

ASSEMBLAGES OF PLATINUM-GROUP MINERALS AND SULFIDES IN SILICATE LITHOLOGIES AND CHROMITE-RICH ROCKS WITHIN THE SHETLAND OPHIOLITE

HAZEL M. PRICHARD

*Department of Geology, University of Wales, College of Cardiff,
P.O. Box 914, Main College, Park Place, Cardiff, CF1 3YE, United Kingdom*

ROB A. IXER

The School of Earth Sciences, Birmingham University, Edgbaston, Birmingham, B15 2TT, United Kingdom

RICHARD A. LORD

*School of the Environment, Benedict Building, University of Sunderland,
St. Georges Way, Sunderland, SR2 7BW, United Kingdom*

JON MAYNARD AND NAOMI WILLIAMS

Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom

ABSTRACT

A large variety of platinum-group minerals (PGM) have been recorded already in chromite-rich lithologies from the Shetland ophiolite complex, in the Shetland Islands, northeast of Scotland. Further work described in this paper documents the nature of the PGM and sulfides from ultramafic lithologies in the ophiolite sequence, including cumulate dunite, wehrlite and pyroxenite. PGM assemblages from all known platinum-group-element-bearing lithologies in the ophiolite are summarized. A paragenetic sequence of PGM formation is described. Primary magmatic laurite is preserved within chromite. Pd- and Pt-rich inclusions isolated in a single crystal of clinopyroxene are considered to represent a re-equilibrated late magmatic phase containing sulfur, base metals and platinum-group elements (PGE). Pt- and Pd-bearing PGM are clustered around the sulfides and enclosed by serpentine or chlorite, suggesting formation after release, during alteration, of PGE from magmatic sulfide assemblages. The PGM enclosed by altered silicates are commonly As-, Sb- and Te-bearing. These elements have been introduced during alteration of the primary silicate minerals. Subsequent removal of the arsenic and antimony produces Pt- or Pd-bearing alloys; late-stage weathering changes the Pt- and Pd-bearing minerals to ochres and, in one case, to a composite Pt-bearing mineral containing oxygen and carbon. Textural evidence from dunite, wehrlite and pyroxenite suggests that the majority of the secondary PGM formed only a few micrometers from the primary source of the PGE. However, longer-range mobility of PGE is indicated by the presence of Pt and Rh in alloclaste – gersdorffite_{ss} along the basal contact of the ophiolite at Cliff, a few hundred meters away from a primary magmatic source of the PGE.

Keywords: ophiolite, Shetland, platinum-group minerals, Pt oxide, ochre, carbonate, gold, Unst, Scotland.

SOMMAIRE

Une grande variété de minéraux du groupe du platine ont été décrits dans les unités riches en chromite du massif ophiolitique de Shetland, affleurant dans les îles Shetland, au nord-est de l'Écosse. Dans cet article, nous nous attardons sur les minéraux du groupe du platine dans les unités ultramafiques de la séquence ophiolitique, c'est-à-dire dans les unités à dunite cumulative, wehrlite et pyroxénite, tout en résumant la distribution des minéraux du groupe du platine dans le massif en entier. Nous présentons une séquence paragenétique de ces minéraux. La laurite magmatique (primaire) est piégée dans la chromite. Les inclusions riches en Pt et Pd qui ont été repérées dans un seul cristal de clinopyroxène représenteraient une phase minérale tardi-magmatique contenant soufre, métaux de base et les éléments du groupe du platine. Dans le cas des minéraux du groupe du platine accolés sur les sulfures et englobés par la serpentine ou la chlorite, leur formation aurait eu lieu après la libération des éléments du groupe du platine suite à l'altération des assemblages de sulfures magmatiques. Les minéraux du groupe du platine englobés par les silicates altérés sont généralement porteurs de As, Sb et Te; ces éléments auraient été introduits pendant l'altération des silicates primaires. Un lessivage tardif de As et Sb mène à la formation d'alliages de Pt ou Pd. L'altération finale due aux eaux de surface a transformé les minéraux du groupe du platine en ochres et, dans un cas, en un minéral platinifère complexe porteur d'oxygène et de carbone. D'après l'évidence texturale, la plupart des minéraux secondaires se seraient formés à peine à quelques micromètres de leur précurseur dans les dunites, les wehrlites et les pyroxénites. Une mobilité plus grande serait à l'origine du Pt et Rh dans la solution solide alloclaste – gersdorffite à Cliff, le long de la semelle de l'ophiolite, à une centaine de mètres d'une source primaire des éléments du groupe du platine.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, oxyde de Pt, ochre, carbonate, or, ophiolite, Shetland, Unst, Écosse.

INTRODUCTION

The platinum-group minerals (PGM) traditionally described from ophiolite complexes are Os-, Ir- and Ru-bearing minerals associated with podiform chromitite (Stockman & Hlava 1984, Talkington *et al.* 1984, Augé 1985, Legendre & Augé 1986). Pt-, Pd- and Rh-bearing PGM have been recorded only rarely (Stockman & Hlava 1984, Augé 1988, Fisher *et al.* 1988, Moring *et al.* 1988), and not necessarily associated with chromitite (Orberger *et al.* 1988). More recent studies have shown that Pt-, Pd- and Rh-bearing PGM are common in some ophiolite sequences (Prichard & Lord 1990b, McElduff & Stumpfl 1990, Corrivaux & Laflamme 1990, Ohnenstetter *et al.* 1991, Leblanc 1991, Leblanc *et al.* 1991). A large variety of PGM occur in the Shetland ophiolite complex; their systematic documentation in the various silicate and oxide lithologies is presented here.

The Shetland Islands lie northeast of mainland Scotland; the ophiolite is exposed on the most northeasterly islands, Unst and Fetlar. The complex represents the lower part of a typical ophiolite sequence (Prichard 1985, Flinn 1985), with mantle harzburgite overlain by cumulate dunite, wehrlite and pyroxenite (Fig. 1). Above this is gabbro, and the uppermost part of this is intruded by dykes. Boundaries between the ultramafic cumulate units are transitional, and a single outcrop commonly contains layers (2–10 cm thick) of dunite, wehrlite and pyroxenite. No orthopyroxene has been observed in either the ultramafic or mafic part of the crustal sequence. Concentrations of chromite in dunite lenses in harzburgite and in discontinuous layers in the overlying dunite have compositions comparable to those of chromitites from other ophiolite complexes (Prichard & Neary 1981, 1982, Gass *et al.* 1982); the geochemistry of the dykes in the upper part of the ophiolite indicates a supra-subduction-zone setting (Prichard & Lord 1988).

The presence of platinum and associated metals in Unst was first noted in heavy-mineral concentrates from the chromite-ore crushing mill (Hitchen 1929). Subsequently, Ru-, Ir- and Os-bearing PGM have been described from two chromite-rich localities in the northern part of the ophiolite (Prichard *et al.* 1981). This discovery led to a systematic survey of PGM in chromite-rich samples from abandoned chromite quarries, which revealed the presence of Os-, Ir- or Ru-bearing PGM at 13 localities (Prichard *et al.* 1986). Anomalous Ir and Au values were discovered in chromite-rich samples from a dunite lens enclosed within mantle harzburgite at Cliff (Prichard *et al.* 1984). Pt-, Pd- and Rh-bearing minerals were observed in chromite-enriched samples from both Cliff and Harold's Grave, which is another lens of dunite in harzburgite (Neary *et al.* 1984, Prichard *et al.* 1986, 1987, Ixer 1990). Pt and Pd are extremely enriched (Pt + Pd values of over 60 ppm) at Cliff,

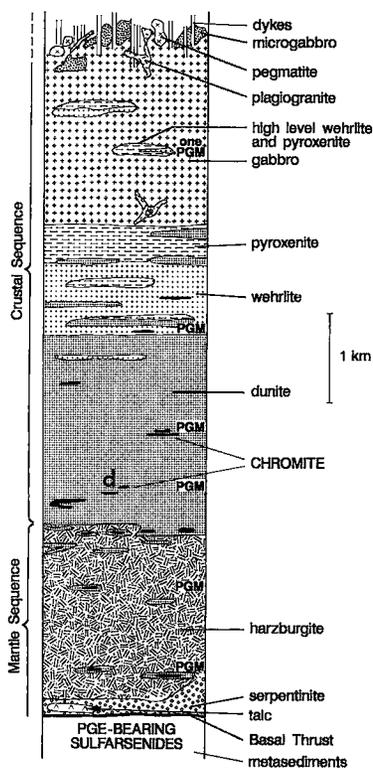


FIG. 1. Section through the ophiolite showing the locations of the PGM-rich assemblages. The letter *d* marks the stratigraphic level of the drill core from north of Baltasound. The symbol PGM indicated in the harzburgite refers to PGM within pods of dunite. PGE-bearing sulfarsenides occur in serpentine and talc at the basal thrust.

giving positive slopes on chondrite-normalized diagrams, and Os, Ir and Ru are enriched (Os + Ir + Ru values of up to 3–4 ppm) at Harold's Grave, giving negative slopes on chondrite-normalized diagrams (Neary *et al.* 1984, Prichard *et al.* 1986). These results have been confirmed by Gunn *et al.* (1985) and Gunn (1989).

The occurrence of all six platinum-group elements (PGE) in the chromite-rich lithologies at Cliff and Harold's Grave is expressed mineralogically by a diverse suite of PGM (Tarkian & Prichard 1987, Prichard & Tarkian 1988). The major observations made by these authors were that PGM within chromite grains are Ru-, Ir- and Os-bearing, whereas Pt-, Pd- and Rh-bearing PGM only occur within the serpentinized silicate matrix interstitial to the chromite. The Os-, Ir- and Ru-bearing minerals crystallized prior to or with the chromite, whereas Pt-, Pd- and Rh-bearing phases appeared later, postdating the formation of the chromite grains. The presence of Pt-, Pd- and Rh-bearing PGM within the altered silicate matrix

TABLE 1. SULFIDE AND PLATINUM-GROUP MINERAL ASSEMBLAGES

Assemblage name	Primary silicates	Secondary minerals	Opaque oxides	Sulfides, arsenides and antimonides	Major platinum-group minerals	Native metals, alloys, amalgams
(1) Basal thrust	None	Talc, magnetite, dolomite, serpentine, minor chlorite	Magnetite, ferrichromit, chromite	Pyrrhotite, pentlandite, allociase-gersdorffite ^{ss} , niccolite, cobaltite, violarite, chalcopyrite	Rhodium and platinum-rich cores in gersdorffite	Very rare native Cu, very rare native Au
Harzburgite	Olivine, orthopyroxene, minor clinopyroxene	Serpentine, minor chlorite	Chromite, ferrichromit, magnetite	Sparse sulfides. Pentlandite, heazlewoodite, millerite, Ni-arsenides and Cu-sulfides	N.R.	Native Cu
(2) Chromitite from dunite in harzburgite and from cumulate dunite	None	Serpentine, ± kammererite, Ni carbonate	Chromite, ferrichromit, magnetite	Ruthenianpentlandite, niccolite, maucherite	Laurite [Ru(r, Os) ₂], irarsite IrAs ₃ , native Os, hollingworthite RuAs ₃	N.R.
(3) Chromite-rich, As-rich, sulfide-bearing dunite from Cliff	None	Serpentine, nickel carbonate, kammererite	Chromite, ferrichromit, magnetite	Ni-arsenides, minor pentlandite, heazlewoodite, millerite, Cu sulfides: bornite, chalcocite and covellite	Sperryite, stibiopalladinite, hongshiite, Pd, Pt, Au, base metal alloys, potarite (PtHg), Pt and Pd tellurides, Pt and Pd ocres	Native Cu, Au, Ag
(4) Sulfide-bearing dunite pods and sulfide-bearing cumulate dunites	Olivine	Serpentine, minor chlorite, carbonate	Chromite, ferrichromit, magnetite	Pentlandite, cobaltpentlandite, heazlewoodite, millerite, godlevskite, orcelite, maucherite, ± Pd-bearing Ni, Cu antimonides, chalcopyrite, chalcocite, digenite, djurite, bornite, cuprite, ± covellite, ± spionkopite	Stibiopalladinite (Pd ₅ Sb ₂), geversite (PtSb ₂), genkinite (PtPd) ₄ Sb ₃ , Pt, Fe, Cu alloy, hongshiite (PtCu), Pt and Pd ocres	Ni, Fe alloy, native Cu, native Au, Ag amalgam, Ag, Cu alloy, Ni, Pb alloy
(5) Sulfide-bearing wehrlite and pyroxenite	Clinopyroxene, olivine	Serpentine, actinolite, minor chlorite	Chromite, ferrichromit, magnetite	Pyrrhotite, pyrite, pentlandite, heazlewoodite, millerite, maucherite, orcelite, chalcopyrite, bornite, digenite, covellite	Sperryite (PtAs ₂), Pd antimonides, Pt ocres	Native Cu, native Au, Au, Ag alloy
(6a) Fresh pyroxene crystal, MR45	Clinopyroxene	None	None	Pentlandite, chalcopyrite	Pd, Cu, sulfides ± Pt ± Au, Pd, Pb alloys ± Pt ± Au	N.R.
(6b) Altered cleavage of pyroxene crystal, MR45	None	Serpentine, chlorite	Magnetite	Heazlewoodite	Pd antimonides and tellurides Pt and Pd arsenides	Au, Pd, Ag, Cu alloy
(7) High-level sulfide-bearing wehrlite	Clinopyroxene, olivine	Serpentine, chlorite, calcite	Magnetite, chromite, ferrichromit, ilmenite	Pyrrhotite, pyrite, pentlandite, allociase-gersdorffite ^{ss} , niccolite, cobaltite, chalcopyrite	Sperryite	N.R.
Gabbro, plagiogranite and dolerite dykes	Clinopyroxene	Actinolite, albite, epidote, chlorite, quartz	Magnetite, chromite, ferrichromit	Pyrrhotite, pyrite, cobaltpentlandite, chalcopyrite	N.R.	N.R.

N.R. - not recorded, Numbers (1) etc. refer to PGE-bearing assemblages described in the text.

was used to infer that the original PGE-bearing minerals were replaced by low-temperature assemblages. Previous studies of the chromite-rich lithologies also showed that Pt and Rh anomalies are not restricted to Cliff and Harold's Grave. Before this study, Rh-bearing PGM had been located in a chromite-rich sample from another lens of dunite in harzburgite at Nikkavord North, and Pt- and Rh-bearing PGM had been found in a chromite-rich sample from Jimmie's quarry within the dunite unit (Prichard *et al.* 1987). PGM also were found in sulfide-bearing dunite from Cliff (Prichard & Lord 1988, Ixer & Prichard 1989, Ixer & Prichard in Prichard & Lord 1990a, Ixer 1990).

The unusually high concentrations of the PGE discovered at Cliff in the Shetland ophiolite (Neary *et al.* 1984, Prichard *et al.* 1986, 1987) prompted a MIRO (Minerals Industry Research Organisation) exploration program for PGE concentrations throughout the complex (Prichard & Lord 1990a). The result was a systematic survey of PGE concentrations within the ophiolite (Lord & Prichard 1989, 1991, Lord 1991, Prichard & Lord 1993) that revealed the extent to which the PGE are concentrated both in chromite-rich and chromite-poor rocks. This paper documents the assemblages of PGM located in all the PGE-bearing lithologies, especially the newly documented assemblages from the chromite-poor rocks (Table 1). Textural relationships between the PGM and with their host silicates are described and interpreted in terms of their parageneses.

TECHNIQUES

More than 750 whole-rock samples of 1 kg were crushed and analyzed for Pt and Pd by Ni sulfide fire assay and inductively coupled plasma – emission spectrometry (ICPES) (Prichard & Lord 1990a). Samples selected for mineralogical study included those with the most anomalous total PGE values and others close to the analytical detection limit of 10 to 20 ppb. PGM were located by combined use of conventional oil immersion, reflected-light optical microscopy and scanning electron microscopy using back-scattered electron imagery. All the PGM described were analyzed qualitatively using an X-ray detector (EDX) attached to a scanning electron microscope (SEM). Initial determinations of composition were obtained using a Philips 501 SEM with a LINK EDX system, and later using a JEOL 820 SEM with a KEVEX analytical EDX. The latter instrument has a higher resolution, and many PGM were re-analyzed, including all the 350 or more grains of PGM associated with a single pyroxene crystal. A spectrum for each of the hundreds of PGM grains analyzed was examined and systematically identified, with particular attention paid to overlapping peaks and small peaks close to the background noise. To test for homo-

TABLE 2. COMPOSITION OF Pt- AND Pd-BEARING MINERALS

	1	2	3	4	5
Pt	nd	nd	0.46	0.57	41.04
Pd	0.93	0.26	5.67	1.88	0.15
Fe	0.15	0.18	3.70	1.42	1.79
Ni	41.18	42.01	28.55	29.69	1.20
Cu	11.78	4.12	4.05	0.47	0.22
Ag	0.10	nd	nd	nd	nd
S	0.10	2.56	nd	0.14	0.19
As	0.30	0.21	nd	nd	nd
Sb	47.05	50.13	58.30	65.74	53.51
Total	101.59	99.47	99.98	100.20	98.17

Columns 1–4: palladium Ni,Cu antimonides, column 5: geversite. The grain of geversite is adjacent to a grain of pentlandite. Fe and Ni in the geversite may result from excitation of the adjacent pentlandite; nd: not detected. Results expressed in weight %.

geneity, several spot-analyses were performed across the larger grains of PGM. For composite or inhomogeneous PGM, X-ray maps of each constituent element were plotted. Quantitative determinations of PGM compositions are beyond the scope of this paper. The compositions of the more common PGM from Cliff and Harold's Grave are given in Tarkian & Prichard (1987) and Prichard & Tarkian (1988). Many of the PGM described here, which are new to the Shetland ophiolite, are too small (0.5 – 5 μm) for quantitative analysis; X-ray spectra are included to indicate their compositions. The composition of a few of the larger PGE-bearing minerals, previously unanalyzed from Shetland, was quantified on a Cambridge Mark 9 electron microprobe (Table 2).

METHODS OF ANALYSIS OF PGM CONTAINING LIGHT ELEMENTS

Analysis at 25 kV of a strongly anisotropic mineral with a low reflectance showed the presence of Pt only (Fig. 2a). To test the possibility that oxygen and carbon are present, this mineral was analyzed using a Kevex detector with a thin window designed to detect light elements. At 25 kV, the strong X-ray emission from Pt obscures X rays that would be produced by the presence of oxygen, but at a lower voltage, reduced excitation of the heavy elements enables observation of the lighter elements. At 5 kV, comparison of the spectra of the Pt-bearing mineral with those of the adjacent silicate (Figs. 2b, c) reveals a large peak due to oxygen in the silicate and a smaller but significant peak due to oxygen in the Pt-bearing mineral. Also at 5 kV, a carbon peak is recorded (Fig. 2b), and its size is equal to the sum of contributions from carbon in the mineral, carbon in the coating and a small Pt *M* line escape peak, which overlaps the carbon peak. The peak attributed to the carbon coating is small [assumed equivalent to that in the otherwise carbon-poor adjacent silicate (Fig. 2c)], and the Pt

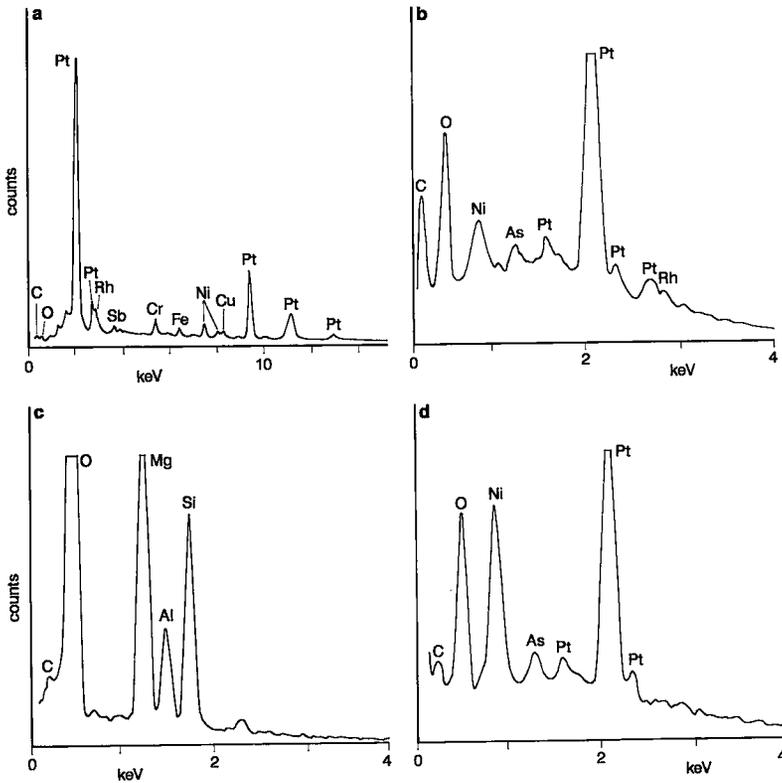


FIG. 2. Spectra obtained using a Kevex energy-dispersion analytical facility attached to the SEM. (a)–(c) Silicate and a Pt-bearing mineral containing carbon and oxygen from Harold's Grave. (a) Spectrum recorded at 25 kV and an energy range of 20 keV, showing Pt peaks with minor Rh, Sb, Cr, Fe, Ni, and Cu. (b) Spectrum recorded at 5 kV and an energy range of 5 keV, showing a major Pt peak and minor Ni, Rh and As peaks. An oxygen peak is clear and is adjacent to a substantial carbon peak. (c) Spectrum of the silicate adjacent to the Pt-bearing mineral, also recorded at 5 kV and an energy range of 5 keV, showing large oxygen, Mg, Al and Si peaks from the silicate and a small carbon peak from the carbon coating. (d) Spectrum of Pt oxide-ochre from Cliff measured at 5 kV and an energy range of 5 keV, showing a major Pt peak and minor Rh and As peaks. An oxygen peak is clear and is adjacent to a small carbon peak from the carbon coating and a minor overlapping Pt escape peak. A relatively large Ni peak is likely to be a contribution from the adjacent Ni-Cu-bearing mineral.

escape peak also is small (estimated from its ratio with the Pt *M* line). When these two peaks are removed, a significant carbon peak from the Pt-bearing mineral remains. Thus, this Pt-bearing mineral is inferred to contain oxygen and carbon and would seem to be a Pt carbonate or a very fine mixture (smaller than the resolution of the SEM) of a Pt mineral and an unidentified carbonate.

A second low-reflectance Pt-bearing mineral, with an irregular shape and intergrown with a Ni,Cu mineral, was analyzed at 5 kV (Fig. 2d), as it had been suggested that this might be a Pt ochre or oxide (Ixer

& Prichard 1989). In this case, a large oxygen peak and only a small carbon peak are recorded. This small peak has approximately the same size as the peak due to the carbon coating seen in the spectrum from the adjacent silicate, and so is believed to be due to the carbon coating and the small overlapping Pt *M* line escape peak. Thus carbon is not present in this mineral, but the presence of oxygen indicates that it is an oxide or hydroxide. Further work is in progress to confirm and determine the abundance, distribution and compositional variation of Pt and Pd minerals containing light elements in these rocks.

PGM-BEARING LITHOLOGIES

The following sections present a detailed description of all the PGM-bearing assemblages, including newly recognized types. They are defined according to the lithology of the host silicate and associated sulfides and oxides (Table 1), and are listed in order of ascending stratigraphic level (Fig. 1). Within these assemblages, two distinct groups of PGM occur, distinguished by their compositions and associated minerals. The first group consists of Os-, Ir-, and Ru-rich PGM associated with chrome-spinel or chromite. These minerals are present in chromite-rich rocks (more than 30% chromite). The second is an assemblage of Pt- and Pd-rich PGM associated with sulfides and found in dunite, wehrilite and pyroxenite. Chromite and sulfides commonly occur together, and so both groups of PGM are present in some samples.

Pt- and Rh-bearing sulfarsenides from the basal thrust (1, Table 1)

Harzburgite is completely serpentized along the basal thrust and is altered partially to talc-carbonate-rich rocks that carry minor sulfides and arsenides. This basal thrust assemblage is composed of pyrrhotite and chalcopyrite, but includes niccolite, mixed intergrowths of hexagonal pyrrhotite – pentlandite – minor chalcopyrite and euhedral, faintly anisotropic crystals of alloclaste – gersdorffite_{ss} with an average composition of $(\text{Co}_{0.6}\text{Ni}_{0.4}\text{Fe}_{0.1})\text{AsS}$ (three analyses). Although located close (200 – 300 m) to the PGE-rich Cliff locality, this assemblage is different from that at Cliff because of the presence of pyrrhotite and alloclaste – gersdorffite_{ss}. No discrete PGM were observed. The sulfarsenides, however, have euhedral cores 1–5 μm in diameter that are Rh- and Pt-enriched, with up to 0.17 wt% Pt (detection limit 0.05 wt%), showing up as harder centers surrounded by very faint zoning in hardness and reflectance in the alloclaste – gersdorffite_{ss}. Whole-rock PGE analyses of these samples containing Rh- and Pt-bearing alloclaste – gersdorffite_{ss} indicates Pt levels below the detection limit of 20 ppb.

Chromitites (2, Table 1)

The more chromite-rich lithologies (over 30% chromite and approaching massive chromitite, with more than 90% chromite) occur at all levels within the ultramafic sequence, as lenses in dunite pods within the harzburgite, as discontinuous layers in the overlying dunite and, rarely, as discontinuous chromite-rich layers at higher levels in the low-level wehrilite. Laurite is the only common PGM in these chromite-rich samples; it is ubiquitous, and generally totally

enclosed by chromite (Prichard *et al.* 1987). Where laurite is situated on the edge of a chromite grain or in contact with a serpentine-filled crack, it is altered to composite grains of Ir- and Os-poor laurite, irarsite and native osmium. At the edges of chromite grains, irarsite locally is rimmed by hollingworthite. Ru-rich pentlandite occurs in these chromite-rich lithologies, in dunite lenses with irarsite, laurite and native osmium (Tarkian & Prichard 1987). The chromite-rich material in the dunite lens in mantle harzburgite at the extremely PGE-rich locality at Cliff also belongs to this category. However, the most chromite-rich samples from Cliff do not have anomalously high PGE values (less than 250 ppb total PGE) and only contain laurite. The chromite-rich lithology from Harold's Grave, which contains anomalous (ppm) levels of Os, Ir and Ru, also is classed in this group, and has a similar mineralogy of laurite, irarsite and native Os, but the PGM are more abundant and larger, the largest grain of laurite having a diameter of 0.4 mm. These chromite-rich lithologies tend to be poor in base-metal sulfides.

As-rich assemblage at Cliff (3, Table 1)

At Cliff, a dunite lens in harzburgite contains massive and disseminated discontinuous chromite-rich layers. Extremely Pt- and Pd-enriched concentrations (up to 60 ppm Pt + Pd) occur in arsenic-rich, chromite-bearing (up to 30% chromite), sulfide-bearing dunite. Nickel arsenides are more common than pentlandite; heazlewoodite and millerite intergrowths and minor Cu sulfides occur (Ixer 1990, Ixer & Prichard 1989, Ixer & Prichard in Prichard & Lord 1990a). Breithauptite has not been observed. Trace amounts of native copper, silver, gold and spionkopite are present. Pd antimonides and rare geversite are joined in this assemblage by arsenic-bearing PGM, including sperryllite (Prichard & Tarkian 1988) and by Pt and Pd tellurides.

Sulfide-bearing dunites (4, Table 1)

Sulfide-bearing dunites occur in dunite lenses in harzburgite and in the overlying dunite cumulates, both in the area north of Baltasound and east of Caldbeck. The dunites examined in this study are relatively undeformed. Relict Mg-rich olivine (Fo_{87-91}) (Gass *et al.* 1982) is moderately common at 10–20% levels, but up to 60–70% is locally present. Generally, however, olivine is completely serpentized, leading to pseudomorphism of the igneous textures. The sulfide assemblage is similar throughout the dunites and consists of pentlandite (commonly altered to awaruite, heazlewoodite and magnetite), with rare cobaltian pentlandite, breithauptite, a Ni,Pb alloy, and chalcop-

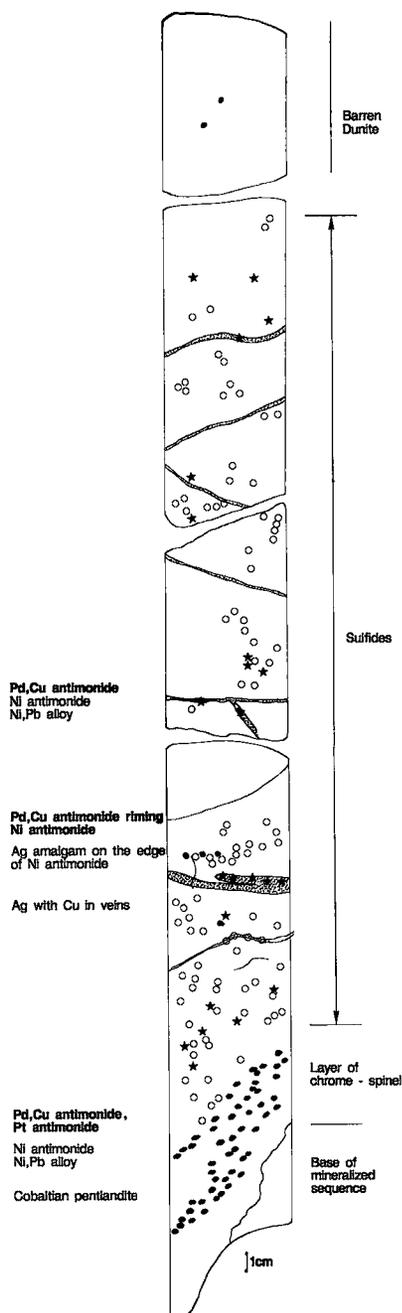


FIG. 3. Sketch of the minerals visible on the flat surface of a section of drill core showing the sequence of chromite, sulfides and PGM typical of the PGE-bearing assemblage in the dunite unit. Thin sections were cut across this section of core and revealed the distribution of the PGM. Unnamed minerals, analyzed qualitatively, are noted beside the section at the horizon where they were located. Symbols: ●: chromite, ○: sulfides, and ★: native copper. Length of the scale bar is 1 cm.

pyrite, bornite and chalcocite altering to native Cu. Ag amalgams have been identified and, in one case, an Ag amalgam partially encloses a Pd-bearing Ni,Cu antimonide and is itself surrounded by an intergrowth of pentlandite and native Cu. Sulfide-bearing dunites from Cliff are similar, except that awaruite is absent; they contain godlevskite, millerite and orcelite (Ixer 1990). Only one grain of pyrrhotite has been found.

The PGM-bearing sulfide-rich dunites are usually associated with chromite-rich discontinuous layers, either in dunite lenses or in the dunite cumulates. Study of drill core from the dunite unit north of Baltasound revealed specific relationships among the PGM, sulfides and chromite-rich layers (Fig. 3). Typically, sulfide-free dunite passes up stratigraphically to a (1-cm thick) layer of disseminated chromite containing cobaltian pentlandite. On the strength of its geochemical characteristics, this is interpreted as the base of a magmatic cycle. Over a short distance (0.5 cm), the chromite becomes less abundant, and concentrations of pentlandite (commonly altered to heazlewoodite and Ni,Fe alloy) are developed in a cluster around chromite. This zone of sulfides can be 10–50 cm thick; passing upward, the sulfides become progressively less abundant, and the rock grades into barren dunite. Minor chalcopyrite occurs within the sulfide zone, and cross-cutting veins commonly contain native Cu locally associated with native Ag and a Cu-bearing Ag amalgam. Pt-bearing PGM are concentrated in the lower part of the sulfide sequence closer to, but above, the chromite, whereas the Pd-bearing PGM occur slightly higher. Grains of gold have been observed both within sulfide and in serpentine. This assemblage has a primary magmatic origin, demonstrated by its precise relationship with primary lithologies, for it overlies layers of disseminated chromite within the dunite. The present assemblage of sulfides and the PGM, however, is secondary, and there is evidence of local (millimeter to centimeter scale) remobilization of elements, for example the movement of Cu into cross-cutting veins.

Pt- and Pd-bearing PGM have been observed in these sulfide-bearing dunites, but Os-, Ir-, Ru- and Rh-bearing minerals have not. The PGM are dominantly Pd antimonides and geversite. Antimonides of Pd occur in silicates surrounding the clusters of sulfides (Fig. 4), in fractures cross-cutting chromite grains, as rims to breithauptite, or in Ni,Fe alloy rims to heazlewoodite or pentlandite. Minor amounts of Pd, ± Pt, are present within Ni and Cu antimonides in different types of occurrence, for example: (i) up to 1 wt% Pd has been documented in large (90 μ m) grains of isotropic, euhedral Ni,Cu antimonides intergrown with awaruite, altered silicates and a vermiform intergrowth of pentlandite and native Cu (Table 2, analysis 1); (ii) trace amounts of Pd (0.26 wt%) occur in spheroidal 20- μ m composite grains comprising intergrowths of breithauptite and a Ni,Cu-bearing

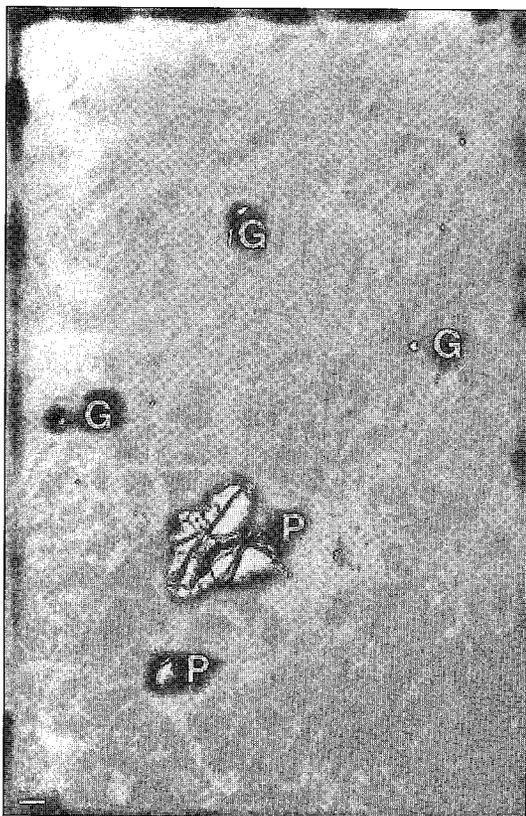


FIG. 4. Photomicrograph (reflected light) of pentlandite P broken by a Ni,Fe alloy alteration product located along the fractures. The pentlandite (0.25 mm in diameter) lies in serpentinized olivine in dunite. Satellite grains of geversite G (25 μ m) are situated around the pentlandite. The section is taken from dunite from the cumulate unit north of Balta Sound. Scale bar represents 100 μ m.

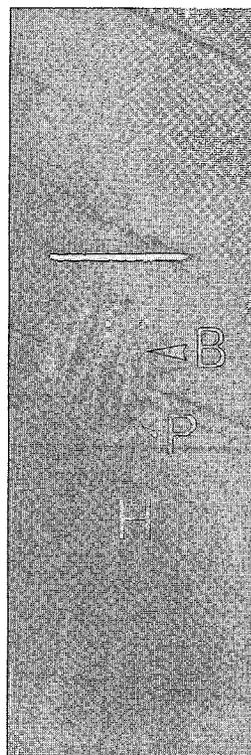


FIG. 5. Photomicrograph (reflected light) of a spherical grain of Pd-bearing breithauptite (B) (25 μ m in diameter) intergrown with a Ni,Cu antimonide. Pentlandite (P) partially surrounds the grain, and all these phases are enclosed by heazlewoodite (H). The section is taken from dunite from the cumulate unit north of Balta Sound. Scale bar represents 25 μ m.

antimonide (Figs. 5, 6) (Table 2, analysis 2), the Pd locally being present in lamellae in anhedral breithauptite enclosed in magnetite or altered silicates. Trace amounts of Pt (0.5–0.6 wt%) were also noted in these Pd-rich lamellae (Table 2, analysis 3) and adjacent host breithauptite (Table 2, analysis 4). Breithauptite *sensu stricto* without detectable PGE occurs as 1–10 μ m spherical inclusions in heazlewoodite and, more rarely, in pentlandite. The most common Pt-bearing mineral is geversite (Fig. 5), but two grains of a Pt,Fe,Cu alloy have been located in a chlorite rim surrounding a cluster of sulfides asso-

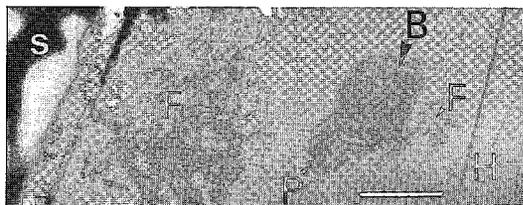


FIG. 6. Photomicrograph (reflected light) of an oval grain of Pd-bearing breithauptite (B) (40 μ m in diameter) intergrown with a Ni,Cu antimonide. Pentlandite (P) partly surrounds the grain and contains intergrowths of a Ni,Fe alloy (F). All these phases are enclosed by heazlewoodite (H), which is altered to a Ni,Fe alloy (F) on its edge adjacent to serpentine (s). The section is taken from dunite from the cumulate unit north of Balta Sound. Scale bar represents 40 μ m.

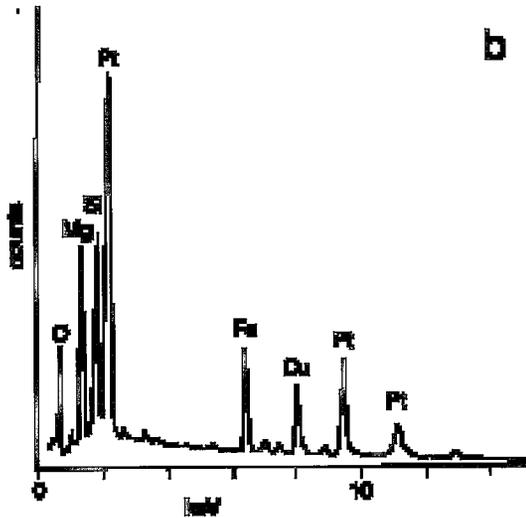
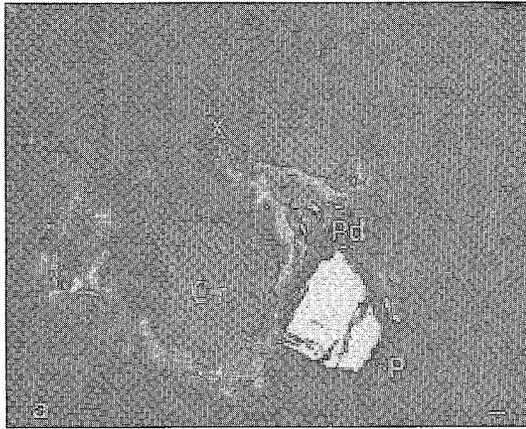


FIG. 7. (a) Photomicrograph (reflected light) of two grains of a Pt,Fe,Cu alloy (x) in a chlorite rim surrounding a cluster of sulfides (pentlandite P) and chromite (Cr). Section cut from a sample of drill core in dunite cumulate north of Baltasound. Pd is a Pd,Cu alloy on the edge of a copper sulfide on the edge of chromite and in contact with chlorite. Scale bar represents 20 μm . (b) Spectrum (measured at 25 kV and with an energy range of 20 keV) of the larger grain of Pt,Fe,Cu alloy shown in (a).

ciated with chromite grains (Figs. 7a, b). Where Pt- and Pd-bearing minerals occur in the same sample, they are closely associated with each other (Fig. 7a) and with Au grains of similar size (1 – 10 μm in diameter). Examples of the PGM, large enough to be analyzed, are given in Table 2. These include two Pd-bearing Ni,Cu antimonides: (1) $(\text{Ni}_{1.81}\text{Cu}_{0.48}\text{Pd}_{0.02})\text{Sb}$, and (2) $(\text{Ni}_{1.74}\text{Cu}_{0.16}\text{Pd}_{0.01})(\text{Sb}_{1.0}\text{S}_{0.19})$, and geversite, $\text{Pt}_{0.96}\text{Fe}_{0.14}\text{Sb}_2$. Despite good analytical totals, these minerals apparently have poor stoichiometry; their true stoichiometry is still unknown.

Sulfide-bearing wehrlite and pyroxenite (5, Table 1)

PGM have been identified in wehrlite and clinopyroxenite lying stratigraphically above the dunite unit and overlain by gabbro. The wehrlite and pyroxenite form a unit that extends westward from Ordale and the

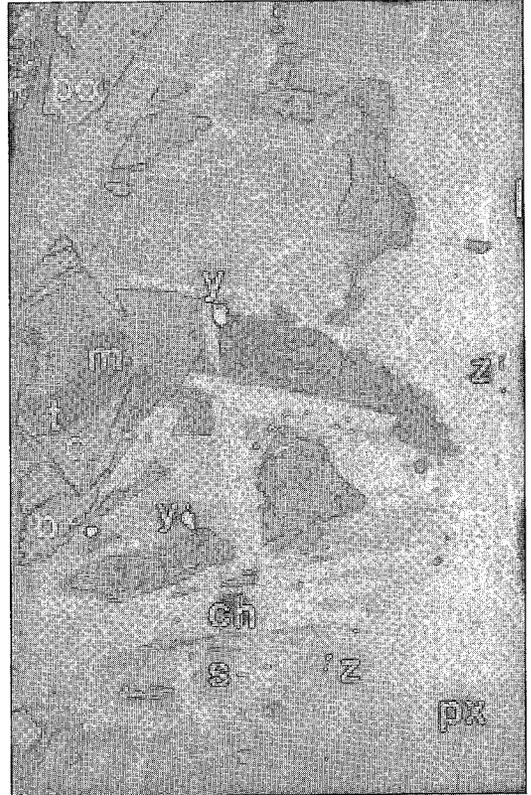


FIG. 8. Back-scattered electron image of a cluster of sulfides associated with PGM in pyroxenite in a section of wehrlite from the ultramafic sequence at Ordale. Chalcopyrite (c) has altered to bornite (b). Pyrrhotite (po) occurs within the silicate matrix separate from the chalcopyrite. The sulfides are surrounded by chlorite (ch) and serpentine (s) interstitial to fresh clinopyroxene (px). Rounded grains of sperrylite (y) (2 – 5 μm in diameter) occur within or on the edges of chalcopyrite. Smaller grains (1 μm) of sperrylite (z) are located along the junction between the fresh pyroxene and the serpentine – chlorite matrix, which hosts the sulfides. Magnetite (m) is enclosed by chalcopyrite and contains tiny (less than 0.5 μm) Pt-bearing grains that form the apices of a triangle containing the letter (t). These grains of PGM are too small to analyze, but qualitatively they give Pt and Fe peaks; Fe may be a contribution from the enclosing magnetite. They are white in this back-scattered image, but in reflected light, they are dark grey. Vertical scale bar is 10 μm .

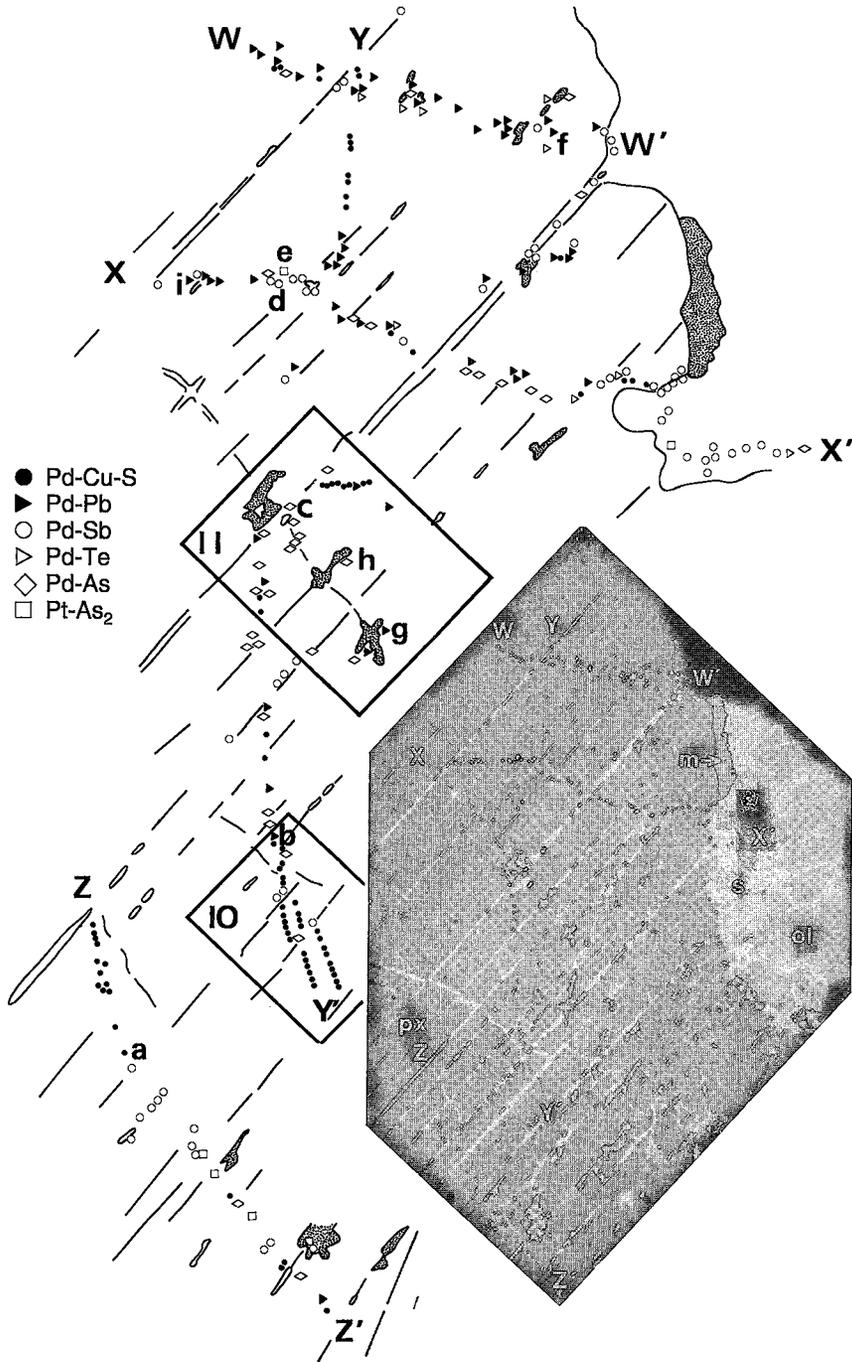


FIG. 9. Sketch of PGM enclosed within a clinopyroxene crystal from typical wehrlite, MR45; inset is the back-scattered electron image of the PGM-rich part of the clinopyroxene crystal. Rows of PGM (W-W', X-X', Y-Y' and Z-Z') traverse the clinopyroxene (px), which exhibits a prominent {110} cleavage (black lines). The junction between the fresh olivine (ol) and the pyroxene is marked by serpentine (s) and magnetite (m). Length of the largest grain of magnetite (m) is 130 μm . Black, filled symbols represent PGM enclosed entirely by fresh pyroxene, and open, unfilled symbols represent secondary PGM surrounded by serpentine in altered cleavage. Fine dots enclosed by a black outline are magnetite grains. The letters a to i correspond to locations of the PGM analyzed (Fig. 12).

Keen of Hammar, and then swings southward through the middle of Unst. Samples with anomalous PGE values have been studied from a number of localities, including those south of Unst airport and at Ordale.

The clinopyroxene in both rock types is commonly extremely fresh and is the least altered primary igneous mineral in the ophiolite complex. In both wehrlite and pyroxenite, fresh clinopyroxene is accompanied by almost totally serpentinized olivine. In the wehrlite, olivine commonly surrounds clinopyroxene, whereas in the pyroxenite, serpentinized olivine may be almost entirely enclosed by fresh clinopyroxene. The wehrlite and pyroxenite are also relatively undeformed in the samples studied, and their

igneous textures are preserved. The sulfide assemblage consists of pentlandite (altering to heazlewoodite), chalcocopyrite (altering to blue "chalcocite", bornite, digenite, covellite and native copper), and pyrrhotite (altering to pyrite). Whereas arsenides are almost absent in the dunite north of Baltasound, they are common in wehrlite and pyroxenite, where orcelite (10–50 μm in diameter) is encountered.

Like in the dunite, the PGM are associated with aggregates of base-metal sulfides, approximately 1 mm in diameter. These are composed of chalcocopyrite (altering to bornite) and pyrrhotite, and commonly are found where the abundance of pyroxene is sufficiently great to surround interstitial serpentine (after olivine)

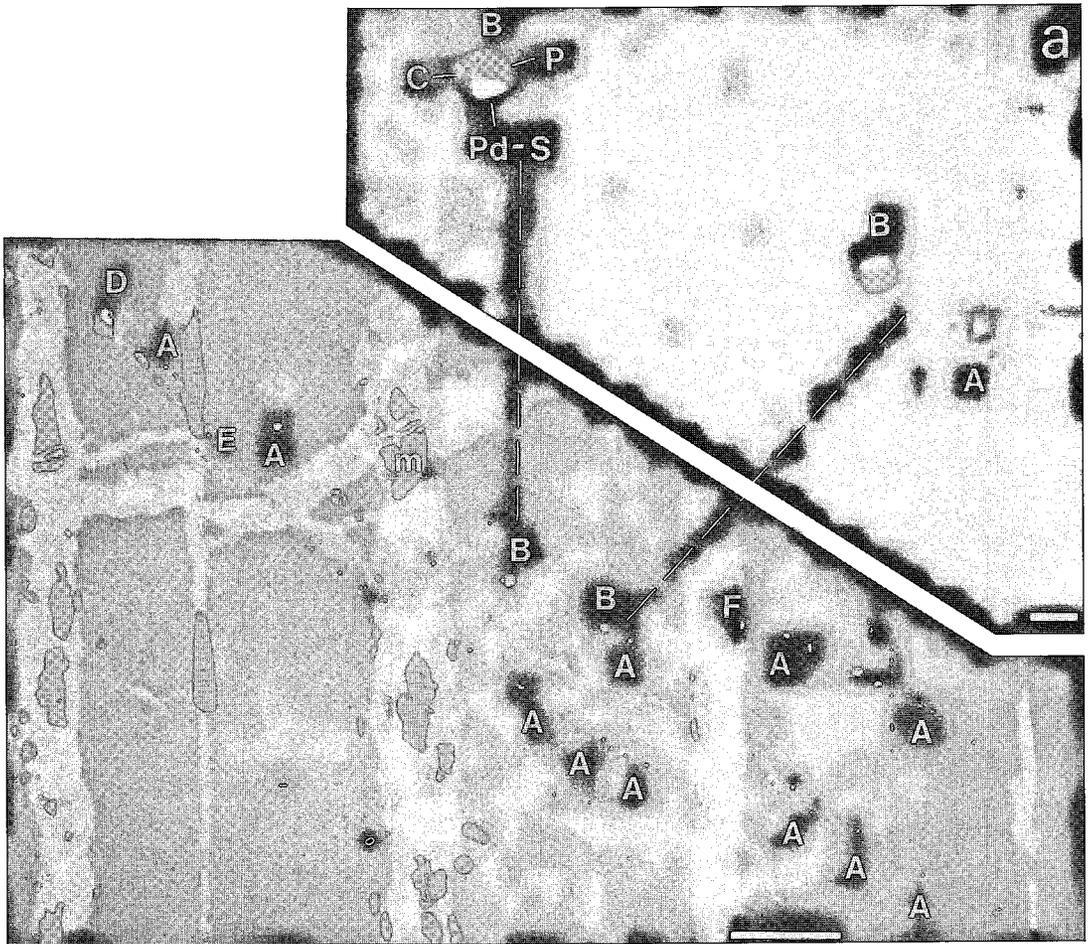


FIG. 10. Back-scattered electron image of part of the PGM-rich clinopyroxene crystal shown in Fig. 9 (Box 10). Rows of Pd,Cu sulfide (A) traverse the fresh clinopyroxene. Composite grains (B) and inset (10a) lie in these rows. These composite grains are composed of pentlandite (P), Cu,Fe sulfide (C) and Pd,Cu sulfide \pm Pt \pm Au (Pd-S). A Pd,Pb alloy (D) also occurs in these rows. Pd,As (E) and Pd,Sb (F) grains are located in serpentine in the altered cleavage. Magnetite (m) is abundant in the vertical {110} cleavage zones. Scale bar is 10 μm in length (1 μm in length for Fig. 10a).

and chlorite. This is illustrated in Figure 8, where larger grains of PGM (5 μm in diameter) lie in contact with chalcopyrite, and smaller grains of PGM (1 μm in diameter) are aligned along the junction between the adjacent fresh pyroxene and the chlorite – serpentine matrix hosting the sulfides. Other minerals at this junction include chalcopyrite, bornite and a single grain of Ag,Au alloy. In the wehrlite and pyroxenite (as in the dunite), Au grains (1 – 10 μm diameter) occur in similar textural positions to the Pt- and Pd-bearing PGM and are associated with them. Palladium occurs in antimonides, and Pt is present in sperrylite. Osmium-, Ir-, Ru- and Rh-bearing minerals have not been observed in these lithologies.

PGM within clinopyroxene from wehrlite
(6, Table 1)

In one case, more than 350 grains of PGM, displaying great compositional variation, were found within a

single grain of clinopyroxene, surrounded by olivine crystals, in a sample (MR45) of typical wehrlite from southern Unst. The whole-rock analysis revealed that the PGE concentrations are not anomalous (60 ppb Pt, 40 ppb Pd). The clinopyroxene is extremely fresh and is only altered at the crystal margins and along cleavages. It is an unzoned diopside close to the end member, typical both of other grains of pyroxene in the same thin section and of those in the host wehrlite unit, having the formula $(\text{Ca}_{0.92}\text{Na}_{0.02})(\text{Mg}_{0.91}\text{Fe}_{0.06}\text{Cr}_{0.03}\text{Al}_{0.03})(\text{Si}_{1.9}\text{Al}_{0.1})\text{O}_6$. In the plane of the thin section, the pyroxene displays one good {110} cleavage (Figs. 9–11) and two less-well-developed serpentine- and, rarely, magnetite-filled planes of exsolution.

The pyroxene grain measures 3 \times 3 mm, and the PGM lie mainly in four rows [W–W', X–X', Y–Y' and Z–Z' (Fig. 9)] within an area 1 \times 0.5 mm near an edge of the crystal. The rows of PGM are exposed on the surface of the polished thin section, these rows being the surface expression of PGM that extend

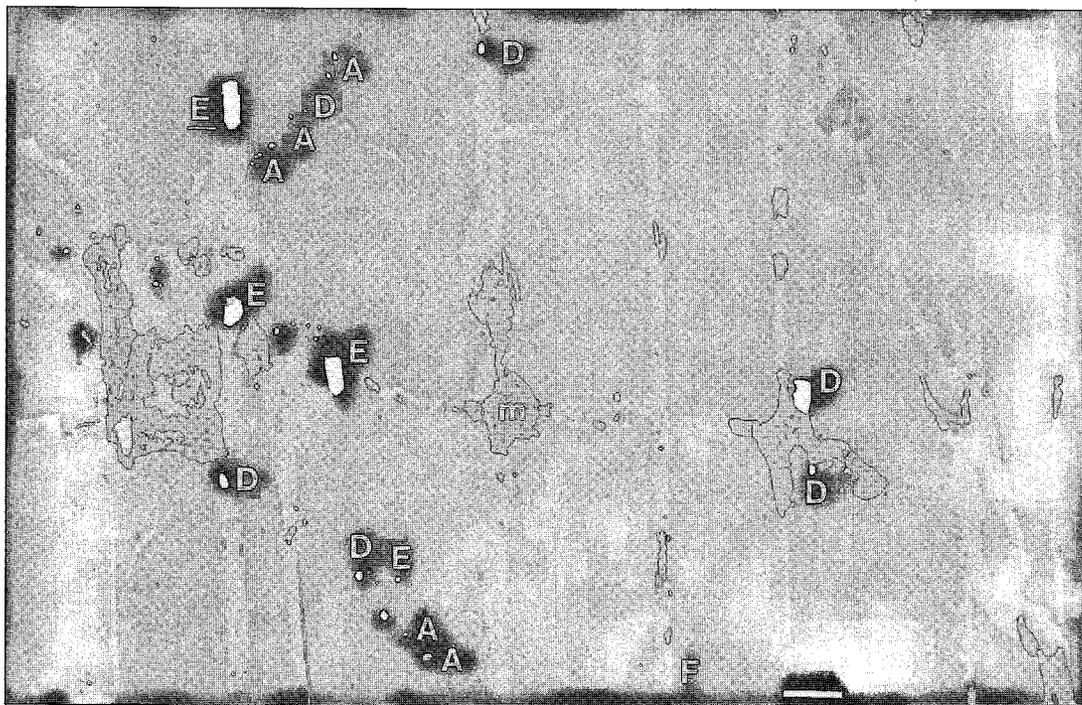


FIG. 11. Back-scattered electron image of part of the PGM-rich clinopyroxene crystal shown in Fig. 9 (Box 11). A row of predominantly Pd,Cu sulfide (A) (less than 1 μm in diameter) traverses the fresh clinopyroxene. A larger grain of Pd arsenide (E) occurs in the serpentinized cleavage zone displaced approximately 5 μm from the intersection of the row of PGM and the cleavage. The Pd in this arsenide may have derived from grains of Pd,Cu sulfides that crossed the cleavage and have now been replaced as a result of the introduction of the arsenic; the Pd was remobilized a few micrometers along the cleavage before crystallizing as the arsenide. Other Pd,As grains are present (E). The Pd,Pb alloy (D) is present both in the rows of PGM and in the vertical serpentinized {110} cleavage zones. Magnetite (m) grains occur in the cleavage. Scale bar is 10 μm .

downward into the 50 μm -thick section. At the surface, two subparallel rows ($W-W'$ and $X-X'$) traverse inward from the edge of the pyroxene crystal for approximately 300 μm . $X-X'$ extends at X' for 50 μm into the altered pyroxene edge but does not penetrate the adjacent partially serpentinized olivine. Two more subparallel rows ($Y-Y'$ and $Z-Z'$) lie approximately at right angles to the first two rows. $Y-Y'$, the longer one (approximately 500 μm) cross-cuts $W-W'$ and $X-X'$, and at one end, Y' , terminates by splitting into two branches (Fig. 10). The rows of PGM are curved and do not follow any of the pyroxene cleavage or exsolution directions. The PGM range in size from $0.5 \times 0.5 \mu\text{m}$ to the largest, at $4 \times 15 \mu\text{m}$. The remarkable variation in the composition of the PGM in this small area is very closely related to the textural position of the PGM (Fig. 9), as will be described in the following two paragraphs.

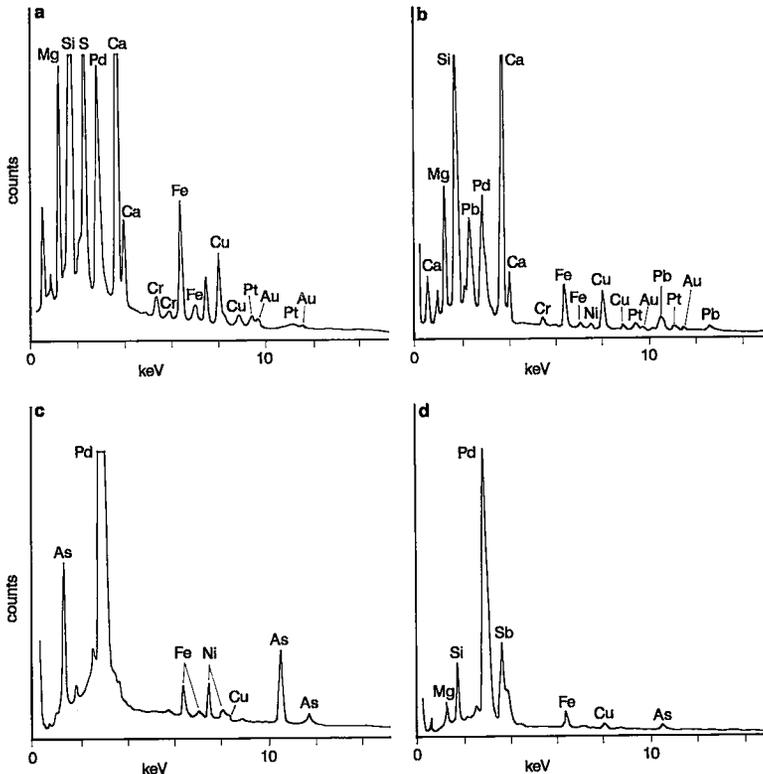
PGM in the unaltered clinopyroxene
(6a, Table 1)

Without exception, the PGM grains completely enclosed by the unaltered clinopyroxene are uncharac-

terized Pd,S and Pd,Pb minerals. These two phases have not been found anywhere else in the ophiolite. Ten or more Pd sulfide grains commonly occur in a line in fresh pyroxene between two cleavage planes. They are circular and small, with diameters of 0.5 – 3 μm , and in several cases form circular composite grains with pentlandite and chalcopyrite (Fig. 10a). Grains of a Pd,Pb alloy also are spherical and more common in the rows extending inward from the edge of the pyroxene ($W-W'$ and $X-X'$) compared to the Pd sulfides, which are more abundant in the cross-cutting rows ($Y-Y'$ and $Z-Z'$). Some Pd sulfides and Pd,Pb alloys contain Cu and traces of Pt or Au or both (Figs. 12a, b).

PGM in the altered cleavage of the clinopyroxene
(6b, Table 1)

Pyroxene cleavages are filled with serpentine and magnetite, and heazlewoodite is present in contrast to pentlandite, which only occurs within fresh pyroxene. Grains of PGM tend to occur in the cleavage planes, where rows of PGM traverse the cleavage, although they may be slightly offset along the cleavage



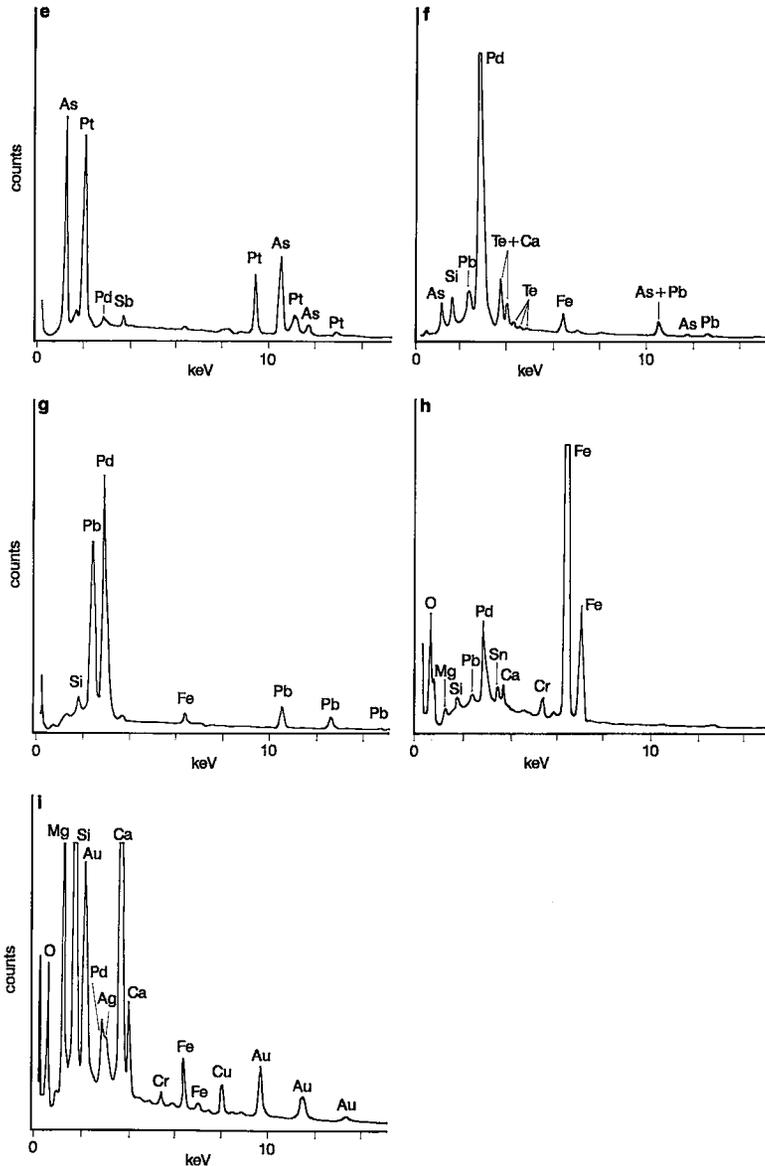


FIG. 12. Spectra (measured at 25 kV and with an energy range of 20 keV) of PGM from the clinopyroxene crystal in MR45. The positions of the unnamed minerals (a–i) corresponding to the spectra are shown on Fig. 9. Clinopyroxene (enclosing PGM) is represented by peaks of Mg, Si, Ca and Fe. (a) Pd sulfide with peaks indicating major Pd and S, minor Cu, and traces of Pt and Au. (b) Pd,Pb alloy with peaks indicating major Pd and Pb, minor Cu and traces of Pt and Au. (c) – (f) PGM situated in serpentine (Mg and Si peaks) with rare magnetite (Fe peak) in the clinopyroxene cleavage; (c) Pd arsenide with minor Ni and Cu, (d) Pd antimonide with minor Cu, (e) Pt arsenide with major Pt and As peaks, adjacent to a Pd antimonide shown by minor Pd and Sb peaks. (f) Pd telluride with major Pd and Te peaks. There is an overlap between CaK α and K β peaks and Te peaks, but the presence of Te is confirmed by the presence of all five Te peaks, three of the smaller peaks being completely separate from Ca peaks. Ca is considered to be absent in this spectrum despite its potential presence due to the close proximity of the clinopyroxene. The Si and Fe peaks correspond to serpentine and magnetite, not pyroxene. (g) Pd,Pb alloy represented by major Pd and Pb peaks located on the edge of magnetite (Fe peak) and adjacent to serpentine (Si peak). Pt and Au peaks are missing, in contrast to the case of the Pd,Pb alloy enclosed in clinopyroxene (b). (h) Unidentified Pd-bearing mineral with a major Pd peak and minor Sn and Pb peaks in magnetite (Fe and O peaks). (i) Au,Pd,Ag,Cu alloy, with major peaks of Au and minor peaks of Pd, Ag and Cu, in serpentine enclosed by clinopyroxene, jointly represented by peaks of Mg, Si, Ca and Fe.

(Fig. 11). In the cleavage planes, the grains of PGM are usually slightly larger than those in the fresh pyroxene, and locally are elongate in the direction of the cleavage. In these cleavage zones (Fig. 12f), the PGM are predominantly uncharacterized minerals containing Pd and As, Pd and Sb, Pt and As (Figs. 12c–e), and Pd and Pb. Still in these cleavage zones but toward the edge of the fresh pyroxene and in the altered edge (at X'), an unnamed Pd,Te mineral occurs (9 grains). The grains of Pd,Pb alloy in the cleavage zones are similar to those in fresh pyroxene, but are Pt- and Au-poor (Fig. 12g). In general, however, they appear compositionally unaffected by alteration, which changes the Pd sulfides in the fresh pyroxene to arsenides, antimonides and tellurides along the cleavages. Rarely, Au and Cu occur in Pd arsenides, and Cu is enriched on the edge of Pd arsenide grains. Very locally, where Pd arsenides predominate over Pd antimonides, traces of Sn occur in the PGM. Figure 12h shows a grain of Pd,Sn alloy enclosed in magnetite within a cleavage zone. Rarely, Pd,Cu,Au alloy forms lath-shaped crystals in the altered cleavage zones, and one grain of Au,Pd,Ag,Cu alloy was located (Fig. 12i).

Sulfide-bearing high-level wehrlite (7, Table 1)

High-level wehrlite occurs as ultramafic lenses in gabbro; it is more Fe-rich than the wehrlite in the sequence of ultramafic cumulates (Gass *et al.* 1982). It also is sulfide-bearing, containing pyrrhotite, pentlandite, pyrite, chalcopyrite, allocase – gersdorffite_{ss} and niccolite. These lenses have Pt + Pd concentrations of up to 310 ppb. In one sample spanning the junction between a wehrlite layer and a pyroxene layer, one grain of Pt arsenide, less than 5 µm across, was found and inferred to be sperrylite.

Pt and Pd oxides and ochres

Many of the assemblages of Pt- and Pd-bearing PGM include low-reflectance minerals that form composite grains with other PGM. Their textural associations suggest that they are products of alteration of earlier PGM; analyses show that they contain oxygen and, more rarely, carbon. They are secondary oxides or ochres and carbonates formed as a result of weathering. The following are descriptions of the types of oxides and carbonates that have been found in the Shetland ophiolite.

The Pt-, Pd- and Rh-bearing PGM at Harold's Grave occur in clusters with irarsite and laurite in serpentine that is interstitial to the chromite grains. The Pt-, Pd- and Rh-bearing PGM include hollingworthite, geversite, hongshiite and genkinite. Associated with these PGM is a low-reflectance Pt-rich mineral that may be a Pt carbonate (Figs. 2b, 13).

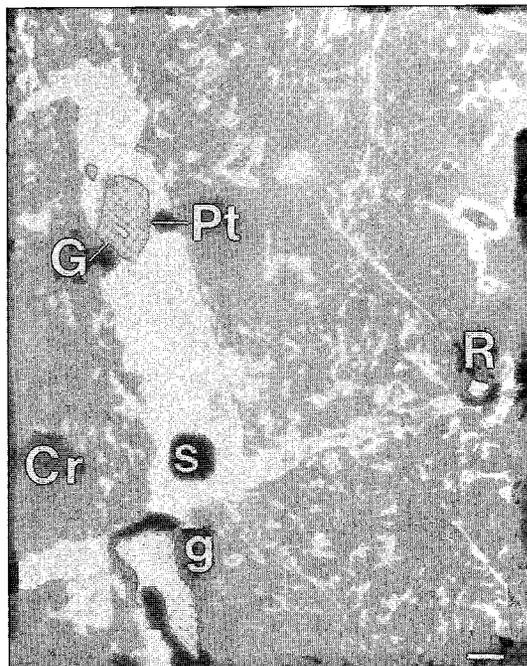


Fig. 13. Photomicrograph (reflected light) of a chromite-rich, sulfide-bearing dumite from Harold's Grave, showing the Pt-rich low-reflectance PGM (15 µm in diameter) (Pt), which may be a Pt carbonate. The mineral has variable reflectance, giving it a zoned appearance, with greater reflectance around the edge, creating a bright rim to the mineral, and a darker halo around a small inclusion of a Pt antimonide (G). The optical zoning does not correspond to any chemical zoning that could be resolved using X-ray mapping. The mineral is euhedral with strong anisotropy, has a good basal cleavage, and shows many of the optical properties of valleriite, but has a bright back-scattered image in the SEM. This mineral occurs in serpentine (s), filling a pull-apart crack between chromite grains (Cr). The PGM (Pt) clearly has lower reflectance than the other PGM (G), genkinite (g) and a Pt,Rh-rich antimonide (R). Scale bar represents 10 µm.

It contains a small, higher-reflectance, elongate inclusion of a Pt antimonide identified as geversite. Trace amounts of As, Cr, Fe, Ni, Cu and Rh (Fig. 2a) occur within the mineral. It is interpreted as a pseudomorph after sperrylite. The Pt antimonide may have been an original inclusion in the sperrylite that remained unaffected by the processes that altered the sperrylite. Such Sb-rich inclusions enclosed in PGE arsenides have been observed elsewhere in Shetland (Prichard & Tarkian 1988), indicating a general relationship of As-bearing PGM surrounding Sb-bearing ones, and thus giving additional support to the suggestion that the host to this Sb-bearing PGM was once an arsenide.

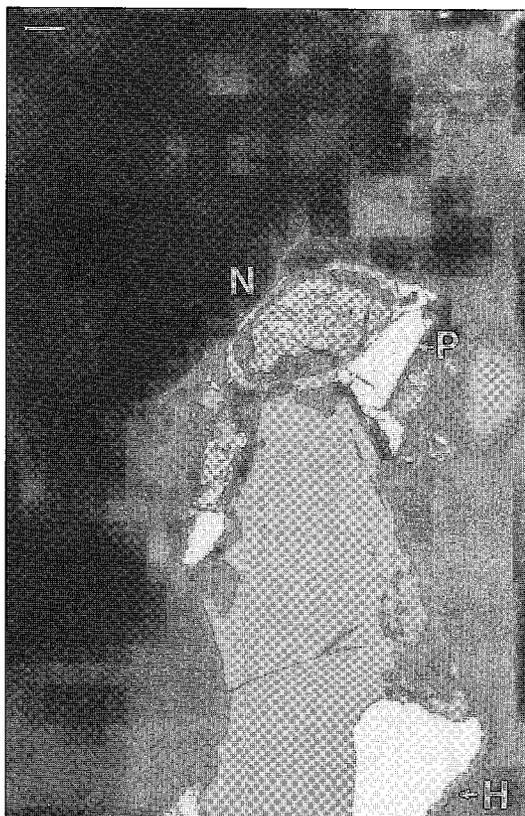


FIG. 14. Photomicrograph (reflected light) of a chromite surrounded by heazlewoodite (H), pentlandite (P) and native Cu (C) in serpentinized dunite. A colloform-textured Pt,Ni intergrowth (N) (80 μm in length) has a low reflectance and occurs on the edge of the chromite. This may be an ochre. The section is cut from dunite from drill core through the cumulate unit north of Balta Sound. Scale bar represents 20 μm .

A low-reflectance anhedral Pt-rich mineral is present adjacent to sperrylite within a sample of chromite-rich, As-rich, sulfide-bearing dunite from Cliff. It has been interpreted as a Pt-oxide or ochre (Ixer & Prichard 1989). Several spectra from this mineral were recorded; they reveal the presence of oxygen (Fig. 2d). The phase contains minor As, Ni, Cu and Fe; its position adjacent to sperrylite, in an area where a chlorite vein cross-cuts this composite PGM, suggests that it formed during alteration of sperrylite. At Cliff, Pd antimonides commonly are altered to Pd ochres which, like the Pt ochres, have a low reflectance (Ixer & Prichard 1989).

In drill core that intersects Pt- and Pd-bearing sulfides in cumulate dunites, a low-reflectance Pt,Ni intergrowth lies adjacent to chromite and is partially surrounded by pentlandite (Fig. 14). This has a similar

reflectance and shape to the light-element-, Pt-bearing minerals described from Cliff and Harold's Grave, but the lack of As in this phase and the absence of As-bearing minerals in general in this assemblage suggest that it may not be an alteration product of sperrylite. Magnetite associated with sulfide clusters in a pyroxenite (Fig. 11) locally contains low-reflectance Pt-bearing inclusions that are too small (up to 1 μm) for quantitative analysis, but also may be Pt-bearing ochre. All these examples emphasize the wide distribution of ochres throughout the PGE-bearing lithologies in this ophiolite complex.

DISCUSSION

The discussion firstly compares PGM in ophiolite and layered complexes. Secondly, it focuses on the formation and alteration of the PGM in the Shetland ophiolite complex, starting with the genesis of the primary igneous PGM and then their successive stages of alteration and weathering.

PGM in ophiolite and layered complexes

Despite the reported differences in final PGM mineralogy between ophiolite and layered complexes, their original mineralogy and mineralogical associations seem to be similar. Theoretically, Ru, Os and Ir are the high-melting-point PGE (Barnes *et al.* 1988, Peck & Keays 1990); these are the first PGE to form, with laurite crystallizing from the magma before chromite. This is seen in layered complexes, where laurite is the most common PGM to be enclosed in chromite, as exemplified by the Merensky Reef and UG-2 of the Bushveld Complex (von Gruenewaldt *et al.* 1986). Theoretically, Pt and Pd are chalcophile, and therefore are concentrated with base metals in an immiscible sulfide melt that scavenged these PGE from the silicate melt (Crocket 1979, Naldrett *et al.* 1979, Barnes *et al.* 1985, Gain 1985, Naldrett *et al.* 1989). As a result, Pt and Pd are usually associated with sulfides in basic and ultrabasic layered intrusions, as in the Sudbury (Chyi & Crocket, 1976) and Bushveld complexes (Wagner 1929, Kinloch 1982, McLaren & De Villiers 1982). In addition, there is a common association of Pt and Pd with chromite in layered basic and ultrabasic complexes; the Bushveld complex is the classic example of this (von Gruenewaldt *et al.* 1986). Hence, comparison with layered complexes shows that the basic and ultrabasic rocks of the Shetland ophiolite are not unusual in containing laurite associated with chromite, and Pt- and Pd-bearing PGM associated with sulfides, especially where these are close to chromite-rich lithologies. Since the associations of precious-metal minerals of ophiolite and layered complexes are very similar, so the processes that concentrate the PGE in them both may also be similar.

TABLE 3. PRIMARY AND SECONDARY PGE-BEARING MINERALS IN SHETLAND

Primary PGM	Secondary PGM
Enclosed by primary magmatic minerals	Enclosed by serpentine or chlorite
Laurite Ru(Ir,Os) ₂ enclosed in chromite	Os-, Ir-poor laurite, native Os Irarsite-hollingworthite IrRhAsS Speyrylite PtAs ₂ , Pt antimonide including geversite PtSb ₂
Pd, Cu, S ± Au ± Pt, enclosed in clinopyroxene	Pd, Sb including stibiopalladinite Pd ₅ Sb ₂
Pd, Pb ± Au ± Pt, enclosed in clinopyroxene	Pd-bearing Ni antimonides Pd, As, Pd, Te, Pt, Pd, Au and base metal alloys Pt, Rh cores to the allocrase-gersdorffite ₉₈ Pt and Pd ocifers

PGM and early magmatic processes

Table 3 shows the major primary and secondary PGM in the Shetland ophiolite complex. The PGM nearest to a magmatic composition are sulfide-rich and enclosed in primary silicates and oxides. All other PGM are surrounded by chlorite and serpentine and are inferred to be secondary. Ultramafic lithologies in ophiolite complexes are commonly altered; as a consequence, primary PGM are rarely seen or described. The exception is laurite, which is common and usually enclosed in chromite grains (Constantinides *et al.* 1980, Talkington *et al.* 1984, Augé 1986); thus it is preserved from alteration. Laurite is ubiquitous in Shetland in chromite at all stratigraphic levels within the ultramafic sequence (Prichard *et al.* 1987).

The precipitation of PGE from a sulfide-rich melt is indicated also by a general strong spatial association between Pt- and Pd-bearing PGM and base-metal sulfides. These PGM-sulfide associations are located at specific igneous horizons, which indicates that the sulfides are original magmatic concentrations; for example, in the drill core in the dunite unit, sulfides occur above layers of disseminated chromite. Either the PGE sulfides crystallized as discrete minerals associated with the base-metal sulfides or were in solid solution with them. Experimental studies (Makovicky *et al.* 1986) have shown that Pt and Pd are soluble in sulfides at high temperatures (Pd enters pyrrhotite and pentlandite, whereas Pt favors chalcopyrite), but are less soluble at lower temperatures. Therefore, on cooling and alteration, the PGE could be released from sulfides and recrystallize as PGM in close proximity to the sulfides.

Late concentration of PGE enclosed in a clinopyroxene crystal

The other inferred primary PGM (which may have re-equilibrated on cooling) is the unnamed Pd sulfide containing small quantities of Pt and Au, seen in fresh clinopyroxene and also preserved from alteration. This Pd sulfide only rarely has been described from ophiolite complexes, but is known from layered intrusions.

It is proposed that PGM trapped within the unaltered clinopyroxene are products of crystallization of a magmatic sulfide melt rich in Pd, Pt, Ni, Cu and Pb. The variation in composition of the PGM within the rows may indicate that crystallization of the PGM was not entirely homogeneous on a very local scale. Pd,Pb alloys crystallized from a more sulfur-poor portion of the melt located nearer the edge of the crystal, whereas a more sulfur-rich Pd-Ni-Cu-Fe-bearing portion of the melt crystallized toward the center of the crystal. Composite grains of Pt- and Au-bearing Pd sulfide, pentlandite and chalcopyrite may be products of re-equilibration of this trapped melt. The timing of formation of the PGM inclusions in the pyroxene is constrained by: (a) the morphology of the rows, which suggests that injection of the PGE-bearing melt occurred along cooling fractures, indicated by their irregular curved configuration, branching and oblique to the cleavage, (b) the absence of any PGM in the adjacent partially serpentinized olivine, which implies that the introduction of the PGE into the clinopyroxene occurred prior to juxtaposition of the pyroxene with the adjacent olivine, (c) the rounded shape of the PGM grains, which are aligned and separated by fresh pyroxene. These resemble rows of secondary fluid inclusions; in a like manner, a late-stage sulfide and PGE-rich magmatic fluid could have been injected into fractures in the pyroxene and have become isolated into droplets as the fractures closed by annealing during postmagmatic cooling of the pyroxene. The clinopyroxene is located at a high level in the sequence of ultramafic cumulates, where late magmatic volatiles are likely to have accumulated. As-, Sb- and Te-bearing PGM are not present within the fresh pyroxene, indicating crystallization of sulfide-rich PGM in the absence of and prior to the introduction of As, Sb and Te. The timing of the introduction of these elements is considered in the next section, dealing with alteration.

The concentration of the PGE in an immiscible sulfide melt depends on the concentration of the PGE in the parental liquid and the partition coefficient of the PGE into that sulfide melt. In Shetland, the level of concentration of Pt and Pd in the sulfides varies. It is comparatively low in sulfides associated with base-metal concentrations in the sulfide-bearing dunite, wehrlite and pyroxenite, where the PGE have been expelled from the primary magmatic sulfides subsequently, upon cooling and alteration. In contrast, the Pd sulfide inclusions in the clinopyroxene crystal are so PGE-enriched that they can be classed as discrete PGM rather than as PGE-bearing sulfides. Changes in the partition coefficients could be responsible for these different concentrations. Indeed, there is much discussion in the literature about the values of partition coefficients of PGE into sulfide. Estimated values of the partition coefficients D_{Pt} of 1,000 and D_{Pd} of 1,500 proposed by Naldrett (1981) are low compared with

empirical values of up to 1,000,000 calculated by Campbell & Barnes (1984). Three possible explanations for the extremely high PGE contents of the sulfide-rich inclusions in the clinopyroxene crystal are considered.

1. PGE are believed to be concentrated by C–H–O-bearing fluids within the magma (Ballhaus & Stumpfl 1986). If these volatile species were concentrated within this sulfide-bearing base-metal-, Pd- and Pt-rich melt, then the solubility of the PGE in the sulfide melt may have been enhanced, thus providing an explanation for the high tenor of the PGE in the inclusions within the pyroxene.

2. Where the concentration of PGE in the melt is locally high and the sulfur concentration is low, the sulfides may become very rich in the PGE, with the partition coefficients approaching infinity. This may be the case for the late-stage melt enriched in sulfide – base metals – PGE trapped within the clinopyroxene crystal, which occurs in a wehrlite that is not enriched in base-metal sulfides. High ratios of PGE to sulfide are described, for example, from the Bushveld complex, where Hiemstra (1985) explained the discrepancy between what is observed and what is expected from low partition coefficients (Naldrett 1981) by appealing to extremely high partition coefficients.

3. High partition coefficients may be apparent if there has been subsequent loss of base metals or sulfur from the inclusions. Naldrett & Lehmann (1988) suggested a postmagmatic loss of Fe as an explanation of high levels of Ni and Cu and PGE-enriched sulfides in chromitites. Authors favoring lower partition coefficients for the Bushveld suggest sulfur loss after formation to explain high ratios of PGE to sulfide (von Gruenewaldt *et al.* 1986). There is, however, no textural evidence for loss of base metals or sulfur in the PGM in the clinopyroxene crystal in the Shetland ophiolite complex. The high PGE content of these inclusions is best explained, therefore, by PGE accumulation in an immiscible volatile- and sulfur-rich melt separated from a late-stage low-sulfur magma in partially crystallized wehrlite.

PGM assemblages produced as a result of alteration and the introduction of As, Sb and Te

There is much debate as to whether PGE-bearing arsenides are late magmatic or secondary phases. The possibility of an As- and S-rich late magmatic immiscible liquid was first proposed by Oen (1973), and Gervilla & Leblanc (1990) suggested, for Alpine-type lherzolite massifs, that the PGE concentrate in such a liquid. At both the major PGE-bearing Ni–Cu sulfide deposits, Sudbury and Noril'sk–Talnakh, volatile-rich fluids are thought to have separated from an immiscible sulfide magma. Li *et al.* (1992) described the separation of a late magmatic Cl-rich fluid from a residual liquid in the Strathcona mine at Sudbury. The

crystallization of PGE in this case was controlled by Te, Bi, Sn and As in the late hydrothermal liquid. Genkin & Evstigneeva (1986) proposed that Pt, Pd, Sn, Te, Pb, As, Sb and Bi concentrated into a residual liquid in the case of the Noril'sk–Talnakh ores. Proton-microprobe studies confirm this hypothesis; they show that in these ores, small quantities of As, Sb, Te and PGE occur in solid solution in magmatic base-metal sulfides (Czamanske *et al.* 1992), and on cooling they are expelled from these sulfides to form PGE-bearing arsenides, antimonides and tellurides. This process, described for massive Ni–Cu sulfide deposits, could occur in ophiolite complexes. However, the quantities of sulfide involved are much smaller, rarely more than a maximum of 1–2% of the rock, and so the associated very small concentrations of As, Sb and Te would be insignificant and insufficient to form As-, Sb- and Te-bearing PGM in ophiolite complexes. In spite of this, examples of PGE-bearing arsenides from ophiolite complexes are commonly described and usually can be interpreted as secondary, due to late introduction of As during, or after, serpentinization and emplacement of the ophiolite (Corriavaux & Laflamme 1990). Sperryllite and other PGE sulfarsenides have been located in schlieren-type chromitites within serpentinized dunites from the Hochgrossen ultramafic massif in Austria. These are interpreted as secondary hydrothermal in origin (Thalhammer & Stumpfl 1988). Despite their preference for a late magmatic origin, even Gauthier *et al.* (1990) do not exclude the possibility that the PGE-bearing arsenides in the Ordovician ophiolite complexes of southern Quebec are associated with later, low-temperature alteration.

The ultramafic lithologies are extensively altered in Shetland. Except for chromite and clinopyroxene, the minerals, including olivine and orthopyroxene, are 75–100% altered, making recognition of primary PGM enclosed in these silicate minerals difficult. The majority of the PGM are surrounded by chlorite or serpentine and are arsenides and antimonides with minor tellurides. PGE-bearing arsenides (and their texturally associated antimonides and tellurides) are interpreted as having been formed after emplacement of the ophiolite, as low-temperature, secondary minerals during a hydrothermal event that produced talc along the basal thrust (Neary & Prichard 1985). The event was accompanied by the formation of both molybdenite-bearing chlorite and tourmaline-bearing quartz veins, some of which cross-cut the ophiolite and the adjacent metasedimentary units, thus dating this event as being post-emplacment. Arsenic anomalies commonly correlate with talc-rich lithologies, suggesting that the As was introduced during the hydrothermal event (Prichard & Lord 1993); widespread Ni arsenides and antimonides occur in fault zones and areas of greater alteration. Calculations suggest that As tends to immobilize the PGE (Mountain & Wood

1988a, b), because As will readily combine with Pt to form stable compounds. Where As was introduced along emplacement faults that cross-cut PGE-bearing igneous lithologies, the PGM have been altered to arsenides but remain within millimeters to centimeters to their original magmatic positions, as indicated by their close association with magmatic concentrations of sulfide and chromite. Sperrylite is not found in the crustal dunite, probably owing to a lack of major fault-zones near PGE-bearing dunite, and hence a lack of As [less than 30 ppm in samples from this area (Lord 1991)], rather than as a consequence of the variations in levels of magmatic As. Although As may have been derived from the magma, it would have been swamped by the large arsenic anomaly introduced during the hydrothermal event. These As anomalies are much higher (up to 2,000 ppm) than the highest As concentrations (350 ppm) caused by the As-rich late magmatic fluids of Ronda (Gervilla & Leblanc 1990) which, in turn, are 10 to 100 times normal magmatic values of As for ultramafic rocks (Onishi 1978).

Secondary PGM in the clinopyroxene cleavages

On a very local scale (micrometers), in the clinopyroxene crystal, all the Pd sulfides are enclosed within fresh pyroxene, and all the arsenides, antimonides and tellurides are along the altered cleavage, suggesting that Sb and Te are secondary and introduced. This relationship supports our theory that As, Sb and Te were introduced into the cleavages during or after serpentinization; if they had been released from the sulfides on cooling, they would be present also in the inclusions within the fresh pyroxene. The unfractured pyroxene provided an effective barrier to the penetration of As, Sb and Te, so preserving the Pd sulfides enclosed within it. In contrast, a very penetrative process of As, Sb and Te introduction throughout the serpentine, accompanied by local remobilization of the PGE, completely altered the PGM within the open-ended cleavages. The Sb-, As- and Te-bearing minerals are zoned within the cleavage. The origin of this zoning is problematical, but it may represent some kind of evolution of the low-temperature Sb-, As- and Te-rich fluid or the result of diffusional zoning. Antimonides are more abundant deeper in the cleavages, away from the edge of the pyroxene crystal, than are the arsenides, and hence slightly earlier than the As or more mobile, whereas the presence of the Pd tellurides nearer the edge of the pyroxene crystal may indicate that Te was introduced slightly later than the arsenides or is less mobile.

The only description of PGM in a similar textural setting to those PGM described here in the clinopyroxene crystal is provided by Edwards (1990). A fresh orthopyroxene, with a serpentinized cleavage, from the mantle sequence of the Lewis Hills in the

Bay of Islands, contains a trail of Pt- and Pd-bearing PGM. These are interpreted as late magmatic Pt and Pd arsenides formed as arsenic built up in the magma. The photomicrograph in Edwards (1990) shows that all the inclusions are in contact with serpentine and fractures (S.J. Edwards, pers. comm.). These inclusions may all have been modified by arsenic introduced during low-temperature alteration and could have had a primary PGE-sulfide mineralogy similar to that preserved in the fresh clinopyroxene crystal in Shetland. This suggests that there may have been a PGE- and sulfide-rich magmatic fluid in the mantle sequence of the Lewis Hills.

Serpentinization and weathering

The complex has been subjected to a number of periods of metamorphism and alteration, all of which could have caused serpentinization and associated alteration of the PGM. Sequentially, starting with the earliest event, they include (i) sea-floor hydrothermal circulation, more likely to have affected the upper parts of the ophiolite sequence, (ii) ophiolite emplacement, (iii) the post-emplacement hydrothermal event responsible for introduction of the As, with alteration focused along emplacement thrusts and internal faults, (iv) a pervasive regional greenschist-facies metamorphism (Read 1936), which affected the basement metasedimentary units and the whole ophiolite sequence. The relative degree of alteration during these events is difficult to determine. Heazlewoodite, millerite, godlevskite, magnetite, Ni,Fe alloy and native metals such as Cu, common in Shetland, are characteristic of serpentinization under reducing conditions (Ramdohr 1967, Dick 1974, Eckstrand 1975, Moody 1976). The formation of PGE alloys may coincide with this process. Such alloys have been described with similar assemblages from a number of ophiolite complexes, including Thetford (Corrivaux & Laflamme 1990). Prichard & Tarkian (1988) suggested that late-stage removal of arsenic led to the formation of alloys in the PGE-rich chromite-bearing lithologies at Cliff. This study shows that PGE-bearing alloys are present elsewhere in the Shetland ophiolite complex. For example, a Pt,Fe,Cu alloy occurs in a late-stage chlorite-rich alteration rim that surrounds chromite in dunite (Fig. 7a) and an Au,Pd,Ag,Cu alloy also occurs in the cleavage of the pyroxene crystal. Evidence of As removal is indicated by Pd arsenides, which locally have a Cu-enriched rim, also in these cleavage zones. The serpentinization event that caused the formation of these alloys is not identified, but may have been late, postdating the hydrothermal event that introduced As, because the PGE-bearing arsenides are locally seen to be altering to an alloy.

Oxides of the PGE are currently being described from a number of other PGE-bearing complexes (Legendre & Augé, pers. comm., Weiser 1991,

Milliotti & Stumpfl 1993). The low-reflectance Pt- and Pd-bearing oxides or ochres first identified in the Shetland ophiolite at Cliff (Iser & Prichard 1989) are shown here to be quite widespread in this ophiolite and present wherever Pt- and Pd-rich PGM occur. They take a poor polish and are friable. Texturally, they occur around the other PGM, suggesting that they were the last PGM to form. They are considered to be products of oxidation formed by present-day weathering, characterized by high fugacity of oxygen. Drill core from north of Baltasound contains a Pt,Ni ochre at a depth of 15 m, such that the ochres are not confined to the surface. If the Pt-bearing mineral containing carbon and oxygen is a Pt carbonate, this is very unusual, as Pt carbonates are considered unlikely to exist (Mountain & Wood 1988a, b). There are numerous low-reflectance Pt- and Pd-bearing minerals in these Shetland samples. The thin window detector capable of light element identification makes the study of these oxides or ochres and carbonates possible. Further work is in progress to more fully characterize and categorize these minerals.

Remobilization of the PGE

Textural evidence (Figs. 4, 8 and 11) suggests limited (1 mm scale) movement of PGE during alteration and serpentinization. This is demonstrated by clustering of the PGM around sulfides situated in serpentinized olivine, entirely surrounded by grains of pyroxene (Fig. 8). Here, the PGE have moved away from the sulfides during alteration until they reached fresh pyroxene, which formed a barrier to further dispersion and a suitable substrate for PGM precipitation. Also, slight movement of the PGE in the cleavage of the pyroxene crystal is recorded, where Pd arsenides and antimonides are displaced from the intersection of the cleavage and the rows of primary PGM. The alteration of these PGE sulfides to arsenides, antimonides and tellurides probably took place virtually *in situ*, with the introduction of As, Sb and Te effectively immobilizing the PGE. Local remobilization (with a maximum movement of a few meters and probably only a few centimeters) within the chromite-rich dunite lens at Cliff explains the extremely anomalous PGE values within the As-rich chromite-rich dunite (Lord 1991, Lord & Prichard 1991, Lord *et al.* 1992).

The presence of Pt and Rh in the alloclose – gersdorffite_{ss} at the basal thrust indicates remobilization of very small concentrations of Pt and Rh from the very highly anomalous PGE occurrence at Cliff to the nearby basal thrust (a distance of 200–300 meters). The suggestion that Cliff is the source of the Pt and Rh is supported by evidence concerning Au (an integral part of the highly anomalous assemblage of noble metals at Cliff), which has been mobilized into the basal thrust-zone near Cliff (Lord & Prichard 1989, Prichard & Lord 1993). No PGE anomaly was located

with this Au along the basal thrust at Cliff because the detection limits for the PGE were too high, but their reconcentration is shown mineralogically by the presence of Pt and Rh in the alloclose – gersdorffite_{ss}.

CONCLUSIONS

Assemblages of base-metal and PGE-bearing sulfides, arsenides, antimonides and alloys in the Shetland ophiolite complex are: (1) Pt- and Rh-bearing alloclose – gersdorffite_{ss} from the serpentinized basal thrust, associated with pyrrhotite, pentlandite, violarite and minor chalcopyrite; (2) Os-, Ir-, Ru-bearing PGM in chromite; (3) PGE-, As-rich, chromite-bearing dunite at Cliff; (4) Pt- and Pd-bearing antimonides in dunites, associated with pentlandite (altering to heazlewoodite, magnetite and Ni,Fe alloy), breithauptite, chromite, native copper, minor chalcopyrite and chalcocite; (5) Pt arsenides and Pd antimonides in wehrlite and pyroxenite, associated with pentlandite (altering to violarite), pyrrhotite (altering to pyrite) and chalcopyrite (altering to bornite); (6a) rounded inclusions of Pd sulfides and Pd,Pb alloy, each with or without trace amounts of Pt and Au, locally forming part of composite inclusions with pentlandite, enclosed within a single unaltered clinopyroxene crystal in a typical wehrlite; also, (6b) Pd arsenides, Pd antimonides, Pd tellurides and sperrylite with heazlewoodite and magnetite in the serpentinized cleavage of this clinopyroxene crystal in (6a), and (7) rare sperrylite in high-level wehrlite within gabbro, associated with pyrrhotite, pentlandite, pyrite, chalcopyrite, alloclose – gersdorffite_{ss} and niccolite.

Initially, the PGE were concentrated at a magmatic stage in the Shetland ophiolite complex. Os-, Ir-, Ru- and Rh-bearing PGM occur within chromite-rich lithologies. Pt and Pd are found in more fractionated lithologies enriched in base-metal sulfides closely associated with concentrations of chromite. In cumulate dunite, Pt- and Pd-bearing PGM occur in lithologies enriched in base-metal sulfides overlying discontinuous layers of chromite.

The magmatic PGM are PGE sulfides and, although rare, are preserved within primary chromite and clinopyroxene. In addition, the association of Pt- and Pd-bearing PGM with sulfide assemblages suggests that these PGE have been concentrated into an immiscible sulfide liquid that crystallized to form a primary magmatic assemblage. Small volumes of late-stage magmatic base-metal sulfide melts in the upper part of the ultramafic sequence may also have been volatile-rich and collected high concentrations of Pt and Pd. This step resulted in the formation of discrete Pd ± Pt ± Au sulfides that were preserved in fresh clinopyroxene.

Textural evidence indicates that PGM typically are very close to their original "igneous" locations, in the

order of 10 to 100 μm from their primary PGE source. Laurite is in its original position enclosed by chromite; Pt- and Pd-bearing PGM cluster around secondary sulfides in dunite, wehrlite and pyroxenite, and are considered to have been released from sulfides during alteration. Pd \pm Pt \pm Au sulfides and Pd,Pb alloys are preserved in annealed fractures in clinopyroxene. Larger-scale movement of the PGE is evident in the Cliff area, where very small concentrations of Pt and Rh occur along the basal thrust 200–300 m from the primary source.

Many of the observed PGE-bearing minerals have been formed in response to later alteration, and so are regarded as secondary. The PGM within serpentinite and chlorite are altered to arsenides, antimonides and tellurides. Later modification has resulted in removal of the As, Sb and Te to give PGE alloys, and very late-stage alteration has produced the light-element-rich PGM.

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