AND HAROLD'S GRAVE

The PGM species and relative abundance at Cliff and Harold's Grave are summarized in Table 1. Both localities contain PGM in which all six PGE occur

TABLE 1. FREQUENCY AND SIZE OF PGM FROM CLIFF AND HAROLD'S GRAVE

	Cliff	Harold's Grave	No. of grains measured	Ave. Size µm	Standard deviation of average size
Pt					
Sperrylite	Most abundant		37	11 x 4	± 8.4 x ± 2.9
Genkinite	-	2 grains	2	8 x 2 and 12 x 4	
Hongshiite	1 grain	1 grain	2	6 x 2 and 5 x 4	
Pt-Pd-Cu alloy	-	1 grain	1	6 x 5	
Pt-Pd-Au-Cu	4 grains	-	4	2 x 2	± 1.6 x ± 1.0
Pd					
Mertieite or stibiopalladinite	Abundant	2 grains	26	9 x 4	± 7.8 x ± 1.4
Potarite	1 grain	-	1	3 x 2	
Au Pd alloy	5 grains	-	5	3 x 3	± 0.5 x ± 0.5
Rh					
Hollingworthite	Moderately common	Moderately common	7	11 x 7	± 8.2 x ± 2.7
Rh, Sb, S	1 grain	2 grains	3	4 x 3, 4 x 2 and 3 x 2	
Rh, Ni, Sb	-	1 grain	1	6 x 2	
Ir					
Irarsite	Moderately common	Common	9	27 x 10	± 33 x ± 11.5
Ir, Sb, S	-	1 grain	1	6 x 6	
Ru					
Laurite	Rare	Common	33	13 x 10	± 14.1 x ± 15.5
Ruthenian pentlandite	Common	Common	4	30 x 10	± 15.6 x ± 4.5
Os					
Native	1 grain	Common	50	3 x 2	± 1.5 x ± 0.5

as major components. However, sperrylite is the most abundant PGM at Cliff; it has not been found at Harold's Grave. Similarly, mertieite or stibiopalladinite is the second most abundant PGM at Cliff but has been encountered at Harold's Grave only as two grains measuring 2 by 3 µm. The average maximum and minimum diameters and standard deviations, of the PGM, as exposed on the polished thin sections, are given in Table 1. The range of sizes is quite variable. For example, sperrylite ranges from 2 × 1 µm to 85 × 45 µm, and laurite from 1 × 1 µm to 250 × 200 µm. In contrast, the abundant grains of native osmium have been observed not to have dimensions greater than 5 µm. It is not always possible to accurately measure all PGM, as many are present in irregular shapes and contain inclusions. Hongshiite (Fig. 3) may be present as a single relatively large crystal that encloses a Ni–Cu alloy.

TECHNIQUES

The PGM were studied using both reflected- and transmitted-light microscopy. Analyses of the PGM were obtained using a Cameca Camebax Microbeam CD wavelength-dispersion electron microprobe at the University of Hamburg. The analytical conditions were 15 kV and 15 nA. Pure metals, FeS_2, FeAsS, as well as synthetic PbSb and PbBiTe, were used as standards. Corrections were applied using the computer program PAP. It was possible to analyze quantitatively minerals with a diameter of greater than 5 µm.

Many of the PGM are less than 5 µm in diameter and commonly form composite grains with abundant inclusions of different PGM, so that it was not always possible to obtain quantitative analytical data. In these cases, single-element scans have been used to demonstrate the complexity of the composite PGM and to provide qualitative data. A back-scattered electron image defines the surface outline of the different PGM in such composite grains. The outline of the single-element scan does not always exactly match the outline of the mineral of which it forms a part: extension of the PGM below the surface of the section, beneath surrounding minerals, or the presence of hidden PGM also at a shallow depth within the composite grain may contribute an additional signal to the scan.

In the following section we describe the Pt- and Pd-bearing PGM and give compositions. For the rare PGM, their characteristics are described using reflected-light microscopy; where no quantitative analysis was possible, records of single-element scans are used.

MINERALOGY

Sperrylite, $PtAs_2$

The Shetland sperrylite is anhedral (Fig. 1c), but some grains have adjacent euhedral crystal edges meeting at 120°. Crystals commonly show cleavage in two directions at 120° (Fig. 1a). Sperrylite intergrown with chlorite has a zig-zag shape (Fig. 1b). The composition of the sperrylite is rather constant; typical compositions are given in Table 2.

Genkinite, $(Pt,Pd)_4Sb_3$

Genkinite has been located in two chromite-rich rocks from Harold's Grave. In one it forms part of a composite cluster of minerals (Fig. 2), whereas in the other it is situated in a cluster of PGM but is isolated from them by silicate matrix. In both cases the genkinite forms irregular crystals with dimensions of approximately 12 × 4 µm and 8 × 2 µm. The optical properties of the genkinite are given in Table 3. A typical composition is Pt 41.86, Rh 8.23, Pd 7.01, Ni 3.41, Sb 38.96, total 99.47 wt.%, giving a formula of $(Pt_{2.04}Rh_{0.76}Pd_{0.62}Ni_{0.55})_{\Sigma 3.97}Sb_{3.03}$. Genkinite has been described only three times previously (Tarkian & Stumpfl 1975, Cabri *et al.* 1977, 1981); this paper reports the fourth occurrence, in this case from a chromite-rich lithology from an ophiolitic environment.

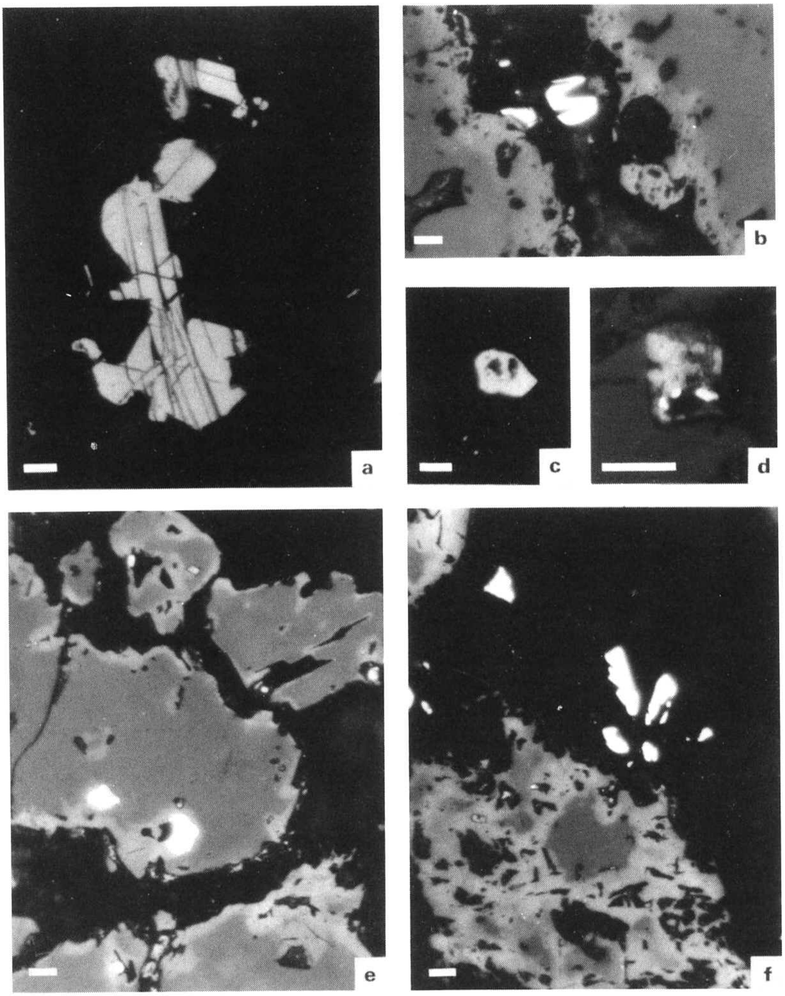

FIG. 1. Reflected-light photomicrographs of Pt- and Pd-bearing minerals from Cliff. (a and c) Sperrylite (pale grey) in a silicate matrix (dark grey). (b) Sperrylite (white) in a silicate vein (dark grey) between two chromite grains (pale grey). (d) Pt–Pd–Cu–Au alloys (white) associated with native copper (pale grey) surrounded by chromite (dark grey) (see Fig. 4). (e) Mertieite or stibiopalladinite (white) in the rim of a chromite grain (pale grey) and associated with pentlandite (white). Silicate matrix appears dark grey. (f) Mertieite or stibiopalladinite (white) in the silicate matrix (dark grey) near a chromite grain (pale grey). Scale bar represents 10 μm.

Hongshiite, PtCu

A Pt–Cu phase that occurs adjacent to genkinite (Fig. 2) and has an irregular form is also present as a network of branches that enclose a Ni–Cu alloy adjacent to a sperrylite crystal (Fig. 3). The composition of the Pt–Cu phase is given by scans only, as it is too small (6×2 μm) for quantitative analysis, but no other elements were detected. The mineral is likely to be hongshiite. Its optical properties, in agreement with those reported by Cabri (1981), are given in Table 3. Hongshiite previously had been described only from Hung, China (Peng *et al.* 1978).

Pt-rich alloys

An irregular grain of a Pt–Pd–Cu alloy lies adjacent to genkinite (Fig. 2) and in contact with irarsite and hollingworthite. The optical properties are given in Table 3. The mineral has a rough, chequered surface, possibly suggesting a fine intergrowth. The grain has an approximate diameter of 5 μm, and the

TABLE 2. MICROPROBE COMPOSITIONS OF SPERRYLITE

	1	2	3	4
Pt	55.79	55.69	55.69	55.60
As	43.79	41.79	42.42	41.82
Fe	0.27	0.12	0.46	0.11
Sb	0.91	1.99	1.96	2.92
total	100.76	99.59	100.53	100.45

1. $(Pt_{0.98}Fe_{0.01})$ Σ=0.99 $(As_{2.00}Sb_{<0.01})$ Σ=2.00

2. $(Pt_{0.99}Fe_{0.01})$ Σ=1.00 $(As_{1.94}Sb_{0.06})$ Σ=2.00

3. $(Pt_{0.99}Fe_{0.03})$ Σ=1.02 $(As_{1.94}Sb_{0.06})$ Σ=2.00

4. (Pt0.98Fe0.01) Σ=0.99 (As1.93Sb0.08) Σ=2.01

elements present are given qualitatively by scans (Fig. 2). An analysis gave Pt 63.00, Pd 16.86, Cu 3.21, Sb 0.56, total 83.63 wt.%.

Figures 1d and 4 show four small (less than 5 μm) irregular grains of a Pt–Pd–Au–Cu alloy clustered around an undefined nickel arsenide and associated with native copper. Optical properties of the alloys are given in Table 3. No occurrence of such alloys is known other than in Shetland (Prichard *et al.* 1986).

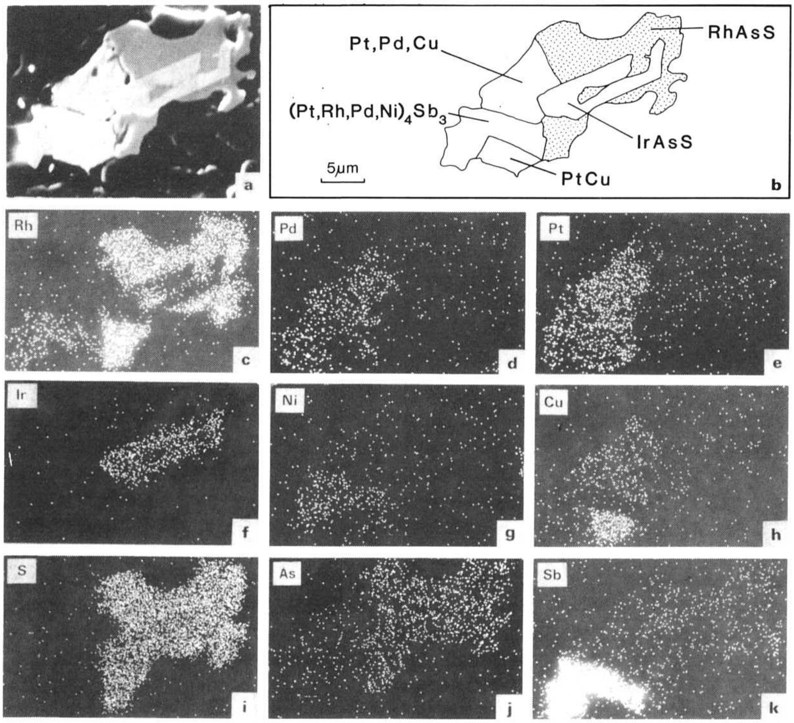

FIG. 2. (a) Back-scattered electron image. (b) Mineral-location map. (c-k) Single-element scans for Rh, Pd, Pt, Ir, Ni, Cu, S, As and Sb, respectively. The PGM in this composite grain from Harold's Grave are irarsite (IrAsS), hollingworthite (RhAsS), hongshiite (PtCu), genkinite [$(Pt, Rh, Pd, Ni)_4Sb_3$], and a Pt-Pd-Cu alloy.

Mertieite or stibiopalladinite

These crystals are subhedral, irregular (Fig. 1e), elongate and commonly lath-shaped. Some crystal edges meet at 120° (Fig. 1f). Two grains of an intergrowth of Pd antimonide and a nickel telluride have been found in the interstitial silicate matrix of the same polished section of material from Cliff. One grain is rhomb-shaped and the other, surrounded by millerite, is tabular. Although apparently optically homogeneous, higher-magnification scans show a fine intergrowth of crystals. The lamellae of the intergrowth are approximately 1 μm wide, but larger areas of each member of the intergrowth are developed locally (Fig. 5). Some typical compositions of these minerals are given in Table 4.

Stibiopalladinite and mertieite I and II can be distinguished from one another only by X-ray-diffraction data (Cabri 1981), as there are no significant optical differences among them. No special reflectance data have yet been given for mertieite I, and the reflectance curves of mertieite II and stibiopalladinite are very similar, as is the microhardness. All three minerals are anisotropic, and there are no differences in the extinction color of the anisotropism. Mertieite I is not fully characterized by crystal-structure analysis but may be pseudohexagonal. Mertieite II is rhombohedral, and stibiopalladinite is hexagonal. According to Cabri (1981), mertieite I may have the composition $(Pd,Cu)_{5+x}(Sb,As)_{2-x}$ or $(Pd,Cu)_{11}(Sb,As)_4$; mertieite II may have the composition $(Pd,Cu)_8(Sb,As)_3$, and stibiopalladinite may have the composition $(Pd,Cu)_{5+x}(Sb,As)_{2-x}$ or $(Pd,Cu)_{8+x}(Sb,As)_{3+x}$, where $x = 0.05$ for all the compositions.

The compositions of Pd–Sb phases from Shetland, calculated on the basis of each of these ideal formulae, are given in Table 4. Composition 6 (Table 4) shows a lower ratio of metal to Sb than the others, but mertieite I, mertieite II and stibiopalladinite can-

TABLE 3. OPTICAL PROPERTIES FOR THE MORE UNUSUAL Pt- AND Pd-BEARING PGM FROM SHETLAND

Name	Composition	Color	Reflectance	Bireflection	Anisotropy	Hardness
Genkinite	$(Pt,Rh,Pd,Ni)_4Sb_3$	pale brown	50%	nd	strongly anisotropic grey to brown	Harder than hongshiite but softer than the Pt-Pd-Cu alloy
Hongshiite	PtCu	creamy yellow	60%	nd	anisotropic grey to greenish grey	softer than genkinite
Alloy	Pt-Pd-Cu	dark brownish	<40%	weak	anisotropic grey to creamy yellow	harder than genkinite but softer than hollingworthite
Alloy	Pt-Pd-Au-Cu	creamy yellow	50%	no data available	anisotropic no color data available	

Note: Reflectance was estimated in white light (air). Color and anisotropism were recorded using oil.
nd = not detectable

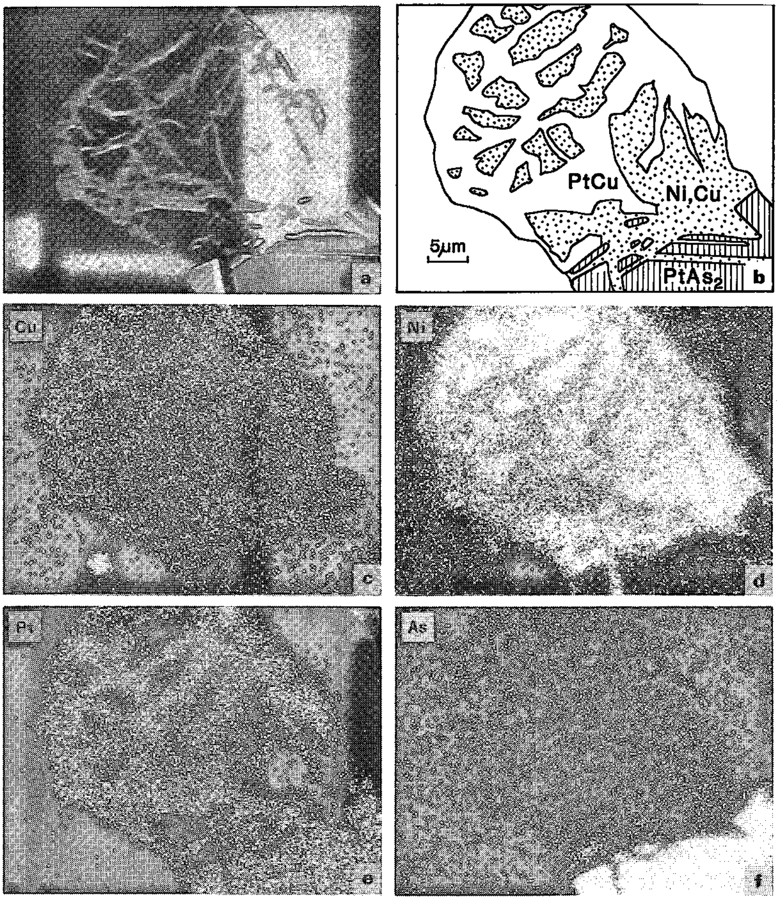

FIG. 3. (a) Back-scattered electron image. (b) Mineral-location map. (c-f) Single-element scans for Cu, Ni, Pt and As, respectively. The minerals in this composite grain from Cliff are sperrylite ($PtAs_2$), hongshiite (PtCu), and a Ni–Cu alloy. The single-element scans define this composite mineral grain, cited and shown in plate 9 in Prichard *et al.* (1986).

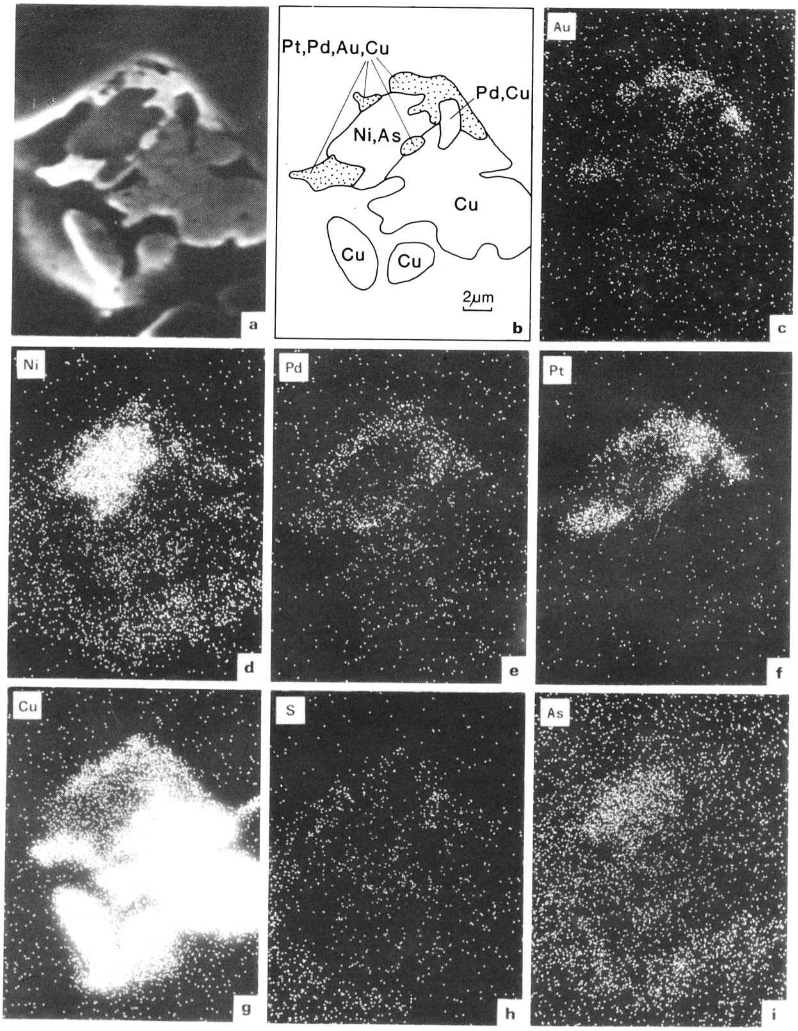

FIG. 4. (a) Back-scattered electron image. (b) Mineral-location map. (c-i) Single-element scans for Au, Ni, Pd, Pt, Cu, S, and As, respectively. The Pt–Pd–Au–Cu alloys from Cliff are associated with native copper and a nickel arsenide. The single-element scans define this composite mineral grain, cited and shown in plate 12 in Prichard *et al.* (1986).

not be distinguished by the differences in chemical composition that were found.

Potarite, PdHg

One grain of potarite from Cliff has been qualitatively analyzed (Prichard *et al.* 1986).

Pd–Au alloys

Small (3 × 3 μm) anhedral grains of Pd-bearing gold have been qualitatively identified from Cliff. Most grains are located in chromite rims, but some are in the interstitial silicate or are associated with pentlandite.

TEXTURAL RELATIONSHIPS OF THE PGM

PGM in relation to their host minerals

All the PGM studied in this paper are from chromite-rich samples, containing 50 to 90% chrome spinel. The interstitial silicates are secondary serpen-

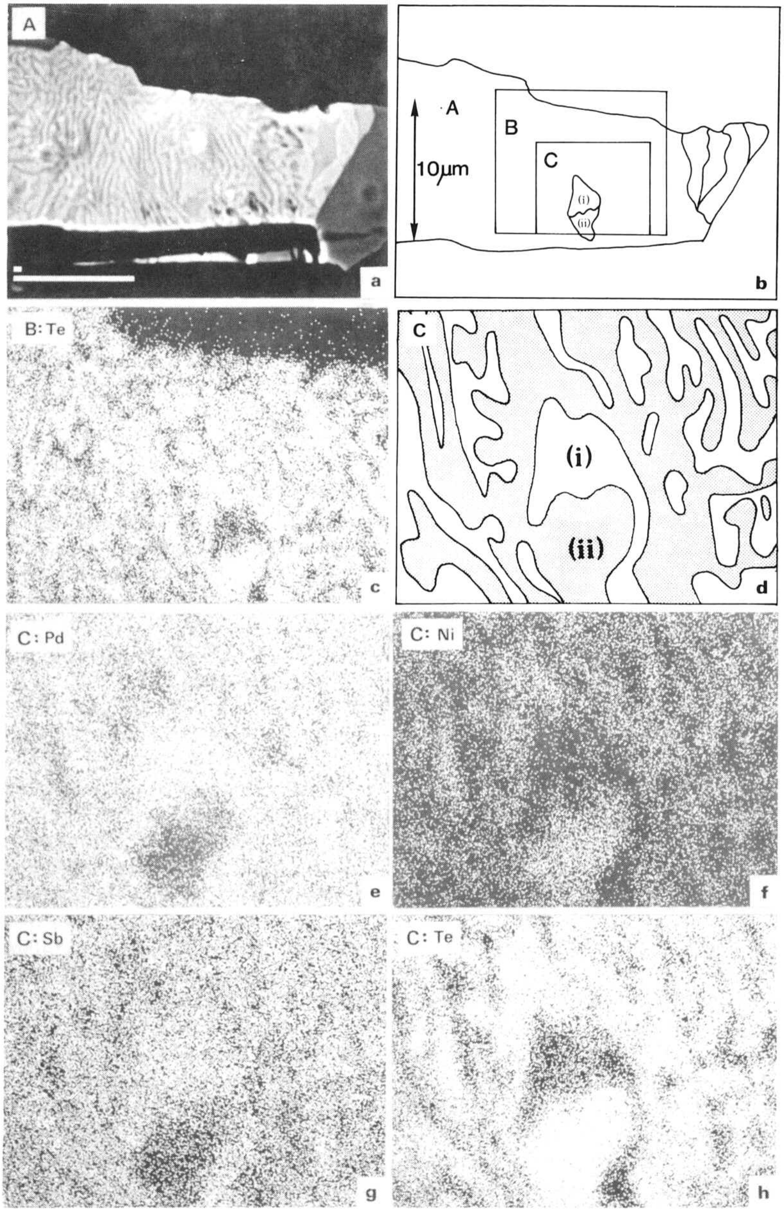

FIG. 5. (a) Back-scattered electron-microscope image. (b) Location-map showing areas A, B and C. (e-h) Single-element scans for Pd, Ni, Sb, and Te, respectively, in area C. This grain from Cliff consists of an intergrowth of a palladium antimonide and a nickel telluride, marked (i) and (ii), respectively.

tine, chlorite associated with magnetite, and nickel carbonate (Prichard *et al.* 1987). The PGM occur in the center and 'spongy' rim of chromite grains and in the silicate matrix interstitial to the chromite. A schematic diagram of the textural settings of the PGM is shown in Figure 6. The only PGM found entirely enclosed within the center of chromite grains is an Os-rich laurite (RuS_2). Os-free laurite, with native osmium inclusions and irarsite, occurs in the rim of chromite grains. Euhedral native osmium also

TABLE 4. MICROPROBE ANALYSES OF MERTIEITE OR STIBIOPALLADINITE FROM CLIFF

	1	2	3	4	5	6
Pd	66.31	67.68	66.57	67.55	67.02	65.61
Cu	2.79	1.71	2.74	1.75	2.84	3.26
Pt	0.48	0.78	0.61	0.60	0.42	0.49
Ni	-	-	-	-	-	-
Sb	28.34	29.27	29.05	27.24	30.47	31.21
As	0.60	0.32	0.36	1.72	-	-
total	98.52	99.76	99.33	98.86	100.75	100.57

	Pd_5Sb_2 (ideal) Pd:Sb = 30:12	**$Pd_{11}Sb_4$ (ideal) Pd:Sb = 33:12**	**Pd_8Sb_3 (ideal) Pd:Sb = 32:12**
1.	$(Pd_{4.79}Cu_{0.34}Pt_{0.02})_{\Sigma=5.15}(Sb_{1.79}As_{0.06})_{\Sigma=1.85}$	$(Pd_{10.27}Cu_{0.72}Pt_{0.04})_{\Sigma=11.03}(Sb_{3.84}As_{0.13})_{\Sigma=3.97}$	$(Pd_{7.53}Cu_{0.53}Pt_{0.03})_{\Sigma=8.09}(Sb_{2.81}As_{0.10})_{\Sigma=2.91}$
2.	$(Pd_{4.89}Cu_{0.21}Pt_{0.03})_{\Sigma=5.13}(Sb_{1.84}As_{0.03})_{\Sigma=1.87}$	$(Pd_{10.47}Cu_{0.44}Pt_{0.07})_{\Sigma=10.98}(Sb_{3.95}As_{0.07})_{\Sigma=4.02}$	$(Pd_{7.68}Cu_{0.32}Pt_{0.05})_{\Sigma=8.05}(Sb_{2.90}As_{0.05})_{\Sigma=2.95}$
3.	$(Pd_{4.79}Cu_{0.33}Pt_{0.02})_{\Sigma=5.14}(Sb_{1.82}As_{0.04})_{\Sigma=1.86}$	$(Pd_{10.25}Cu_{0.71}Pt_{0.05})_{\Sigma=11.01}(Sb_{3.91}As_{0.08})_{\Sigma=3.99}$	$(Pd_{7.52}Cu_{0.52}Pt_{0.03})_{\Sigma=8.07}(Sb_{2.87}As_{0.06})_{\Sigma=2.93}$
4.	$(Pd_{4.87}Cu_{0.21}Pt_{0.02})_{\Sigma=5.10}(Sb_{1.72}As_{0.18})_{\Sigma=1.90}$	$(Pd_{10.44}Cu_{0.45}Pt_{0.05})_{\Sigma=10.94}(Sb_{3.68}As_{0.38})_{\Sigma=4.06}$	$(Pd_{7.66}Cu_{0.33}Pt_{0.04})_{\Sigma=8.03}(Sb_{2.70}As_{0.27})_{\Sigma=2.97}$
5.	$(Pd_{4.75}Cu_{0.34}Pt_{0.01})_{\Sigma=5.10}Sb_{1.90}$	$(Pd_{10.19}Cu_{0.72}Pt_{0.04})_{\Sigma=10.95}Sb_{4.05}$	$(Pd_{7.47}Cu_{0.53}Pt_{0.03})_{\Sigma=8.03}Sb_{2.97}$
6.	$(Pd_{4.65}Cu_{0.39}Pt_{0.02})_{\Sigma=5.06}Sb_{1.94}$	$(Pd_{9.98}Cu_{0.84}Pt_{0.04})_{\Sigma=10.86}Sb_{4.15}$	$(Pd_{7.32}Cu_{0.61}Pt_{0.03})_{\Sigma=7.96}Sb_{3.04}$

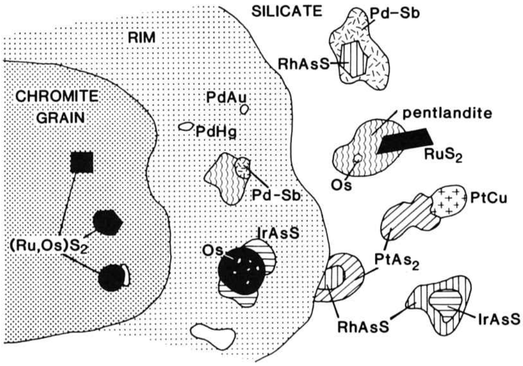

FIG. 6. Schematic diagram of the PGM and their textural positions in relation to chromite grains.

is present, enclosed by ruthenian pentlandite, which is located in the silicate matrix in association with nickel carbonate. Pure laurite and irarsite also occur in the interstitial silicate matrix; the irarsite is commonly rimmed by hollingworthite (RhAsS). No Rh-bearing minerals have been observed in the center or rim of chromite grains (Tarkian & Prichard 1987).

Most Pd-bearing PGM occur in the altered silicate matrix, but some are located in chromite rims. Generally, the mertieite or stibiopalladinite is situated in chlorite or serpentine between chromite grain, and only rarely is it in chromite rims, where it is associated with silicate inclusions and occasionally pentlandite (Figs. 1e, f, 6). Potarite also is found within these rims, as are the majority of the Pd-bearing gold grains.

All sperrylite is associated with the interstitial silicates between chromite grains. Only rarely is sperrylite attached to the edge of the chromite grains, and none has been found within the center or rim of chromite grains. Nearly all the sperrylite is surrounded by chlorite, and some is intergrown with chlorite to form zig-zag crystals. Some sperrylite is associated with nickel carbonate, and one sperrylite grain is enclosed by mesh-textured serpentine. Genkinite and hongshiite also occur in the interstitial silicate matrix.

Textures of the composite PGM grains

PGM commonly form composite grains, examples of which are illustrated in Figures 2 and 3. In Tarkian & Prichard (1987), the composite Ru-, Ir-, Os- and Rh-bearing PGM are discussed in detail, but a general summary is included here to enable the genetic sequence of formation of the Pt- and Pd-bearing PGM to be discussed. Figure 7 is a diagrammatic representation of the textural relationships of the PGM at Cliff and Harold's Grave.

In general, PGM sulfides and antimonides are enclosed by arsenides where they are found in association. For example, laurite (RuS_2), commonly containing abundant small (2–3 μm) inclusions of native osmium, is commonly intergrown and rimmed by irarsite (IrAsS) (Fig. 8). Irarsite also contains a number of antimony-rich phases including Rh–Sb–S, Ir–Sb–S, Rh–Ni–Sb, small grains of a Pd antimonide and breithauptite (NiSb). Another example of an Sb-bearing phase enclosed by an As-rich phase is a Rh–Sb–S inclusion, which is surrounded by sperrylite. The majority of the Pd forms Pd antimonide, which is mostly isolated from the other phases but is found within and adjacent to irarsite and partly enclosed by sperrylite. In one case the Pd antimonide encloses hollingworthite, which has a pure end-member composition devoid of Pt. In the reverse case, where hollingworthite encloses Pd antimonide, the hollingworthite is Pt-bearing (Tarkian & Prichard 1987). Hollingworthite commonly rims irarsite (Fig. 2) and is itself enclosed by sperrylite, the latter being the most arsenic-rich phase. Genkinite, hongshiite, and the Pt–Pd–Cu alloy are all found in association with other Pt-bearing PGM.

GENESIS OF THE PGM

These textural relationships suggest constraints on the order of PGM formation and changes in availability of PGE and arsenic. If chromite crystallization preceded that of the primary igneous interstitial silicates, then the PGM inclusions in chromite grains formed prior to those in the silicate matrix. PGM in the spongy rim of chromite grains, and commonly associated with silicate inclusions, probably formed at an intermediate stage. On this basis the earliest mineral to form was Os-rich laurite, which occurs as isolated crystals in chromite grains (Tarkian & Prichard 1987). Irarsite inclusions associated with silicates in chromite rims represent increasing availability of arsenic. Antimony-rich inclusions that occur within As-rich phases such as irarsite and sperrylite may indicate increasing availability of As in place of Sb.

The presence of Pd-rich PGM in chromite rims and interstitial silicate, and the restriction of PGM containing Pt as a major PGE, to the silicate matrix, suggest that Pd preceded Pt availability for PGM formation. Similarly, Rh-bearing PGM are found only in the silicate matrix. Hollingworthite commonly rims irarsite grains in the silicate matrix, but no such rims are found around irarsite within chromite rims. As for Pt, this relationship is interpreted to reflect increasing availability of Rh after the formation of chromite, Ru-, Os- and Ir-bearing PGM, and early Pd-bearing PGM within chromite rims. There is also evidence from the hollingworthite compositions that Pt became available later than Rh. Hollingworthite is Pt-free where surrounded by Pd antimonide, suggesting formation prior to the availability of Pt. However, the hollingworthite is Pt-bearing where it surrounds Pd antimonide and also where it is surrounded by sperrylite.

The last PGM to form are the Pt- and Pd-rich alloys. For example, hongshiite occurs adjacent to sperrylite and appears to be an alteration product of the sperrylite, which breaks down along cleavages (Fig 3). This hongshiite is adjacent to a late cross-cutting silicate vein that may be associated with a late phase of hydrothermal alteration involving the removal of As. Hongshiite has been described as an alteration product by Cabri (1981), who suggested that it replaced cooperite (PtS). The Pt–Pd–Au–Cu alloy (Fig. 4) also may be a late phase, as it is adjacent to native copper, probably a product of low-temperature alteration. Stockman & Hlava (1984) suggested that the PGM may be reduced in the natural environment, and they cited alteration of laurite to a Ru-rich alloy. Shetland Ru-bearing pentlandite has been found to surround laurite and euhedral native osmium. This pentlandite is associated with nickel carbonate and contains Ru that may have been released from the laurite during low-temperature alteration. This process may also have recrystallized native osmium into euhedral crystals within the Ru-bearing pentlandite.

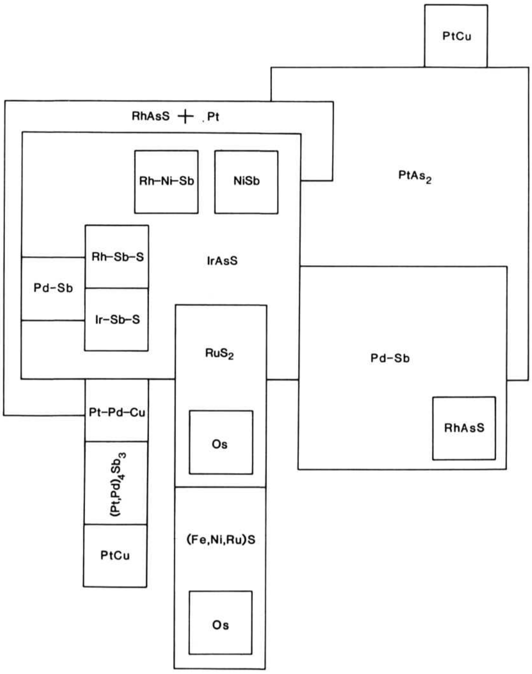

FIG. 7. Schematic diagram showing the textural relationships of PGM within composite grains. Only minerals found in mutual contact are considered, the size of the area representing a particular PGM giving an indication of its relative abundance; *e.g.*, the square representing Os is enclosed by RuS$_2$, indicating that inclusions of native osmium occur within laurite. The minerals represented are: native osmium, laurite, rhodium nickel antimonide, rhodium antimony sulfide, iridium antimony sulfide, breithauptite, irarsite, Pt-free hollingworthite, Pt-rich hollingworthite, mertieite or stibiopalladinite, sperrylite, Pt–Pd–Cu alloys, genkinite, hongshiite and ruthenian pentlandite.

DISCUSSION

Primary igneous silicate minerals are absent in the chromite-rich Shetland samples examined in this study. It is not possible, therefore, to compare directly the PGM in primary igneous assemblages with those in altered silicate lithologies in order to determine whether the present PGM are a modified assemblage of primary minerals or the result of PGE

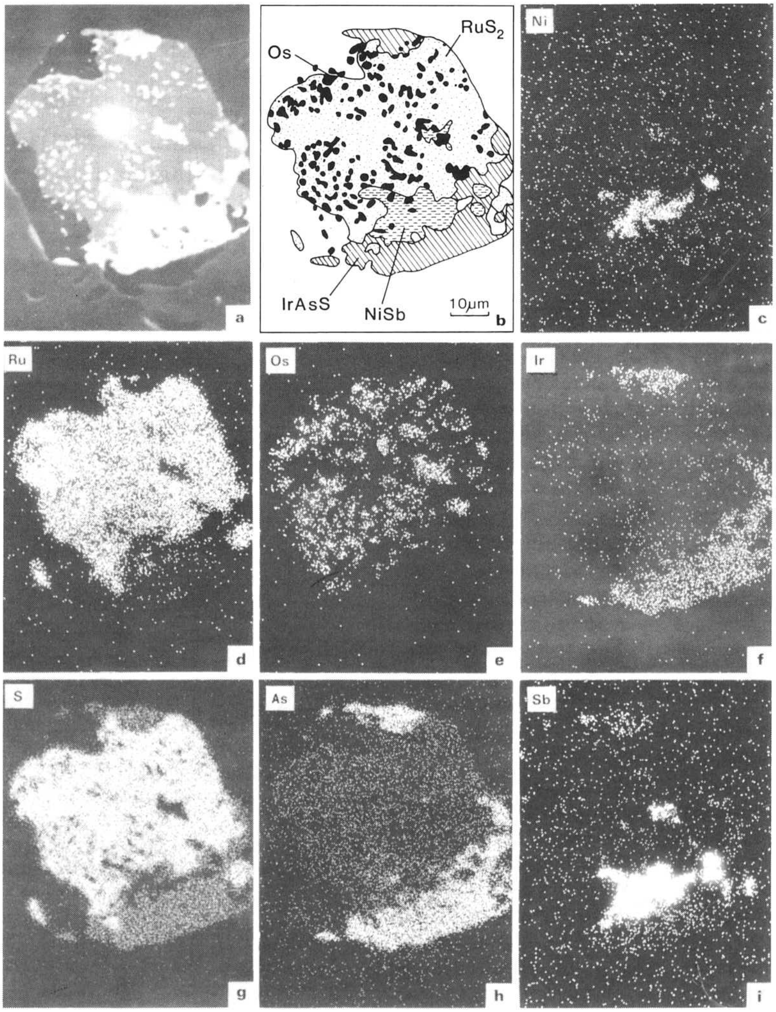

FIG. 8. (a) Back-scattered electron image. (b) Mineral-location map. (c-i) Single-element scans for Ni, Ru, Os, Ir, S, As and Sb. The minerals in this composite grain from Harold's Grave are laurite, irarsite, native osmium and breithauptite.

addition by secondary processes of enrichment. At Cliff, however, PGM have been found in dunite containing unaltered olivine (Prichard & Lord 1988). The PGM-bearing chromite-rich samples from both Cliff and Harold's Grave occur as chromite-rich lenses surrounded by a dunite envelope within harzburgite. These lenses are typical of ophiolite complexes and are thought to form by crystallization from diapirs of basaltic magma that rise through the mantle to feed the overlying crustal magma-chamber (Gass & Smewing 1981). The association of PGM with the dunite envelope and with the chromite-rich samples suggests a primary magmatic origin. The textural relationships between the PGM and their hosts indicate that laurite crystallization preceded or was contemporary with chromite formation, whereas all Pt-bearing minerals are in the interstitial silicate matrix and postdate chromite. Assuming a magmatic origin, the trend may represent a fractionation sequence.

Superimposed on the effects of igneous processes are those of lower-temperature processes of alteration, which may have modified and redistributed the PGM. For example, chlorite and sperrylite, which occur interstitially to the chromite grains, are intergrown. The sperrylite forms an unusual zig-zag-shaped crystal among the chlorite laths, suggesting that the sperrylite formed at the same time or postdates the chlorite. As and Sb could have been introduced with late magmatic fluids, or by some later, lower-temperature process; nevertheless the chlorite–sperrylite association suggests the presence of an As-rich environment during or after the low-temperature hydrous conditions of chlorite formation. Work in progress on both the associated Ni- and Cu-bearing minerals and the variably altered chromite-rich host lithologies may enable the processes of PGM formation to be determined more exactly.

PGM associated with serpentinization include the Pt–Pd–Au–Cu alloys, which occur adjacent to other PGM, but within late serpentinite veins that cut composite PGM. These alloys contain no As or Sb (unlike the adjacent PGM), suggesting that this process of PGM formation, associated with vein formation, led to removal of the As and Sb. This depletion is illustrated for As in the example where chlorite, interstitial to chromite, is cut by a serpentinite vein; sperrylite occurs in the chlorite, whereas the adjacent hongshiite is in the serpentinite vein. In the case of Sb, geversite is surrounded by native Pt; possibly the geversite was altered to native Pt (Prichard *et al.* 1987). Although the platinum-group mineralogy has changed during low-temperature alteration, the PGE apparently remained *in situ,* suggesting that there is little redistribution of the PGE within the host lithology during the process of serpentinization.

CONCLUSIONS

Reports of Pt- and Pd-bearing PGM in ophiolite complexes are rare. Sperrylite is the most common PGM at Cliff, and mertieite or stibiopalladinite is the most abundant Pd-bearing PGM in Shetland; these minerals are traditionally thought to be uncommon in ophiolite complexes. The other Pt- and Pd-bearing PGM described here, including genkinite, hongshiite and potarite, apparently are new to ophiolite complexes. The Pt–Pd–Cu and Pt–Pd–Au–Cu alloys are thought to be new minerals. The abundance and variety of PGM described here suggest that Pt- and Pd-bearing minerals may be more common in ophiolite complexes than previously assumed.

In the chromite-rich samples from Shetland, textural relationships between PGM and their host silicate or chromite, and relationships within composite PGM grains, suggest an order of formation of the PGM. Os- and Ru-rich PGM appear to have formed first, and were followed by Ir-, Pd-, Rh- and, lastly, Pt-bearing PGM. An increase in availability of arsenic for the formation of PGM was followed by the last period of PGM formation, in a low-temperature environment in which Pt- and Pd-rich alloys and Ru-bearing pentlandite formed in association with nickel carbonate.

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