

HARZBURGITES AND REFRACTORY MELTS IN THE LEWIS HILLS MASSIF, BAY OF ISLANDS OPHIOLITE COMPLEX: THE BASE-METALS AND PRECIOUS-METALS STORY

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ABSTRACT

The immobility of the platinum-group elements (*PGE*) during serpentinization enables these elements to provide important information on the history of ophiolite mantle. In the Springers Hill area, Lewis Hills Massif, Bay of Islands Ophiolite Complex, Newfoundland, a residuum of harzburgite and minor dunite is intruded successively by a suite of dunite \pm chromite, orthopyroxenite and clinopyroxenite veins and dykes. These intrusive bodies represent crystal fractionates rather than liquid compositions. The fractionation sequence is typical of refractory melts such as boninites. Platinum-group minerals (*PGM*) and chondrite-normalized *PGE* patterns show that as the melt evolves, solid grains of Os-bearing laurite become entrapped in chromite, whereas solid Pt-Pd arsenide phases are incorporated in pyroxene. Consequently, the Pd/Ir value of the melt increases with progressive crystal fractionation, as the immiscible liquid phase changes from S-saturated to As-saturated. Harzburgites of residual origin have Pd/Ir < 1 . The Springers Hill harzburgites are *PGE*-enriched (Pd/Ir = 1.2–1.7), but otherwise possess residual characteristics arising from a minimum of 17% partial melting. Partial melting would have partitioned all sulfide in the source into the melt. Melt extraction was highly efficient, and no sulfide or silicate melt remained in the Springers Hill harzburgites. Therefore, *PGE* in the Springers Hill harzburgites are not present in sulfides. Field and petrographic evidence shows that enrichment of the *PGE* in Springers Hill harzburgites resulted from addition of an early-suite orthopyroxenite component (average Pd/Ir = 51). Orthopyroxene addition occurred by melt impregnation or mechanical mixing.

Keywords: Bay of Islands ophiolite, Newfoundland, harzburgite, dunite, chromite, pyroxenite, melt impregnation, platinum-group elements, base-metal sulfides.

SOMMAIRE

L'immobilité des éléments du groupe du platine (*EGP*) pendant la serpentinisation permet l'utilisation de ces éléments pour déduire de l'information utile concernant le manteau à la base des ophiolites. Dans la région de Springers Hill, dans le massif de Lewis Hills de l'ophiolite de Bay of Islands, à Terre-Neuve, un résidu de harzburgite et de dunite accessoire est recoupé successivement par une suite de dunite \pm chromite, orthopyroxénite et clinopyroxénite en veines et en filons. Ce cortège de roches intrusives comagmatiques représenterait des produits d'un fractionnement de cristaux plutôt que des compositions de liqui-

des. La séquence de fractionnement est typique de celle que suivrait un magma résiduel, comme un magma boninitique. Les minéraux des *EGP* et les teneurs de ces éléments, normalisées par rapport à une chondrite, montrent qu'à mesure que le magma évoluait, des cristaux de laurite contenant de l'osmium ont été englobés par la chromite, tandis que les arsénures de Pt et de Pd ont été incorporés dans le pyroxène. Par conséquent, la valeur Pd/Ir du magma augmentait à mesure que progressait le fractionnement et que la phase liquide immiscible devenait saturée en As plutôt qu'en S. Dans les harzburgites résiduelles, le rapport Pd/Ir est beaucoup plus faible que 1. Les harzburgites de Springers Hill sont enrichies en *EGP* (1.2 < Pd/Ir < 1.7), mais sont autrement typiquement résiduelles, ayant résulté d'un minimum de 17% de fusion partielle. Cette étape de fusion aurait causé tout sulfure disponible à la source à favoriser la phase liquide. L'extraction du bain fondu aurait été très efficace, de telle sorte que ni liquide sulfuré, ni liquide silicaté ne restait dans la harzburgite. C'est donc dire que dans la harzburgite de Springers Hill, les *EGP* ne sont pas situés dans les sulfures. À la lumière des relations de terrain et de la pétrographie, l'enrichissement des *EGP* semble avoir accompagné l'addition d'une composante orthopyroxénitique, partie d'une suite précoce, qui avait, en moyenne, un rapport Pd/Ir de 51. Cette fraction d'orthopyroxénite s'est ajoutée soit par imprégnation d'un liquide, soit par mélange mécanique.

(Traduit par la Rédaction)

Mots-clés: ophiolite de Bay of Islands, Terre-Neuve, harzburgite, dunite, chromite, pyroxénite, imprégnation d'un liquide, éléments du groupe du platine, sulfures des métaux de base.

INTRODUCTION

It is now well established that stratiform complexes such as those of the Bushveld, Great Dyke and Stillwater are important hosts for the platinum-group elements (*PGE*); on the other hand, economic concentrations of these elements have yet to be found in ophiolite complexes, in spite of their close similarity to stratiform complexes. To date, there have been very few complete studies of the base- and precious-metal concentrations in an ophiolite section. Oshin & Crocket (1982, 1986) carried out the most thorough investigation, and focused on the ultramafic, gabbroic and volcanosedimentary sections of the Thetford Mines Ophiolite, Quebec.

This paper combines field, petrographic, and base- and precious-metal data in order to explain the occurrence and origin of base and precious metals in residual and magmatic lithologies of the Springers Hill area, Lewis Hills Massif, Bay of Islands Ophiolite Complex (BIOC), western Newfoundland. Emphasis is placed upon trends of magmatic fractionation defined by the *PGE*, and the use of these elements to document modifications to pyroxenite and peridotite mineralogy and chemistry.

GEOLOGICAL SETTING AND FIELD RELATIONSHIPS

On the western coast of Newfoundland, the Humber Arm Allochthon (Williams & Cawood 1989) of

the Humber Zone (Williams 1979) preserves two ophiolite terranes: the BIOC and the Coastal Complex (CC). These adjacent terranes form an approximately north-south-trending zone some 100 km long and 25 km wide (Fig. 1). The CC lies to the west of the BIOC. The BIOC comprises four ophiolite massifs that, from north to south, crop out as the Table Mountain, North Arm Mountain, Blow Me Down Mountain and Lewis Hills massifs, respectively. The Lewis Hills is unique in that it preserves an original, subvertical contact between the CC to the west and BIOC to the east (Karson 1977, 1979, Karson & Dewey 1978). The BIOC formed at a spreading center (Casey *et al.* 1983, 1985), whereas the CC represents oceanic crust that has experienced a transform-

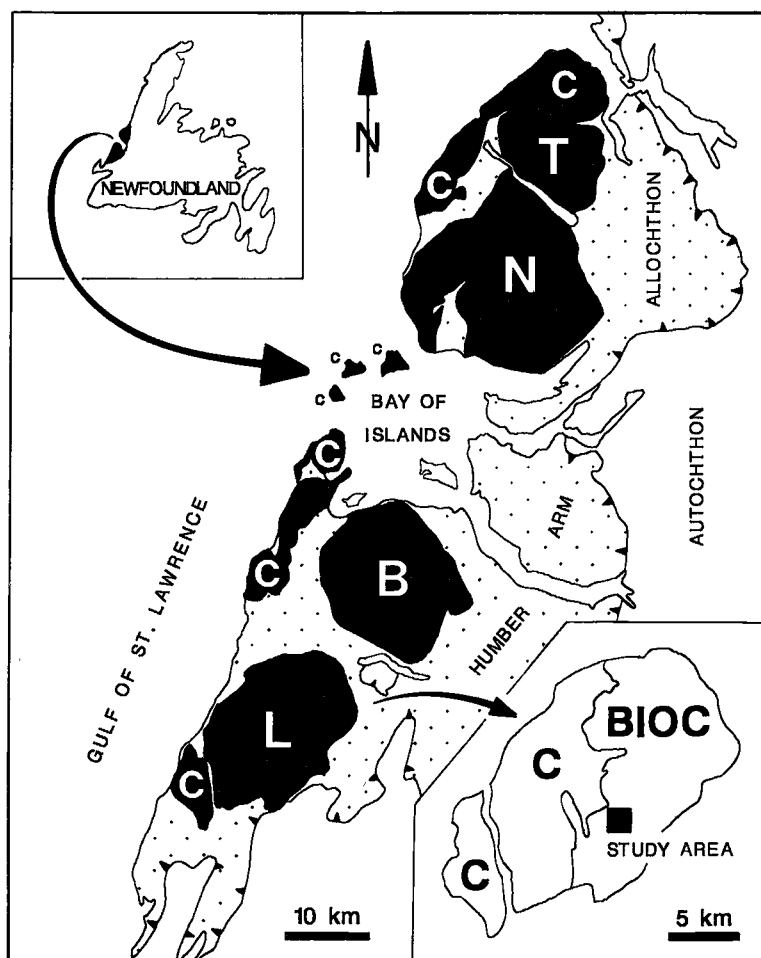


FIG. 1. Generalized geological map of the Humber Arm Allochthon (Williams & Cawood 1989). Geology of the Lewis Hills Massif is taken from Karson (1979). BIOC: Bay of Islands Ophiolite Complex, T: Table Mountain, N: North Arm Mountain, B: Blow Me Down Mountain, and L: Lewis Hills Massif; C stands for the Coastal Complex.

fault tectonic history within an oceanic fracture-zone (Karson & Dewey 1978, Karson 1984).

The Springers Hill area is located in the southern part of the Lewis Hills Massif, within the BIOC (Fig. 1). The area has been studied by Karson (1979), Dahl & Watkinson (1986), Dunsworth *et al.* (1986), Suhr & Calon (1987) and Edwards (1988a). Two magmatic suites are hosted within a harzburgite–dunite residuum (Edwards 1988a, b). The early suite is defined by successive intrusions of variably deformed dunite (with or without chromitite), orthopyroxenite and clinopyroxenite, as millimeter- to meter-wide veins and dykes lying parallel and subparallel to the plane of mantle flow defined by the tectonite fabric of the residuum. The order of crystallization among silicate minerals mimics the sequence of crystallization of melts derived from highly refractory mantle sources. The later suite is relatively undeformed, cropping out as a kilometer-sized body of dunite, wehrlite, clinopyroxenite and gabbro. The margin of the late suite cross-cuts the foliation defined by the residual tectonites and early-suite veins and dykes. This margin contains xenoliths of residuum and early-suite lithologies. The abundance of early-suite veins and dykes and the presence of the massive, late-suite intrusive body are unique to the Springers Hill area. In no other part of the BIOC has such a concentration of varied intrusive phases been observed in the mantle sequence. The late suite is not considered in this study; attention will focus on the origin and evolution of the residuum and early-suite lithologies.

The residual nature of the harzburgite is supported by the absence of clinopyroxene, presence of chromite, occurrence of porphyroclastic orthopyroxene with margins corroded to olivine, and occurrence of minor residual dunite. The latter is produced either by 35–45% partial melting of pyrolite (Jaques & Green 1980), or by reaction of peridotite with an introduced fluid, resulting in incongruent melting of orthopyroxene (*e.g.*, Dick 1977). In the Springers Hill area, residual dunites contain isolated grains of orthopyroxene and a chromite foliation and concentration similar to those in the adjacent harzburgite (Edwards 1987, 1988a). As the modal abundance of orthopyroxene decreases, harzburgite grades into residual dunite. Residual dunites are most easily recognized where they cross-cut the foliation of the harzburgite; remnants of the foliation they cross-cut are preserved. Massive bodies of pure harzburgite are rare owing to the presence of abundant early-suite veins and dykes.

Magmatic dunites are generally dyke-like in appearance, preserve a higher concentration of chromite than their harzburgite host, and parallel or cross-cut the harzburgite foliation. The margins of some magmatic dunites have residual characteristics. Chromitite bodies are always hosted in a dunite

envelope.

The orthopyroxenite and clinopyroxenite bodies occur as coarse-grained to pegmatitic veins and dykes and their boudinaged equivalents. Both types of pyroxenite preserve magmatic textures such as olivine–pyroxene parallel growth, adcumulus texture and consertal intergrowth texture. The pyroxenites rarely occur together, and it is very rare for clinopyroxenite to intrude orthopyroxenite. Orthopyroxenites are hosted by harzburgite, whereas clinopyroxenites are usually hosted by dunite. Consequently, the pyroxenites and their associated host-rocks define domains, which can be several hundred meters in width.

The orthopyroxene content of harzburgite is highly variable and ranges from <10 modal % (orthopyroxene dunite) to <90 modal % (olivine orthopyroxenite). However, the majority of harzburgites have an intermediate composition, *i.e.*, between 10 and 50 modal % orthopyroxene. The low end of this range is associated with dunite, whereas elevated orthopyroxene contents almost always occur in the vicinity of orthopyroxenite veins and dykes.

Two types of harzburgite have been defined on the basis of field and petrographic observations. The first type is residual, and has characteristics of a residue, as already described. The other type is residual harzburgite, or in rare cases, residual or magmatic dunite, with an overprint of up to 20 modal % orthopyroxene derived from the early-suite orthopyroxenites. The addition of orthopyroxene to harzburgite occurs either by mechanical mixing or melt impregnation. The former case arises by partial to complete tectonic disaggregation of orthopyroxenite veins and narrow dykes (<1 m) in harzburgite during progressive flow of mantle. The distribution of orthopyroxene in the resulting harzburgite is partly to completely homogenized, and orthopyroxene has a porphyroclastic texture. Melt impregnation occurs where orthopyroxenite veins and dykes become diffuse. The diffuse bodies occur in zones where melt could no longer hydraulically fracture the host rock to form dykes. Petrographically, the impregnations of undeformed orthopyroxene are present as delicate, interstitial grains, whereas impregnations of deformed orthopyroxene also exhibit a porphyroclastic texture. Nicolas & Prinzhofer (1983) and Nicolas & Dupuy (1984) have used melt impregnation to explain the enrichment of clinopyroxene and feldspar in harzburgite and dunite to yield lherzolite, wehrlite and troctolite.

PETROGRAPHY

Polished thin sections were examined in detail using transmitted- and reflected-light microscopy in order to determine the nature and occurrence of base- and precious-metal sulfides, arsenides, alloys and

native metals. A Hitachi S-570 scanning electron microscope was used to identify mineral grains and obtain semiquantitative analyses where appropriate. The distribution of base-metal phases and *PGM* is heterogeneous at the scale of a thin section.

Platinum-group minerals (PGM)

Discrete *PGM* have been identified in only three samples belonging to the early suite: a chromitite (L245), a pegmatitic orthopyroxenite dyke (L068), and a clinopyroxenite dyke that intrudes an orthopyroxenite dyke (L283).

A single grain of Os-bearing laurite (RuS_2) has been found in the chromitite sample. The grain is located within unaltered chromite, in association with native Cu and a Ca-Mg-Al silicate (Fig. 2A). Os-bearing laurite is commonly found in chromitite from ophiolites (Talkington *et al.* 1984).

The orthopyroxenite sample preserves a trail of Pt- and Pd-arsenide mineral grains at the margin of a pegmatitic orthopyroxene grain that is in contact with Ca-amphibole (Fig. 2B). Of the seven grains in Figure 2B, six are Pd-arsenide and one is Pt-arsenide. The Pd/As value is lower in the Pd-arsenide associated with the Pt-arsenide than in any other grain of Pd-arsenide. Low concentrations of Fe and Ni occur in Pd-arsenide.

In the clinopyroxenite sample, a single, hexagonal, composite grain of *PGM* occurs fully enclosed within the margin of a clinopyroxene grain (Fig. 3). Phases present in the composite grain are native Pt, native Cu, Pd-Cu and minor Pt-Cu alloys, and Pt-Pd arsenide phases with or without Fe, Co and Ni. The Pt-Cu alloy probably is hongshiite (PtCu), which has only been described from Hung, China (Peng *et al.* 1978) and the Shetland Ophiolite (Prichard & Tarkian 1988). The Pd-Cu alloy identified in the Springers Hill area may be a new mineral.

Sulfides, alloys and native metals

In harzburgite, residual dunite, and dunite, chromitite and orthopyroxenite of the early suite, rare base-metal phases occur as minute wisps, flecks and grains in serpentine. Grains are commonly too small to be identified positively. Awaruite (Ni-Fe alloy) and magnetite are the most common phases identified. In some harzburgites, wüstite has altered to magnetite and native Fe. Pentlandite, heazlewoodite (Ni_3S_2), awaruite and millerite (NiS) occur in some dunites. Copper sulfides and native Cu are found in orthopyroxene, parallel to the cleavage and in fractures, respectively. All the base-metal phases are believed to be of secondary origin, related to serpentinization. In the harzburgite-dunite tectonite,

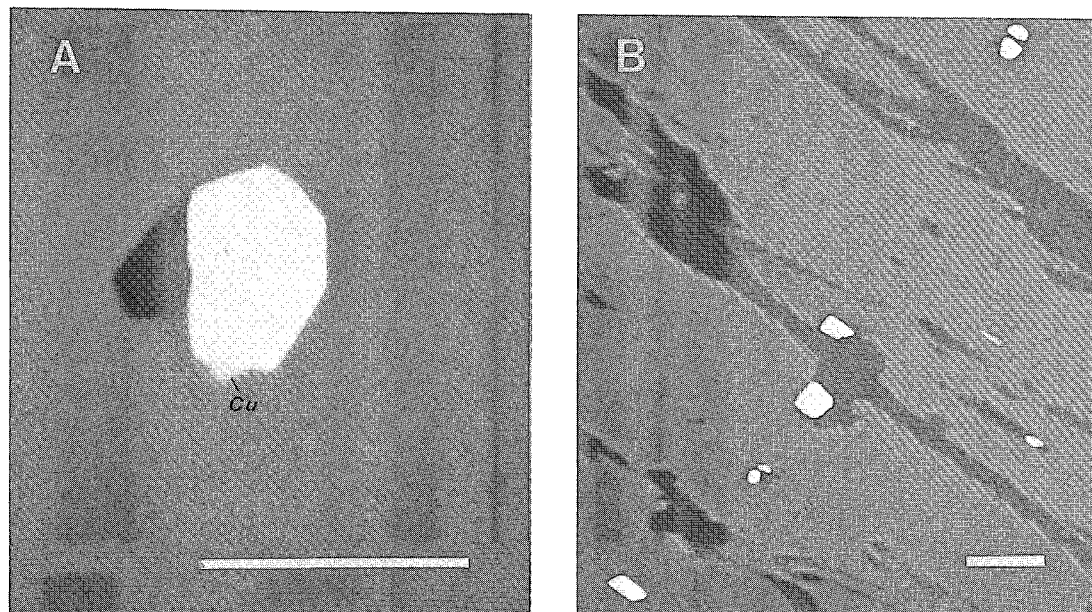


FIG. 2. Scanning electron photomicrographs. (A) Euhedral Os-bearing laurite (white), euhedral Ca-Mg-Al silicate (black), and tongue of native Cu in a grain of unaltered chromite (grey). Early-suite chromitite, L245. (B) Trail of euhedral Pt- and Pd-arsenide grains (white) in unaltered orthopyroxene (grey). The trail of arsenide grains is perpendicular to the cleavage in orthopyroxene, which is partly altered (dark grey). Early-suite orthopyroxenite, L068. Scale bar 10 μm in both cases.

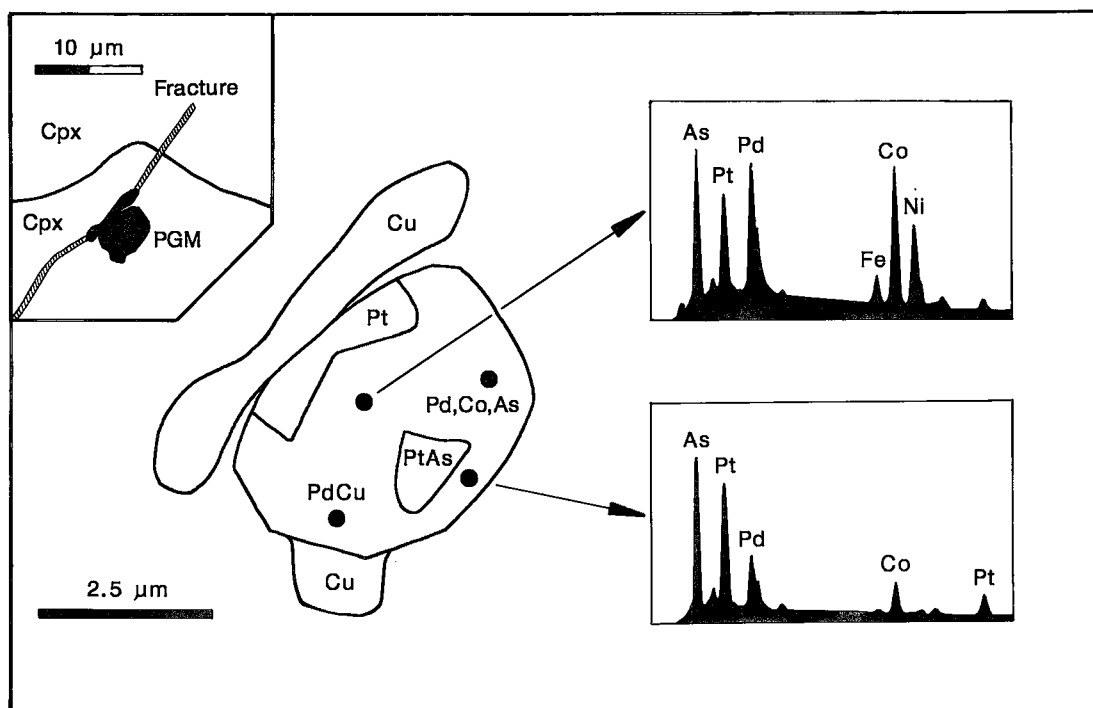


FIG. 3. Line drawing of a scanning electron photomicrograph that illustrates the composite nature of a *PGM* grain hosted by clinopyroxene. Early-suite clinopyroxenite, L283.

magnetite and Fe–Ni–Cu–S phases are undeformed and show no evidence of recrystallization, which supports their late origin.

In *clinopyroxenite of the early suite*, Fe–Ni–Cu–S phases form grains <0.15 mm in diameter, and are more abundant in the early-suite clinopyroxenites than in any other lithology of the early suite. Moreover, within meter-wide dykes of clinopyroxenite, which contain variable amounts of olivine, the Fe–Ni–Cu–S phases occur ubiquitously, but not exclusively, in clinopyroxene-rich areas. Hence, the distribution of Fe–Ni–Cu–S phases is heterogeneous and suggestive of localized zones of S saturation in clinopyroxene-rich areas.

Pentlandite and native Cu with minor associated Cu sulfide are the most common phases found, both within clinopyroxene and at clinopyroxene–clinopyroxene grain boundaries. These base-metal phases may or may not be associated with chromite and amphibole. Pentlandite and native Cu commonly exhibit a symplectitic texture (Fig. 4), which probably resulted from the exsolution of native Cu from pentlandite and its subsequent migration to the margin of the grain. In places, pentlandite fragments are wholly enclosed in native Cu. Discrete ovoid grains of native Cu occur in unaltered, unfractured clinopyroxene grains.

The occurrence of pentlandite and native Cu as inclusions in clinopyroxene, and at grain boundaries of clinopyroxene, is best explained in terms of immiscible globules of liquid forming at or near the surface of growing crystals of clinopyroxene. Some globules became entrapped, whereas others were pushed ahead of the crystallization front (Peterson & Francis 1977, Sharkov 1983, Andersen *et al.* 1987). This would also explain why the majority of inclusions in the Springers Hill samples are hosted in the margin of clinopyroxene crystals. Alternatively, native Cu could have exsolved from clinopyroxene, especially in cases where native Cu occurs as irregular blebs parallel to the cleavage in grains of unaltered clinopyroxene.

During late-stage alteration, Cu was mobile, and was removed from pentlandite. Other reactions include the formation of awaruite at the contact between pentlandite and native Cu, the replacement of pentlandite by magnetite, and the formation of cuprite where native Cu is oxidized in the presence of magnetite.

Cobalt-bearing awaruite or a composite awaruite–wairauite (Co–Fe alloy) grain has been identified at the silicate–chromite contact of a silicate inclusion in a chromite grain hosted by clinopyroxene.

Semiquantitative analyses of pentlandite and

awaruite show that they are Ni-rich. The absence of olivine in the vicinity of the assemblage pentlandite + awaruite may explain the elevated Ni/Fe value.

WHOLE-ROCK BASE-METAL AND PRECIOUS-METAL CHEMISTRY

Analytical techniques

Eighteen whole-rock samples were analyzed for *PGE* and Au using the SCIEX ELAN inductively coupled plasma – mass spectrometer (ICP–MS) at Memorial University. Nickel and Cu concentrations were determined by X-ray fluorescence (XRF) in fourteen whole-rock samples using the Philips PW1450 instrument at Memorial University. Large samples were powdered in order to minimize sampling error arising from grain size and mineral distribution.

Pellets of pressed powdered sample (10 g sample, 1.45 g Bakelite brand phenolic resin binder) were analyzed on the XRF. Based on standards, Cu values are considered to be consistently much lower than true values. Consequently, Cu values are reported solely for the purpose of comparing Cu-rich and Cu-poor samples, and the data are not used quantitatively. Standards demonstrate that Ni values are precise and accurate (Table 1).

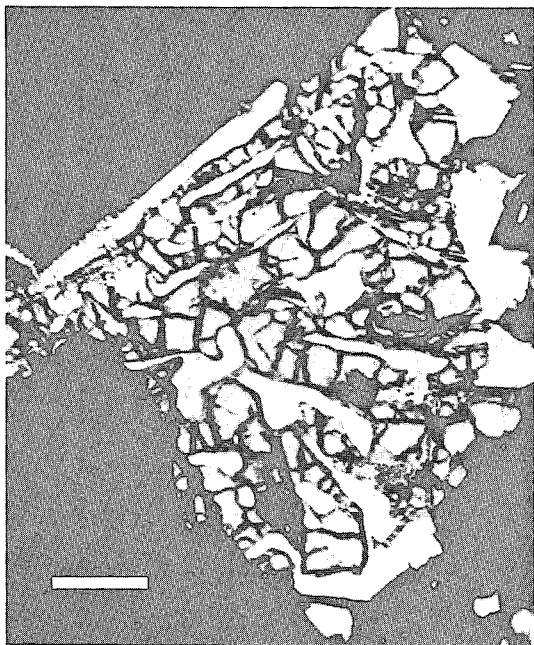


FIG. 4. Scanning electron photomicrograph of vermiciform exsolution blebs of native Cu (white) in Ni-rich pentlandite (grey) hosted by clinopyroxene (black). Early-suite clinopyroxenite, L214. Scale bar 20 μ m.

Samples run on the ICP–MS were prepared by fusing a mixture of rock (15.0 g), Ni carbonyl (9.6 g), S (6.0 g), Na_2CO_3 (18.0 g), $\text{Na}_2\text{B}_4\text{O}_7$ (36.0 g) and SiO_2 (15.0 g) to produce a NiS button. This button was then dissolved in HCl, and the *PGE* and Au were collected by Te precipitation (Jackson *et al.* 1988). Detection limits are at or below 0.3 ppb (Table 1). The precision and accuracy of the Au and *PGE* analyses vary widely, but Pd and Ir both exhibit good precision and accuracy (Table 1). The average blank composition (Table 2) has been subtracted from all Springers Hill data in order to remove the effects of contamination from samples yielding low elemental concentrations. Prior to correction, samples low in Pd and Ir exhibited Pd/Ir values biased by the blank component. Some corrected values lie at or below the detection limit (Tables 1, 2). These values are still considered because they were above the detection limit before correction.

Whole-rock chemistry

Nickel, Cu and *PGE* values (Table 2) support the petrographic evidence for the presence of pentlandite, awaruite, native Cu and *PGM*. Based on all of the analyses, only the early-suite orthopyroxenites consistently show significant enrichment in *PGE*. Gold exhibits an affinity for clinopyroxenites. The highest Au values are restricted to those samples with high Cu values.

ORIGIN OF THE BASE AND PRECIOUS METALS

Prior to an interpretation of the base- and precious-metal data, it is first necessary to determine whether the measured values reflect primary or secondary processes. The distribution of the elements may reflect conditions during initial crystallization of the melt, subsequent subsolidus re-equilibration, and later low-temperature alteration related to serpentinization.

Primary grains of base- and precious-metal minerals

It is assumed that grains of base- and precious-metal minerals enclosed in unaltered and unfractured chromite and silicate grains are primary because subsolidus reactions occurred as a closed system (Lorand 1987a). Phases interstitial to chromite and silicate grains have clearly reacted with serpentinizing fluids.

The laurite – native Cu – silicate assemblage in chromite (Fig. 2A) is primary and *in situ*. The euhedral nature of the laurite and silicate grains indicates that they were incorporated into chromite as solid grains during chromite growth. Johan & Le Bel (1978), Constantinides *et al.* (1980), Prichard *et al.* (1981), Stockman (1982) and Talkington *et al.* (1983) also have found that euhedral grains of *PGM* are

TABLE 1. PRECISION AND ACCURACY OF ANALYTICAL METHODS

Standard	Element	n	DL	Precision	Mean	MUN	Ref
PGC-1	Ni	19	2	1.1	2291	-	2400
PTC-1	Au	4	0.14	23.2	551	463	650
PTC-1	Ru	4	0.08	14.2	436	440	650
PTC-1	Rh	4	0.02	3.1	605	609	620
PTC-1	Pd	4	0.13	5.8	11354	11405	12700
PTC-1	Re	4	0.04	18.2	67	67	-
PTC-1	Os	4	0.31	32.8	160	192	240
PTC-1	Ir	4	0.01	7.5	171	164	170
PTC-1	Pt	4	0.05	18.4	2583	2699	3000
	Pd/Ir				66.4	69.5	74.7

Concentrations in ppm for Ni and ppb for Au and PGE. n = number of analyses of the standard. DL = detection limit. Precision (as %) reported as the coefficient of variation. MUN are the Memorial University reported values for PTC-1. Ref are accepted standard values: Ni (Abbey 1983), Au and PGE (McAdams *et al.* 1973).

The origin of As in *PGM* is equivocal, and the origin of the Pt-Pd arsenide phases is reserved for the following section on alteration.

The primary composition of the base-metal sulfide in the early-suite clinopyroxenites is most likely approximated by grains of pentlandite that host exsolution blebs of native Cu (Fig. 4). If subsolidus re-equilibration of such grains was isochemical, the bulk composition of the original sulfide phase was that of a Cu-bearing, Ni-rich pentlandite. Such a sulfide phase is likely derived from a mantle source that had previously undergone partial melting, which decreased the Fe and S content of the mantle sulfide component (Garuti *et al.* 1984).

TABLE 2. Ni, Cu, Au AND PGE CONTENT OF SPRINGERS HILL AREA LITHOLOGIES

Sample	Lithology	ppm					ppb					Sum PGE	Pd/Ir
		Ni	Cu	Au	Ru	Rh	Pd	Re	Os	Ir	Pt		
L106	Harz	1908	bdl	0.14	8.75	1.53	8.16	0.39	4.61	4.76	9.54	37.74	1.71
L218	Harz	1992	bdl	0.32	7.23	1.84	3.87	0.05	3.16	3.13	5.19	24.47	1.24
L054	ES Serp	na	na	0.09	20.98	3.59	2.67	0.00	4.04	9.60	1.13	42.01	0.28
L254	ES Dn	2186	bdl	0.38	3.56	0.44	0.71	bdl	1.90	2.00	0.20	8.81	0.36
L203	ES Chrm	na	na	0.14	50.66	4.62	2.79	0.06	14.61	15.05	1.58	89.37	0.19
L244	ES Chrm	na	na	4.57	50.41	2.83	0.00	0.00	22.41	11.91	2.13	89.69	-
L289	ES Chrm	na	na	0.12	25.60	2.35	5.31	0.00	13.31	6.05	2.13	54.75	0.88
L068	ES Opxt	721	bdl	0.59	0.13	0.48	170.38	0.00	0.14	0.36	170.85	342.34	473.28
L071	ES Opxt	775	bdl	0.94	0.19	1.60	15.92	16.43	bdl	0.44	14.58	49.16	36.18
L267	ES Opxt	711	bdl	0.50	0.56	10.12	104.74	0.30	1.29	3.32	141.70	262.03	31.55
L268	ES Opxt	703	bdl	0.63	2.02	30.92	405.68	0.00	2.79	9.51	517.20	968.12	42.66
	Av Opxt	728	bdl	0.66	0.73	10.78	174.18	4.18	1.06	3.41	211.08	405.41	51.08
L026	ES Cpxt	744	313	29.23	0.17	0.74	67.98	0.00	0.26	0.31	61.24	130.70	219.29
L211	ES Cpxt	948	176	28.81	bdl	0.31	10.38	0.94	0.13	0.01	3.47	15.24	1038.00
L212	ES Cpxt	794	132	23.11	bdl	0.13	0.44	0.54	0.63	bdl	0.18	1.92	-
L213	ES Cpxt	558	bdl	2.13	bdl	0.13	3.83	1.05	0.53	0.03	0.77	6.34	127.67
L214	ES Cpxt	1354	125	16.34	bdl	0.03	6.05	13.28	bdl	0.07	1.00	20.43	86.43
L283	ES Cpxt	493	bdl	7.94	0.23	3.73	193.71	0.05	0.35	1.62	520.53	720.22	119.57
L293	ES Cpxt	560	bdl	0.13	0.16	0.08	10.16	0.00	0.05	0.06	3.41	13.92	169.33
	Blank			0.56	bdl	0.05	0.92	0.15	bdl	0.03	0.33	1.48	30.67

Au and PGE values are reported as the original values minus the reagent blank composition. bdl = below detection limit; na = not analyzed; Av = average; Harz = harzburgite; ES = early-suite; Serp = chromite-rich serpentinite; Dn = dunite; Chrm = chromitite; Opxt = orthopyroxenite; Cpxt = clinopyroxenite.

entrapped in chromite, whereas silicates become initially trapped as liquids or euhedral crystals (Talkington *et al.* 1984). Therefore, the suggestion by Gijbels *et al.* (1974), Agiorgitis & Wolf (1978), Crockett (1979) and Mitchell & Keays (1981) that the *PGE* are in solid solution in the spinel structure does not apply to the Springers Hill samples. Gijbels *et al.* (1974) have suggested that grains of *PGM* are produced by expulsion of the *PGE* from structural sites in spinel during subsolidus re-equilibration. Inclusions in chromite from the Springers Hill chromitite sample do not support this process. The occurrence of sulfide in chromite probably results because the crystallization of chromite locally reduces the FeO content of the melt, allowing sulfide to precipitate (Page 1971, Haughton *et al.* 1974).

Alteration

In order to use base- and precious-metal concentrations in whole-rock samples as petrogenetic tracers, the effects of alteration must be known. The present Fe-Ni-Cu-S assemblage represents the end product of serpentinization reactions, which yielded an assemblage of magnetite, awaruite, native metals (Cu), pentlandite and other minor phases. Such an assemblage is characteristic of serpentinized ultramafic rocks (Eckstrand 1975, Moody 1976). The pentlandite - magnetite - awaruite - native Cu assemblage is common in all environments where relict olivine and serpentine coexist, as a result of low $f(\text{O}_2)$ and low $f(\text{S}_2)$ conditions (Eckstrand 1975). The magnetite-awaruite assemblage in serpen-

tinite is evidence for a very O_2 -deficient, H_2 -rich environment at temperatures below $420^\circ C$ (Moody 1976).

Under conditions of nonconstant volume, serpentinization is an isochemical process except for the introduction of H_2O and loss of Ca (Coleman & Keith 1971, Eckstrand 1975). Groves & Keays (1979) predicted that a system undergoing serpentinization may gain S from an external source and lose Ni from the silicate fraction into opaque phases, or from the system altogether. In terms of mobility, Fe, Ni, Co and S can move as much as 10 cm during the most active stage of serpentinization (Shiga 1987); Fe^{2+} is more mobile than Ni^{2+} because NiS has a smaller solubility product than FeS (Groves & Keays 1979). The petrographic examination of the Fe-Ni-Cu-S assemblages in samples from the Springers Hill area indicates that Fe and Ni remained essentially *in situ* in pentlandite, awaruite and magnetite, or moved a short distance (mm scale) to be incorporated into other opaque phases in serpentine. Copper was the most mobile element (mm-cm scale); in cases, it was removed from pentlandite and precipitated along fractures (Fig. 3) and grain boundaries. Hence, Fe, Ni and Cu are *in situ*, at least at the scale of a hand specimen; data on these elements should, therefore, be representative of the original composition of the whole rock prior to serpentinization.

Platinum-group elements are immobile during serpentinization (Keays & Davison 1976, Groves & Keays 1979, Oshin & Crockett 1982, Prichard & Tarkian 1988); therefore, primary magmatic abundances should survive this alteration (Oshin & Crockett 1982). Prichard & Tarkian (1988) have found, however, that the phases comprising the *PGM* assemblage will change during serpentinization; for example, hongshiite may be an alteration product of sperrylite ($PtAs_2$) (Prichard & Tarkian 1988) or cooperite (PtS) (Cabri 1981). By inference, hongshiite in the Springers Hill samples probably has a similar origin. If so, the source of Cu could be native Cu blebs and pentlandite in the early-suite clinopyroxenites. Copper remobilization in clinopyroxenite is probably related to serpentinization of the harzburgite and dunite hosting the clinopyroxenite. The preference of native Cu and Cu-*PGE* alloys for the margins of *PGM* arsenide grains (Fig. 3) strongly suggests that arsenide minerals existed prior to the introduction of Cu.

Another example of a modification in the *PGM* assemblage may result from the introduction of As. The origin of As in *PGM* is unclear; Naldrett & Cabri (1976) reported that during cooling, sulfides undergo phase transformations and the *PGE* exsolve, recrystallize, and combine with As, Te, Bi and Sb to form complex *PGM* phases. The low S/As values reported by Groves & Keays (1979) for some serpentinites (mainly talc-carbonate rocks) suggest that As

was introduced by an alteration fluid. Similarly, Prichard & Tarkian (1988) argued that As could be introduced with late-magmatic fluids, or during or after low-temperature hydrous conditions suitable for chlorite formation. In the Springers Hill samples, the euhedral nature of the arsenide grains in relatively unaltered pyroxene (Figs. 2B, 3) implies that the arsenides precipitated as primary phases from a fractionating melt. Support for this was provided by Oen (1973), Lorand (1987b) and Leblanc *et al.* (1989), who proposed that the *PGE* are fractionated in an immiscible As-S-rich liquid in the early stages of crystal fractionation during mantle upwelling.

Gold may be lost during serpentinization (*e.g.*, Keays & Davison 1976), but Oshin & Crockett (1982) showed that Au may be added to harzburgite during the formation of asbestos veins. Groves & Keays (1979) proposed that the dissolution and removal of Au in an alteration environment are enhanced by high $f(O_2)$, but strongly oxidizing conditions do not appear to have prevailed in the Springers Hill area.

In conclusion, the concentrations of Fe (as total Fe), Ni, Cu and *PGE* in lithologies of the residuum and early-suite rocks in the Springers Hill area are most likely primary in origin, despite local remobilization. Solid sulfide and arsenide grains were incorporated into chromite and pyroxene as the melt evolved. Osmium-Ru-S saturation was followed by Pt-Pd-As and Fe-Ni-Cu-S saturation, respectively, all under magmatic conditions.

PETROGENETIC CONSTRAINTS

The concentrations of *PGE* enable constraints to be placed upon the origin of the lithologies in the Springers Hill area. The *PGE* data are presented as Pd/Ir values (Table 2) and in chondrite-normalized *PGE* plots (Fig. 5). Gold is not considered because it is more mobile than the *PGE* during serpentinization.

Origin of the Springers Hill harzburgite

Before examining the *PGE* chemistry of the Springers Hill harzburgite, it is necessary to understand the origin of these rocks. The sulfide component of the upper mantle has a low melting point (Naldrett 1973) and is largely involved in mantle melting (Garuti *et al.* 1984). This phenomenon allows the abundance of Fe-Ni-Cu-S phases to be used as an index of depletion, especially as their abundance correlates with the modal abundance of clinopyroxene and plagioclase in residual mantle material (Lorand 1988). The Springers Hill harzburgites are devoid of primary Fe-Ni-Cu-S phases, clinopyroxene and plagioclase. They have highly depleted trace-

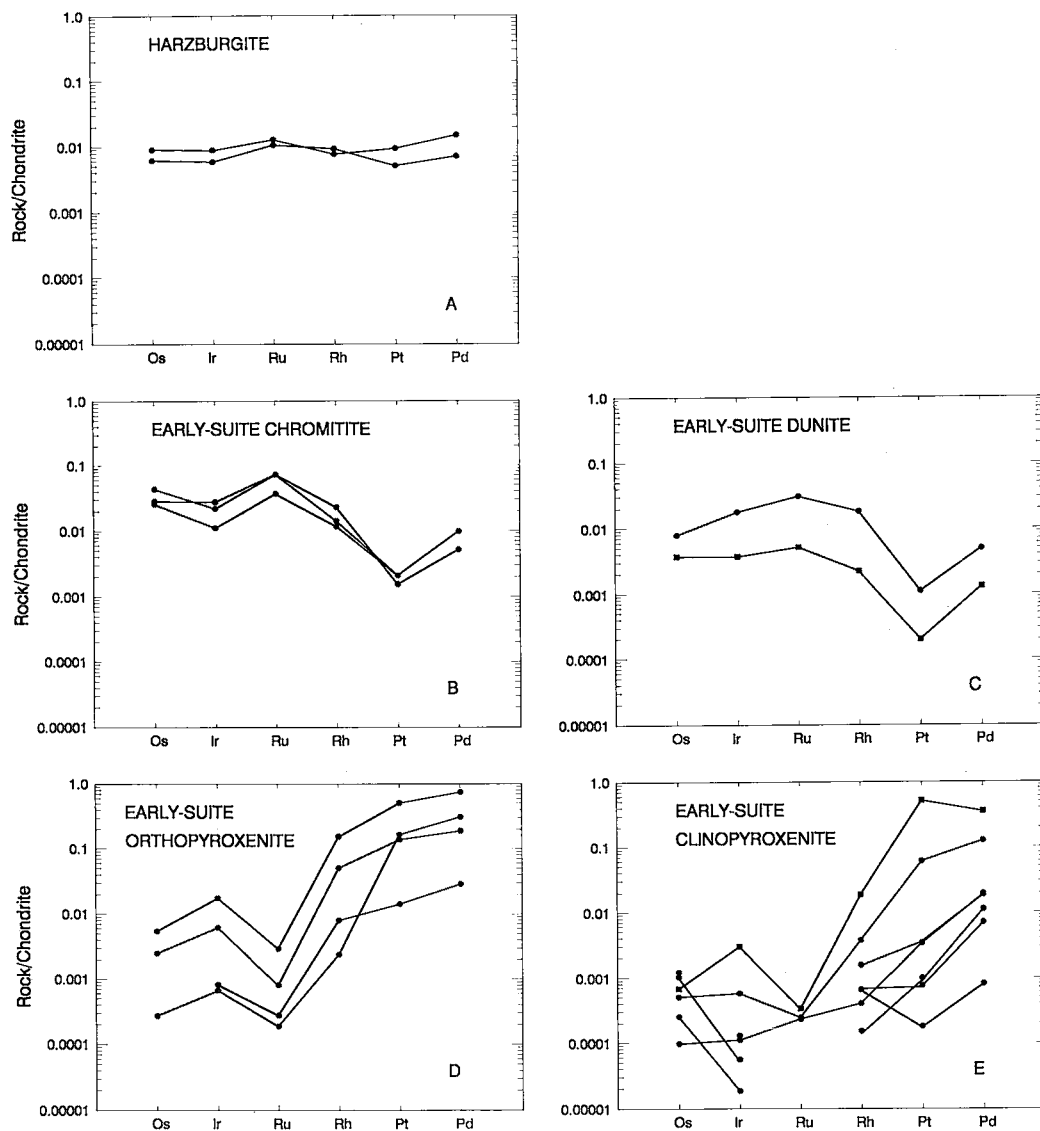


FIG. 5. Chondrite-normalized PGE abundances in harzburgite (A) and lithologies of the early suite (B, C, D and E) from the Springers Hill area, BIOG. All samples are represented by circles, except in C (circle: chromite-rich serpentinite, square: dunite) and E (square: clinopyroxenite dyke containing xenocrysts of orthopyroxene derived from orthopyroxenite). PGE values used for normalization are those compiled by Naldrett & Duke (1980) for an average C1 chondrite.

and rare-earth-element characteristics, and they contain chromite associated with Mg-rich olivine and orthopyroxene. These features are all characteristic of a highly depleted mantle residuum.

It is possible to estimate the degree of partial melting required of a mantle source to yield a harzburgite residue totally barren of sulfide (Barnes *et al.* 1985). Garuti *et al.* (1984) reported an Fe-depleted,

Ni- and Cu-enriched mantle sulfide component for the Baldissero and Balmuccia lherzolites of the Ivrea-Verbano mantle peridotites, western Italian Alps. These lherzolites preserve S contents of 140–320 ppm, which are representative of the S content of undepleted to partly depleted upper mantle (Garuti *et al.* 1984). For the Springers Hill harzburgites, it is assumed that the initial S content of the

mantle source was 140–320 ppm, that partial melting occurred at a depth of <40 km (Duncan & Green 1987), and that S solubility in basic silicate melts is 0.19 wt. % (Wendlandt 1982). For these parameters, 7% to 17% partial melting is required to remove all of the mantle sulfide into the melt for, respectively, S contents between 140 and 320 ppm in the initial mantle source. Depleted mantle peridotites in the BIOC were produced by 23% partial melting of BIOC spinel lherzolite (Malpas 1978), which would leave a harzburgite residue totally devoid of any primary sulfide phase after complete extraction of melt. Basal spinel lherzolites in the BIOC have an Fe–Ni–Cu–S component of <0.005% by volume, and they grade into harzburgites totally devoid of a sulfide component (Lorand 1987a). Springers Hill harzburgites contain no petrographically visible sulfide phase, apart from that resulting from serpentinization of the silicate phases. During partial melting, the dissolution of all the mantle sulfide leaves no sulfide residue into which the *PGE* can partition. Melt has been very effectively removed from the Springers Hill harzburgites, as there is no evidence for trapped silicate or sulfide melt residing in the residuum.

The Springers Hill harzburgites contain 24–38 ppb total *PGE*. Because there is no sulfide in which the *PGE* can exist, they must be present in either chromite and silicate phases, or an intergranular phase. It has been postulated that refractory Cr-spinel and olivine in S-poor ultramafic rocks may act as a sink for Ir (Crocket 1979, Naldrett *et al.* 1979). In addition, Mitchell & Keays (1981) predicted that high-temperature Ir alloys may exist under upper-mantle *P–T* conditions in environments of low $f(S_2)$. Iridium in this form would remain as a residual phase during partial melting of the mantle (Mitchell & Keays 1981). In contrast to Ir, Pd is more volatile (Arculus & Delano 1981); therefore, during partial melting Pd fractionates from Ir, which is left in the residue (Hertogen *et al.* 1980, Mitchell & Keays 1981). Hence, highly depleted mantle peridotites have low total *PGE* contents, fractionated chondrite-normalized *PGE* patterns with negative slopes from Ir to Pd, and Pd/Ir <1. Such patterns have been reported from the Thetford Mines Ophiolite, Quebec (Oshin & Crocket 1982) and the Ronda peridotite massif, Spain (Stockman 1982), and calculated for the Vourinos Ophiolite Complex, Greece (Cocherie *et al.* 1989). The chondrite-normalized *PGE* patterns (Fig. 5A) and Pd/Ir values (1.2–1.7) of the Springers Hill harzburgites are completely inconsistent with a residual origin. In fact, the flat *PGE* patterns for Springers Hill harzburgites coincide with the chondrite-normalized *PGE* data compiled by Arculus & Delano (1981) for undepleted upper mantle (Jagoutz *et al.* 1979, Morgan & Wandless 1979, Morgan *et al.* 1980, Mitchell & Keays

1981), and yet the Springers Hill harzburgite is clearly residual in origin. In order to explain the apparent discrepancy between the *PGE* data and the residual origin for the harzburgite, it is necessary first to consider the origin and *PGE* chemistry of the early-suite lithologies.

The early suite

Lithologies of the early suite are magmatic in origin, as demonstrated earlier, and both their silicate mineralogy and *PGE* chemistry define a fractionation sequence. All of the chromitite samples (Fig. 5B) have characteristic chondrite-normalized *PGE* patterns typical of ophiolites (e.g., Page *et al.* 1982, 1983, Page & Talkington 1984), but exhibit a positive slope from Pt to Pd, which appears to be a diagnostic feature of Newfoundland ophiolites (Page & Talkington 1984). The V-shaped Os–Ir–Ru patterns of the chromitites reflect the occurrence of Os-bearing laurite inclusions in chromite grains. It is important to note that a discrete Ir-bearing phase has not been found in any lithology investigated in this study.

Dunite has a nearly identical chondrite-normalized *PGE* pattern to that of serpentinite (Fig. 5C), which strongly suggests that serpentinization has not affected whole-rock *PGE* chemistry. The *PGE* patterns in Figure 5C are best explained by chromite fractionation (*cf.* Fig. 5B), and the higher *PGE* content of the serpentinite is attributed to its greater abundance of chromite relative to the dunite. The low Os/Ru value of the serpentinite may argue for the presence of Os-poor or Os-free laurite in this sample. Osmium-free laurite has been observed in serpentinite and chlorite interstitial to chromite grains in chromite-rich samples from the Shetland Ophiolite (Tarkian & Prichard 1987).

Chondrite-normalized *PGE* patterns for the orthopyroxenites (Fig. 5D) show an inverse correlation with respect to the chromitite and dunite patterns (Figs. 5B, 5C), which reflects the presence of Pt and Pd phases in the orthopyroxenite. Oshin & Crocket (1982), Page & Talkington (1984), Barnes *et al.* (1985) and Prichard & Tarkian (1988) have suggested that as a magma evolves, it becomes enriched in Pt and Pd relative to Ir, implying a fractionation trend. The *PGE* patterns presented in Figures 5B, 5C and 5D suggest that the orthopyroxenites precipitated from a basic melt that had previously undergone fractionation of a chromite component. The intrusive relationships, magmatic textures, fractionated *PGE* patterns, and high Pd/Ir values exhibited by the orthopyroxenites all argue against their origin as residues after partial melting. Loubet *et al.* (1976) and Loubet & Allègre (1979) proposed a residual origin for the garnet pyroxenites of Beni-Bousera, Morocco.

Chondrite-normalized *PGE* patterns are highly variable in clinopyroxenites (Fig. 5E). The clinopyroxenite richest in *PGE* has a *PGE* pattern almost identical to those of the orthopyroxenites. This clinopyroxenite intrudes an orthopyroxenite and contains orthopyroxene xenocrysts derived from the orthopyroxenite. As a result, in places, the clinopyroxenite becomes a websterite, and inherits a significant component of its *PGE* pattern from the orthopyroxene xenocrysts. Primary sulfides first appear in the clinopyroxenites, but their influence on the *PGE* patterns presently is unknown.

During fractionation in the early suite, there was a significant fluctuation in the concentration of Ir fractionating from the melt relative to Os and Ru. If an Ir-rich alloy remained in the residuum upon melt extraction (Mitchell & Keays 1981), then this could account for the V-shaped Os–Ir–Ru pattern of chromitite. However, even if this were the case, the *PGM* in chromitites should be Ir-depleted, relative to Os and Ru, in order to account for the upward V-shaped Os–Ir–Ru pattern in orthopyroxenite. This trend suggests that the relative proportions of Os, Ir and Ru present in *PGM* are very sensitive to the crystallization environment in terms of whether chromite or pyroxene is precipitating.

The complementary evolution of the *PGE* chemistry with mineralogy of the early-suite veins and dykes strongly suggests that the veins and dykes of this suite may be comagmatic and that the *PGE* patterns have not arisen through alteration. Clearly the veins and dykes are crystal fractionates and do not represent

liquid compositions. The fractionation sequence olivine → orthopyroxene → clinopyroxene is typical of highly refractory melts such as boninites. The corresponding fractionation of the *PGE* to yield high Pd/Ir values in the early-suite pyroxenites also is consistent with a boninitic origin for this suite, as boninites and low-Ti lavas have Pd/Ir values in the range 20–200 (data compiled by Barnes *et al.* 1988).

Modification of the Springers Hill harzburgite

The relatively unfractionated *PGE* chemistry exhibited by the otherwise highly depleted Springers Hill harzburgites is best explained in terms of the field and petrographic evidence for addition of an early-suite orthopyroxenite component to residual harzburgite. As described earlier, the addition of orthopyroxene involves either melt infiltration of orthopyroxenite into residual harzburgite, or mechanical mixing of orthopyroxenite into harzburgite by the stretching and pulling apart of orthopyroxenite veins and narrow dykes (<1 m) hosted within residual harzburgite. These processes would increase the orthopyroxene content of depleted harzburgite. In a similar way, it is possible to produce harzburgites by adding orthopyroxene to residual or magmatic dunites.

Plotted in Figure 6 are the Pd and Ir data for the *PGE*-depleted Black Lake harzburgite (sample 1C) from the Thetford Mines Ophiolite (Oshin & Crocket 1982), the *PGE*-enriched Springers Hill harzburgite (sample L106), and the average Springers Hill

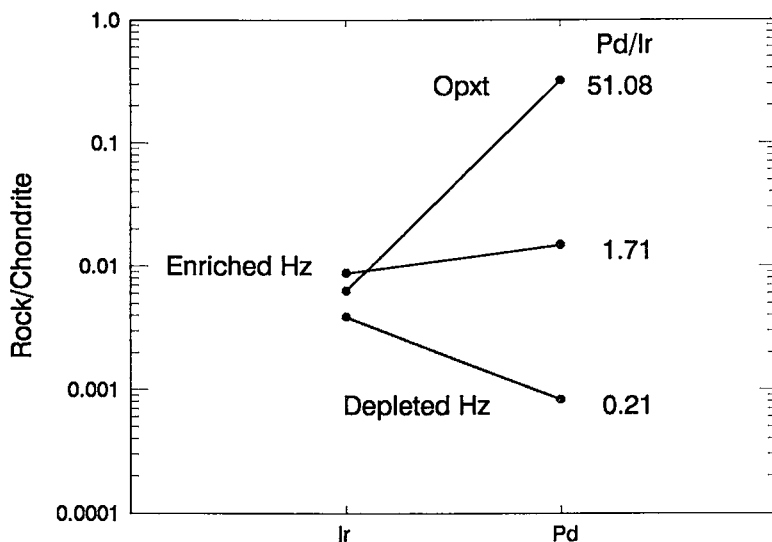


FIG. 6. Pd, Ir and Pd/Ir values for *PGE*-depleted harzburgite [sample 1C from Oshin & Crocket (1982)], *PGE*-enriched harzburgite (L106) from Springers Hill, and average early-suite orthopyroxenite composition, also from Springers Hill.

orthopyroxenite composition (Table 2). The *PGE* content of the Black Lake harzburgite is assumed to represent the *PGE* content of residual mantle. Iridium-Pd slopes pivot about an essentially constant Ir value for large variations in Pd concentration (Fig. 6). Consequently, the addition of early-suite orthopyroxenite to *PGE*-depleted harzburgite will greatly alter the Pd content of the harzburgite without significantly modifying the Ir content. This trend is further supported by the differences in Pd/Ir and Pd/Pt values of the *PGE*-enriched harzburgite, compared to those of the average orthopyroxenite. Whereas Pd/Ir values for the two lithologies are vastly different, 1.7 and 51, respectively, Pd/Pt values are essentially identical, 0.86 and 0.83, respectively. The proportion of average early-suite orthopyroxenite required to change residual harzburgite compositions (sample 1C of Oshin & Crocket 1982) into Springers Hill harzburgite (sample L106) can be calculated from simultaneous equations involving the Pd, Ir and Pd/Ir values of these three components. The *PGE* chemistry suggests that the enriched Springers Hill harzburgite (L106) is composed of 98% residual harzburgite and 2% orthopyroxene from early-suite Springers Hill orthopyroxenite. The addition of 2% orthopyroxene to residual harzburgite is clearly inconsistent with the field and petrographic data, which suggest that up to 20 modal % orthopyroxene from orthopyroxenite is added to harzburgite. One explanation for this discrepancy appeals to the heterogeneous distribution of *PGM* in orthopyroxenite; the addition of orthopyroxene thus need not result in a proportional addition of *PGE* to the harzburgite. As an alternative, the *PGE*-enriched harzburgites may have experienced a small degree of partial melting to remove Pd relative to Ir. This is unlikely, however, because the fine, delicate, impregnated orthopyroxene in the harzburgite exhibits no evidence for corrosion resulting from partial melting. More *PGE* data from harzburgites are required in order to better understand the behavior of the *PGE* in mantle residuum in ophiolite sequences.

The question now arises as to how significant are the orthopyroxene-addition processes in terms of modifying harzburgite compositions in mantle sequences in ophiolites. In the Springers Hill area, orthopyroxenite veins and dykes are abundant, and a significant proportion of the harzburgite appears to be modified. However, the area mapped in this study is only 2 km². A more regional study of the BIOC mantle section is presently under way, and there is evidence for orthopyroxene impregnation in other massifs (G. Suhr, pers. comm.). A survey of the literature data on the *PGE* content of other harzburgites from ophiolites indicates that many of them preserve Pd/Ir values greater than 1, e.g., Troodos Ophiolite Complex, Cyprus (Becker & Agiorgitis

1978), Thetford Mines Ophiolite, Quebec (Oshin & Crocket 1982), Vourinos Ophiolite Complex, Greece (Cocherie *et al.* 1989). Without detailed field and petrographic studies of the harzburgites from these ophiolites, it is premature to attribute the elevated Pd/Ir values to orthopyroxene addition. However, if such a process does operate in these ophiolites, then modifications of Pd/Ir values of harzburgite by orthopyroxene addition would appear to be the rule rather than the exception.

CONCLUSIONS

The main conclusions drawn from the Springers Hill area of the BIOC are summarized as follows:

- 1) The *PGE* are essentially immobile during serpentinization, despite modifications of *PGM* phase assemblages resulting from the addition of Cu. Consequently, chondrite-normalized *PGE* diagrams and *PGE* values are useful tools to determine the petrogenesis of ultramafic rocks.
- 2) Copper is locally mobilized during serpentinization, but Fe, Ni and Cu remain essentially *in situ* at the hand-specimen scale. Original Fe-Ni-Cu-S phase assemblages are affected by serpentinization.
- 3) The early-suite veins and dykes fractionate olivine \pm chromite \rightarrow orthopyroxene \rightarrow clinopyroxene, which is the order of crystallization of refractory melts, e.g., boninites. Fractionation of the *PGE* from a melt occurs by removal of sulfides in chromite (Os, Ru and possibly Ir) and arsenides in pyroxene (Pt and Pd). Base-metal sulfides do not seem to play a role in this fractionation.
- 4) Partial melting of mantle with a chondritic distribution of the *PGE* yields melt and residue with high and low Pd/Ir values, respectively. Precipitation of chromite from this melt enhances the Pd/Ir value of the residual melt. Pyroxenites with highly elevated Pd/Ir values precipitate from such a residual melt.
- 5) The Springers Hill harzburgites that exhibit a Pd/Ir value greater than 1 contain a component of early-suite orthopyroxenite. These harzburgites contain coexisting residual and magmatic orthopyroxenes. The residual orthopyroxene is porphyroclastic and corroded, whereas the magmatic orthopyroxene is porphyroclastic if deformed, or a delicate impregnation if undeformed.
- 6) Refractory pyroxenites in mantle sequences in ophiolites may be of economic interest for future mineral exploration.

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