Potential of ophiolite complexes to host PGE deposits

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Abstract

All six PGE have been recorded as concentrated at parts per million (ppm) in a number of ophiolite complexes. Occurrences of PGE concentrations in ophiolites are common in podiform chromitite where Os, Ir and Ru may be concentrated to give negative slope chondrite normalised patterns. If sulphur saturation of the magma occurred during chromite crystallisation then Pt and Pd $\pm$ Rh will also be concentrated in the chromitite giving positive chondrite normalised patterns. PGE-rich ophiolite complexes are those where there has been sufficient mantle melting, in a subduction zone, to extract the PGE at a critical melting interval. Too much melting will dilute this melt with PGE-barren melt and too little melting will not extract the PGE. The Scottish Shetland ophiolite is an example in which all 6 PGE have been concentrated in base metal sulphide-bearing podiform chromitite. It is proposed that if all the PGE are concentrated in podiform chromitite then they crystallised from one PGE-rich melt that was close to sulphur saturation. Exploration for PGE within ophiolites is likely to be enhanced by growing evidence that there is a link between chromite composition and PGE concentration.

Introduction

Ophiolite complexes are slices of oceanic crust that have been emplaced onto continents. They consist of, from top to bottom, pillow lavas, sheeted dykes, gabbros and mafic and ultramafic cumulates underlain by mantle peridotite consisting of harzburgite and/or lherzolite. Podiform chromitite hosts most of the ophiolitic platinum-group element (PGE) concentrations. This chromitite occurs in the ultramafic cumulate sequences of ophiolites, mainly either in crustal dunite or in the underlying mantle, where commonly chromitite is enclosed in envelopes of dunite. Ophiolites have very variable abundances of PGE, sometimes with grades similar to those in the Bushveld layered complex and in base metal sulphide-rich ores in feeder sills in Noril'sk, which together host the two major PGE resources of the world (Lee 1996; Cabri 2002; Naldrett et al., 1996). In contrast, the known tonnages of PGE concentrations in ophiolites are very small compared to the major deposits but they do contain sporadic and very anomalous grades of PGE. Unlike continental stratiform chromitite, ophiolitic chromitite pods are discontinuous, unpredictable in outcrop and subcrop and relatively poorly understood in terms of PGE grade. Mining of podiform chromitite ores is often haphazard due to the unpredictable *en echelon* arrangement of podiform

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chromitite and occurrences of high grades of PGE are rarely located or recovered during mining of the chromite.

Traditionally it was thought that the dominant PGE in ophiolites are osmium (Os), iridium (Ir) and ruthenium (Ru), collectively known as the IPGE, and are associated with podiform chromitites (Constantinides et al. 1980; Prichard et al. 1981; Page et al. 1982; Talkington et al. 1984; Augé 1985, 1986, Zhou et al. 1998). Over the last 20 years platinum (Pt) and palladium (Pd) $\pm$ rhodium (Rh), collectively known as the PPGE, have been located in ophiolites associated with sulphide-bearing chromitites. The Shetland ophiolite complex was one of the first ophiolite complexes in which Pt and Pd concentrations as great as a few ppm were identified (Neary et al. 1984; Prichard et al. 1984, 1986; Gunn et al. 1985). Now many other Pt and Pd occurrences have been described from ophiolite complexes including from Leka in Norway (Pedersen et al. 1993), Acoje in the Philippines (Bacuta et al. 1988; Orberger et al. 1988), New Caledonia (Augé et al. 1998), Bulquiza in Albania (Ohnenstetter et al. 1991, 1999), Al 'Ays in Saudi Arabia (Prichard et al. 1996a Prichard et al. 2008a), Pindos in Greece (Economou-Eliopoulos 1996; Tarkian et al. 1996; Eliopoulos et al. 1998, Prichard et al. 2008b), Troodos in Cyprus (Prichard & Lord 1990), Inazumi-yama in Japan (Arai et al. 1999), Thetford in Canada (Corrivaux & LaFlamme, 1990), Cabo Ortegal in Spain (Moreno et al. 2001) and Bragança in Portugal (Bridges et al. 1993). Maps of the world showing the position of major podiform chromite deposits and of IPGE and PPGE concentrations in podiform chromitites are shown in Figure 1.

Figure 1. Map of the world showing the major PPGE, IPGE and PGE-barren podiform chromitites. Included are Leka, Cabo Ortegal, Veria and Pindos which contain anomalous PGE concentrations without substantial podiform chromitite mineralization. References to ophiolites/ PGE occurrences not included in the text. (Acharyya 2007; Ahmed and Bilgrami 1987; Ahmed et al. 2005; Arai et al., 1999; Arenas et al. 2004; Bédard et al. 2008; Bortolotti and Principi 2005; Casey et al. 1985; Cassard et al. 1981; Cawood and Korsch 2008; Coombs et al. 1976; Economou-Eliopoulos 1996; Escayola et al. 2004; GeoMapApp 2009; Ghazi and Hassanipak 2000; Guilmette et al. 2008; Hall 2002; Ishiwatari and Tsujimori 2003; Keller and Fisk 1992; Matsumoto & Arai, 2001; Melcher et al. 1997; Monnier et al. 1995; Najafzadeh et al. 2008; Ortiz et al. 2004; Paladines 2004; Pessagno et al. 2000; Peters 2000; Proenza et al. 2004; Pubellier et al. 2004; Qiu et al. 2007; Robinson and Zhou 2008; Schellart et al. 2009; Scott et al. 1989; Skobelev et al. 2004; Spadea and Scarrow 2000; Stern et al. 2004; Stowe 1987; Sturt and Roberts 1991; Suita et al. 2004; Tapponnier et al. 1981; Tsoupas and Economou-Eliopoulos 2008; Tsukanov et al. 2007; USGS 2009; Varne et al. 2000; Veloso et al. 2005; Wang et al. 2007; Wang et al. 2008; Whattam 2009; Yang et al. 1996; Yihunie and Hailu 2007; Yumul Jr et al. 2003; Zaccarini et al. 2008; Zhang et al. 2008; Zhou et al., 1998).
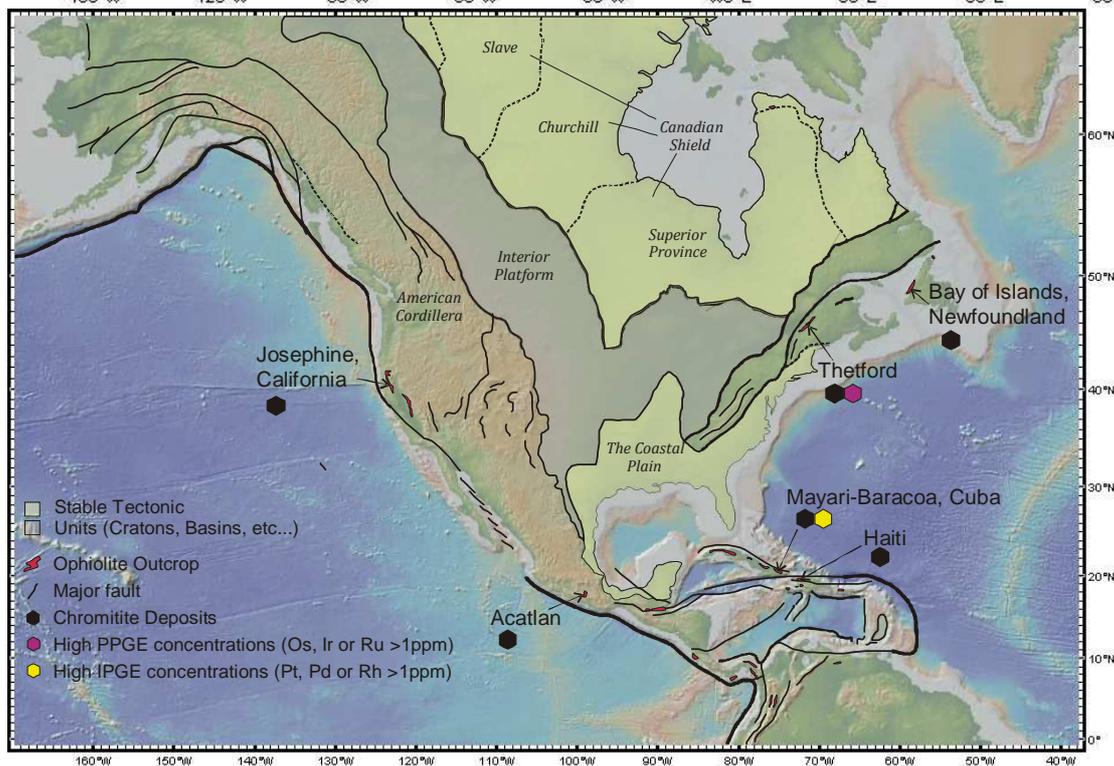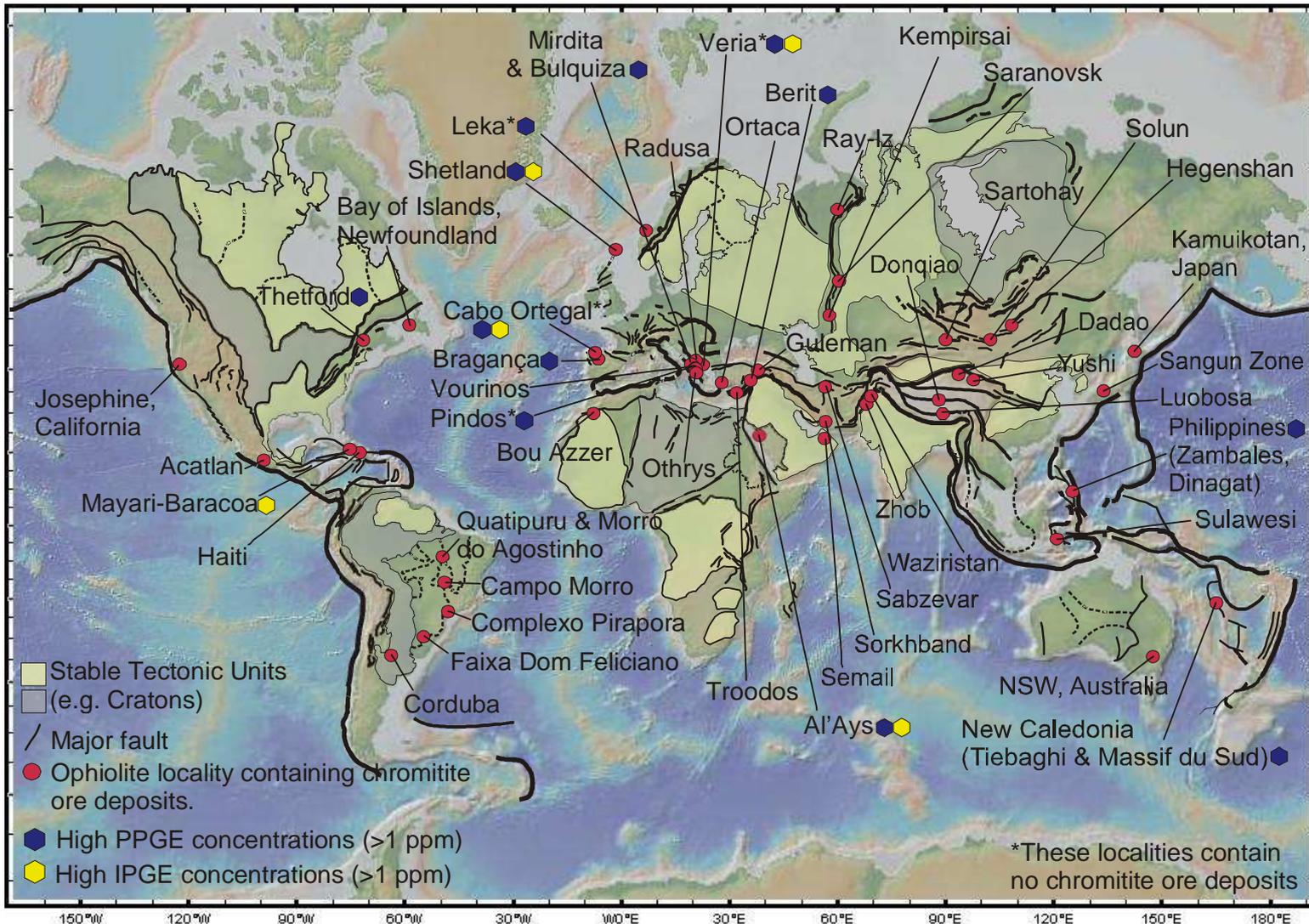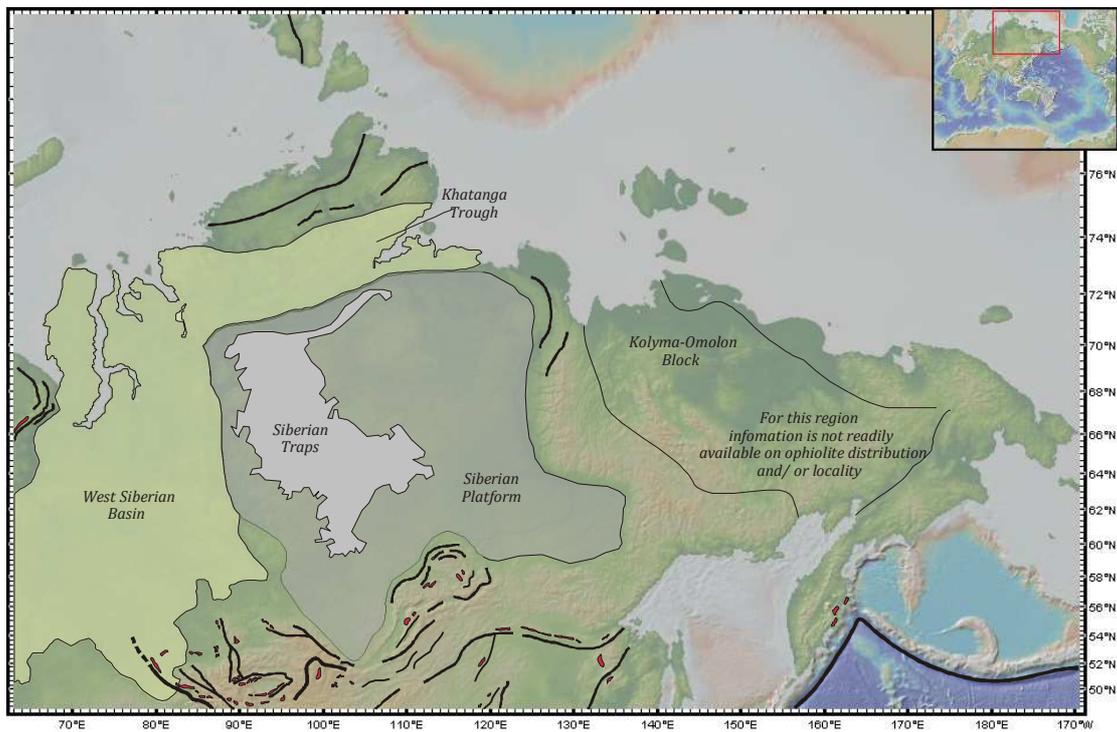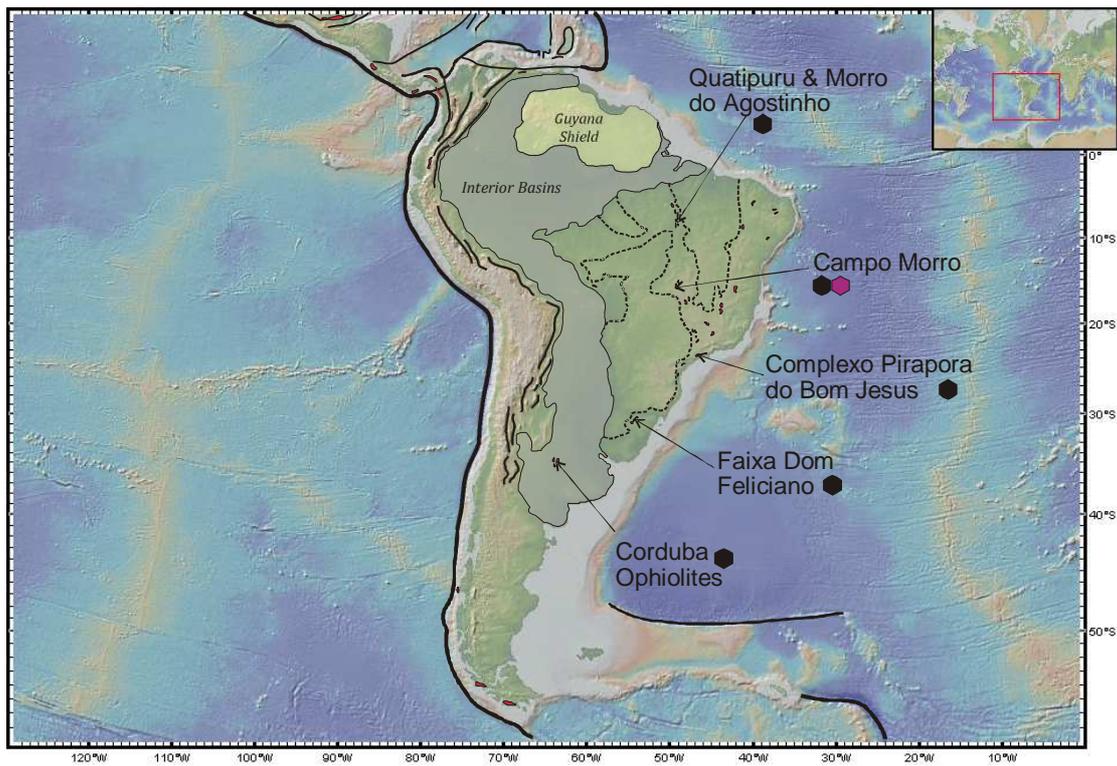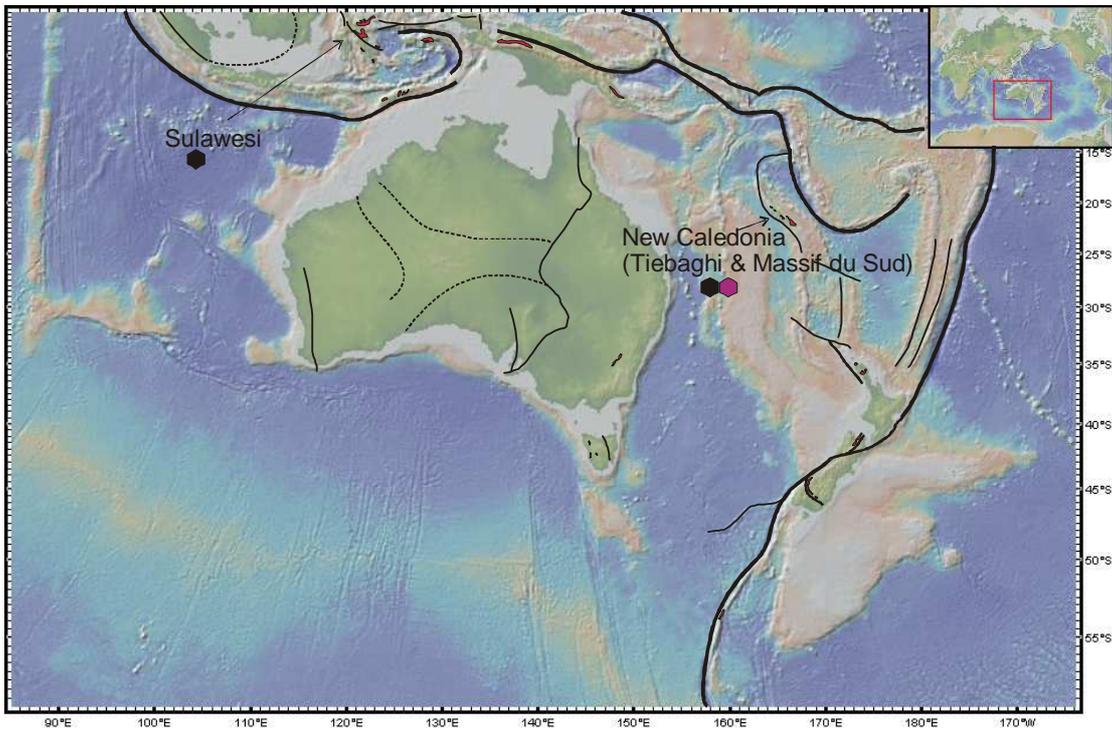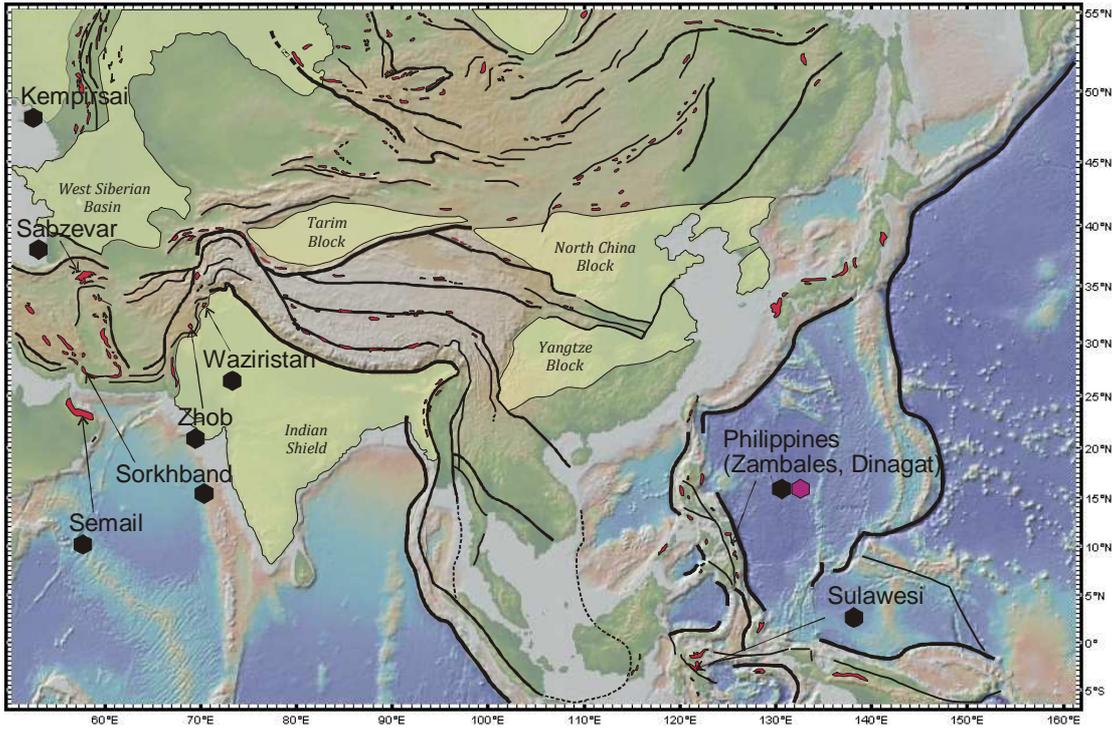
PGE patterns

PGE concentrations normalised to chondrite allow the relative enrichment of individual PGE relative to chondrite to be observed. Ophiolitic podiform chromitite enriched in Os, Ir and Ru, especially in base metal sulphide-poor chromitites, give negative slope chondrite normalised patterns (Figure 2a). Pt- and Pd- $\pm$ Rh- rich concentrations in sulphide-bearing ultramafic lithologies including chromitites, dunites (often associated with chromitites), wehrlites and pyroxenites give positive slope chondrite normalised patterns (Figure 2b). If base metal sulphide crystallisation occurred with chromite then the combined concentrations of Os, Ir and Ru with enriched Pt and Pd $\pm$ Rh give a positive slope chondrite normalised pattern.

It is important to note that in layered complexes, such as the Bushveld, base metal sulphide-poor chromitites have negative slope chondrite normalised patterns and base metal sulphide-bearing ultramafic rocks which may include chromitite have positive slope chondrite normalised patterns. Ophiolite complexes can also exhibit positive slope and negative slope chondrite normalised patterns as described above. Negative slope chondrite normalised patterns do not characterise ophiolite complexes and positive chondrite normalised patterns do not characterise layered complexes. Rather positive and negative slope patterns characterise different magmatic processes that produce lithologies with specific mineralogies that can occur in both ophiolite and layered complexes.

Figure 2 (a) Negative slope chondrite normalised patterns in samples from the Shetland ophiolite, chromitite RL070 (black square) and RLM003 (white square) and (b) positive slope chondrite normalised patterns associated with base metal sulphides for S-bearing dunite RLM063 (black square), Cr-rich S-bearing dunite RLM066 (white square) and RLM068 (black diamond),) sulphide-bearing chromitite RLM007 (white diamond) and S-bearing pyroxenite pegmatite NA25 (white triangle). Chondrite values used to plot the chondrite normalised patterns are Os 514, Ir 540, Ru 690, Rh 200, Pt 1025 and Pd 545 after Naldrett and Duke (1980). (adapted from Prichard and Lord 1993).
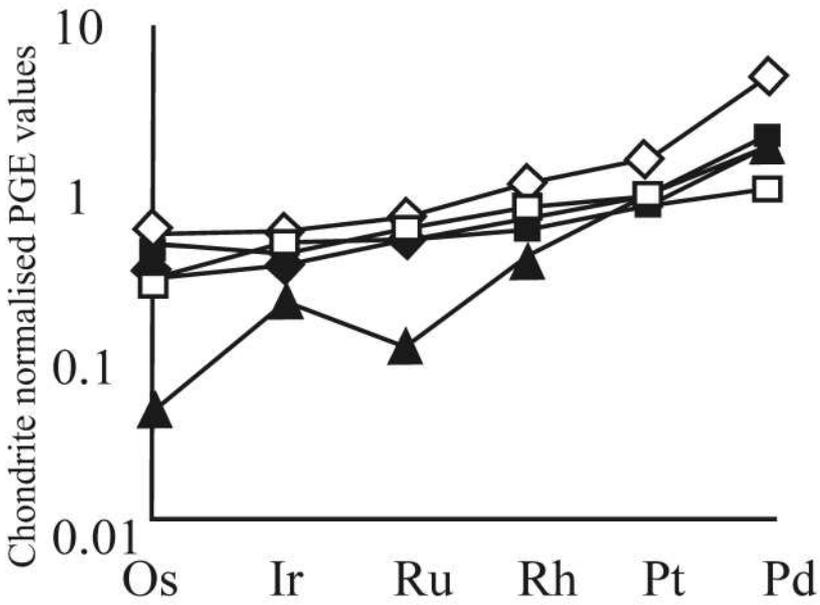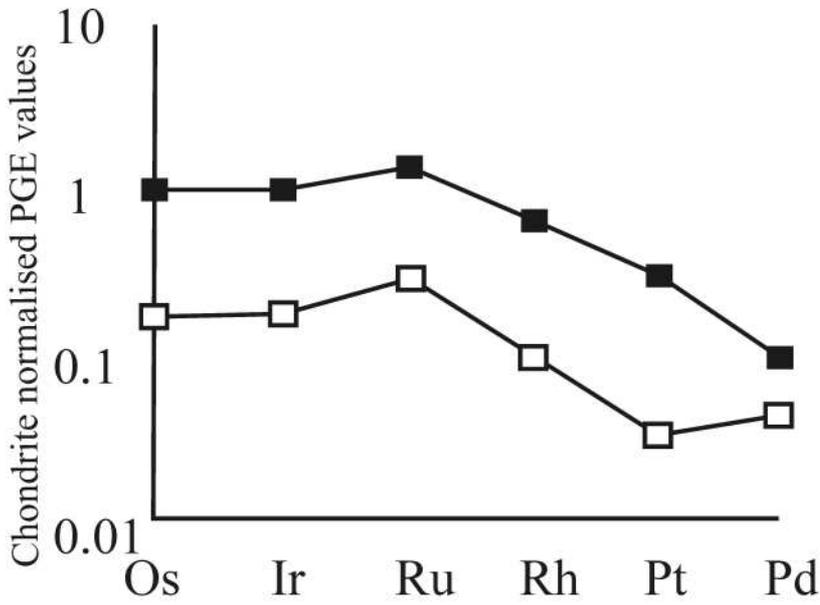
The slope of chondrite normalised patterns between Pt and Pd often varies. This probably reflects the degree of alteration of the lithologies with steep positive slopes being typical of unaltered lithologies and gentle positive slopes to flat or even negative slopes are produced during most types of alteration processes. This is because the preferential removal of Pd rather than Pt during alteration increases the Pt/Pd ratio.

Platinum-group minerals

Laurite ($Ru[Os,Ir]S_2$) is the most commonly described platinum-group mineral (PGM) in ophiolite complexes, and usually occurs enclosed in chromite (for example Prichard et al. 1981; Constantinides et al. 1980; Augé 1986). Also primary Ru-Os-Ir alloys have been recorded enclosed in chromite. In Pt- and Pd-bearing ophiolties a much greater variety of PGM have been described (for example Prichard et al. 1994, Augé 1988, Prichard & Lord 1990, Tarkian et al. 1996, Corrivaux & LaFlamme, 1990). Pt-, Pd- and Rh-bearing PGM include sperrylite $PtAs_2$, stibiopalladinite Pd_5Sb_2, hongshiite PtCu, geversite $PtSb_2$, genkinite $(PtPd)_4Sb_3$, Pt and Pd tellurides, potarite (PdHg), AuPd alloys, hollingworthite (RhAsS), Rh antimonides and Pt and Pd oxides (Prichard et al. 1994, Prichard et al. 2008a). A schematic diagram of PGM distribution in podiform chromitite is shown in Figure 3.

The PGM record the igneous and subsequent secondary alteration processes affecting them. Magmatic PGM include laurites and Ru-Os-Ir alloys within chromite and rarely Pt- and Pd-sulphides within primary clinopyroxene. These PGE-bearing Ni- and Cu-sulphides probably reflect the primary igneous mineralogy with the PGE-being strongly associated with sulphur in the magma. In chromite-rich lithologies Pt-, Pd- and Rh-bearing PGM generally occur interstitially to chromite, usually in secondary serpentine and chlorite whereas Os-, Ir- and Ru-bearing PGM occur mainly within chromite. These textural associations indicate an in situ magmatic fractionation of PGE from early Os, Ir and Ru trapped within the centres of relict primary chromite to later Pt-, Pd- and Rh-bearing PGM formed after the crystallisation of chromite (Figure 4).

Figure 3 shows the different mineralogical associations of the PGM in ophiolite complexes.
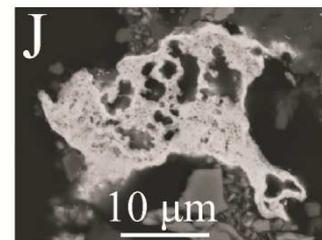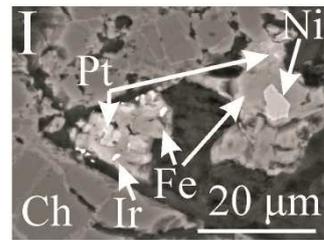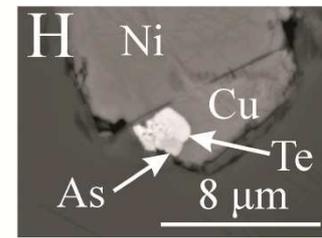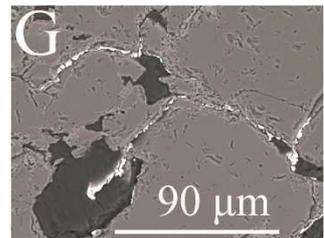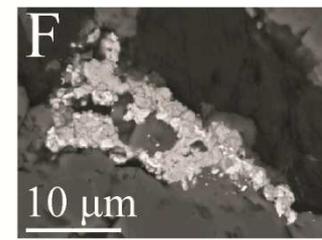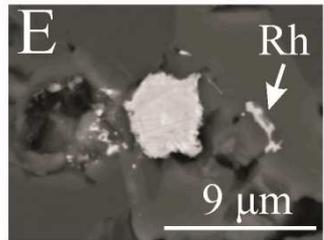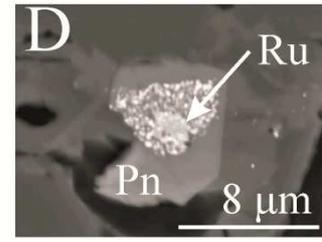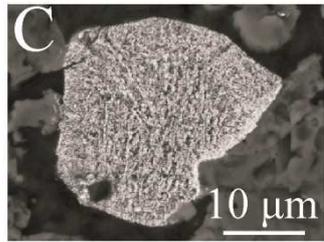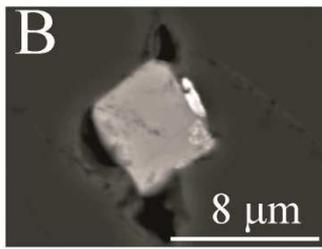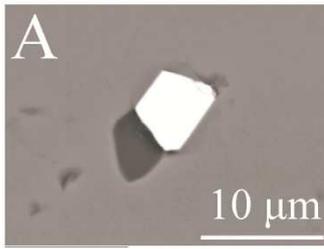
A   Euhedral laurite crystal enclosed in a chromite grain.

B   Subhedral rectangular laurite (grey) with a small attached irarsite (white) in a silicate filled crack (black) surrounded by chromite.

C   Mottled Os-Ir alloy pseudomorphing an earlier PGM on the edge of chromite (grey) and partially surrounded by silicate (Black).

D   Rhodium arsenide (white dots) surrounding a laurite (Ru, pale grey) all within a ruthenian cobalt-bearing pentlandite (Pn, grey) surrounded by chromite (darker grey) and silicate (black).

E   Anhedral rounded Ru-Ir-Os alloy (pale grey) surrounded by chromite close to an elongate rhodium antimonide (Rh)

F   Mottled irregular elongate shaped Ir-Pt alloy (pale grey) located on the edge of chromite (grey) and adjacent to silicate (black).

G   Stringers of Pt-Ni alloy (white) in silicate filled cracks (black) in chromite (grey).

H   Composite PGM composed of Pd telluride (Te, white) and Pd-Ni arsenide (As, very pale grey) located on the edge of a composite base metal sulphide composed of Cu and Ni sulphides (Cu and Ni, pale grey) all surrounded by chromite (darker grey).

I   Ru-Ir alloy (Ir, white) and Pt-Fe oxide (Pt, pale grey) located in Fe-Ni-oxide (Fe, grey) pseudomorphing a former PGM and surrounded by mottled silicate (black) close to a Ni-Fe alloy containing traces of Rh and Pt, (Ni, pale grey) enclosed in Fe-Ni-oxide also surrounded by the mottled silicate and all close to chromite (Ch).

J   Mottled Pd-Cu oxide (pale grey) surrounded by silicate (grey) and holes (black).

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Figure 4 Schematic diagram showing the different textural arrangements of PGM grains .
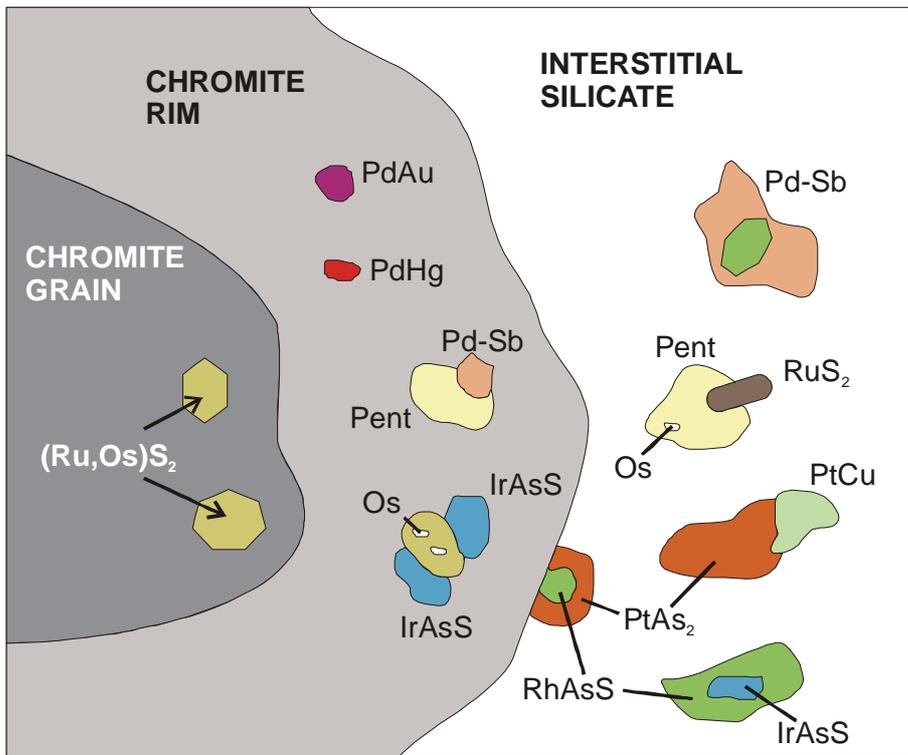
Laurite enclosed in chromite is usually euhedral in shape and contains Ir and Os in solid solution. However where the laurite occurs on the edge of chromite, in contact with altered silicate, or is crossed by serpentine-filled fractures in the chromite, then the laurite is often irregular in shape. Serpentinisation may cause recrystallisation of the laurite to form pure RuS_2, expelling the Ir and Os that now form irasite (IrAsS) and native osmium which often accompany it. Laurite may also lose sulphur during serpentinisation and in extreme cases native Ru is produced (for example Stockman & Hlava 1984; Tarkian & Prichard 1987). Also Ru is present in minor amounts in ruthenian pentlandite occurring with serpentine.

PGM enclosed by altered silicates are often As-, Sb and Te-bearing. Examples of these include irarsite, hollingworthite RhAsS, sperrylite and stibiopalladinite. These PGM have been altered during serpentinisation that was accompanied by the introduction of As, Sb and Te. Further alteration of the PGM removes As, Sb and Te producing PGE-alloys with base metals and gold, including hongshiite PtCu, Pt-Pd-Au-Cu and Pd-Au. Finally, probably during surface weathering, PGE-oxides are formed. These have been observed in a number of ophiolite complexes (Prichard et al., 2008a and b, Prichard et al. 1994, Moreno et al. 1999, Augé & Legendre. 1994, Garuti and Zaccarini 1997, Garuti et al. 1997).

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Exploration significance

a) Geochemical pathfinders for the PGE

Os, Ir and Ru are especially concentrated with chromitites and therefore Cr is a pathfinder for these elements. Pt and Pd $\pm$ Rh are associated with base metal sulphides hosted by pentlandite, heazlewoodite, millerite, chalcopyrite, chalcocite and bornite and therefore Cu and Ni correlate with these PGE. The sulphides may be visible in hand specimen, form 1-2 % of the rock (Lord et al. 1994) and give rise to Ni and Cu anomalies in PGE-rich areas.

Exploration for PGE in Shetland revealed that the highest values of the pathfinder elements Cu and Ni in the PGE-rich areas in the dunite crustal sequence are up to 8,500ppm Ni and up to 1,500ppm Cu (Lord et al. 1994). In addition to Ni, Cu and Cr being good geochemical pathfinders for the PGE, Au is also elevated, for example to between 20-65ppb in the PGE-rich lithologies (Lord & Prichard 1998). This lithological association of the PGE with chromitite and Ni- and Cu-sulphides is common and indicates a magmatic process of concentration. Arsenic is not a pathfinder for the magmatic PGE occurrences, although where a magmatic PGE concentration is cross cut by faults, and PGE are re-concentrated by secondary processes then arsenic values may be high as at the extremely anomalous PGE-enriched Cliff locality in Shetland.

b) PGE mobility –

Pd is widely acknowledged to be more mobile than Pt (for example Fuchs & Rose 1974) and this is also the case for ophiolite complexes. Analysis of soils in Shetland, in the area where Pt and Pd anomalies are associated with the sulphide-bearing dunite and chromitite, showed that Pt and Pd tend to occur in the soils above rocks containing Pt and Pd. Pt /Pd ratios in these soils tend to be greater than one suggesting a faster removal of Pd than Pt during surface weathering (Prichard & Lord, 1994). Os, Ir and Ru present in laurite or alloys are often enclosed in chromite and are protected during mechanical weathering of the chromite. Therefore they tend to be concentrated in stream panned concentrate which is rich in chromite. Pt and Pd are also mobile in umbers in Cyprus with high Pt/Pd ratios found near faults, where Pd has been remobilised preferentially to Pt, and low ratios found in basal umbers where only Pd has precipitated (Ravizza et al. 2001).

The types of ophiolite characterised by their PGE

Although unpredictable the PGE content of different ophiolites can be divided into three main groups; ophiolites that have Pt- and Pd-bearing chromitite, ophiolites with Pt- and Pd-poor chromitite but with minor Pt- and Pd- enrichment in the gabbro and ophiolites that are poor in both PGE and chromitite. Three examples have been chosen to illustrate these subdivisions and the processes that produced these different types of PGE concentration.

The Shetland ophiolite

An example of a PGE-rich ophiolite occurs in the Shetland Islands, NE of the Scottish mainland in the UK. The PGE in this ophiolite are associated with base metal sulphide-bearing ultramafics, usually close to podiform chromitite, either in dunite lenses in the mantle or in overlying crustal dunites and wehrlites (Prichard & Lord 1993). Thus the major PGE concentrations correspond to the distribution of the chromitite (Figures 5 and 6). These are located at a number of stratigraphic levels within the ultramafic lithologies of the ophiolite. Starting at the highest stratigraphical level, Pt and Pd concentrations occur in the high level wehrlite within gabbro with maximum Pt and Pd values of only 120 and 190 ppb. Lower in the sequence Pt and Pd are concentrated in base metal sulphide-bearing wehrlite and pyroxenite that form part of cyclic units in the upper part of the lower crustal ultramafics. A sulphide-bearing pegmatitic pyroxenite from this unit gave Pt and Pd values of 510 and 590 ppb and also within the pyroxenite unit a Ru value of 710 ppb is associated with a thin Fe-rich chromitite lens.

Stratigraphically below this, Ni- and Cu- sulphide-bearing dunite, within the lower part of the crustal ultramafics, has Pt plus Pd values of 1,000-3,000ppb. This dunite hosts a zone of PGE enrichment (2.5km x 0.5km) that includes many discontinuous chromitite layers, the thicker of which have been extracted leaving several small disused quarries. The highest Pt and Pd values occur in the sulphide-bearing dunites adjacent to chromitite layers close to the disused chromite quarries; especially those situated entirely within the dunite rather than those located at the dunite / harzburgite boundary (Lord & Prichard 1998). A section showing the distribution of the PGM, base metal sulphides and chromite within the crustal dunite is shown in Figure 7. The PGE concentrations occur within magmatic cycles marked at the base by a discontinuous layer of chromitite, overlain by dunite containing Pt, Pd and base metal sulphides and grading up into barren

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Figure 5. Shetland ophiolite showing distribution of PGE (adapted from Prichard and Lord 1993).
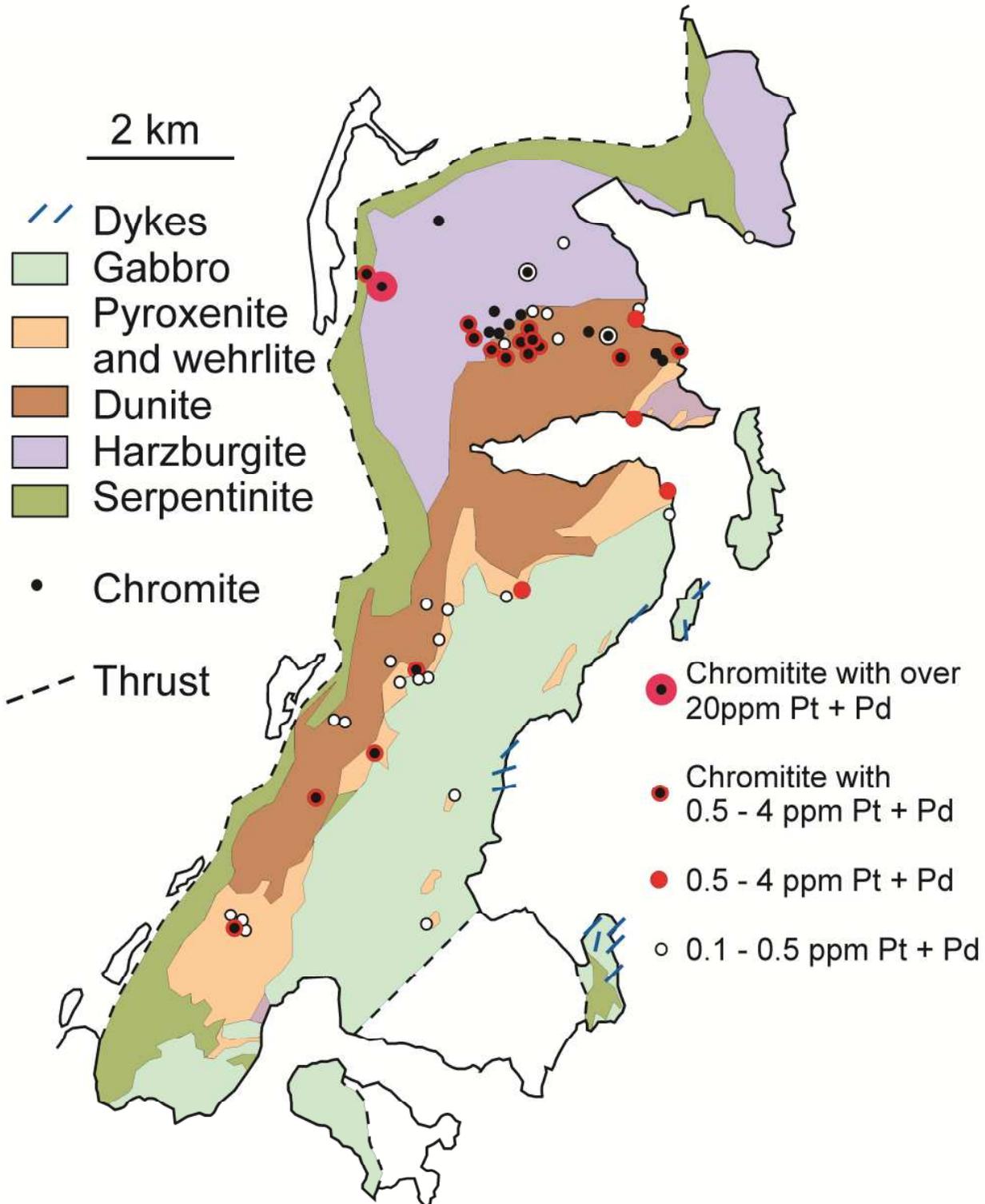
Figure 6. Section through the Shetland Ophiolite showing the occurrence of PGE horizons (adapted from Prichard et al. 2004).
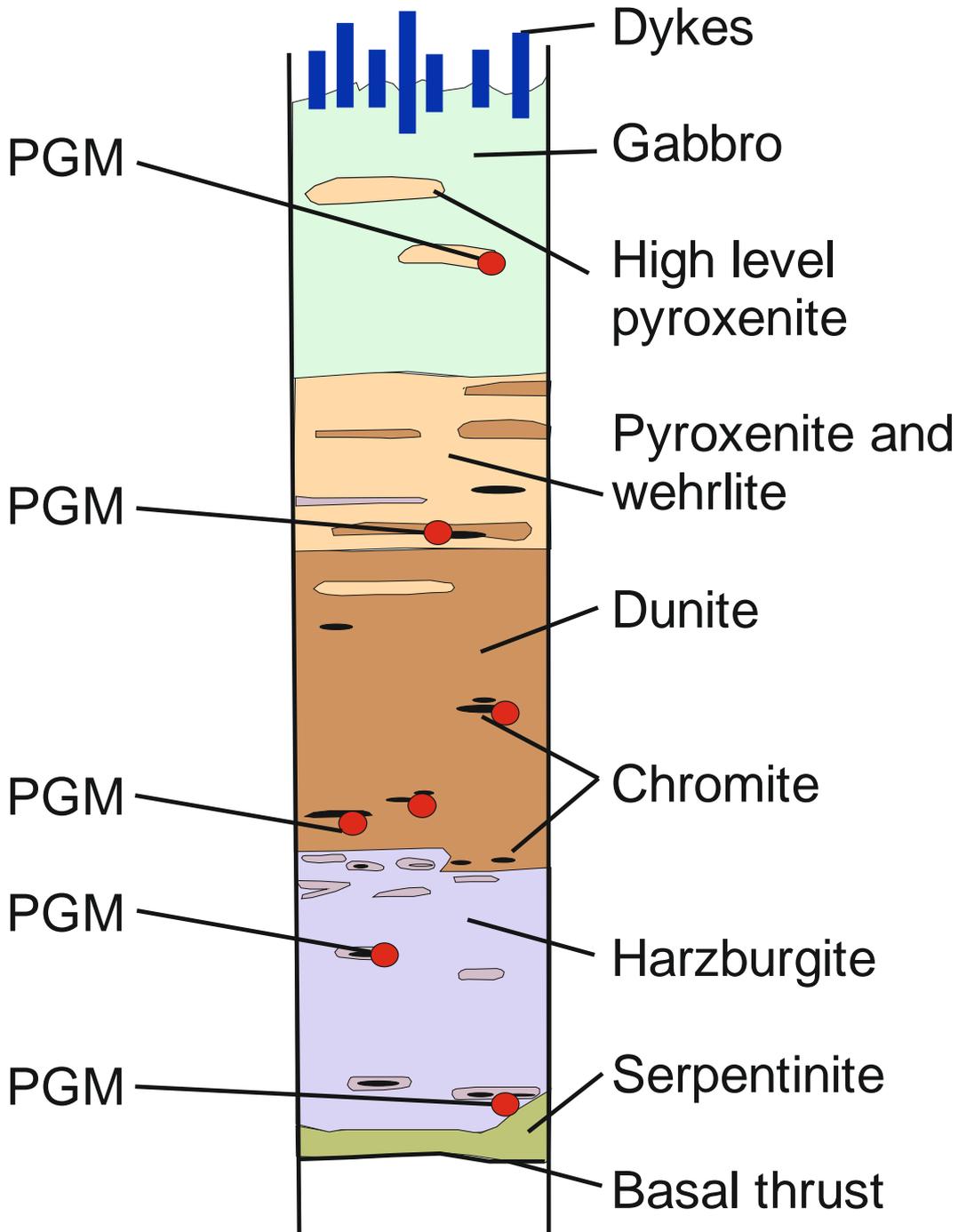
dunite. The variation in delta^{34}S of -1 to +4 over 1.5 metres of mineralized core material from this area is explained by magmatic fractional crystallization (Maynard et al. 1997).

Stratigraphically lower in the sequence, below the petrological Moho (marked by the junction between the crustal dunite and the underlying residual mantle harzburgite) dunite lenses, often chromite-rich, occur within harzburgite. These are variably PGE-enriched with some of these chromitites relatively Os, Ir and Ru enriched, others relatively Pt, Pd and Rh enriched and some completely barren of PGE. The greatest PGE concentrations in the ophiolite occur in these chromite-bearing dunite lenses. Chromitite in one of these lenses, at Harold's Grave, contains enriched Os, Ir and Ru with IPGE values of 1,000-4,000 ppb. Another chromitite-rich dunite lens in harzburgite, at Cliff, 300 m from the basal thrust of the ophiolite, hosts extremely anomalous PPGE values of 60,000ppb (Prichard et al. 1986). The Cliff locality consists of five small pits formerly containing *en echelon* chromitite lenses over a distance of 100m by 20m. These lenses are surrounded by thin envelopes of dunite which are variably base metal sulphide-bearing. One such Ni- and Cu-sulphide-bearing dunite from Cliff, which contains a Pt plus Pd value of 4,000ppb, has an average d^{34}S value of +4.2 that is indistinguishable from sulphur isotope values from dunites from the PGE-enriched crustal dunite. Therefore by comparison the origin of the base metal sulphide in the dunite at Cliff is also magmatic (Maynard et al. 1997).

The extremely PGE-rich lithology at Cliff consists of a disseminated chromite containing between 10 and 60 percent chromite surrounded by serpentinised olivine. Base metal sulphides are rare but this lithology often has a greenish colour probably caused by the presence of nickel carbonate. The only other PGE-rich concentration in the Cliff area is in a small chromitite closer to the basal thrust. The Cliff chromitite is unique in Unst in that it contains elevated As, Sb and Au. Therefore it has been suggested that the extremely high PGE values at Cliff were formed by local hydrothermal reconcentration of PGE within the chromite-bearing dunite lens that hosted magmatic concentrations of PGE at Cliff. This re-concentration to produce the very high PGE values may have occurred during the introduction of fluids from the basement along both the basal thrust and the internal faults (Prichard and Lord 1993; Lord et al. 1994).

Figure 7. Section through a PGE-rich layer in the crustal dunite showing the distribution of the PGE with Os, Ir and Ru in the basal chromite-rich layer and Pt and Pd in the first base metal sulphides to form in the overlying dunite (adapted from Prichard et al. 2004).

PGE mineralisation in dunite in Shetland

Barren dunite

Veins with native Cu

Pd-bearing PGM

Ni and Cu sulphides

Pt- and Pd-bearing PGM

A layer of chromite

Os, Ir and Ru-bearing PGM

Base of mineralisation

1 cm
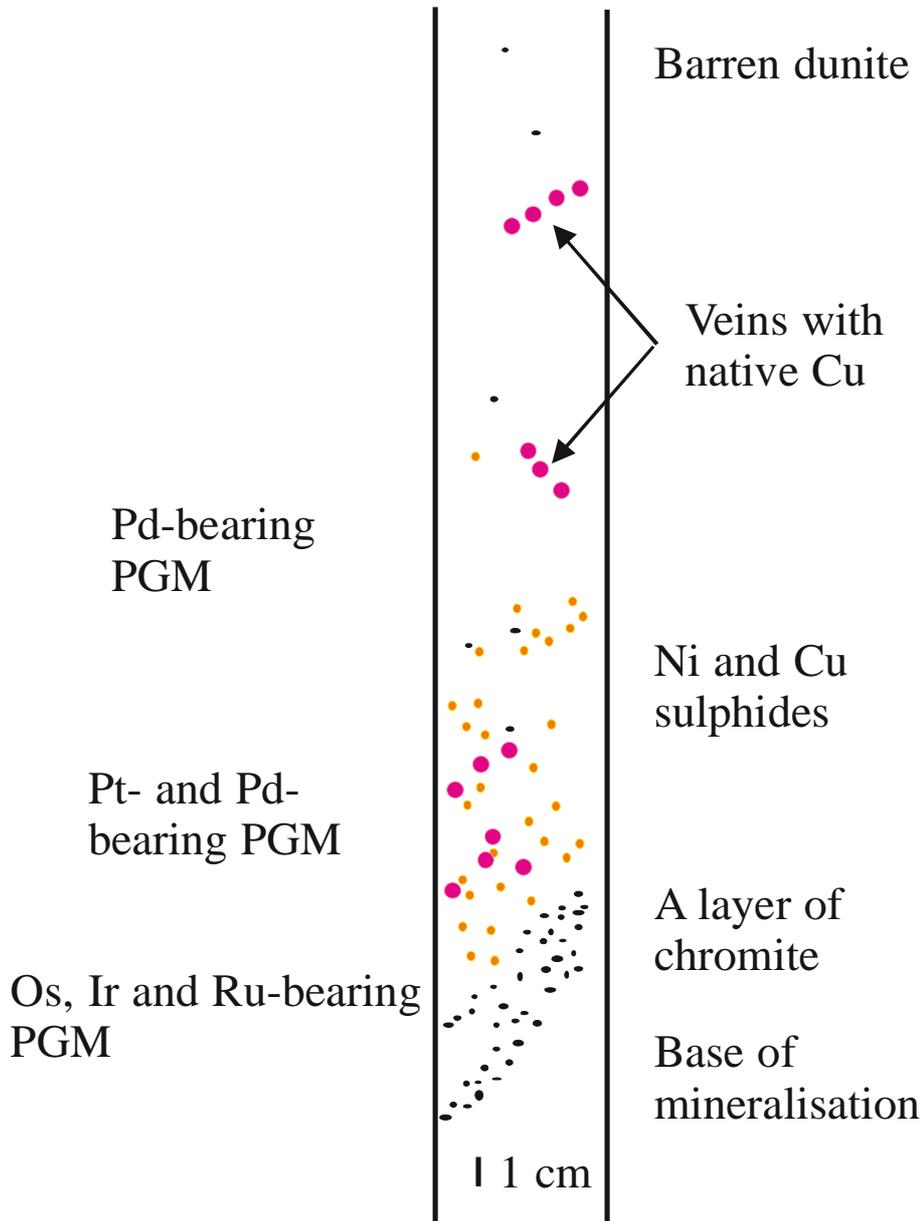
The Troodos Ophiolite in Cyprus

The Troodos ophiolite is an example of an ophiolite with Pt- and Pd- poor chromitite but minor Pt- and Pd-enrichment in the gabbro. The PGE concentrations in Cyprus are rather different from those in Shetland, thus demonstrating the variability of concentration and distribution between ophiolite complexes. This complex has been chosen as a second example to illustrate the distribution of PGE in ophiolites because in addition to magmatic PGE concentrations there are also minor hydrothermal PGE concentrations in this ophiolite. The Troodos ophiolite in Cyprus is the classic ophiolite complex where it was first realised the sheeted dyke complex represents fossilized dolerite dykes formed by ocean spreading (Gass 1968). Unlike Shetland this ophiolite in Cyprus has a complete sequence from mantle to lavas (Figure 8).

Figure 8. Map of the Troodos ophiolite in Cyprus showing Pt and Pd occurrences. Pt and Pt in the lavas are within umbers (adapted from Prichard et al. 2004).
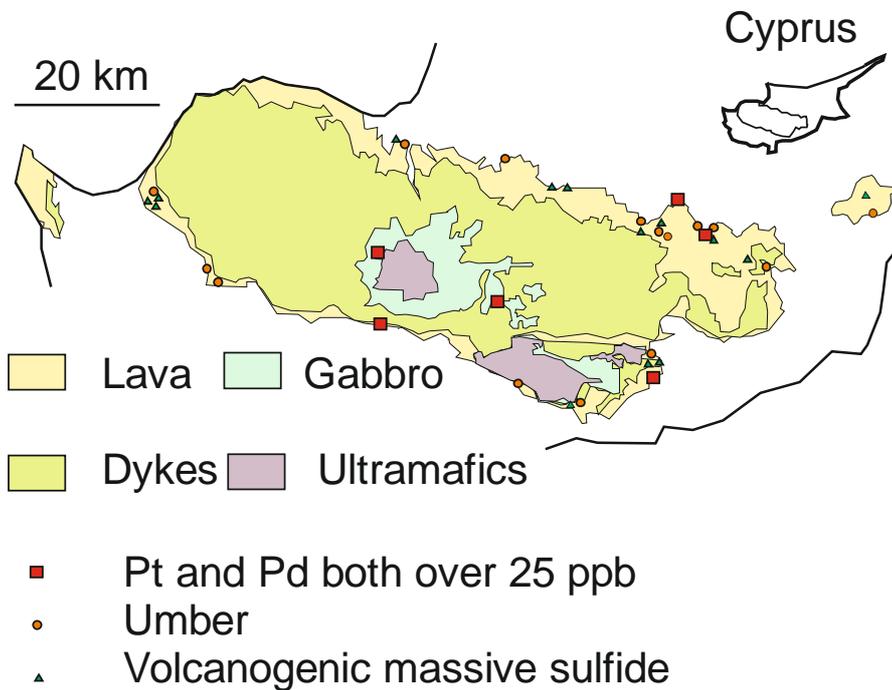
Os, Ir and Ru are concentrated in the podiform chromitites both within the mantle and in chromitites at the base of the overlying crustal sequence (Constantinides et al. 1980). In contrast to Shetland, sulphide saturation and the crystallisation of the first magmatic base metal sulphides was delayed until the crystallisation of the first gabbros. The ultramafic crustal sequence is virtually devoid of

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magmatic sulphides. Pt and Pd occur in low concentrations with these Ni- and Cu-sulphides in the gabbros (Prichard & Lord 1990). The presence of Pt and Pd at a higher level than in the Shetland ophiolite allowed the Pt- and Pd-bearing gabbros to be exposed to hydrothermal circulation associated with the formation of the volcanogenic massive sulphide deposits. A study of these deposits and their associated Mn-bearing umbers showed that the umbers are slightly Pt and Pd enriched. This re-concentration is particularly apparent at the base of umbers, along faults within the umbers or with precipitation of sulphides within the umbers (Ravizza et al. 2001 and Prichard 2004) (Figure 8).

The Lizard ophiolite complex

This example of a PGE- and chromitite-poor ophiolite is situated on the southern most peninsula in Cornwall in the UK and only the lower part of the ophiolite is preserved with the upper most level being the at the base of the sheeted dyke complex. Unlike the Shetland and Troodos ophiolite complexes the Lizard has a very thin unit of ultramafic cumulate with very little dunite and a predominance of pyroxenites and troctolites at the base of the crustal sequence just above the mantle peridotite. This mantle is composed mainly of lherzolite rather than the harzburgitic mantle present in Shetland and Troodos. The only PGE concentrations located to date occur associated with poikilitic clinopyroxene and rare base metal sulphides occurring in patches in the mantle. It was suggested by Hutchinson et al. (1999) that these represent partial melts trapped in the mantle as they ascended towards the overlying crustal sequence.

PGE-rich and -poor magmas in ophiolite complexes

These three examples illustrate the main different types of PGE concentration in ophiolite complexes and their PGE concentrations have been explained by differences in the degree of partial melting of the mantle. Prichard et al. (1996b) suggested that for ophiolites to contain some Pt- and Pd-enriched chromitite they would need to have formed in tectonic regimes where high degrees of mantle melting extracted the Pt and Pd from the mantle; for example in a supra-subduction zone. Release of PGE from the mantle into a melt will be dependent on the melting regime and the stages of destruction of the PGE carrier phases. These ideas have been discussed by Hamlyn and Keays (1986), Naldrett and Barnes (1986), Rehkämper et al. (1999) and modelled by Mungall (2005) and O'Hara et al. (2001a and b) who predicted a critical melting stage when PGE are released into mantle melts over a relatively narrow interval of partial melting (Figure 9). Thus too little melting

will not remove the PGE from the mantle, critical melting will extract the PGE as the last base metal sulphides are removed and too much melting will dilute the PGE as PGE-poor mantle is melted. These three stages of melting cause the three types of PGE concentrations in ophiolites.

Figure 9. Model showing the removal of PGE from the mantle (dashed line) and the resulting spike of PGE concentration as critical melting is reached.

Perfect fractional melting

Suprasubduction
PGE-rich chromitite
critical melt

Concentration spike

Dilution →

PGE-poor MORB

Initial melting

Liquid

Suprasubduction
PGE-poor chromitite

Solid residue

PGE concentration

0   0.25   0.5   0.75   1.0
% of partial melting →
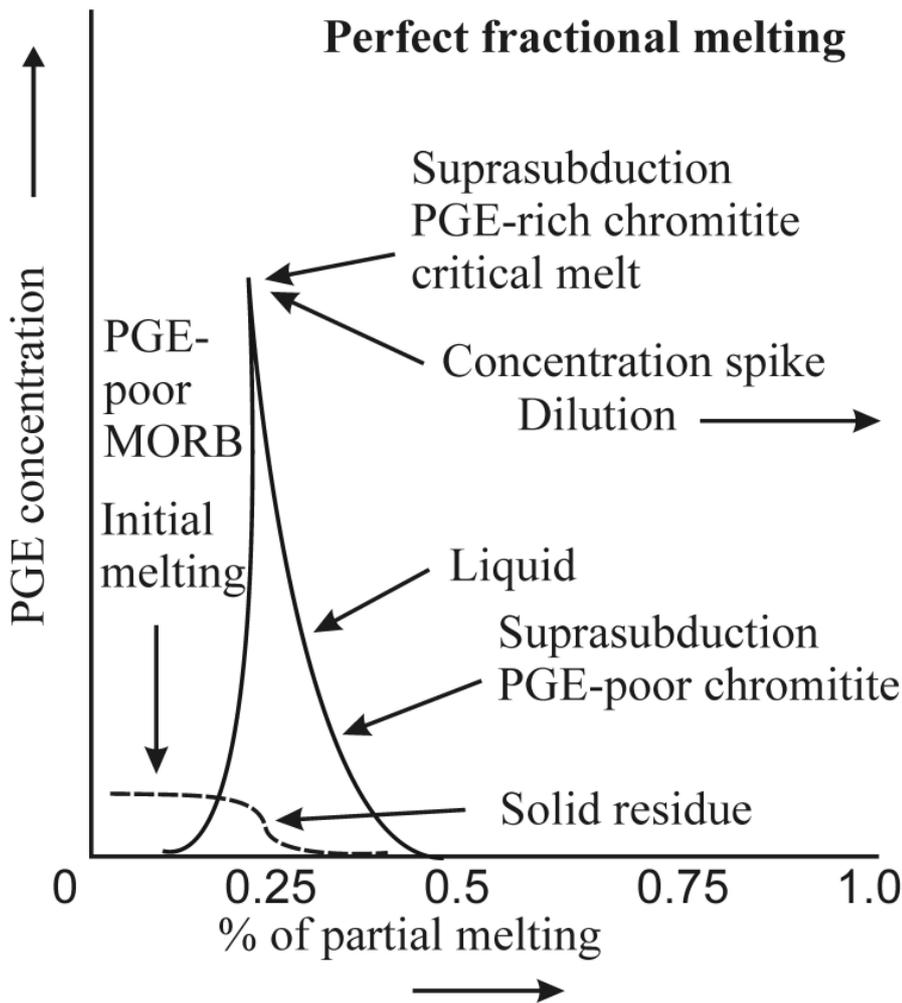
Melting in PGE-poor ophiolites

Within PGE-poor ophiolites there has been insufficient melting to extract the PGE, and therefore most of the PGE will be retained in sulfides within the mantle and will not be released into the melt. As such both the dunite lenses within the mantle and the crustal sequences contain insignificant Pt and Pd concentrations. Examples of MORB type ophiolites are the Lizard in Cornwall, UK and the

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Bay of Islands in Newfoundland (Kirby 1979; Malpas & Strong 1975; Edwards 1990). The inference is that Pt and Pd $\pm$ Rh remain in the mantle peridotite. MORB ophiolites often have ultramafic crustal sequences which are thin or absent, lack podiform chromitite and have undepleted lherzolitic mantle sequences (Pearce et al. 1984 and Roberts & Neary 1993).

Melting in PGE-rich ophiolites

Within PGE-rich ophiolites the degree of partial melting and the melting regime will be just right to extract PGE without overly diluting them. This critical mantle melting will produce some PGE-enriched chromitite with ppm concentrations. The podiform chromitites occur within dunite lenses which are themselves hosted within mantle harzburgite as well as in the overlying crustal sequence. These ophiolites often contain thick crustal dunites overlying mantle harzburgite. The Shetland ophiolite is an example of this type of ophiolite (Prichard and Lord, 1993) with magmatic values of Pt + Pd of up to 3000 ppb (Prichard et al., 1996a). Other examples include Leka with Pt + Pd values of up to 7300 ppb (Pedersen et al., 1993), Thetford with Pt + Pd values of up to 2590 ppb (Corrivaux and LaFlamme, 1990), Pindos (Augé, 1985; Tarkian et al., 1996) with Pt + Pd values of up to 5120 ppb (Economou-Eliopoulos, 1996) and New Caledonia (Augé et al., 1998) with average Pt values of 2000-10000 ppb and the highest Pd value of 2300 ppb (Augé and Legendre, 1994). Some ophiolites contain Pt and Pd concentrations in base-metal sulfide-bearing dunite in the vicinity of the chromitite as in Shetland with Pt + Pd values in the base-metal-bearing dunite of 6400 ppb and in this case the adjacent chromitite is also Pt- and Pd-enriched (Prichard and Lord, 1993). In the Zambales ophiolite (Orberger et al., 1988; Bacuta et al., 1990) the dunite has recorded values of Pt + Pd of up to 14300 ppb (Bacuta et al., 1988) and here the chromitite is apparently barren of Pt and Pd. In the eastern ophiolite complexes in Albania Pt and Pd concentrations occur in base-metal sulfide-bearing dunite stratigraphically above the Bulquiza chromitite with Pt + Pd values of up to 8700 ppb (Ohnenstetter et al., 1991; 1999).

Melting in ophiolites with Pt- and Pd- poor chromitites

Finally, within some ophiolite complexes, the degree of partial melting will be so high that extraction of PGE is followed by dilution due to addition of subsequent PGE-poor melt. These ophiolites have minor concentrations of Pt and Pd in their overlying ultramafic and mafic crustal sequences. These ophiolites contain a thick layer of ultramafic cumulates that overlie infertile mantle harzburgite. Their chromitite is usually barren of Pt and Pd. Examples of this group of

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ophiolite complex are the Troodos and the Semail ophiolite complexes (Prichard and Lord, 1990;

Lachize et al., 1991). These 3 types of PGE enrichment in ophiolites are summarized in Figure 10.

Figure 10. Schematic diagram showing the different tectonic settings for the three types of ophiolite based on PGE content. (i) PGE-poor, PGE remain dispersed in the mantle with too little melting to extract the PGE e.g. Lizard ophiolite complex (ii) PGE-rich, all 6 PGE are associated with chromitite, critical melting achieved e.g. Shetland ophiolite complex (iii) and Pt and Pd occur with base metal sulphide in the gabbro with too much melting that dilutes the PGE e.g. Cyprus and Oman (adapted from Prichard et al. 2008a)
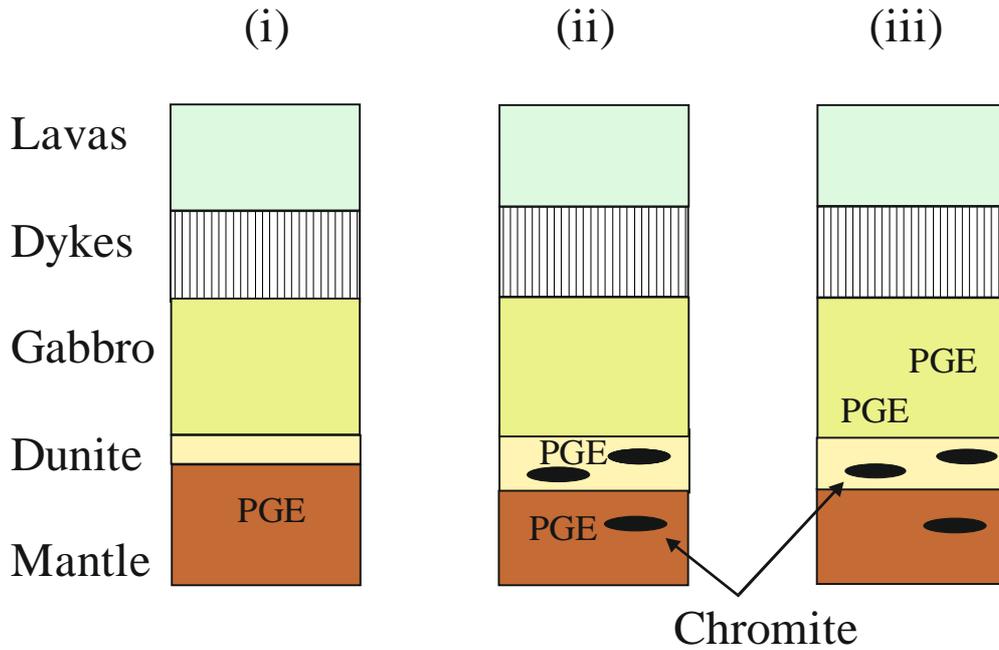
Tectonic setting and PGE in ophiolites

Many ophiolite complexes are formed in basins behind island arcs and above subduction zones. The dependence of degree of mantle melting experienced within an ophiolite and the tectonic setting means that the likely PGE content of the melt and the ophiolite can be linked to particular tectonic settings (Figure 11). In subduction zone settings the initial melts will be produced by high degrees of partial melting due to the high water content of the downgoing slab. These melts will be PGE-diluted as the melting will likely be beyond the critical melting window. However as subduction continues and less water becomes available, lower degrees of partial melting will occur until eventually PGE-poor MORB type melts will be produced (Prichard et al., 1996a). At an intermediate point between these two extremes, critical melting will produce PGE-rich melts (Prichard et al 2008a). A particular sequence of melting common to many ophiolites occurs when a

first PGE-poor partial melt is removed at a midocean ridge setting, followed by a hiatus in melting until a switch to a suprasubduction type setting. With the influx of water from the downgoing slab, a second stage, higher degree partial melt is possible. Perfect fractional melting will produce a melt in isolation from other melts and has the potential to produce a more enriched PGE melt than those melts that mix with other melts as in equilibrium partial melting. As such a second stage closely approximates perfect fractional melting (Prichard et al. 2008a) and has the potential to produce a particularly PGE-enriched pulse of magma undiluted by the lower partial melts separated from it in the first melting event (Hamlyn & Keays, 1986). These second melts are often boninitic and may erupt as either PGE-enriched boninites or precipitate its PGE in cumulate sequences. The silica-rich nature of boninitic magmas makes sulphur saturation more likely (Naldrett & Macdonald 1980) and the resulting base metal sulphides will be PGE enriched. Arc root zones may also be formed by magmas derived from high degrees of partial melting and therefore these will be PGE enriched as for example in Bragança in Portugal (Bridges et al. 1993) and Cabo Ortegal in Spain (Moreno et al. 2001).

Figure 11. Stratigraphic sections for PGE-poor and-rich ophiolite sections (adapted from Prichard et al. 2008a).

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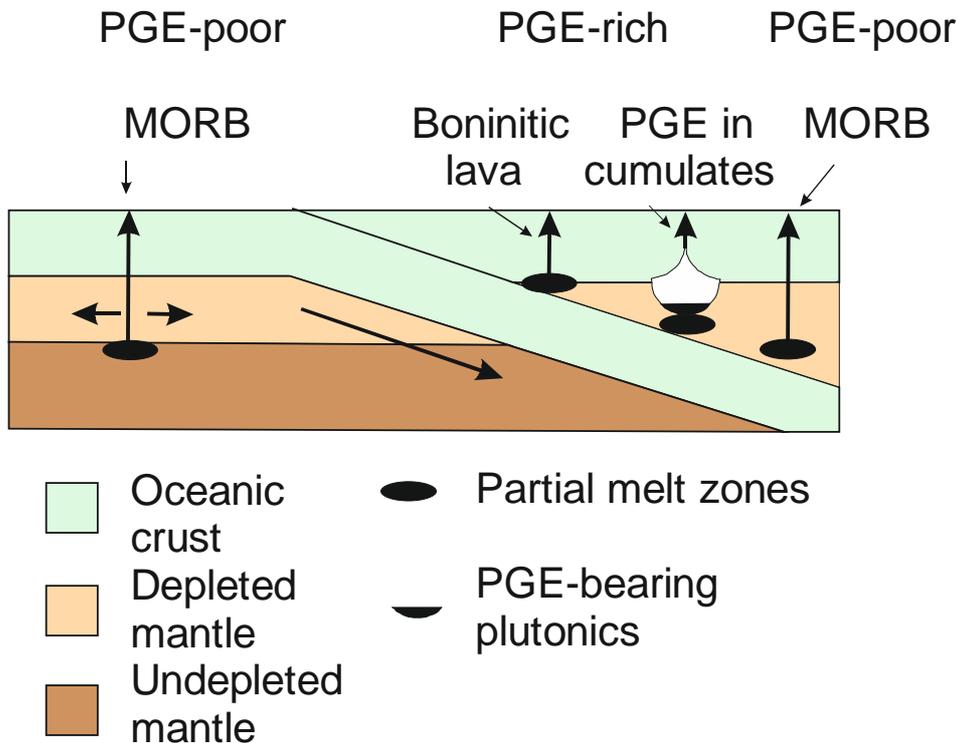
Fractionation of the PGE and sulphur saturation

The separation of Os, Ir and Ru from Pt, Pd and Rh during igneous crystallisation is commonly observed in ophiolites. Os, Ir and Ru tend to be concentrated within chromite grains and Pt and Pd $\pm$ Rh with disseminated base metal sulphides. Ru tends to be more enriched relative to Pt in chromitites located in mantle pods and less enriched than Pt in overlying chromitites among the crustal dunites as in New Caledonia (Augé 1998) and Cabo Ortegal (Moreno et al. 2001), which also suggests separation of the PGE during crystallisation. The strong association of Pt and Pd with sulphides means that the timing of sulphur saturation is crucial to crystallization of Pt- and Pd- type PGM. It is known that removal of FeO (e.g. by chromite crystallization) increases the likelihood of sulphur saturation (e.g. Mungall, 2005). Also silica may be added to the melt, through dissolution of pyroxene and reprecipitation of olivine as chromitite forms in a dunite lens in the mantle. This will lower the sulphur solubility (Zhou et al., 1998), increasing the likelihood of sulphur saturation during the formation of podiform chromitite. If sulphide-saturation occurred in a magma at the same time as chromite crystallisation then all six PGE occur together although, even in this case, it may be demonstrated mineralogically (Prichard & Tarkian 1988; Lee 1996) that Os-, Ir- and Ru-bearing minerals are enclosed in chromite and crystallised earlier than the Pt-, Pd- and Rh-bearing minerals which occur among the interstitial silicates and presumably crystallised later. If sulphide-saturation was not coincident with chromite crystallisation then Os, Ir and Ru may be present in chromitite and Pt, Pd and Rh absent, thereby causing a separation of the PGE during crystallisation. If sulphide-saturation occurs in the absence of, or long after, chromite crystallisation then Pt and Pd may be the major PGE associated with the base metal sulphides as in the gabbros in Cyprus.

Conventionally, magma mixing of sulphur undersaturated PGE-bearing magma and sulphur saturated PGE-poor magma is preferred for continental layered complexes (e.g. Irvine 1977, Hamlyn & Keays, 1986). This could be considered as a mechanism for the formation of PGE concentrations in ophiolites. If a sulphur saturated MORB type melt mixed with a silica-rich boninitic melt that is PGE-rich then PGE should crystallize with base metal sulphides as in continental stratiform deposits. However crystallisation of PGE may be possible without magma mixing. At the critical partial melting stage, the PGE will be concentrated into the last base metal sulphides and then melted to produce a PGE-enriched melt which is close to sulphur saturation. On crystallisation of this melt the PGE will precipitate with base metal sulphides especially when podiform chromitite begins to crystallize (Prichard et al. 2008a and b). Any subsequent melting

causes the resultant magma to become sulphur undersaturated. Thus with greater sulphur undersaturation, it is less likely that chromitite and Pt- or Pd-PGM will be associated.

The link between chromite composition and PGE concentrations

There is growing evidence that there is a link between chromite composition and the potential for PGE enrichment in podiform chromitite (Prichard et al. 2008a and b). It has been suggested (Prichard et al. 2008a) that two main processes are operating during PGE crystallization within the Al'Ays ophiolite. Firstly IPGE are crystallizing across the whole range of chromite composition with some associated Pt- and Pd- crystallization occurring interstitial to the chromite grains. Secondly, sulphur saturation occurs at an approximate Cr_2O_3% of 48% and Cr_2O_3/ Al_2O_3 ratio of 1 to 3 producing PGE-rich chromitites over a narrow range of Cr_2O_3 composition. It is predicted that ophiolites containing PPGE-rich chromitite will have that enrichment located within a narrow chromite range, associated with the timing of sulphur saturation, although the exact range of Cr2O3 and Cr# will vary form ophiolite to ophiolite (Prichard et al. 2008a).

PGE and ophiolites of different ages

Ophiolites vary in age from very recent young to PreCambrian ones which are dismembered but still retain characteristics identifying them as of oceanic origin. For example they may have oceanic lava or podiform chromitite that have textures and geochemistry characteristic of ophiolite complexes. The original magmatic PGE content and so the PGE concentrations within these ophiolites varies not with age but with the tectonic setting in which the ancient ocean crust formed and hence the degree of partial melting that produced the magma. This was further confirmed by Walker et al. (2002) who examined the variation in Os isotopes in podiform chromitites through geological history and showed a constant evolution of mantle Os with time, re-enforcing the stability of the processes forming ophiolite complexes.

Conclusions Exploration for PGE in ophiolite complexes

Magmatic concentrations of PGE in ophiolite complexes are controlled by the degree of partial melting of the mantle from which the magma was extracted and the crystallisation processes of that magma. High degrees of partial melting associated with wet mantle melting in subduction zones will produce PGE-enriched boninitic magmas. Too much melting will dilute the Pt and Pd and they

will crystallise with the first base metal sulphides in the crustal gabbros whereas Os, Ir and Ru are concentrated in the chromitite. Critical melting will produce PGE-rich almost sulphur saturated magma that will crystallise with podiform chromitite of low Cr# to produce chromitites enriched in all six PGE. Too little melting will not extract the PGE from the mantle. Thus in order to locate the PGE of more economic interest, that is Pt and Pd $\pm$ Rh, in ophiolite complexes it is necessary to determine whether there has been sufficient melting to extract the PGE from the mantle and if so locate the first base metal sulphides within the crustal sequence, whether in podiform chromitite or higher in the gabbroic sequence. If the first base metal sulphides crystallised with the podiform chromitites then it is likely that the PGE concentrations will be located with chromitite of a specific composition. This will vary between ophiolites depending on the particular melting regimes caused by local tectonic settings. Therefore it is possible to predict the location of PGE concentrations within ophiolite complexes and if prolonged mantle melting at the critical partial melting interval occurred then it is likely that a significant concentration of high grade PGE could have crystallised and would be worthy of discovery.

References

Acharyya, S. K. (2007) Collisional emplacement history of the Naga-Andaman ophiolites and the position of the eastern Indian suture. *J. Asian Earth Sci.* 29(2-3), 229-242.

Ahmed, A. and Bilgrami, S. (1987) Chromite Deposits and Ophiolites of Pakistan. *In* C. W. Stowe (ed.) *Evolution of Chromium Ore Fields*. New York: Van Nostrand Reinhold Company Inc.

Ahmed, A. H., Arai, S., Abdel-Aziz, Y. M. and Rahimi, A. (2005) Spinel composition as a petrogenetic indicator of the mantle section in the Neoproterozoic Bou Azzer ophiolite, Anti-Atlas, Morocco. *Precamb. Res.* 138(3-4), 225-234.

Arai, S., Prichard, H. M., Matsumoto, I. and Fisher, P. C. (1999) Potarite (PdHg) in thermally metamorphosed dunite from the Inazumi-yama ultramafic complex, Japan: an implication for the behaviour of mercury in PGE mineralisation in peridotite. *Min. Mag.* **63**, 369-377.

Arai, S., Prichard, H. M., Matsumoto, I. and Fisher, P. C. (1999) Platinum-Group Minerals in podiform chromitite from the Kamuikotan zone, Hokkaido, Northern Japan. *Res. Geol.* **49**, 39-47.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Arenas, R., Catalan, M., Martinez, S., Garcia, D., Abati, J. and Fernandez-Suarez, J. (2004) Ofiolitas paleozoicas de la sutura varisca de galicia (nw del macizo iberico, espana): distribucion, caracteristicas y significado. *In* (ed. Pereira, R. Castroviejo and F. Ortiz). *Complejos Ofioliticos en Iberoamerica*. Madrid.

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

Augé, T. (1986) Platinum-group mineral inclusions in ophiolitic chromitites from the Oman ophiolite. *Bull. Mineral*. **109**, 301-304.

Augé, T. (1988) PGM in the Tiebaghi and Vourinos ophiolitic complexes: genetic implications. *Can Min*. **26**, 177-192.

Augé, T. and Legendre, O. (1994) PGE oxides from the Pirogues ophiolitic mineralization. New Caledonia: origin and significance. *Econ. Geol.* **89**, 1454-1468.

Augé, T., Legendre, O, and Maurizot, P. (1998) The distribution of Pt ande Ru-Os-Ir minerals in the New Caledonia ophiolite. *In* Laverov, N. P. and Distler, V. V. (eds.) *International Platinum*. Theophrastus publications, Athens, 141-154.

Bacuta, G. C. Jr., Lipin, B. R., Gibbs, A. K. and Kay, R. W. (1988) Platinum-group element abundance in chromite deposits of the Acoje ophiolite block, Zambales ophiolite complex, Phillipines. *In* Prichard, H. M., Potts, P. J., Bowles, J. F. W. and Cribb, S. J. (eds.) *Geoplatinum-87*, Elsevier, London, 381-382.

Bacuta, G. C., Kay, R. W, Gibbs, A. K. and Lipin, B. R, (1990) Platinum-group element abundance and distribution in chromite deposits of the Acoje block, Zambales ophiolite complex, Philippines. *Jl Geophys. Res.* **37**, 113-145.

Bédard, É., Hébert, R., Guilmette, C. and Dostal, J. (2008) The supra-ophiolitic sedimentary cover of the Asbestos ophiolite, Québec, Canada: First geochemical evidence of transition from oceanic to continental sediment flux. *Lithos* **105**(3-4), 239-252.

Bortolotti, V. and Principi, G. (2005) Tethyan ophiolites and Pangea break-up. *Isl. Arc* **14**(4), 442-470.

Bridges, J. C., Prichard, H. M., Neary, C. R. and Meireles, C. A. (1993) Platinum-group element mineralization in the chromite-rich rocks of the Braganca massif, northern Portugal. *Trans. Inst. Min. Metal.* **B 102**, 103-113.

Cabri, L. J. (2002) The geology, geochemistry, mineralogy and mineral beneficiation of platinum-group elements. *Can. Inst. Min. Metal. Sp. Vol.* **54**, 852pp.

Casey, J. F., Elthon, D. L., Siroky, F. X., Karson, J. A. and Sullivan, J. (1985) Geochemical and geological evidence bearing on the origin of the Bay of Islands and Coastal Complex ophiolites of western Newfoundland. *Tectonophysics* **116**(1-2), 1-40.

Cassard, D., Nicolas, A., Rabinovitch, M., Moutte, J., Leblanc, M. and Prinzhofer, A. (1981) Structural classification of chromite pods in southern New Caledonia. *Econ. Geol.* **76**, 805-831.

Cawood, P. A. and Korsch, R. J. (2008) Assembling Australia: Proterozoic building of a continent. *Precamb. Res.* **166**(1-4), 1-35.

Coombs, D. S., Landis, C. A., Norris, R. J., Sinton, J. M., Borns, D. J. and Craw, D. (1976) The Dun Mountain ophiolite belt, New Zealand, its tectonic setting, constitution, and origin, with special reference to the southern portion. *Amer. J. Sci.* **276**, 561-603.

Constantinides, C.C., Kingston, G. A. and Fisher, P. C. (1980) The occurrence of platinum-group minerals in the chromitites of the kokkinorostos chrome mine, Cyprus. *In* Panayiotou, A (ed.) *Ophiolites: Proc. Int. Ophiolite Symp.Cyprus*. Geol. Surv. Dep. Nicosia, 93-101.

Corrivaux, L and Laflamme, J. H. G. (1990) Mineralogie des elements du grouped u platine dans les chromitites de l'ophiolite de Thetford mines, Quebec. *Can. Min.* **28**, 579-595.

Economou-Eliopoulos, M. (1996) Platinum-group element distribution in chromite ores from ophiolite complexes: Implications for their exploration. *Ore Geol. Rev.* **11**(6), 363-381.

Edwards, S. J., (1990) Harzburgites and refractory melts in the Lewis Hills massif, Bay of Islands ophiolite complex: the base metals and precious metals story. *Can. Min.* **28**, 537-552.

Eliopoulos, D., Skounakis, S. and Economou-Eliopoulos, M (1998) Geochemical characteristics of sulfide mineralisations from the Pindos ophiolite complex: Preliminary data. *Bull. Geol. Soc. Greece*. **32**, No. 3, 179-185.

Escayola, M., Proenza, J. A., Schalamuk, A. and Cabana, C. (2004) La secuencia ofiolitica de la faja ultramafica de sierras pampeanas de cordoba, argentina. *In* E. Pereira, R. Castroviejo and F. Ortiz (eds.) *Complejos Ofioliticos en Iberoamerica* Madrid, 133-156.

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

Garuti, G. and Zaccarini, F. (1997) In situ alteration of platinum-group minerals at low temperature evidence from serpentinized and weathered chromitites of the Vourinos complex (Greece). *Can. Min.* **35**, 611-626.

Garuti, G., Zaccarini, F., Cabella, R. and Fershtater, G.B. (1997) Occurrence of unknown Ru–Os–Ir–Fe oxides in the chromitites of the Nurali ultramafic complex, southern Urals, Russia. *Can. Min.* **35**, 1431–1439.

Gass, I. G. (1968) Is the Troodos massif of Cyprus a fragment of Mesozoic oceanic floor? *Nature* **220**, 39-42.

Geomapapp (2009) *Marine Geoscience Data System.*

Ghazi, A. M. and Hassanipak, A. A. (2000) Petrology and Geochemistry of the Shahr-Babak Ophiolite, central Iran. *In* Y. Dilek, E. M. Moores, D. Ethon and A. Nicolas (eds.) *Ophiolites and Oceanic Crust: New Insights from field studies and the Ocean Drilling Program*, Colorado: Geol Soc. Am. Sp. Paper 485-497.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Graham, I. T., Franklin B. J. and Marshall, B. (1996) Chemistry and mineralogy of podiform chromitite deposits, southern NSW, Australia: A guide to their origin and evolution. *Min. Pet.* **57,** pp129-150.

Guilmette, C., Hébert, R., Dupuis, C., Wang, C. and Li, Z. (2008) Metamorphic history and geodynamic significance of high-grade metabasites from the ophiolitic mélange beneath the Yarlung Zangbo ophiolites, Xigaze area, Tibet. *J. Asian Earth Sci.* **32**(5-6), 423-437.

Gunn A. G., Leake R. C., Styles M. T. and Bateman J.H.(1985) Platinum-group element mineralisation in the Unst ophiolite, Shetland. British Geological Survey, *Mineral Reconnaissance Programme Report*, no. 73.

Hall, R. (2002) Cenozoic geological and plate tectonic evolution of SE Asia and the SW Pacific: Computer-based reconstructions, model and animations. *J. Asian Earth Sci.* **20**(4), 353-431.

Hamlyn, P. R. and Keays, R. R., (1986) Sulfur saturation and second stage melts; application to the Bushveld Pt metal deposits. *Econ. Geol.* **81**, 1431-1445.

Hutchionson, D., Prichard, H. M. and Macleod, C. J. (1999) Evidence for partial melting and melt impregnation of mantle peridotites leading to PGM deposition: a comparison of samples from the Lizard and Troodos ophiolites and the Tonga Trench. *In* Stanley C. J. et al. (eds.) *Extended abstract in Mineral Deposits: Processes to processing.* Balkema, Rotterdam, SGA London. 729-732.

Irvine, T.N. (1977) Origin of chromitite layers in the Muskox intrusion and other stratiform intrusions: a new interpretation. *Geol.* **5**, 273-276.

Ishiwatari, A. and Tsujimori, T. (2003) Paleozoic ophiolites and blueschists in Japan and Russian Primorye in the tectonic framework of East Asia: A synthesis. *Isl. Arc* **12**(2), 190-206.

Keller, R. and Fisk, M. (1992) Quaternary marginal basin volcanism in the Bransfield Strait as a modern analogue of the southern Chilean ophiolites. *In* L. M. Parson, B. J. Murton and P. Browning (eds.) *Ophiolites and their Modern Oceanic Analogues*. Geol Soc. Sp. Pub. 155-169.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Kirby, G. A., (1979) The Lizard complex as an ophiolite. *Nature.* **282**, 58-61.

Lachize, M., Lorand, J. P. and Juteau, T. (1991) Cu-Ni-PGE magmatic sulfide ores and their host layered gabbros in the Haymiliyah fossil magma chamber (Haylayn block, Semail ophiolite nappe, Oman), *In* Peters, T. J., Nicolas, A. & Coleman,R. G. (eds.) *Ophiolite Genesis and Evolution of the oceanic lithosphere.* Proceedings of the ophiolite conference held in Muscat, Oman. Kluwer academic publishers, 209-229.

Lee, C. A., (1996) A review of mineralisation in the Bushveld complex and some other layered intrusions. *In* Cawthorn, R. G. (ed.) *Layered intrusions*. Elsevier, 103-147.

Lord, R. A. and Prichard, H. M. (1998) Exploration and origin of stratigraphically controlled platinum-group element mineralisation in crustal sequence ultramafics, Shetland ophiolite complex. *Trans. Inst. Min. Metal.* **B 106**, 179-193.

Lord, R. A. Prichard, H. M. and Neary, C.R. (1994) Magmatic PGE concentrations and hydrothermal upgrading in the Shetland ophiolite complex. *Trans. Inst. Min. Metal.* **B 103**, 87-162.

Malpas, J. and Strong, D. F., (1975) A comparison of chrome-spinels in ophiolites and mantle diapirs of Newfoundland. *GCA* **39**, 1045-1060.

Matsumoto, I. & Arai, S. (1999) Morphological and chemical variations of chromian spinel in dunite-harzburgite complexes from the Sangun Zone (SW Japan): Implications for mantle/melt reaction and chromite formation processes. *Mineral. And Petrol.* **73** (4) 305-323

Maynard, J., Prichard, H. M., Ixer, R. A., Lord, R. A., Wright, I. P., Pillinger, C. T., McConville, P., Boyce, A. J. and Fallick, A. E. A (1997) A sulphur isotope study of Ni-Fe-Cu mineralisation in the Shetland ophiolite complex. *Trans. Inst. Min. Metal.* **B 106**, 205-234.

Melcher, F., Grum, W., Simon, G., Thalhammer, T. V. and Stumpfl, E. F. (1997) Petrogenesis of the Ophiolitic Giant Chromite Dposits of Kempirsai, Kazakhstan: a Study of Solid and Fluid Inclusions in Chromite. *J Petrol.* **38**(10), 1419-1458.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Monnier, C., Girardeau, J., Maury, R. C. and Cotten, J. (1995) Back-arc basin origin for the East Sulawesi ophiolite (eastern Indonesia). *Geol.* **23**(9), 851-854.

Moreno, T., Prichard, H.M., Lunar, R., Monterrubio, S. and Fisher, P.C. (1999) Formation of a secondary PGM assemblage in chromitites from the Herbeira ultramafic massif, Cabo Ortegal, NW, Spain. *Eur. J. Mineral.* **11**, 363-378.

Moreno, T., Gibbons, W., Prichard, H. M. and Lunar, R. (2001) Platiniferous chromitite and the tectonic setting of ultramafic rocks in Cabo Ortegal, NW Spain. *J. Geol. Soc. Lon.* **158**, 601-614.

Mungall. J. E. (2005) Magmatic geochemistry of the platinum-group elements. *In* Mungall. J. E. (ed) *Exploration for platinum-group element deposits, Mineralogical Association of Canada, Short Course Series,* **35,** 1-34.

Najafzadeh, A. R., Arvin, M., Pan, Y. and Ahmadipour, H. (2008) Podiform Chromitites in the Sorkhband Ultramafic Complex, Southern Iran: Evidence for Ophiolitic Chromitite. *Jl Sci, Islamic Republic of Iran* **19**(1), 49-65.

Naldrett, A.J. and Barnes, S-J., (1986) The behaviour of platinum-group elements during fractional crystallization and partial melting with special reference to the composition of magmatic sulfide ores. *Fortschritte der Mineralogie* **64**, 113-133.

Naldrett, A. J. and Duke, J. M. (1980) Pt metals in magmatic sulphide ores: the occurrence of these metals is discussed in relations to the formation and importance of these ores. *Science*, **208**, 1417 – 1424.

Naldrett, A. J. and Macdonald, A., J., (1980) Tectonic settings of some Ni-Cu sulfide ores: their importance in genesis and exploration. *In* Strangway, D. W. (ed) *The continental crust and its mineral deposits.* Geol Ass. Can. Sp. Pap. **20**, 633-657.

Naldrett, A. J., Fedprenko, V. A., Asif, M., Shushen, L., Kunilov, V. E., Stekhin, A. I., Lightfoot, P. C. and Gorbachev, N. S. (1996) Controls on the composition of Ni-Cu sulfide deposits as illustrated by those at Noril'sk, Siberia. *Econ. Geol.* **91**, 751-773.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Neary, C.R., Prichard, H.M. and Potts, P.J. (1984) Chromite, platinoids, gold and moly in the Shetlands. *Min. Mag.,* 559-60.

O'Hara, M.J., Fry, N. and Prichard, H. M. (2001a) Minor phases as carriers of trace elements in non-modal crystal-liquid separation processes I: basic relationships. *J. Petrol.* **42**, 1869-1885.

O'Hara, M.J., Fry, N. and Prichard, H. M. (2001b) Minor phases as carriers of trace elements in non-modal crystal-liquid separation processes II: illustrations and bearing on behavior of REE, U, Th and PGE in igneous processes. *J. Petrol.* **42**, 1887-1910.

Ohnenstetter, M., Karaj, N., Neziraj, A., Johan, Z. and Cina, A. (1991) Le potentiel platinifere des ophiolites: mineralisations en elements du groupe du platine (PGE) dans les massifs de Tropoja et Bulquiza, Albanie. C. R. *Acad. Sci.* Paris **13**, SerieII, 201-208.

Ohnenstetter, M., Johan, Z., Cocherie, A., Fouillac, A. M., Guerrot, C., Ohnenstetter, D., Chaussidon, M., Rouer, O., Makovicky, E., Makovicky, M., Rose-Hanson, J., Karup-Møller, S., Vaughan, D., Turner, G., Pattrick, R. A. D., Gize, A. P., Lyon, I. and McDonald, I. (1999) New exploration methods for Pt and Rh deposits poor in base-metal sulfides-NEXTPRIM. *Trans. Inst. Min. Metal.* **B 108**, 119-150.

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

Ortiz, F., Gaviria, A., Parra, L., Arango, C., Ramirez, G., Pereira, E. and Prichard, H. (2004) Guias geologicas para localizacion de metales preciosos en las ofiolitas del occidente de colombia. *In* E. Pereira, R. Castroviejo and F. Ortiz (eds.) *Complejos Ofioliticos en Iberoamerica* Madrid, 169-199.

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

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Paixão, M. A. P., Nilson, A. A. and Dantas, E. L. (2008) The Neoproterozoic Quatipuru ophiolite and the Araguaia fold belt, central-northern Brazil, compared with correlatives in NW Africa. *In*: Pankhurst, R. J., Trouw, R. A. J., Brito Neves, B.B. & de Wit, M. J. (eds.) *West Gondwana: Pre-Cenozoic Correlations Across the South Atlantic Region*. Geol. Soc. Lon. Sp. Pub. **294**, 297–318.

Paladines, A. (2004) Mineralizaciones asociadas a ofiolitas en el ecuador. *In* E. Pereira, R. Castroviejo and F. Ortiz (eds.) *Complejos Ofioliticos en Iberoamerica*. Madrid, 157-168.

Pearce, J. A., Lippard, S. J. and Roberts, S. (1984) Characteristics and tectonic significance of supra-subduction zone ophiolites. *In* Kokelaar, B. P. & Howells, M. F. (eds.) *Marginal Basin Geology.* Geol Soc. Lon Sp. Pub. **16**, 77-94.

Pedersen, R. B., Johnnesen, G. M. and Boyd, R. (1993) Stratiform PGE mineralisations in the ultramafic cumulates of the Leka ophiolite complex, central Norway. *Econ. Geol.* **88**, 782-803.

Pessagno, E. A., Hull, D. M. and Hopson, C. A. (2000) Tectonostratigraphic significance of sedimentary strata occurring within and above the Coast Range ophiolite (California Coast Ranges) and the Josephine ophiolite (Klamath Mountains), northwestern California. *In* Y. Dilek, E. M. Moores, D. Elthon and A. Nicolas (eds.) *Ophiolites and Oceanic Crust: New Insights from field studies and the Ocean Drilling Program*. Colorado: Geol Soc. Am. Sp. Paper, 383-394.

Peters, T. (2000) Formation and evolution of the western Indian Ocean as evidenced by the Masirah ophiolite: A review. *In* Y. Dilek, E. M. Moores, D. Elthon and A. Nicolas (eds.) *Ophiolites and Oceanic Crust: New Insights from field studies and the Ocean Drilling Program*. Colorado: Geol Soc. Am. Sp. Paper, 525-536.

Prichard, H. M. (2004) Elementos del groupo del platino (EGP) en complejos ofiolíticos. Complejos ofiolíticos en Iberoamérica; guías de prospectión para metales preciosos. Pereira, E, Castroviejo, R and Ortiz, F. (eds.) *Proyecto Xlll.1.-CYTED* 71-96. ISBN 84-96023-24-9.

Prichard, H.M. and Tarkian, M. (1988) Pt and Pd minerals from two PGE- rich localities in the Shetland ophiolite complexes. *Can. Min.* **26**, No. 4, 979-990.

Prichard, H. M. and Lord, R. A. (1990) Platinum and palladium in the Troodos ophiolite complex, Cyprus. *Can. Min.* **28**, No. 3, 607-617.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Prichard, H. M. and Lord, R. A. (1993) An overview of the PGE concentrations in the Shetland ophiolite complex. *In* Prichard, H. M., Alabaster, T, Harris, N. B. W. and Neary, C. R. (eds.) *Magmatic processes and plate tectonics*, Geol. Soc. Lon Sp. Pub. **76**, 273-294.

Prichard, H. M. and Lord, R. A. (1994) Evidence for the mobility of PGE in the secondary environment in the Shetland ophiolite complex. *Trans. Inst. Min. Metal.* **B 103**, 79-86.

Prichard H. M., Potts, P. J. and Neary, C. R. (1981) Platinum group minerals in the Shetland ophiolite complex. *Trans. Inst. Min. Metal.* **B 90**, 186-188.

Prichard H. M., Neary, C. R. and Potts, P. J. (1984) Platinum and gold in the Shetland ophiolite. *Min. Jl.* **303**, No. 7772, 77.

Prichard, H. M., Neary, C. R. and Potts, P. J. (1986) Platinum-group minerals in the Shetland ophiolite complex. *In* Gallagher M.J., Ixer R.A., Neary C.R. & Prichard H.M. (eds.) *Metallogenesis of basic and ultrabasic rocks.* I. M. M. Symp. Vol., Edinburgh, 395-414.

Prichard, H. M., Ixer, R. A., Lord, R. A., Maynard, J and Williams, N.(1994) Assemblages of platinum-group minerals and sulphides in silicate lithologies and chromite-rich rocks within the Shetland ophiolite. *Can. Min.* **32**, No. 2, 271-294.

Prichard, H. M., Lord, R. A. and Neary, C. R. (1996a) A model to explain the occurrence of Pt-and Pd-rich ophiolite complexes. *J. Geol. Soc. Lon.* **153**, 323-328.

Prichard, H. M., Puchalt, H., Eckhardt, J-D. and Fisher, P. C. (1996b) Platinum-group element concentrations in mafic and ultramafic lithologies drilled from the Hess Deep. *In* Mevel, C., Gillis, K. M. and Meyer, P. S (eds.) *Proceedings of the Ocean Drilling Program, Scientific Results.* **147**, 77-90.

Prichard, H. M., Neary, C.R., Fisher, P. C. and O'Hara, M. J. (2008a) PGE-rich podiform chromitites in the Al 'Ays ophiolite complex, Saudi Arabia: an example of critical mantle melting to extract and concentrate PGE. *Econ. Geol.*, **103**, 1507-1529.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Prichard, H. M. Economou-Eliopoulos, M. and Fisher, P. C (2008b) Platinum-group minerals in podiform chromitite in the Pindos ophiolite complex, Greece. *Can Min.* **46,** 2, 329-341; DOI: 10.3749/canmin.46.2.329

Proenza, J. A., Ortega-Gutiérrez, F., Camprubí, A., Tritlla, J., Elías-Herrera, M. and Reyes-Salas, M. (2004) Paleozoic serpentinite-enclosed chromitites from Tehuitzingo (Acatlán Complex, southern Mexico): A petrological and mineralogical study. *J. S Amer. Earth Sci* **16**(8), 649-666.

Proenza, J. A., Rodríguez-Vega, A, Díaz-Martínez, R., Gervilla, F., Melgarejo, J. C., Ramayo, L. and Vila, A. R. (2004) Distribuición de elementos del grupo del platino (EGP) y Au en la faja ofiolitica Mayarí-Baracoa (Cuba oriental). *In*: Pereira, E., Castroviejo, R., Ortiz, F. (eds.), *Complejos ofiolíticos en Iberoamérica*, Proyecto XIII.1— CYTED, 309–336.

Pubellier, M., Monnier, C., Maury, R. and Tamayo, R. (2004) Plate kinematics, origin and tectonic emplacement of supra-subduction ophiolites in SE Asia. *Tectonophysics* **392**(1-4), 9-36.

Qiu, R. Z., Zhou, S., Li, T. D., Deng, J. F., Xiao, Q. H., Wu, Z. X. and Cai, Z. Y. (2007) The tectonic-setting of ophiolites in the western Qinghai-Tibet Plateau, China. *J. Asian Earth Sci* **29**(2-3), 215-228.

Ravizza, G., Blusztajn, J. and Prichard, H. M. (2001) Re-Os systematics and PGE distribution in metalliferous sediments from the Troodos ophiolite. *EPSL*, **188**, 369-381.

Rehkämper, M., Halliday, A. N., Fitton, J. G., Lee, D. C., Wieneke, M. and Arndt, N. T. (1999) Ir, Ru, Pt, and Pd in basalts and komatiites: new constraints for the geochemical behavior of the platinum-group elements in the mantle: *GCA* **63**, 3915-3934.

Roberts, S. and Neary, C. R. (1993) Petrogenesis of ophiolitic chromitite. *In* Prichard, H. M., Alabaster, T, Harris, N. B.W. & Neary, C. R.(eds.) *Magmatic processes and plate tectonics.* Geol Soc.Lon Sp. Pub. **76**, 257-272.

Robinson, P. T. and Zhou, M. F. (2008) The origin and tectonic setting of ophiolites in China. *J. Asian Earth Sci* **32**(5-6), 301-307.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Schellart, W. P., Kennett, B. L. N., Spakman, W. and Amaru, M. (2009) Plate reconstructions and tomography reveal a fossil lower mantle slab below the Tasman Sea. *EPSL*. **278**, (3-4), 143-151.

Scott, D. J., St-Onge, M. R., Lucas, S. B. and Helmstaedt, H. (1989) The 1998 Ma Purtuniq ophiolite: imbricatred and metamorphosed oceanic crust in the Cape Smith Thrust Belt, northern Quebec. *Geos. Can.* **16**(3), 144-147.

Skobelev, S. F., Hanon, M., Klerkx, J., Govorova, N. N., Lukina, N. V. and Kazmin, V. G. (2004) Active faults in Africa: A review. *Tectonophysics* 380(3-4), 131-137.

Spadea, P. and Scarrow, H. (2000) Early Devonian boninites from the Magnitogorsk arc, southern Urals (Russia): Implications for early development of collisional orogen. *In* Y. Dilek, E. M. Moores, D. Elthon and A. Nicolas (eds.) *Ophiolites and Oceanic Crust: New Insights from field studies and the Ocean Drilling Program*. Colorado: Geol Soc. Am. Sp. Paper, 461-472.

Stern, R. J., Johnson, P. R., Kroner, A. and Yibas, B. (2004) Neoproterozoic Ophiolites of the Arabian-Nubian Shield. *In* T. M. Kusky (ed.) *Precambrian Ophiolites and Related Rocks*. Amsterdam: Elsevier, 95-128.

Stockman, H. W. and Hlava, P.F. (1984) PGM in Alpine chromitites from south western Oregon. *Econ. Geol.* **79**, 491-508.

Stowe, C. W. (1987) Distribution of Chromite Ore Fields. *In* C. W. Stowe (ed.) *Evolution of Chromium Ore Fields*. Van Nostrand Reinhold Company Inc., 49-70.

Sturt, B. and Roberts, D. (1991) Tectonostratigraphic Relationships and Obduction Histories of Scandinavian Ophiolitic Terranes. *In* T. J. Peters, A. Nicolas and R. G. Coleman (eds.) *Ophiolite Genesis and Evolution of the Oceanic Lithosphere*. Dordrecht: Kluwer Academic Publishers, 745-769.

Suita, M., Pedrosa-Soares, A., Leite, C., Nilson, A. and Prichard, H. (2004) Complexos ofioliticos do Brasil e a metalogenia comparada das faixas aracuai e brasilia. *In* E. Pereira, R. Castroviejo and F. Ortiz (eds.) *Complejos Ofioliticos en Iberoamerica*. Madrid. 101-132.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Talkington, R. W., Watkinson, D. H., Whittaker, P.J. and Jones, P. C. (1984) PGM and other solid inclusions in chromite of ophiolite complexes: occurrence and petrological significance. *Tschermaks Mineralogische und Petrographische Mitteilungen,* **32**, 285-301.

Tapponnier, P., Mattauer, M., Proust, F. and Cassaigneau, C. (1981) Mesozoic ophiolites, sutures, and arge-scale tectonic movements in Afghanistan. *EPSL* **52**(2), 355-371.

Tarkian, M., Economou-Eliopoulos, M and Sambanis, G. (1996) PGM in chromitites from the pindos ophiolite complex, Greece. *N. Jb. Miner. Mh.* **4**, 145-160.

Tarkian, M. and Prichard, H.M. (1987) Irarsite-hollingworthite solid solution series and other associated Os, Ir and Rh bearing PGM's from the Shetland ophiolite complex. *Min. Dep.* **22**, 178-184.

Tsoupas, G. and Economou-Eliopoulos, M. (2008) High PGE contents and extremely abundant PGE-minerals hosted in chromitites from the Veria ophiolite complex, northern Greece. *Ore Geol. Rev.* **33**(1), 3-19.

Tsukanov, N. V., Kramer, W., Skolotnev, S. G., Luchitskaya, M. V. and Seifert, W. (2007) Ophiolites of the Eastern Peninsulas zone (Eastern Kamchatka): Age, composition, and geodynamic diversity. *Island Arc* **16**(3), 431-456.

USGS (2009) *United States Geological Survey* www.usgs.gov.

Varne, R., Brown, A. V. and Falloon, T. (2000) Macquarie Island: Its geology, structural history, and the timing and tectonic setting of its N-MORB to E-MORB magmatism. *In* Y. Dilek, E. M. Moores, D. Elthon and A. Nicolas (eds.) *Ophiolites and Oceanic Crust: New Insights from field studies and the Ocean Drilling Program.* Colorado: Geol Soc. Am. Sp. paper, 301-320.

Veloso, E. A. E., Anma, R. and Yamazaki, T. (2005) Tectonic rotations during the Chile Ridge collision and obduction of the Taitao ophiolite (southern Chile). *Island Arc* **14**(4), 599-615.

Walker, R. J, Prichard, H. M, Ishiwatari, A. and Pimentel, M. (2002) The Os isotopic composition of the convecting upper mantle deduced from ophiolite chromites. *GCA*, **66**, No. 2, 329-345.

PRICHARD, H. M. and BROUGH, C. (2009) Potential of ophiolite complexes to host PGE deposits. In New developments in magmatic Ni-Cu and PGE deposits; LI, C. and RIPLEY E. M. (Eds.) Geological publishing house Beijing, 277-290

Wang, Q., Wyman, D. A., Zhao, Z. H., Xu, J. F., Bai, Z. H., Xiong, X. L., Dai, T. M., Li, C. F. and Chu, Z. Y. (2007) Petrogenesis of Carboniferous adakites and Nb-enriched arc basalts in the Alataw area, northern Tianshan Range (western China): Implications for Phanerozoic crustal growth in the Central Asia orogenic belt. *Chem. Geol.* **236**(1-2), 42-64.

Wang, W. L., Aitchison, J. C., Lo, C. H. and Zeng, Q. G. (2008) Geochemistry and geochronology of the amphibolite blocks in ophiolitic mélanges along Bangong-Nujiang suture, central Tibet. *J. Asian Earth Sci*. **33**(1-2), 122-138.

Whattam, S. A. (2009) Arc-continent collisional orogenesis in the SW Pacific and the nature, source and correlation of emplaced ophiolitic nappe components. *Lithos*. (in press)

Yang, J. S., Robinson, P. T., Jiang, C. F. and Xu, Z. Q. (1996) Ophiolites of the Kunlun Mountains, China and their tectonic implications. *Tectonophysics* **258**(1-4), 215-231.

Yihunie, T. and Hailu, F. (2007) Possible eastward tectonic transport and northward gravitational tectonic collapse in the Arabian-Nubian shield of western Ethiopia. *J. Afr. Earth Sci* **49**(1-2), 1-11.

Yumul Jr, J. R., G. P., Dimalanta, C. B., Maglambayan, V. B. and Tamaya Jr, R. A. (2003) Mineralization controls in island arc settings: Insights from Philippine metallic deposits. *Gond. Res.* **6**(4), 767-776.

Zaccarini, F., Pushkarev, E. and Garuti, G. (2008) Platinum-group element mineralogy and geochemistry of chromitite of the Kluchevskoy ophiolite complex, central Urals (Russia). *Ore Geol. Rev.* **33**(1), 20-30.

Zhang, Q., Wang, C. Y., Liu, D., Jian, P., Qian, Q., Zhou, G. and Robinson, P. T. (2008) A brief review of ophiolites in China. *J Asian Earth Sci.* **32**(5-6), 308-324.

Zhou, M. F., Sun, M., Keays, R. R., and Kerrich, W. (1998) Controls on PGE distributions of podiform chromitites: A case study of high-Cr and high-Al chromitites from Chinese orogenic belts. *GCA*, **62**, No. 4, 677-688.