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PLATINUM AND PALLADIUM IN THE TROODOS OPHIOLITE COMPLEX, CYPRUS

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ABSTRACT

Platinum and palladium have been detected in sulfide-bearing gabbros from the classic Troodos ophiolite complex of Cyprus. Concentrations of the platinum-group elements (*PGE*) in the Troodos gabbros give positively sloping chondrite-normalized patterns. Os, Ir and Ru are removed from the magma at an early stage, with chromitites, which have a negatively sloping chondrite-normalized pattern. Pt and Pd are fractionated to higher levels within the magma chamber, and are concentrated at the base of the gabbros, but they also occur at higher stratigraphic levels in the gabbros. The *PGE* in fresher gabbros retain their magmatic chondrite-normalized patterns, though located in secondary platinum arsenide and palladium antimonide associated with actinolite. Evidence from the "type" ophiolite complex, on Troodos, supports the idea that significant levels of Pt and Pd are generally present in ophiolites.

Keywords: Troodos, Cyprus, platinum, palladium, gabbro, ophiolite.

SOMMAIRE

Les gabbros à sulfures du complexe ophiolitique classique du Troodos, en Chypre, contiennent du platine et du palladium. Dans ces roches, les teneurs en éléments du groupe du platine (*EGP*), normalisées par rapport aux teneurs chondritiques, montrent une pente positive. Les éléments Os, Ir et Ru semblent avoir été lessivés du magma à un stade précoce, au cours de la formation des chromitites, qui démontrent une pente négative dans un diagramme où les teneurs des *EGP* sont normalisées à celles des chondrites. Le Pt et le Pd sont enrichis vers les niveaux supérieurs de la chambre magmatique, et concentrés à la base des gabbros, mais ils sont aussi présents à des niveaux plus élevés dans la section gabbroïque. Dans les gabbros les plus sains, les *EGP* conservent leur teneurs primaires, et définissent donc le même enrichissement envers les chondrites, malgré que les *EGP* sont situés dans un arséniure de platine et un antimoniure de palladium secondaires, associés à l'actinote. D'après ces observations sur le massif ophiolitique type qu'est le Troodos, des quantités importantes de Pt et de Pd seraient généralement présentes dans toute séquence ophiolitique.

(Traduit par la Rédaction)

Mots-clés: Troodos, Chypre, platine, palladium, gabbro, ophiolite.

INTRODUCTION

The major source of Pt and Pd in the western world is the Bushveld complex, where horizons with anomalously high levels of the *PGE* extend for kilometers. In these zones, Pt and Pd concentrations are generally greater than 1 ppm, and occur with lower levels of the other platinum-group elements (Rh, Ru, Os and Ir). The concentrations in the Bushveld are very anomalous if compared with average crustal abundances of 5 ppb Pt and 1 ppb Pd (Naldrett 1981). Recently, analysis of rocks for the platinum-group elements (*PGE*) has become more routine with the use of ICP-MS analytical techniques. This approach has enabled examination of other types of geological environments for *PGE*. Formerly, Os, Ir and Ru were considered to be the only *PGE* of any significant concentration in ophiolite complexes, where they occur at ppb levels in association with chromitites (Page *et al.* 1982a). Recently, it has become clear that a number of basic and ultrabasic complexes with the characteristic ophiolite stratigraphy contain Pt and Pd, and, in at least one case, at concentrations similar to those in the Bushveld (Prichard *et al.* 1986). The aim of this research was to re-examine the "type" Troodos ophiolite to establish whether or not Pt and Pd concentrations are characteristic of ophiolite complexes.

GEOLOGY OF THE COMPLEX

The Upper Cretaceous basic and ultrabasic complex exposed in the Troodos mountains of Cyprus is the classic, Penrose-type of ophiolite complex (Gass 1980). Tectonized upper-mantle harzburgite is overlain by layered dunites, wehrlites and gabbros. Above this are high-level gabbros, granophyres, plagiogranites, a sheeted dyke complex and an extrusive sequence with lithologies ranging from MORB type to boninitic. The plutonic unit is made more complex by the presence of late intrusive gabbros and wehrlites (Allen 1975, Benn & Laurent 1987). Chromitites occur in the ultrabasic part of the complex (Greenbaum 1977), both in dunite lenses in the harzburgite (*e.g.*, at Kannoures) and at the base of the overlying dunite unit (*e.g.*, at Kokkinorotsos) (Fig. 1). The enrichment of Os, Ir and Ru in the chromitites of Troodos is well known. *PGE* assays of the Kokkinorotsos chromitite indicate greater concentrations of Ru, Ir or Os than either Pt or Pd (Constantinites *et al.* 1980). This is reflected by the presence in these samples of laurite (RuS_2), which

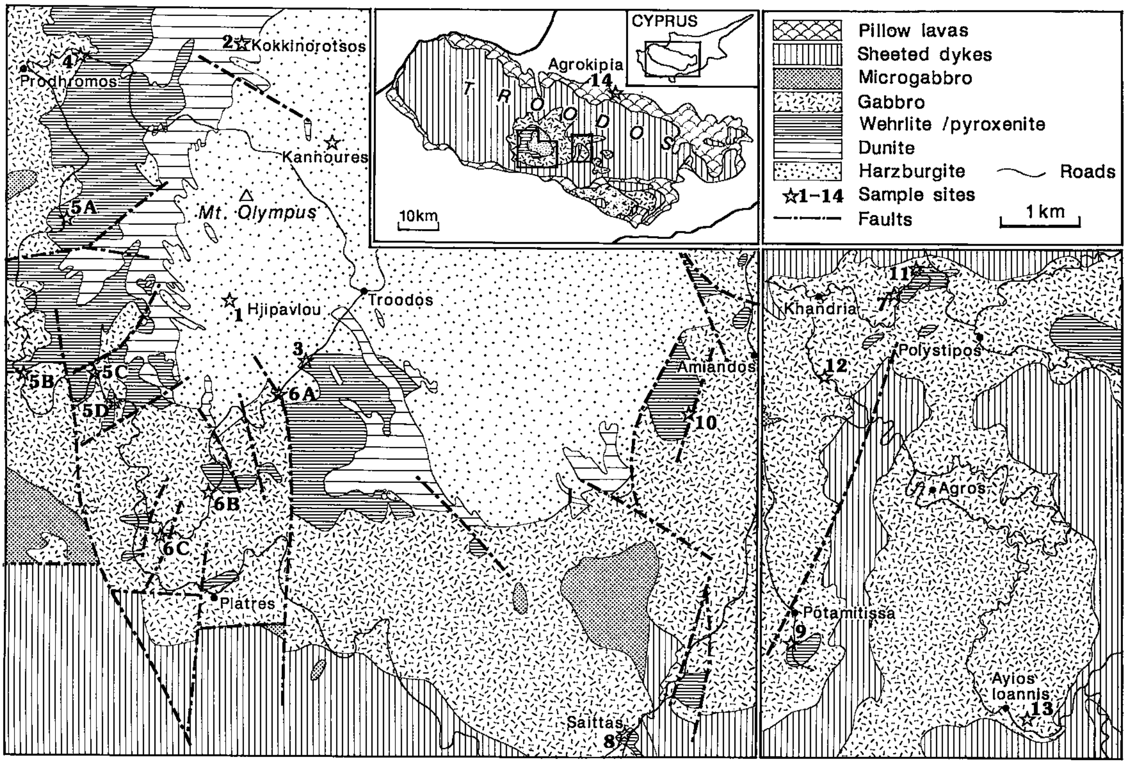

FIG. 1. Geological map of the plutonic part of the Troodos mountains (Gass 1980, Bear & Morel 1960, Wilson 1959) showing the sample sites. A few ultrabasic lithologies were sampled, including a dunite, harzburgite and chromitite from Hdjipavlou (1), chromitites from Kokkinorotsos (2), and wehrlites from the Troodos – Platres road section (3). Basal sulfide-bearing gabbros adjacent to an unfaulted ultramafic contact were obtained east of Prodhromos (4). Low-level layered gabbros were collected south of Katoikiai on the Troodos–Limassol road (6). The junction of the peridotites with the gabbros is faulted on the west side of Troodos, but a number of gabbros and ultrabasic samples were collected south of Prodhromos (5). High-level gabbros and ultramafic rocks were collected north of the Cyra road junction (7), at Sattis (8) and at Potamitissa (9). A wehrlite, adjacent to a gabbro with cross-cutting dykes, was sampled at Amiandos (10). High-level layered gabbros, cut by occasional dykes, were collected 100 meters west of the junction of the Polistipos-Kandria and Spilia roads (11) and by the Kandria–Agros road (12). Sulfide-bearing samples were obtained from the massive sulfide deposit within the gabbros at Ayios Ionnis (13). A sulfide-rich sample was collected from the volcanogenic massive sulfide deposit within the pillow lavas at Agrokipia (14).

may contain Os and Ir, and erlichmanite (OsS_2), which may contain Ir and Ru. Pt- and Pd-bearing minerals have not been reported. More recent analyses for the *PGE* from Kokkinorotsos and Kannoures confirm the presence of more Ru than Os or Ir (average concentrations of 122, 41 and 21 ppb, respectively), Pt, Pd or Rh (averages for Pt and Pd of 12.5 ppb and 10 ppb, respectively, and maximums of 15 ppb, 25 ppb and 6 ppb, respectively) (Johan *et al.* 1982). Becker & Agiorgitis (1978) showed that Os and Ir concentrations occur in the Troodos ultramafic rocks: the highest Pd value they recorded is only 13.4 ppb, and occurs in a pyroxenite. The literature concerning the distribution of *PGE* in the Cyprus ophiolite supports the traditional view of ophiolite complexes, with greater enrichment of Os, Ir and Ru than Pt and Pd, which occur in association with chromitite (Crocket 1981, Agiorgitis & Wolf 1978). Recently, the presence of rare Pt and Pd minerals associated with Os, Ir and Ru minerals was reported in the Troodos chromitites (McElduff & Stumpfl 1989).

Conventionally, *PGE* data are normalized to chondrite and plotted in the order Os, Ir, Ru, Rh, Pt and Pd. Samples with greater normalized Os, Ir and Ru than Pt, Pd and Rh therefore have a negatively sloping pattern, which is considered typical of chromite-rich samples from ophiolite complexes (Page *et al.* 1982a, b, 1984, Page & Talkington 1984). More rarely, positively sloping chondrite-normalized trends have been recorded in chromite-poor cumulate ultramafic lithologies from ophiolite complexes, *e.g.*, in the Thetford ophiolite complex (Oshin & Crocket 1986). It is mainly Os-, Ir- and Ru-bearing platinum-group minerals (*PGM*) that have been described from ophiolite complexes (Prichard *et al.* 1981, Stockman & Hlava 1984, Talkington *et al.* 1984, Augé 1985, 1986, 1988, Legendre & Augé 1986); the most commonly recorded *PGM* is laurite. Recently, Pt- and Pd-bearing minerals have been described from ophiolites including: the Josephine peridotite and Onion Mountain, southwestern Oregon (Stockman & Hlava 1984), Vourinos, Greece and Tiébaghi, New Caledonia (Augé 1988), Zambales, Philippines (Orberger *et al.* 1988), the Pole Corral podiform chromite, northern California (Moring *et al.* 1988), Bou-Azzer, Morocco (Fisher *et al.* 1988) and Shetland, Scotland (Prichard & Tarkian 1988).

TABLE 1. CONCENTRATIONS (ppb) OF THE PGE IN WHOLE-ROCK SAMPLES FROM THE TROODOS COMPLEX*

Sample no.	Rock type	Locality	Au	Pt	Pd	Ru	Rh	Ir	Os	Cu	Ni	Cr
RCY10	Dunite	[1]	0.0	2.5	3.5	6.0	0.0	2.5	4.0	0	2656	1632
RCY11	Harzburgite		0.0	3.5	6.0	6.5	1.0	3.0	4.0	0	2381	1918
RCY12	Chromitite		0.0	0.0	2.0	74.0	3.0	13.0	22.0	0	1234	326620
RCY4	Chromitite	[2]	0.0	2.0	3.0	21.0	1.5	6.5	10.0	11	2771	79914
RCY5	Chromitite		0.0	5.0	1.0	38.0	2.0	17.0	22.0	0	1213	259999
RCY6	Chromitite		0.0	2.5	5.5	40.0	3.0	9.5	18.0	0	1179	274244
RCY14	Wehrlite	[3]	0.0	4.5	5.0	2.0	0.5	0.0	0.0	0	1563	2580
HCY10	Wehrlite		0.0	1.5	5.0	1.5	0.0	0.0	0.0	21	1489	1587
HCY9	Wehrlite		0.0	2.0	2.0	4.0	0.5	2.5	2.0	0	2513	1469
EM34	Gabbro	[4]	0.0	30.0	21.0	3.0	2.0	4.5	0.0	0	225	3165
EM35	Gabbro		6.0	30.0	41.0	2.5	1.0	4.5	0.0	8	189	1635
EM36	Gabbro		0.0	42.0	56.0	1.5	2.0	5.0	0.0	20	189	1538
EM36B				62.0	62.0	16.0	5.5	9.0	2.0			
EM37	Basic layer		8.0	32.0	53.0	0.0	1.5	6.0	4.0	11	207	1064
EM38	Gabbro		4.0	39.0	30.0	1.5	1.0	4.5	2.0	5	203	1839
EM39	Gabbro		6.0	6.5	7.5	0.5	0.0	3.0	0.0	91	73	134
EM40	Gabbro		2.0	1.5	2.5	1.5	0.0	3.5	0.0	81	116	239
EM41	Gabbro		0.0	1.0	5.0	2.0	0.0	4.5	2.0	46	82	119
EM42	Basic lens	[5]	6.0	5.0	4.5	3.0	0.5	4.5	0.0	32	1333	2978
EM42A			6.0	4.5	4.5	1.5	1.0	4.5	0.0			
EM46	Wehrlite		0.0	19.0	14.0	2.5	1.5	4.5	2.0	5	235	1586
EM48	Wehrlite		4.0	3.0	3.5	2.0	2.0	5.0	0.0	3	1079	341
EM49	Wehrlite		2.0	20.0	12.0	4.0	2.5	6.0	0.0	0	1242	505
EM43-45,47,50 Ave	Gabbro		4.0	5.2	9.1	1.9	0.5	5.3	0.4	70	228	394
EM51-58 Ave	Gabbro	[6]	3.8	4.5	9.1	2.1	0.9	4.6	0.0	132	375	389
EM16	Basic layer	[7]	0.0	3.5	0.0	0.0	0.0	1.0	0.0	163	433	2040
EM17	Gabbro		4.0	7.5	12.0	2.0	2.0	5.5	2.0	67	293	799
EM18	Wehrlite		8.0	14.0	16.0	2.0	1.5	4.5	0.0	14	1202	2165
EM19	Basic layer		6.0	8.5	17.0	2.0	1.0	5.0	2.0	61	533	473
EM20	Basic layer		8.0	19.0	4.5	0.0	1.0	4.5	2.0	229	81	198
EM59	Gabbro	[8]	4.0	5.5	8.0	2.5	1.0	4.5	0.0	148	106	192
EM60	Gabbro		0.0	6.5	9.5	3.0	1.5	5.0	4.0	849	186	365
EM62	Gabbro	[9]	6.0	2.5	4.0	3.0	1.0	4.5	2.0	146	45	188
EM62A			6.0	3.0	2.0	1.0	1.0	4.0	0.0			
EM63	Wehrlite		4.0	10.0	14.0	1.5	1.5	3.5	0.0	16	817	1289
EM61	Wehrlite	[10]	4.0	11.0	17.0	3.0	1.5	4.5	4.0	25	1066	1945
EM21-EM33 Ave	Gabbros and Basic layers	[11]	3.1	6.8	8.6	1.0	0.6	4.7	1.7	81	258	154
EM21-EM33 S Dev				2.5	3.3	1.0	0.4	0.4	2.0	23	118	121
EM64	Epidosite		4.0	3.0	3.0	2.5	1.0	3.5	0.0	174	94	759
EM27			2.0	12.0	11.0	1.0	1.0	4.5	2.0			
EM27A				13.0	12.0	3.0	1.5	4.0	0.0			
EM13	Basic layer	[12]	2.0	6.0	3.5	2.5	1.5	5.0	0.0	51	274	49
EM14	Gabbro		4.0	7.5	10.0	1.5	1.5	5.0	4.0	124	72	261
EM4	Gossan	[13]	76.0	4.5	2.5	1.5	1.0	5.5	2.0	323	8	565
EM5	Dyke		8.0	4.5	2.5	1.5	1.0	4.5	2.0	228	48	181
EM6	Gabbro		4.0	9.5	14.0	0.0	1.0	4.5	2.0	132	118	715
EM7	Gabbro		10.0	28.0	30.0	2.0	1.5	4.5	0.0	111	135	725
EM8	Gabbro		16.0	16.0	25.0	0.0	1.0	4.5	2.0	1073	50	1039
EM9	Dyke		10.0	8.5	7.0	0.0	1.0	4.5	0.0	218	134	1005
EM10	Dyke		0.0	5.5	1.0	1.0	0.5	4.5	0.0	119	54	92
EM11	Gabbro		2.0	8.0	9.5	2.0	1.0	3.5	0.0	74	167	397
EM11A			4.0	9.5	9.0	1.5	1.0	4.5	0.0			
EM12	Gabbro		2.0	5.0	2.0	1.0	1.0	4.5	0.0	139	110	170
EM70	Pyrite	[14]	220.0	2.0	4.0	5.5	2.0	14.0	2.0	981	0	2850
EM71	Gossan		32.0	3.0	4.0	0.0	1.0	5.5	0.0	3775	15	255
SARM-7			310	3740	1530	430	240	74	63			
UNK1			170	3000	1400	380	210	75	48			
UNK1A			200	3000	1400	380	220	83	48			
UNK2			310	3000	1300	400	200	82	46			

* Samples are placed in stratigraphic order. Localities refer to Figure 1. Limits of detection are 2 ppb for Au and Os, and 0.5 ppb for the other PGE. Au concentrations are qualitative only. S Dev is the standard deviation of the group of averaged analyses, e.g. EM21-EM33. A is a duplicate analysis in the same batch. B is a duplicate analysis six months later. SARM-7 are the quoted reference values, and UNK1 and 2 are the analytical values for SARM-7 obtained during this study. Wavelength XRF analyses (ppm) are given for Cu, Ni and Cr.

Extremely anomalous levels (over 1 ppm) of all six *PGE* occur in some chromite-enriched lithologies from the Shetland ophiolite complex, with Pt and Pd levels of typically 20 - 30 ppm (Prichard *et al.* 1986). Chondrite-normalized plots of chromitites from this complex include examples of both positively and negatively sloping patterns. The discovery of anomalous levels of the *PGE* and positively sloping chondrite-normalized patterns similar to those found in stratiform complexes prompted a re-examination of the Shetland complex in order to reaffirm its ophiolitic characteristics. The consensus is that this is a Caledonian ophiolite in which the extrusive sequence has been tectonically removed or eroded. Geochemical lines of evidence suggest a supra-subduction zone (SSZ) site for formation of the ophiolite (Prichard & Lord 1988). The analogy of the Troodos data with new evidence from Shetland and elsewhere led to the inference that concentrations of Pt and Pd should be present in Troodos.

Analytical Techniques

Analyses of 50-g portions taken from pulverized samples weighing 1 kg were obtained using nickel sulfide fire assay and ICP–MS at Analytical Services Ltd., Williton, Western Australia (Table 1). Duplicate analyses on 10% of the samples (three of which are given in Table 1) show good precision. The international standard SARM-7 was analyzed twice as an unknown and gave results in accordance with the quoted reference values, which indicates good accuracy as well as precision (Table 1). The reliability of the data also is supported by the occurrence of anomalous Pt and Pd values that are repeated at similar levels in different samples at the two most Pt- and Pd-enriched sites. To further check the analyses for reproducibility, two powders, EM27 and EM36, were re-analyzed as unknowns in another batch six months after than the first. These results confirm that *PGE* levels in EM27 are low, with values within 2 ppb of the previous analysis. The

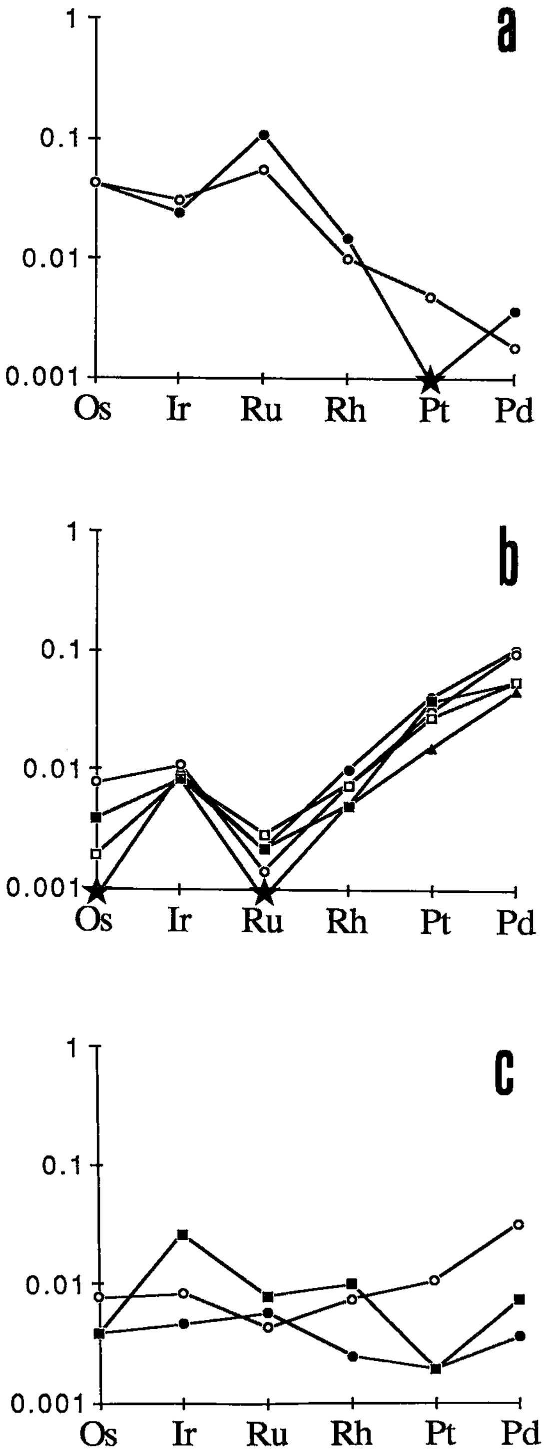

FIG. 2. Chondrite-normalized plots (Table 1) showing samples with significant levels of the *PGE*. (a) Chromitites from Hdjipavlou (1) (black circle, RCY 12) and Kokkinorotsos (2) (white circle, RCY 5) showing negative slopes typical of ophiolites. A peak at Ru may correspond to the presence of laurite. (b) Sulfide-bearing basal gabbros from Prodhromos (4) (black circle, EM 36, white circle, EM 37, and black square, EM 38) and Ayios Ionnis (13) (white square, EM 7, and black triangle, EM 8), showing positive slopes. A trough at Ru may indicate that these gabbros crystallized from a magma depleted in Ru. (c) Wehrlites, from the ultrabasic part of the complex (3) (black circle, HCY 9) and from a layer in gabbro (10) (white circle, EM 61). The volcanogenic massive sulfide (14) (black square, EM 70) shows an irregular pattern. Chondrite values used for normalization are Os 514, Ir 540, Ru 690, Rh 200, Pt 1025 and Pd 545 (Naldrett & Duke 1980). A star indicates an undetected element.

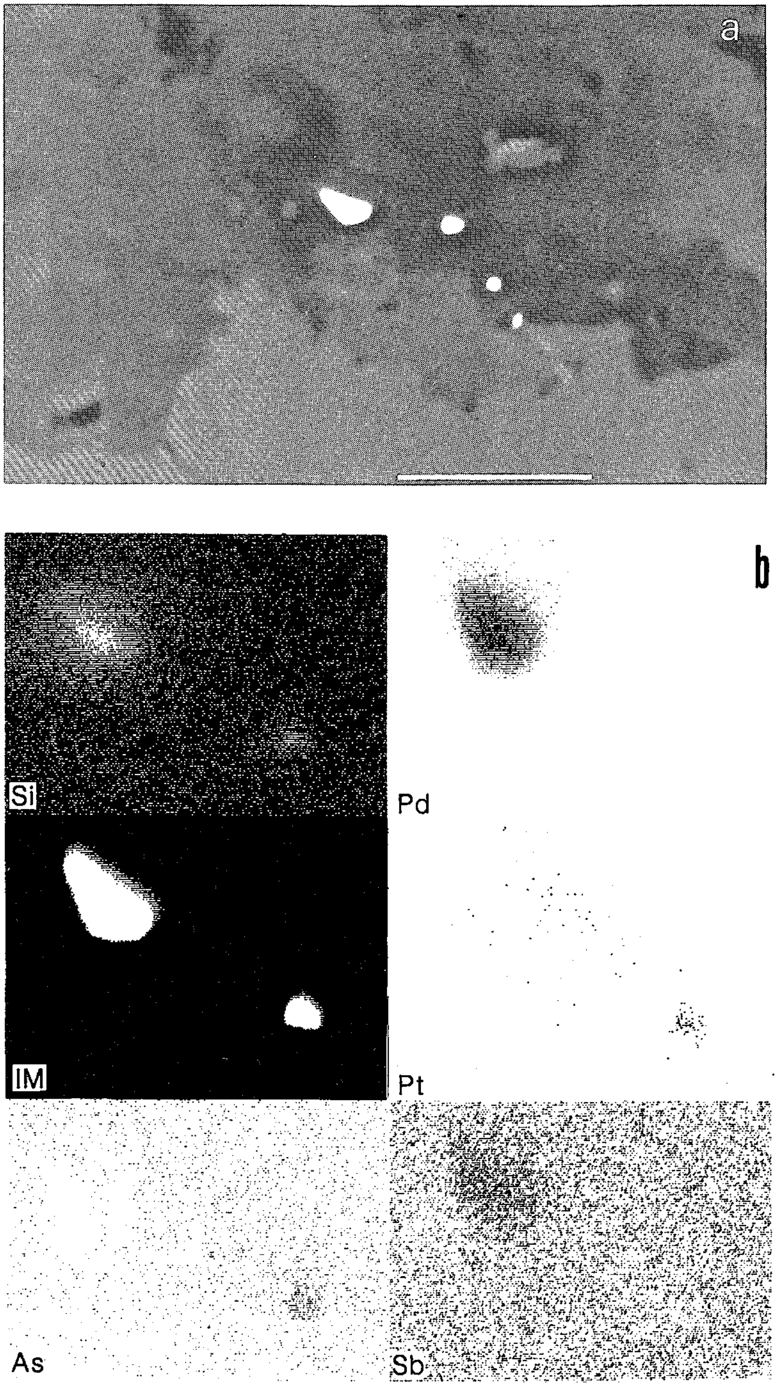

FIG. 3. (a) Scanning electron micrograph of *PGM* (white) in actinolite (black) on the edge of clinopyroxene (grey) from a gabbro east of Prodhromos, EM 37. Scale bar: 10 μm. (b) X-ray maps and a back-scattered image (IM) of the *PGM*. The largest grain (4 × 3 μm) contains Pd, Sb, and is possibly Pt-bearing; the smaller one (1.5 × 1.5 μm) contains Pt and As.

values of EM36 are slightly higher than in the first analysis, with Pt and Pd of 62 and 62 as compared with 42 and 56. This may be due to variation in the precision of the analyses, but may also be due to a real variation between the powders taken from the original sample. The discovery of four tiny (less than 4 μm) grains of *PGM* during a thorough study of three polished thin sections by optical microscopy and scanning electron microscopy confirms the presence of Pt and Pd at low abundance. These *PGM* were analyzed qualitatively using a JEOL JSM-820 scanning electron microscope equipped with a Kevex energy-dispersion system, at the Open University. The *PGM* grains, being less than 4 μm across, are too small to be analyzed quantitatively.

Distribution of the *PGE* in the Troodos Complex

This paper describes the distribution of *PGE* in the Troodos ophiolite complex, and in particular in lithologies other than the chromitites. In layered complexes, the *PGE* are known to be concentrated magmatically with base metal sulfides. Special emphasis was placed, therefore, on the collection of sulfide-bearing samples. As there is a virtual absence of visible sulfide in the Troodos ultramafic rocks, most sampling focused on the gabbros, which are sulfide-bearing. Samples were collected along a series of traverses at selected sites (Fig. 1). The majority of the 70 samples analyzed contain individual *PGE* at levels below 10 ppb. In the gabbro samples, however, a number of significantly higher concentrations of Pt and Pd were recorded, and these invariably occur together (Table 1). The levels of the remaining four *PGE* are extremely low in the gabbro sequence, usually just above the detection limit. Average values (in ppb) are Ru 1.9, Rh 1.0, Ir 4.7 and Os 1.5, with maximum levels of 4.0, 2.5, 8.0 and 6.0, respectively (59 analyses). The following paragraph deals with the distribution of the *PGE*.

Of the ultramafic samples analyzed, only the chromitites contain concentrations of *PGE*. These are enriched in Ru, Os and Ir, and display the negatively sloping chondrite-normalized patterns typical of ophiolitic chromitite (Fig. 2a). Moving upward in the ophiolite sequence, the first detected levels of Pt and Pd occur in the basal gabbros east of Prodhromos [Fig. 1 (4)], and these are also the most anomalous values. At this locality, samples were collected stratigraphically upward, from the base of the gabbros; samples closest to the ultramafic contact (EM 34 – 38) have an average Pt + Pd value of 75 ppb (range 51 – 98 ppb) and represent an apparently continuous zone of low-grade mineralization over a vertical stratigraphic distance of 35 m. Here, the samples further from the base of the gabbro are barren. The host olivine- and clinopyroxene-bearing gabbros have poikilitic or neoblastic textures, with euhedral pyroxene crystals in plagioclase; alteration is patchy. All the *PGE*-enriched samples are sulfide-bearing and have significantly higher Ni and Cr values than the barren samples. The gabbros richest in Pt and Pd have the highest proportion of sulfides, are the most mafic, coarsest grained, and also the least altered. Chondrite-normalized plots of these samples have positive slopes (Fig. 2b). *PGM* were discovered at this locality (Fig. 3). The largest grain (4 × 3 μm) contains Pd and Sb, is possibly Pt-bearing, and is a palladium antimonide; the second largest (1.5 × 1.5 μm) contains Pt and As, and is probably sperrylite.

Pt and Pd enrichments are not confined to the lowermost gabbros. A massive sulfide deposit near the top of the gabbros at Ayios Ionnis [(Fig. 1 (13)] also contains anomalous Pt and Pd values (second highest recorded in this study). A number of different lithologies were sampled at this locality, including barren and sulfide-bearing gabbro, cross-cutting dykes and gossan. Massive sulfide ore was not sampled. The most anomalous values occur in the freshest sample of sulfide-bearing gabbro, which has fresh plagioclase and partially amphibolitized clinopyroxene, whereas adjacent, much more altered samples have lower Pt and Pd values. The samples from Ayios Ionnis have positive slopes in a chondrite-normalized plot, very similar to those east of Prodhromos (Fig. 2b). Slightly elevated values of Pt and Pd also occur in some wehrlitic layers in gabbro (Fig. 1, localities 5, 7, 9, 10). These levels are higher than those in the adjacent gabbros and those obtained in wehrlite samples from the ultramafic sequence [(Fig. 1 (3)], and have slightly positive slopes in chondrite-normalized patterns (Fig. 2c). These wehrlites commonly have a poikilitic texture, for example in EM 49 and EM 61, and may belong to late intrusive plutonic suites in the plutonic series.

At locality 11, thirteen samples of wehrlite and gabbro were analyzed for the *PGE*. All samples were found to contain low levels of *PGE* (Table 1). An epidosite (EM64) collected from this same locality was found to have significantly depleted Pt and Pd levels, lower than one standard deviation from the average of the values in the surrounding gabbros and wehrlites. In order to complete examination of sulfide-bearing lithologies at all levels in the ophiolite complex, the Agrokipia exhalative massive sulfide deposit in the lava sequence also was sampled. One sample contains 14 ppb Ir, more than in any other chromite-poor sample, and the chondrite-normalized plot shows a jagged pattern with a positive Ir anomaly (Fig. 2c). Further research is being undertaken to examine the distribution of *PGE* in the extrusive sequence of this ophiolite complex.

Samples were analyzed for Cu, Ni and Cr (ppm) for confirmation of their stratigraphic position, under the assumption that in general Cu increases toward the top of the sequence, whereas Cr and Ni decrease (Lord & Prichard 1989) (Table 1). In addition, these elements are potential pathfinders for the *PGE*. If the *PGE* are concentrated by magmatic sulfide, then they are likely to be associated with base metal sulfides, and hence with anomalous levels of Ni and Cu. Cr also has been described as a pathfinder for the *PGE* (Buchanan 1988). The concentrations of Cu, Ni and Cr do show the expected stratigraphic trends, but there is no overall association of anomalous levels with Pt and Pd. Stratigraphic variations in background levels of these elements would obscure any patterns of association of anomalous levels with Pt and Pd throughout the sequence. Ni is present in olivine as well as in sulfides; since the olivine content is variable in these samples, this would further obscure any correlation with Pt and Pd. At the locality east of Prodhromos, however, a number of similar gabbros were collected that contain variable amounts of Pt and Pd. Samples containing higher levels of Pt and Pd contain more Cr and Ni and less Cu than the *PGE*-poor samples collected from stratigraphically higher levels within this single exposure (Fig. 4).

PROCESSES THAT CONCENTRATE THE *PGE* IN OPHIOLITES

The processes that concentrate the *PGE* in basic and ultrabasic igneous complexes, especially layered stratiform intrusions, have been discussed at length. The magmatic behavior of the *PGE* has been related to the different melting points of the elements (Barnes *et al.* 1985). Os, Ir and Ru have higher melting points than Pt and Pd. In Troodos, the association of Os, Ir and Ru occurs at low stratigraphic levels in the complex, with the chromitites, and the data presented confirm this. It is suggested that Os, Ir and Ru are removed early from the melt, but Pt and Pd are mostly retained, to appear in the more fractionated lithologies. As an alternative, Nicolas (1986) and others interpreted these rocks as highly residual mantle peridotites. Their high Ru, Ir and Os contents might be interpreted as due to higher compatibilities with the solid during melting than Pt and Pd.

It is difficult to determine the extent of the Pt and Pd anomaly from the restricted number of *PGE* analyses from the Troodos gabbro succession of several kilometers. East of Prodhromos, however, Pt and Pd are enriched consistently over a width of 35 m. Further work is required to ascertain whether this anomaly extends along strike; if so, it could represent a significant Pt and Pd concentration at this level, which would thus demonstrate that the Pt and Pd fractionate to higher levels in the complex than Os, Ir and Ru. Lack of exposure of the field relationships make it difficult to identify whether the samples analyzed for *PGE* in this study are from the main sequence of the plutonic series or from late plutonic intrusive bodies. Further petrological and geochemical studies, beyond the scope of this initial paper, would be required to categorize the samples. If the Pt and Pd are associated with the late plutonic series, which may have been formed in an SSZ set-

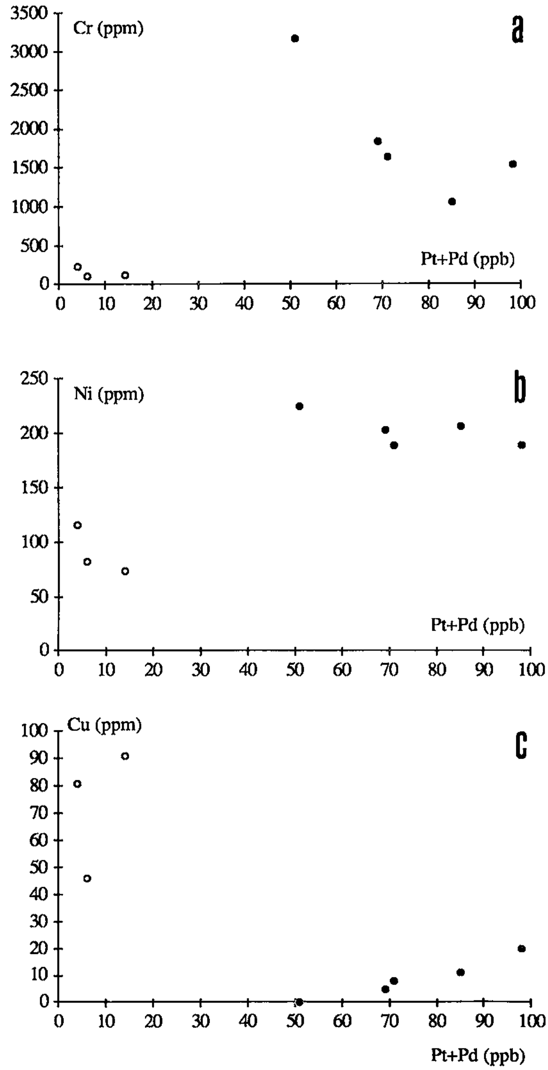

FIG. 4. Graphical comparison of *PGE* content, expressed as the sum of the Pt and Pd concentrations, of gabbros from east of Prodhromos (4) with concentrations of the pathfinder elements Cr (a), Ni (b) and Cu (c). Samples containing higher levels of *PGE* (black circles, EM34–EM38) contain higher levels of Cr and Ni, and lower levels of Cu than *PGE*-poor samples (open circles, EM39–EM41).

ting, then their concentration in the melt may be explained by hydrous partial melting associated with such environments (Prichard & Lord 1988).

This study shows that the Pt and Pd are preferentially concentrated in sulfide-bearing gabbros. The association between Pt, Pd and sulfides is well documented for the Bushveld (McLaren & de Villiers 1982, Gain 1985, Hiemstra 1985, Von Gruenewaldt *et al.* 1986) and other basic and ultrabasic complexes (Talkington & Watkinson 1986, Naldrett & Von Gruenewaldt 1989). As the quantity of *PGE* data accumulates, it seems clear that different ophiolite complexes have anomalous Pt and Pd values at different stratigraphic levels and in different lithologies. In Shetland, chromite-rich Pt- and Pd-bearing samples contain interstitial sulfides (Prichard *et al.* 1986). In the Zambales ophiolite complex, Pt and Pd are associated with base metal sulfides in dunites that are not closely associated with chromite concentrations (Orberger *et al.* 1988), although the origin of the Pt and Pd, whether primary magmatic or remobilized by hydrothermal processes, is uncertain. In the Thetford Mines ophiolite (Oshin & Crocket 1986), Pt and Pd are slightly enriched in the sulfur-rich late dunites and early pyroxenites. In the Karmoy ophiolite, in Norway, Pt and Pd are present in massive sulfide in the sheeted dyke complex (Barnes *et al.* 1988). In this study, the chromitites and the ultramafic part of Troodos in general are found to be poor in sulfides; Pt and Pd are concentrated in the sulfide-bearing gabbros instead. These ophiolite complexes have a similar SSZ origin, and all contain the concentrations of Pt and Pd, but they occur in different silicate lithologies. An association of sulfide with Pt and Pd is apparently the common factor.

The *PGM* described here are arsenides and antimonides. Elsewhere, As-bearing *PGM* are regarded as secondary (Cabri & Harris 1975, Stumpfl & Tarkian 1976, Thalhammer & Stumpfl 1988). The *PGM* in the Troodos gabbros are enclosed in fibrous secondary actinolite on the edge of an augite grain; the *PGM* also may be secondary. Although sulfides are observed in hand specimens of *PGE*-bearing samples, *PGM* are not closely associated with sulfide minerals in thin section (Fig. 3). Some authors (Talkington *et al.* 1984, Prichard & Tarkian 1988) suggest that a change in the platinum-group mineralogy is caused by addition of As, which is not necessarily accompanied by significant remobilization of the *PGE*, and thus preserves the primary relative concentrations. This is apparently the case for Troodos, where Pt and Pd remain concentrated in sulfide-bearing gabbros. It appears that initial minor alteration of the gabbros only changes the mineralogy of the *PGE*, but does not significantly mobilize the *PGE*. Despite their noble characteristics, the *PGE* are now considered to be mobile during extreme alteration; Pd moves more readily than Pt, possibly as a chloride complex (Fuchs & Rose 1974). There is evidence of removal of *PGE* from some intensely altered gabbros, because higher Pt and Pd values occur in fresher gabbros. More altered gabbros have higher Pt/Pd values, suggesting preferential removal of Pd.

It is generally accepted that SSZ ophiolite complexes represent ancient oceanic crust, formed at a spreading axis above a subduction zone. Analogies may be drawn, therefore, about modern oceanic crust in a similar tectonic setting. The depth of penetration of seawater in the oceanic crust is debated (Hekinian *et al.* 1980), but in the Troodos ophiolite complex, hydrothermal circulation of seawater is considered to have reached the upper gabbros at a depth of approximately 4 km (Gass 1980, Adamides 1984). This circulation is known to have leached Au and Cu from the volcanic rocks (Constantinou & Govett 1972), and at a deeper level, transition metals have been removed by hydrothermal processes, producing epidotization of the gabbros and the sheeted dykes (Richardson *et al.* 1987). An epidosite from locality 11 was found to be devoid of significant *PGE*. It is possible that the *PGE* are hydrothermally stripped by saline solutions from alteration zones in gabbros. The *PGE* may be reconcentrated by precipitation from these hydrothermal fluids (McCallum *et al.* 1976). As warm noble-metal-bearing fluids rise through the volcanic rocks into the ocean, they have the potential to precipitate *PGM* in marine sediments. Experimental studies (Mountain & Wood 1988) suggest that saline fluids and hydroxide complexes may transport *PGE* and that in certain conditions, Au and Ir are less mobile than Pt. Consequently, Au and Ir are likely to be precipitated closer to the hydrothermal conduit. Ir is concentrated in hydrothermally altered basalts from Hawaii (Crocket & Kabir 1988). Au is precipitated in modern-day sulfide deposits around black smokers (Hekinian *et al.* 1980) and occurs in association with the exhalative massive sulfide deposits in Cyprus. Au and Ir found in the exhalative massive sulfide at Agrokipia may have been precipitated from hydrothermal fluids. The chondrite-normalized pattern is jagged, which is characteristic of a hydrothermal rather than magmatic concentration. Pt is likely to be dispersed into seawater and may be enriched in Mn nodules on the ocean floor (Hodge *et al.* 1985).

Conclusions

Crocket (1981) noted that there is probably little commercial potential for *PGE* in ophiolites, but observed that sulfides are known to occur in the gabbros (Coleman 1977) and predicted that *PGE* might be associated with them. Although the levels of Pt and Pd documented in Troodos rocks are low, they prove that these elements can be concentrated in ophiolite complexes. These rocks may be enriched in Pt and Pd. Os, Ir and Ru are removed early in chromitites to give the negatively sloping chondrite-normalized pattern. Pt and Pd are fractionated to higher levels within the magma chamber and are concentrated in gabbros in association with sulfides. Fresher gabbros retain positively sloping chondrite-normalized patterns, although the mineralogy is altered to platinum arsenide and palladium antimonide associated with secondary amphibole. More altered gabbros contain less *PGE* than adjacent fresher ones, which suggests that *PGE* are removed during alteration. Some *PGE* concentrations are at a sufficiently high stratigraphic level in the ophiolite complex to be altered by the passage of seawater-derived hydrothermal fluids. If the hypothesis that SSZ ophiolites are fragments of oceanic lithosphere created above fossil subduction zones is accepted, it is likely that *PGE* also are magmatically concentrated in oceanic crust formed above modern subduction zones. Consequently, the *PGE* are available for extraction by seawater-derived hydrothermal fluids and constitute, therefore, an important potential supply of Pt and Pd to the oceanic environment.

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References

Adamides, N.G. (1984): *Cyprus Volcanogenic Sulphide Deposits in Relation to their Environment of Formation.* Ph.D. thesis, Univ. Leicester, Leicester, U.K.

Agiorgitis, G. & Wolf, R. (1978): Aspects of osmium, ruthenium and iridium contents in some Greek chromites. *Chem. Geol.* **23**, 267-272.

Allen, C. R. (1975): *The Petrology of a Portion of the Troodos Plutonic Complex, Cyprus.* Ph.D. thesis, Cambridge Univ., Cambridge, England.

Augé, T. (1985): Platinum-group mineral inclusions in ophiolitic chromitite from the Vourinos complex, Greece. *Can. Mineral.* **23**, 163-171.

______ (1986): Platinum-group mineral inclusions in chromitites from the Oman ophiolite. *Bull. Minéral.* **109**, 301-314.

______ (1988): Platinum-group minerals in the Tiébaghi and Vourinos ophiolitic complexes: genetic implications. *Can. Mineral.* **26**, 177-192.

Barnes, S.-J., Boyd, R., Korneliussen, A., Nilsson, L.-P., Often, M., Pedersen, R.B. & Robins, B. (1988): The use of mantle normalisation and metal ratios in discriminating between the effects of partial melting, crystal fractionation and sulphide segregation on platinum-group elements, gold, nickel and copper: examples from Norway. *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (113-143).

______, Naldrett, A.J. & Gorton, M.P.(1985): The origin of the fractionation of platinum-group elements in terrestrial magmas. *Chem. Geol.* **53**, 303-323.

Bear, L.M. & Morel, S.W. (1960): Geological map to accompany the geological memoir 7 – Agros – Apsiou area. *Geol. Surv. Dep., Nicosia, Cyprus.*

Becker, R. & Agiorgitis, G. (1978): Iridium, osmium and palladium distribution in rocks of the Troodos complex, Cyprus. *Chem. Erde* **37**, 302-306.

Benn, K. & Laurent, R. (1987): Intrusive suite documented in the Troodos ophiolite plutonic complex, Cyprus. *Geology* **15**, 821-824.

Buchanan, D.L. (1988): *Platinum-Group Element Exploration.* Elsevier, London.

Cabri, L.J. & Harris, D.C. (1975): Zoning in Os–Ir alloys and the relation of the geological and tectonic environment of the source rocks to the bulk Pt:Pt + Ir + Os ratio for placers. *Can. Mineral.* **13**, 266-274.

Coleman, R.G. (1977): *Ophiolites – Ancient Oceanic Lithosphere?* Springer-Verlag, Berlin.

Constantinides, C.C., Kingston, G.A. & Fisher, P.C. (1980): The occurrence of platinum group minerals in the chromitites of the Kokkinorotsos chrome mine, Cyprus. *In* Proc. Int. Ophiolite Symp., Cyprus (A. Panayiotou, ed.). Ministry of Agriculture and Natural Resources, Cyprus (93-101).

Constantinou, G. & Govett, G.J.S. (1972): Genesis of sulphide deposits, ochre and umber of Cyprus. *Trans. Inst. Min. Metall.* **81**, B34-46

Crocket, J.H. (1981): Geochemistry of the platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Min. Metall., Spec. Vol.* **24**, 47-64.

______ & Kabir, A. (1988): *PGE* in Hawaiian basalt: implications on hydrothermal alteration on *PGE* mobility in volcanic fluids. *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (259, abstr.).

Fisher, W., Amosse, J. & Leblanc, M. (1988): *PGE* distribution in some ultramafic rocks and minerals from the Bou-Azzer ophiolite complex (Morocco). *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (199-210).

Fuchs, W.A. & Rose, A.W. (1974): The geochemical behavior of platinum and palladium in the weathering cycle in the Stillwater complex Montana. *Econ. Geol.* **69**, 332-346.

Gain, S. B. (1985): The geologic setting of the platiniferous UG-2 chromitite layer on the farm Maandagshoek, eastern Bushveld complex. *Econ. Geol.* **80**, 925-943.

Gass, I. G. (1980): The Troodos massif: its role in the unravelling of the ophiolite problem and its significance in the understanding of constructive plate margin processes. *In* Int. Ophiolite Symp., Cyprus (A. Panayiotou, ed.). Ministry of Agriculture and Natural Resources, Cyprus (23-35).

Greenbaum, D. (1977): The chromitiferous rocks of the Troodos ophiolite complex, Cyprus. *Econ. Geol.* **72**, 1175-1194.

Hekinian, R., Février, M., Bischoff, J.L., Picot, P. & Schanks, W.C. (1980): Sulfide deposits from the East Pacific Rise near 21° north. *Science* **207**, 1433-1444.

Hiemstra, S.A. (1985): The distribution of some platinum-group elements in the UG-2 chromitite layer of the Bushveld complex. *Econ. Geol.* **80**, 944-957.

Hodge, V.F., Stallard, M., Koide, M. & Goldberg, E.D. (1985): Platinum and the platinum anomaly in the marine environment. *Earth Planet. Sci. Lett.* **72**, 158-162.

Johan, Z., Le Bel, L. & Georgiou, E. (1982): Environnement pétrologique des gisements de chromite du complexe ophiolitique du Troodos (Chypre). *Bur. Rech. Géol. Min. - Centre National Rech. Sci., Rapp.*

Legendre, O. & Augé, T. (1986): Mineralogy of platinum-group mineral inclusions in chromitites from different ophiolite complexes. *In* Metallogeny of Basic and Ultrabasic Rocks, Symp. Vol. (M.J. Gallagher, R.A. Ixer, C.R. Neary & H.M. Prichard, eds.). Inst. Min. Metall., London (361-372).

Lord, R.A. & Prichard, H.M. (1989): An igneous source for gold in the Shetland ophiolite. *Trans. Inst. Min. Metall.***98**, B44-46.

McCallum, M.E., Loucks, R.R., Carlson, R.R., Cooley, E.F. & Doerge, T.A. (1976): Platinum metals associated with hydrothermal copper ores of the New Rambler mine, Medicine Bow Mountains, Wyoming. *Econ. Geol.* **71**, 1429-1450.

McElduff, B. & Stumpfl, E.F. (1989): Geochemistry and mineralogy of platinum-group elements in chromitites from Troodos, Cyprus. *Geol. Soc. Finland Bull.* **61(1)**, 36-37 (abstr.).

McLaren, C.H. & de Villiers, J.P.R. (1982): The platinum-group chemistry and mineralogy of the UG2 chromitite layers of the Bushveld Complex. *Econ. Geol.* **77**, 1348-1366.

Moring, B.C., Page, N.J & Oscarson, R.L. (1988): Platinum-group elements mineralogy of the Pole Corral podiform chromite deposit, Rattlesnake Creek Terrane, northern California. *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (257, abstr.).

Mountain, B.W. & Wood, S.A.(1988): Solubility and transport of platinum-group elements in hydrothermal solutions: thermodynamic and physical chemical constraints. *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (57-82).

Naldrett, A. J. (1981): Platinum-group element deposits. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Min. Metall., Spec. Vol.* **23**, 197-231.

______ & Duke, J.M. (1980): Platinum metals in magmatic sulfide ores. *Science* **208**, 1417-1424.

______ & Von Gruenewaldt, G. (1989): Association of platinum-group elements with chromitite in layered intrusions and ophiolite complexes. *Econ. Geol.* **84**, 180-187.

Nicolas, A. (1986): A melt extraction model based on structural studies in mantle peridotites. *J. Petrol.* **27**, 999-1022.

Orberger, B., Fredrich, G. & Woermann, E. (1988): Platinum-group element mineralisation in the ultramafic sequence of the Acoje ophiolite block, Zambales, Philippines. *In* Geo-Platinum Symp. Vol. (H.M. Prichard, P.J. Potts, J.F.W. Bowles & S.J. Cribb, eds.). Elsevier, London (361-380).

Oshin, I.O. & Crocket, J.H. (1986): Noble metals in Thetford Mines ophiolites, Quebec, Canada. II. Distribution of gold, silver, iridium, platinum, and palladium in the Lac de l'Est volcano-sedimentary section. *Econ. Geol.* **81**, 931-945.

Page, N.J, Cassard, D. & Haffty, J. (1982a): Palladium, platinum, rhodium, ruthenium, and iridium in chromitites from the Massif du Sud and Tiebaghi Massif, New Caledonia. *Econ. Geol.* **77**, 1571-1577.

______, ENGIN, T., SINGER, D.A. & HAFFTY, J. (1984): Distribution of platinum-group elements in the Bati Kef chromite deposit, Guleman-Elazig area, eastern Turkey. *Econ. Geol.* **79**, 177-184.

______, PALLISTER, J.S., BROWN, M.A., SMEWING, J.D. & HAFFTY, J. (1982b): Palladium, platinum, rhodium, iridium, and ruthenium in chromite-rich rocks from the Samail ophiolite, Oman. *Can. Mineral.* **20**, 537-548.

______ & TALKINGTON, R. W. (1984): Palladium, platinum, rhodium, ruthenium, and iridium in peridotites and chromitites from ophiolite complexes in Newfoundland. *Can. Mineral.* **22**, 137-149.

PRICHARD, H.M. & LORD, R.A. (1988): The Shetland ophiolite: evidence for a supra-subduction zone origin and implications for platinum-group element mineralisation. *In* Mineral Deposits within the European Community (J. Boissonnas & P. Omenetto, eds.). Springer-Verlag, Berlin (289-302).

______, NEARY, C.R. & POTTS, P.J. (1986): Platinum-group minerals in the Shetland ophiolite. *In* Metallogeny of Basic and Ultrabasic Rocks, Symp. Vol. (M.J. Gallagher, R.A. Ixer, C.R. Neary & H.M. Prichard, eds.). Inst. Min. Metall., London (395-414).

______, POTTS, P.J. & NEARY, C.R. (1981): Platinum group element minerals in the Unst chromite, Shetland Isles. *Trans. Inst. Min. Metall.***90**, 186-188.

______ & TARKIAN, M. (1988): Platinum and palladium minerals from two PGE-rich localities in the Shetland ophiolite complex. *Can. Mineral.* **26**, 979-990.

RICHARDSON, C.J., CANN, J.R., RICHARDS, H.G. & COWAN, J.G. (1987): Metal-depleted root zones of the Troodos ore-forming hydrothermal systems, Cyprus. *Earth Planet. Sci. Lett.* **84**, 243-253.

STOCKMAN, H.W. & HLAVA, P.F. (1984): Platinum-group minerals in alpine chromitites from southwestern Oregon. *Econ. Geol.* **79**, 491-508.

STUMPFL, E.F. & TARKIAN, M. (1976): Platinum genesis: new mineralogical evidence. *Econ. Geol.* **71**, 1451-1460.

TALKINGTON, R.W. & WATKINSON, D.H. (1986): Whole rock platinum-group element trends in chromite-rich rocks in ophiolitic and stratiform igneous complexes. *In* Metallogeny of Basic and Ultrabasic Rocks, Symp. Vol. (M.J. Gallagher, R.A. Ixer, C.R. Neary & H.M. Prichard, eds.). Inst. Min. Metall., London (427-440).

______, ______, WHITTAKER, P.J. & JONES, P.C. (1984): Platinum-group minerals and other solid inclusions in chromite of ophiolitic complexes: occurrence and petrological significance. *Tschermaks Mineral. Petrogr. Mitt.* **32**, 285-301.

THALHAMMER, O.A.R. & STUMPFL, E.F. (1988): Platinum-group minerals from Hochgrossen ultramafic massif, Styria: first reported occurrence of *PGM* in Austria. *Trans. Inst. Min. Metall.* **97**, B77-82.

VON GRUENEWALDT, G., HATTON, C.J., MERKLE, R.K.W. & GAIN, S.B. (1986): Platinum-group element – chromitite associations in the Bushveld complex. *Econ. Geol.* **81**, 1067-1079.

WILSON, R.A.M. (1959): Geological map to accompany the geological memoir 1 – Xeros – Troodos area. *Geol. Surv. Dep., Nicosia, Cyprus.*

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