A.H. Ahmed · S. Arai

Unexpectedly high-PGE chromitite from the deeper mantle section of the northern Oman ophiolite and its tectonic implications

Received: 11 May 2001 / Accepted: 21 December 2001 / Published online: 2 March 2002 Springer-Verlag 2002

Abstract Unusually high, platinum-group element (PGE) enrichments are reported for the first time in a podiform chromitite of the northern Oman ophiolite. The chromitite contains ≤ 1.5 ppm of total PGE, being highly enriched in the IPGE subgroup (Ir, Os and Ru) and strongly depleted in the PPGE subgroup (Rh, Pt and Pd). Its platinum-group minerals (PGMs) are classified into three types arranged in order of abundance: (1) sulphides (Os-rich laurite, laurite–erlishmanite solid solution and an unnamed Ir sulphide), (2) alloys (Os–Ir alloy and Ir–Rh alloy), and (3) sulpharsenides (irarsite and hollingworthite). The high PGE concentrations are observed only in a discordant chromitite deep in the mantle section, which has high-Cr# (>0.7) spinel with an olivine matrix. All the other types of chromitite (in the Moho transition zone (MTZ) and concordant pods in the deeper mantle section) are poor in PGEs and tend to have spinels with lower $Cr#$ (up to 0.6). This diversity of chromitite types suggests two stages of magmatic activity were responsible for the chromitite genesis, in response to a switch of tectonic setting. The first is residual from lower degree, partial melting of peridotite, which produced low-Cr#, PGE-poor chromitites at the Moho transition zone and, to a lesser extent, within the mantle, possibly beneath a fast-spreading mid-ocean ridge. The second chromitite-forming event involves higher degree partial melting, which produced high-Cr#, PGE-rich discordant chromitite in the upper mantle, possibly in a supra-subduction zone setting.

Central Metallurgical Research and Development Institute, P.O. Box 87 Helwan, Cairo, Egypt E-mail: ahmh2@yahoo.com

S. Arai

Department of Earth Sciences, Kanazawa University, Kakuma 920-1192, Japan

Editorial responsibility: T.L. Grove

Introduction

Platinum-group elements (PGEs) are considered to be a potential geochemical monitor of the processes involving material transfer from the mantle to the crust (Naldrett 1981; Garuti et al. 1997). PGE-abundance systematics give us information about the petrological nature and evolution of the mantle source from which they were derived. The wide range of concentration of PGEs in mineral deposits is attributed to the siderophile and, to a lesser extent, chalcophile properties of this group of elements (Cabri 1981). Due to their siderophile nature, PGEs have been concentrated mainly in the Earth's core and mantle during the early stage of the planet's history (Jagoutz et al. 1979; Arculus and Delano 1981; O'Neill 1991). PGEs are strongly fractionated into a sulphide phase and are useful as a measure of sulphur saturation of a melt.

Very little information is available concerning the distribution and mineralogy of PGEs in the Oman ophiolite in general, especially in its northern part. We found high PGE concentrations (up to 1.5 ppm in total) in a chromitite pod from the Wadi Hilti area (Fig. 1) of the northern Oman ophiolite. We also present new data for podiform chromitites in the Moho transition zone (MTZ) and deeper mantle section, including the distribution of PGEs, PGM mineralogy and other solid mineral inclusions in chromian spinel of chromitites and associated rocks. This study also demonstrates the difference of chromitite formation process between the MTZ and deeper mantle section in the context of tectonic evolution of the Oman ophiolite.

The PGE concentrations within ophiolitic chromitites are now well known (Legendre 1982; Page et al. 1982a, 1982b, 1984; Legendre and Augé 1986), and PGEs are considered as one of the targets for mining exploration in ophiolites (Leblanc 1991). Chromitites are small both in size and distribution in the Oman ophiolite and are not commercially attractive for big investments. Since the MTZ-type chromitites are known to be depleted in PGEs (frequently <100 ppb; this study; Brown 1982;

A.H. Ahmed (\boxtimes)

Fig. 1. Simplified geological map of the study localities in the northern Oman mountains; Fizh Block and the northern part of Salahi Block (after Brown 1982). Inset is a simplified geological map of the Oman ophiolite showing the study area

Page et al. 1982b), the discovery of the high-PGE podiform chromitites in the northern Oman ophiolite reported here will be a new target of PGE exploration, especially in the deeper part of the mantle section.

Geological setting

In the northern part of the Oman ophiolite, a complete sequence of ophiolite stratigraphy is well preserved and is exposed from the upper mantle to the upper crust. The mantle sequence is composed of pervasively foliated harzburgite with minor dunites, lherzolites and chromitites (Roberts 1986).

The podiform chromitites occur either within MTZ dunites overlying the mantle harzburgite or in the irregularly shaped dunites within the harzburgite (Nicolas and Al Azri 1991). A number of occurrences have been found at deep levels within the mantle harzburgite section in Wadi Fayd, Wadi Rajmi and Wadi Tayin (Nicolas et al. 1988; Nicolas and Al Azri 1991). Large chromitite pods are also found in the deeper part $($ > 5 km, this study) of the mantle section, as well as in the stratigraphically highest position in the crustal section at Wadi Hilti (Arai et al., unpublished data).

Four chromitite localities in the northern part of the Oman ophiolite complex were examined in this study: three of them are in the uppermost part of the mantle section, just at the MTZ or at a few kilometres $(1-2 \text{ km})$ below the Moho in Wadi Fizh, Wadi Rajmi and Wadi Farfar, whereas the fourth is located in a deeper part of the mantle section at Wadi Hilti $(>5$ km below the Moho; Fig. 1). The Wadi Farfar and Wadi Hilti areas are located in the north-eastern corner and central part respectively, of the Salahi Block whereas Wadi Rajmi and Wadi Fizh are in the Fizh Block.

PGE concentrations in the Oman chromitites: a review

Chromitite occurrences within the dunite pods in the mantle sequence of the Oman ophiolite were first documented by Glennie et al. (1973) and Carney and Welland (1974). The spatial relationship of the chromitite deposits to the petrological Moho was first recognised by Peters and Kramers (1974). However, there are only a few studies of PGE concentrations and distribution in rocks, especially in podiform chromitites, of the Oman ophiolite.

Brown (1982) determined Pd, Pt, Rh, Ir and Ru concentrations on 18 whole-rock chromitite samples from the mantle sequence. He found that the overall PGE abundances are very low, ranging from 0.03 to 0.6 ppm, no PGMs were identified, and there appeared to be no relation between PGE concentrations and chromite chemistry from various stratigraphical positions within the mantle sequence. Brown (1982) concluded that the impoverishment in PGE for the Oman chromitites resulted either from PGE depletion of the source magma involved in the formation of Oman chromitites, or from the lack of PGE concentration processes during chromitite formation in the Oman mantle sequence.

Page et al. (1982b) studied the distribution and concentration of Pd, Pt, Rh, Ir and Ru in the chromitite and chromite-rich rocks from two stratigraphic sections in the basal ultramafic member of the Oman ophiolite: one section is near Ibra in the southern part and the other is from the Wadi Rajmi-Rayy-Jizi area in the northern part of the ophiolite. The rocks have similarly low PGE abundances in both sections; average contents are (in ppb) 8 for Pd, 14 for Pt, 6 for Rh, 48 for Ir, and 135 for Ru (Page et al. 1982b). The authors concluded that (1) PGE contents and ratios are not correlated with chemical properties of silicates and chromite, suggesting PGE occurrence as discrete sulphide or alloy phases; (2) the accumulation processes of the podiform chromitite of the Oman ophiolite may be different from that of stratiform intrusions in terms of concentrations and distribution of PGE; and (3) the magma from which the Oman chromitites were precipitated was possibly derived from a mantle previously depleted in PGEs, particularly Pt and Pd.

Auge´ (1986) examined PGM inclusions in chromian spinel of chromitites from the Oman ophiolite, and found (1) PGM inclusions in six polished sections among 42 investigated from the southern part of the Oman ophiolite; (2) in spite of a systematic investigation of numerous deposits, no PGMs were located in the northern part of the Oman chromitites; (3) the PGM found so far in the Oman chromitites is laurite, occasionally included in, or associated with silicates; (4) chromitites seem to contain PGMs in Oman less frequently than in other ophiolites; (5) PGM distribution in the Oman chromitites is not related to the chromite composition, since most of the PGM-bearing chromitites are relatively Al-rich; (6) the parent melt was relatively poor in Os and Ir with respect to Ru.

Leblanc and Ceuleneer (1992) determined the PGE concentrations and distribution patterns in the chromitite dikes from the Maqsad area, southern Oman ophiolite. Their PGE contents are very low (30–105 ppb in total), and the Au content is also very low $(< 5$ ppb). They concluded from the low contents and strong fractionation patterns of PGEs that the parent magma of the chromitite dikes was probably a MORB-type basalt which had already fractionated most of its initial PGE content at depth.

More recently, Prichard et al. (1996a, 1996b) considered the Oman ophiolite as one of the classic PGE-poor ophiolites, as compared with the PGE-rich ones (e.g. Shetland ophiolite). Although they chose samples specifically to locate anomalies, PGE analyses of 32 samples from the northern Oman ophiolite yielded very low PGE abundances. Maximum values of PGEs were recorded in chromitite within dunite lenses enclosed by mantle harzburgite (maximum $Os+Ir+Ru$ values of 386 ppb with an average of 165 ppb, and maximum $Pt + Pd$ values of 60 ppb with an average of 15 ppb). The authors noted that enriched $Os+Ir+Ru$ values (greater than 1,000 ppb) are present in Shetland and Al'Ays (Saudi Arabia), but not in Cyprus and Oman. In the Oman ophiolite, the ultramafic sequences are barren of magmatic sulphides required to concentrate PGE, whereas Pt and Pd crystallised with first sulphides at the base of the gabbro (Prichard et al. 1996a, 1996b).

From these studies the consensus is that in the Oman ophiolite, chromitites are generally low in PGEs and have very few PGMs, especially in the northern part of the outcrop which we have studied.

Mode of occurrence and petrography

Chromitites and their host rocks

Chromitite pods of the Wadi Farfar area have relatively sharp contacts with surrounding MTZ dunites which, in turn, enclosed lenses from the mantle harzburgite. Wadi Farfar chromitites have less than 74 modal% of chromian spinel, and olivine is relatively well preserved.

Chromitite pods at Wadi Rajmi have lensoidal shapes in a dunite envelope, and both rock types are hosted by mantle harzburgite. Chromitite ores, especially their massive parts, are cross-cut by numerous feldspathic veinlets (Fig. 2A) which are completely absent in the surrounding dunite and harzburgite. Disseminated chromitite is present around the massive ore within the dunite envelope. The modal amount of chromian spinel ranges from 79% in the massive part to 52% in the disseminated part away from the feldspathic veins. Interstitial silicate matrix is mainly composed of amphibole and clinopyroxene in the massive ores (Fig. 2B), whereas it is mainly olivine in the disseminated ones.

The chromitite pod at Wadi Fizh is lensoidal in shape, up to 60 m long and about 30 m thick. The Wadi Fizh chromitite is very massive and has a few feldspathic patches. The interstitial silicate matrix in the massive ores, which have about 90 modal% of chromium spinel, is mainly composed of amphibole and clinopyroxene

and is free of olivine. The dunite envelope reaches 5 m in thickness, grading to the massive chromitite pod via disseminated chromitite with a nodular texture which has about 50 modal% of chromian spinel, mainly with olivine matrix.

On the other hand, the podiform chromitites in the deeper part of the mantle section at Wadi Hilti are different from those around the MTZ. We examined two big chromitite pods, about 500 m apart horizontally from one another: one pod has a lensoidal shape Fig. 2A–F. Photographs of the chromitites and associated rocks. A Feldspathic veinlets within a chromitite pod from Wadi Rajmi. B Massive chromitite with amphibole and clinopyroxene vein and matrix from Wadi Rajmi. C Lensoidal chromitite pod (PGE-poor) in the deeper mantle section at Wadi Hilti (open dotted line). D Spinel-rich orthopyroxenite stratigraphically extended to a large chromitite pod in the deeper level of the mantle section at Wadi Hilti. E Dike-like chromitite pod (PGE-rich) in the deeper mantle section at Wadi Hilti (open dotted *line*). F Anti-nodular chromitite with olivine matrix around the PGE-rich chromitite in the deeper level of the mantle section at Wadi Hilti

(Fig. 2C) and is stratigraphically deeper than the other one, which has a dike-like appearance (Fig. 2E) and is discordant to the foliation of enclosing harzburgite (Fig. 3). The former pod extends to a zone (≤ 6 m thick) rich in concordant spinel-rich orthopyroxenite bands within harzburgite (Figs. 2D and 3). The Hilti chromitites have only olivine as the matrix silicate, even in massive pods with more than 90 modal% of chromian spinel. Nodular to anti-nodular ores with about 60 modal% of chromian spinel are also present within the dunite envelope around the massive pods (Fig. 2F).

The dunites studied have less than 2% of chromian spinel which is smaller in size than spinel in chromitite, and harzburgites have less than 1% of chromian spinel in all cases.

Mineral inclusions in chromian spinel

Silicate mineral inclusions (polymineralic and monomineralic) are common in chromian spinel of all chromitites and associated dunite envelopes studied by us. The silicates have various sizes, being up to a few mm across, with rounded to subhedral shapes (Fig. 4). The constituent minerals are in order of decreasing abundance: amphiboles (pargasite, edenitic hornblende and tremolite), phlogopites (Na and K phlogopites), clinopyroxene, orthopyroxene, and olivine. The most common mineral assemblage within the inclusions is amphibole $+$ phlogopite, followed by amphibole+orthopyroxene, amphibole+orthopyroxene+phlogopite, and orthopyroxene+ clinopyroxene.

Of all chromitites studied, the Wadi Farfar chromitite is the richest in mineral inclusions, especially amphiboles (Fig. 4A). The disseminated, nodular and anti-nodular chromitites are more enriched in mineral inclusions than associated massive ones. For example, chromian spinel is completely free from mineral inclusions in the massive chromitite of Wadi Rajmi, whereas relatively enriched (especially in amphibole and phlogopite inclusions) in associated disseminated ores. On the other hand, there are two distinctive types of chromitite in terms of inclusion mineralogy in the deeper part of the mantle section at Wadi Hilti. The first type (ol-inclusion type) mainly has olivine inclusions which are rounded to subhedral in shape, and are less than $200 \mu m$ across (Fig. 4B). The second one (px-inclusion type) mostly has

clinopyroxene inclusions with irregular shapes and various sizes (Fig. 4C). Orthopyroxene is occasionally associated with clinopyroxene in inclusions (Fig. 4D). Chromian spinel is also highly enriched in clinopyroxene inclusions in the dunite envelope of the second type of chromitite (Fig. 4E). This is in contrast to dunitic chromian spinels from other localities which are highly depleted in mineral inclusions.

PGM inclusions have been detected for the first time in chromitites from the northern Oman ophiolite. PGMs have been observed in the massive chromitites of the two chromitite types (ol- and px-inclusion types) in the deeper part of the mantle section at Wadi Hilti as well as, to a lesser extent, in Wadi Rajmi disseminated chromitite. The PGM paragenesis can be summarised here in a decreasing order of frequency: (1) sulphides (Os-rich laurite, laurite–erlishmanite solid solution, and an unnamed Ir-sulphide phase); (2) alloys (Os–Ir alloy and an unnamed Ir–Rh alloy); and (3) sulpharsenides (irarsite and hollingworthite). Sulphides and alloys mainly occur as discrete inclusions within chromian spinel as well as, to a lesser extent, within the olivine matrix. Sulpharsenides, on the other hand, occasionally occur associated within chromian spinel cracks. PGMs are rarely associated with silicate inclusions, contrary to what has been observed by Augé (1986), but are mostly found as isolated grains within chromian spinel. They have perfect euhedral crystal forms, and are $\leq 50 \,\mu m$ in size (Fig. 4F).

However, detailed mineralogical aspects of PGEs in the northern Oman ophiolitic chromitites will be described in a separate paper.

Chemical compositions

Analytical methods

Analysis of chromian spinel and associated silicate minerals was carried out with a JEOL electron-probe micro-analyzer JXA-8800 (WDS) at the Center for Cooperative Research of Kanazawa University. Analytical conditions were 15-kV accelerating voltage, 12-nA probe current, and 3-um probe beam diameter, and the raw data were corrected with an online ZAF program. The amounts of $Fe³⁺$ and $Fe²⁺$ in spinel were calculated assuming spinel (AB₂O₄) stoichiometry. All Fe is assumed to be $Fe²⁺$ in silicates. Selected analyses of chromian spinels and associated silicates are listed in Tables 1 and 2 respectively.

Thirty samples of chromitites, dunites, harzburgites, and orthopyroxenites as well as gabbroic and feldspathic veins were analysed for all PGEs (Os, Ir, Ru, Rh, Pt, Pd) and Au. The analysis was conducted using ICP-MS, after the Ni-sulphide fire assay collection at the Genalysis Laboratory Services, Australia. Detection limits are 2 ppb for Os, Ir, Ru, Pt and Pd, 1 ppb for Rh, and 5 ppb for Au. Bulk-rock PGE contents for the samples are listed in Table 3. Gold is below detection limits in all analysed samples.

Spinel compositions

Chromian spinel composition of the northern Oman chromitites seems to be dependent on two factors: the stratigraphical position in the mantle section and the modal amount of spinel. Chromian spinel of massive chromitite tends to be more Cr-rich in the mantle sequence than in the MTZ (Fig. 5A, B). Chromian spinel is also Fig. 3. Illustration showing the mode of occurrence and relationship between PGE-poor and PGE-rich chromitites in the deeper mantle section of Wadi Hilti. Note the concordance and discordance of PGE-poor and PGE-rich chromitites respectively, with the foliation plane of enclosing harzburgite and spinel-rich orthopyroxenite bands

more Cr-rich in the disseminated, nodular and anti-nodular ores than in the associated massive chromitites (Table 1). Spinel is much more Al-rich in the massive chromitites than in associated disseminated and nodular ores in the MTZ of Rajmi, Fizh and Farfar (Fig. 5A). The Cr# $(=Cr/(Cr+Al)$ atomic ratios) of spinel in the massive MTZ chromitites is restricted and is around 0.5 (0.567, 0.495 and 0.467 on average in Rajmi, Fizh and Farfar respectively), whereas it is more than 0.6 (0.604 and 0.647 on average in Rajmi and Fizh respectively) in associated disseminated and nodular ores (Table 1; Fig. 6A). The deeper-level mantle chromitites at Wadi Hilti have two compositionally distinctive types, high- and intermediate-Cr# types (Fig. 5B). The former has spinel high in Cr#, usually >0.7 , and is PGE-rich whereas the latter has spinel intermediate in Cr# (~ 0.6) and it is PGE-poor (Fig. 6B). Nodular to anti-nodular chromitite around the high-Cr#, PGE-rich massive chromitite also has high-Cr# (>0.7) spinel (Fig. 6B). Chromian spinel of dunites and harzburgites has intermediate Cr# ranging from 0.5 to 0.6 (Table 2) in all cases studied. Chromian spinel has low TiO₂ contents (usually ≤ 0.3 wt%), both in chromitites and associated peridotites (dunites and harzburgites; Tables 1 and 2).

Silicate mineral inclusions

Amphibole is the most abundant of all inclusion minerals in the MTZ chromitites, especially in the disseminated, nodular and antinodular ones. Edenitic hornblende is more common than pargasitic and tremolitic ones, which seem to continuously vary in compositions. The TiO₂ content is up to 1.04 wt%, (0.57 wt% on average), and the Mg# $(= Mg/(Mg + Fe^{2+}))$ atomic ratios with total Fe assumed to be Fe^{2+}) ranges from 0.92 to 0.95 (Table 2). Amphiboles as inclusions are almost all similar in composition, with slightly higher alkalis, to those interstitial to chromian spinel in the massive MTZ chromitites (Table 2). Both K and Na phlogopites are highly magnesian (Mg# ranging from 0.97 to 0.98), and have TiO₂ contents up to 2 wt^{$\frac{6}{10}$} (0.7 wt^{$\frac{6}{10}$} on average).

Olivine, the most common silicate inclusion in the PGE-poor mantle chromitite, is almost similar in composition to that in the matrix, being highly forsteritic with little variation ($F_{0.95-97}$). Clinopyroxene, the most abundant silicate inclusion in the PGErich chromitite and its host dunite, is mainly diopside with high Mg# ranging from 0.94 to 0.97, and relatively high Al_2O_3 contents ranging from 0.43 to 3.53 wt% (1.52 wt% on average). Orthopyroxene is enstatite with low CaO, Al_2O_3 and Cr_2O_3 contents (Table 2).

Bulk-rock PGE geochemistry

Despite the difference in PGE concentrations, all chromitite samples are distinctly enriched in the Ir subgroup (IPGE= Os , Ir, Ru) in preference to the Pd subgroup (PPGE = \overline{Rh} , Pt, Pd; Fig. 7A, B). All chromitite samples have negatively sloped chondrite-normalised PGE patterns, typical of ophiolitic chromitites elsewhere (e.g. Page et al. 1982a, 1982b; Page and Talkington 1984). PGE concentrations in chromitites, dunites, harzburgites, orthopyroxenites as well as feldspathic and gabbroic veins in the study areas are listed in Table 3. The PGE concentrations are usually below 100 ppb in the MTZ chromitites, and are higher than 100 ppb in the mantle chromitites at a deeper level (Table 3). The lowest PGE contents were obtained from the Wadi Fizh chromitite, where almost all PGEs are below the detection limit for massive varieties, and up to 33 ppb in the associated nodular occurrences (Table 3; Fig. 7A). The Wadi Rajmi and Wadi Farfar chromitites have intermediate PGE contents up to 92 and 73 ppb respectively. The Pd/Ir ratio, one of the best parameters for PGE fractionation (Naldrett et al. 1979), is very restricted in the MTZ chromitites, ranging from 0.105 to 0.75 (Table 3). The chondrite-normalised (CN) PGE patterns of MTZ chromitites exhibit slightly negative slopes from Ru to Pt $(Ru/Pt = 2.17-19.5)$ and positive slopes from Pt to Pd (Fig. 7A), being coincident with CN curves reported from Newfoundland ophiolites (Page and Talkington 1984; Edwards 1990).

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Fig. 4A–F. Backscattered electron micrographs of the mineral inclusions in chromian spinel of A–D, F chromitite and E dunite. A Numerous silicate inclusions with different sizes (mainly amphiboles and phlogopites). MTZ from Wadi Farfar. B Olivine inclusions (0) in spinel from the PGE-poor chromitite from the deeper level of the mantle section of Wadi Hilti. C Irregular clinopyroxene inclusions (cpx) in spinel in the PGE-rich chromitite from the deeper level of the mantle section of Wadi Hilti. D Orthopyroxene (opx) -clinopyroxene (cpx) bimineralic inclusion from the PGE-rich chromitite in the deeper mantle section of Wadi Hilti. Open dotted line indicates the boundary between cpx and opx . E Clinopyroxene inclusions of different sizes within a spinel grain of dunite envelope around the PGE-rich chromitite in the deeper mantle section of Wadi Hilti. F Platinum-group mineral inclusion (single crystal Os rich laurite) within chromian spinel of the PGE-rich chromitite in the deeper mantle section of Wadi Hilti

Table 1. Selected microprobe analyses of chromian spinel in podiform chromitite deposits of the northern Oman ophiolite. MTZ Moho transition zone, diss. ore disseminated chromitite, antin ore anti-nodular chromitite, PGE-poor PGE-poor massive chro-

mitite, *PGE-rich* PGE-rich massive chromitite, $Cr# Cr/(Cr+A)$ atomic ratio, $Mg# Mg/(Mg + Fe^{2+})$ atomic ratio, s. no. sample number

The PGE concentrations are highly variable in the chromitites from the deeper mantle section of Wadi Hilti: the PGE-poor chromitites have less than 130 ppb of total PGE, and the PGE-rich one unusually has high PGE concentrations up to 1,476 ppb (Table 3), more than two and a half orders of magnitude higher than those in ordinary ophiolitic chromitites (Leblanc 1991). The Pd/Ir ratio is very low in the chromitites of the mantle section, being 0.098 in the PGE-poor one and extremely low (0.007) in the PGErich one. The CN curve has a slightly negative slope for the former $(Ru/Pt=2.69)$ and it has a very steep negative slope from Ru to Pt $(Ru/Pt = 173)$ for the latter (Fig. 7B; Table 3). PGE-rich nodular and anti-nodular chromitites have slightly negative slopes from Ru to Pt (Ru/Pt = 5.897 and Pd/Ir = 0.084).

With a few exceptions, the dunites in the northern Oman ophiolite complex have very slightly negative slopes from Ru to Pt $(Ru/Pt=1.25$ to 2; Fig. 8A). Two dunitic samples have slightly positive slopes from Ru to Pt: one is a discordant dunite from a shallow level (2–3 km below the Moho) in the mantle section at Wadi Hilti (Hilti shallow dunite, 31), and the other (Rajmi dunite, 63) is a dunite envelope of a chromitite pod from Wadi Rajmi (Fig. 8A). The harzburgite host has a low and restricted range of PGE contents (24–56 ppb) with nearly flat CN patterns (Pd/ Ir $=0.6-1.8$, Fig. 8B), which are comparable with the values obtained from depleted residual mantle peridotites elsewhere (Barnes et al. 1985; Lorand 1989; Edwards 1990; Lorand et al. 1993).

Discussion

Genesis of chromitites

The tectonic setting of chromitite formation and the mechanism of chromian spinel concentration are still

subject of debate (e.g. Lago et al. 1982; Roberts 1988; Leblanc and Nicolas 1992). The chemical diversity of spinel and its silicate inclusions, and the difference of PGE concentrations between MTZ and deeper mantle chromitites of the northern Oman ophiolite are possibly attributable to the difference in the chemistry of magma involved in the chromitite formation. Assimilation of wall rock by a primitive melt in the mantle (e.g. Kelemen 1990) was thought to affect magmatic evolution and to play an essential role in chromitite formation (e.g. Arai and Yuorimoto 1994; Zhou et al. 1996; Varfalvy et al. 1996, 1997). In contrast to this, assimilation of the crustal rocks by a primitive melt is rarely considered as a source of chromitite pods (Bédard and Hébert 1998; Arai et al., unpublished data). Field and petrographical evidence implies that the assimilation of crustal materials possibly plays an important role in the formation of the MTZ chromitites in the northern Oman ophiolite (Arai et al., unpublished data; this study). The abundance of feldspathic veins and networks only within the chromitite pods in the MTZ, especially at Wadi Rajmi and Wadi Fizh, and the abundance of clinopyroxene and amphibole in the matrix of chromitite are consistent with the assimilation of gabbroic blocks by invaded primitive melt. Addition of CaO, Al_2O_3 and H_2O from the assimilated gabbroic blocks to the magma especially favoured crystallisation of amphibole as matrix and inclusions, and precipitated more aluminous spinel

Table 2. Selected microprobe analyses of silicate mineral inclusions and matrix silicates as well as chromian spinel in the host dunites and harzburgites. Am Amphibole, K -ph K phlogopite, Naph Na phlogopite, cpx clinopyroxene, opx orthopyroxene, ol olivine, MTZ Moho transition zone, *harzb* harzburgite, FeO^* total

iron as FeO, $Cr# Cr/(Cr+Al)$ atomic ratio, $Mg# Mg/(Mg+Fe^{2+})$ atomic ratio, s. no. sample number. Sample localities are 6 Wadi Farfar, 38–40, 43, 67 Wadi Hilti, 60, 61 Wadi Rajmi, 69, 71, 77 Wadi Fizh

a No. atoms for O

Table 3. Selected analyses of bulk-rock PGEs (pbb) of chromitites and associated rocks from the northern Oman ophiolite. MTZ Moho transition zone, m. ore massive chromitite, diss. disseminated chromitite, n. ore nodular chromitite, anti-n anti-nodular chromitite, PGE-p PGE-poor massive chromitite, PGE-r, PGE-rich massive chromitite, harzb harzburgite, felds v. feldspathic veins within chromitite, orthpx orthopyroxenite, s. no. sample number, n.d. not detected

(Bédard and Hébert 1998). Addition of $H₂O$ to the magma, either by the assimilant gabbro or from seawater in the mid-ocean ridge setting, will expand the spinel stability field and promote chromitite formation (Nicholson and Mathez 1991).

The association of PGE-poor chromitite with a zone of spinel-rich orthopyroxenite bands (>6 m thick) in the deeper mantle section at Wadi Hilti suggests that dissolution of orthopyroxene into olivine-spinel-saturated melt possibly produced the intermediate- \tilde{C} r# chromitites

Fig. 5A, B. Variation of Cr_2O_3 wt% versus Al_2O_3 wt% of chromian spinel of the northern Oman chromitites. A MTZ chromitite (Farfar, Rajmi and Fizh). B Mantle chromitite (deeper mantle chromitites at Wadi Hilti; PGE-poor and PGE-rich ones). Note the difference in composition between the massive MTZ chromitites and associated disseminated, nodular and anti-nodular ones, and the deeper mantle ones. MTZ Moho transition zone, $n.$ nodular, $m.$ massive, $diss.$ disseminated

beneath a mid-ocean ridge setting. If a high-pressure olivine-spinel-saturated melt intruded through the shallower mantle and was in contact with such Cr-rich orthopyroxenite, intermediate-Cr# (~ 0.6) spinel would be precipitated from the melt modified by the orthopyroxene dissolution (Arai and Abe 1995). PGE-rich chromitite with high-Cr# spinel (>0.7) , on the other hand, was possibly produced by a high degree of partial melting of mantle peridotite, may be in a supra-subduction zone environment. Chromian spinel from different tectonic environments has distinctive Cr# values which reflect differences in magma composition. For example, chromian spinel with high Cr# (>0.7) is frequently found in magmatic rocks with boninitic or Mgrich andesite composition occasionally found in the supra-subduction zone environment, whereas rocks from mid-ocean ridge settings rarely have chromian spinel with Cr# higher than 0.7 (e.g. Dick and Bullen 1984; Arai 1997). The differences may be due to differences in fertility of the mantle source rocks or different degrees of partial melting (Dick 1989). The less fertile the mantle source or the larger the degrees of partial melting, the higher the Cr# of the resulting chromian spinel (Fujii

1989). The high-degree partial melts are occasionally enriched in refractory elements such as Ni and Cr (Pearce et al. 1984, 1992) as well as PGEs.

Abundances and fractionation of PGEs

Chromitite

Ophiolitic chromitites are characterised by enrichment in Os, Ir and Ru relative to Pt and Pd, and their PGE contents and Pd/Ir ratios are highly variable (Page and Talkington 1984; Barnes et al. 1985; Leblanc 1991). Although most of them contain between 100 and 500 ppb of PGE and have moderate to low Pd/Ir ratios (0.8–0.1) and steep, negatively sloped PGE patterns (Leblanc 1991), they are sometimes PGE-rich $($ >750 ppb) and show very low Pd/Ir ratios (< 0.1) in ophiolites such as the Massif du Sud of New Caledonia (Legendre 1982; Page et al. 1982a). PGE contents of chromitites tend to increase with an increase of volume ratio and Cr# of chromian spinel (Crocket 1979; Page et al. 1982a, 1982b; Economou 1986; Leblanc 1991). This relationship is also confirmed in the northern Oman ophiolite where PGE contents increase with an increase of Cr content, suggesting the coprecipitation of chromian spinel and PGM in a deep-seated magmatic process (e.g. Arai et al. 1999).

Three processes, that is, partial melting, crystal fractionation and alteration, possibly control the PGE concentration in igneous rocks (Barnes et al. 1985). Gold and Pt are more easily mobile than the other PGEs during the alteration process, and Pd may be mobilised by hydrothermal fluids (McCallum et al. 1976; Ross and Keays 1979; Keays et al. 1981, 1982; Barnes et al. 1985; Stumpfl 1986). Since there is no evidence for hydrothermal alteration in the study areas, crystal fractionation and partial melting seem to be the main factors controlling the distribution and fractionation of PGEs in Oman ophiolite. Os, Ir and Ru have higher melting points than Pt and Pd and tend to be concentrated in refractory residue and in early cumulates relative to Pt and Pd which are more incompatible and tend to be retained in the melt (Barnes et al. 1988; Edwards 1990; Prichard et al. 1996a, 1996b). The strong variation of Pd/Ir ratios of PGEs in chromitites from the MTZ to deeper levels in the mantle section of the northern Oman ophiolite, from 0.6–1.8 to 0.098–0.007 respectively, was basically dependent on the variation of PGE contents in magmas responsible for chromitite genesis throughout the MTZ-mantle section.

The PGEs, which are very refractory, require high degrees of partial melting for extraction from the less depleted mantle source and for concentration in appreciable amounts in resultant igneous rocks. A high-degree $(>25\%)$ partial melt is, therefore, expected to be enriched in PPGEs and its residuum enriched in IPGEs (Sun 1982; Barnes et al. 1985; Leblanc 1991). Interstitial sulphides and chromian spinel are the most common hosts of PPGEs and IPGEs respectively, in ultramafic

Fig. 6A, B. Cr–Al–Fe³⁺ plots of chromitite spinels of the northern Oman ophiolite in A MTZ chromitites and B chromitites of deeper level in the mantle section at Wadi Hilti. Average Cr#s $(=Cr/$ $(Cr+A)$ atomic ratios) are also shown

mantle rocks (Mitchell and Keays 1981; Oshin and Crocket 1982; Barnes et al. 1988; Cocherie et al. 1989; Leblanc 1991). At relatively low sulphur fugacity and high temperatures (1,200–1,300 °C), Os, Ir and Ru will be concentrated into alloys and, to a lesser extent, sulphides (i.e. laurite), leaving a melt depleted in these elements (Leblanc 1991). Chromian spinel crystals, the early fractionate of the melt, may include minute Os–Ir–Ru crystals as alloys or sulphide during early stages of their growth. The common abundance of laurite as well as, to a lesser extent, Os–Ir alloys in the PGE-rich chromitite suggests a possibly relatively sulphur-saturated melt involved in the formation of PGE-rich chromitite in the northern Oman ophhiolite. Collection of the PGEs from the magma might be taking place as PGE sulphide and discrete alloys. The residual melt, which was still enriched in PPGEs, may have concentrated its PPGE contents as interstitial sulphides somewhere at a relatively shallower level in the ophiolite succession. Naldrett et al. (1979) suggested that the PGEs are collected as immiscible sulphide droplets from the melt at high temperatures if sulphur saturation is reached.

Accordingly, two possible processes may control the difference in PGE contents between the PGE-rich chromitite in the mantle and the PGE-poor one around the MTZ in the northern Oman ophiolite: (1) fractionation of a single PGE-rich magma, which precipitated PGErich chromitite in the deeper section and a PGE-poor one around the MTZ; and (2) two different magmas involved in chromitite formation in the deeper mantle section and MTZ, depending on the tectonic setting in which these

two chromitite types are formed. Petrological and field characteristics support the second possibility. The presence of PGE-rich with PGE-poor chromitites at the same level deeper within the mantle section, the lensoidal shape of the former and dike-like occurrence of the latter, the common abundance of olivine inclusions within PGE-poor chromitite spinel and clinopyroxene in the PGE-rich one, as well as the intermediate-Cr# spinel in the former (\leq 0.6) against high-Cr# spinel in the latter (0.7) all strongly indicate different magma sources involved in chromitite formation.

The PGE-rich chromitite of the northern Oman mantle section was most probably precipitated from a PGE-rich magma generated by a high degree of partial melting and modified by reaction with mantle orthopyroxene (Arai and Yurimoto 1994; Arai and Abe 1995). The shallower podiform chromitites around the MTZ were possibly precipitated from evolved magmas which originally had low PGE contents, from which the PGEpoor chromitite was precipitated at depth in the same level as the PGE-rich chromitite. Contamination of this evolved magma by crustal materials to various degrees (see Bédard and Hébert 1998) produced the PGE-depleted chromitites at the MTZ. The low-Cr# character of spinel in both MTZ chromitites (~ 0.5) and PGE-poor ones at depth (~ 0.6) is coincident with the chemical characteristics of MORB spinels (Arai 1992). The crustal contamination is supported by abundance of amphibole and clinopyroxene in the matrix of the MTZ massive chromitites of the northern Oman ophiolite (Augé 1987; this study), as well as the abundance of feldspathic veins within MTZ chromitites. Due to the low PGE contents of the crustal materials, their assimilation by primitive melt may contribute to the PGE-poor character of the resultant melt. It is noteworthy that the previous PGE

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Fig. 7A, B. Chondrite-normalised PGE patterns of chromitites from the northern Oman ophiolite. A MTZ chromitite (Farfar, Rajmi and Fizh), and B mantle chromitite (deeper mantle chromitites at Wadi Hilti; PGE-poor and PGE-rich ones). Normalising values currently in use are taken from Naldrett and Duke (1980; cf. 514, 540, 690, 200, 1,020 and 545 for Os, Ir, Ru, Rh, Pt and Pd respectively). Abbreviations as in Fig. 4

studies on the Oman chromitites have dealt mainly with the pods located at the MTZ or even slightly deeper levels of a few kilometres (2–3 km) below the MTZ (Brown 1982; Page et al. 1982a, 1982b; Auge´ 1983, 1986; Leblanc and Ceuleneer 1992), where the PGE-poor chromitites are inevitably found.

Peridotites

The slightly negative slope of PGE distribution patterns of dunites is best explained by the nature of their early precipitates where PGE-bearing phases have relatively high IPGE/PPGE ratios. Exceptional samples which display slightly positive PGE slopes (Fig. 8A) are from a discordant dunite from Wadi Hilti and a dunite envelope from Wadi Rajmi, implying the presence of Pt- and Pdbearing phases (Page and Talkington 1984; Barnes et al. 1985; Prichard and Tarkian 1988; Edwards 1990). The fractionated PGE pattern of these dunites was possibly due to fractionation of the PGE-rich magma, which has

Fig. 8A, B. Chondrite-normalised PGE patterns of A dunites and B harzburgites of the northern Oman ophiolite mantle section. Note the positive slope of dunite samples of Hilti (shallow, 31) and Rajmi (63). Numbers within brackets refer to the sample numbers

lost its IPGEs by forming IPGE-rich chromitite at depth in the mantle. The subsequent magma precipitated dunite higher in PPGE/IPGE ratios (Pd/Ir up to 8.00).

The flat or nearly flat PGE distribution patterns of harzburgite (Fig. 8B) coincide with the CN patterns of the undepleted upper mantle peridotite compiled by Arculus and Delano (1981), and may indicate its unfractionated nature ($Pd/Ir = 0.6-1.8$). By contrast, highly depleted mantle peridotites usually have low total PGE contents and fractionated CN patterns with negative slopes from Ir to Pd, and Pd/Ir<1 (Hertogen et al. 1980; Mitchell and Keays 1981; Edwards 1990). Such patterns have been reported from the Thetford Mines ophiolite, Quebec (Oshin and Crocket 1982), the Ronda peridotite massif, Spain (Stockman 1982), and the Vourinos ophiolite complex, Greece (Cocherie et al. 1989).

Tectonic implications

The geological, petrographical and geochemical diversity of podiform chromitites suggests that two stages of magma generation were involved in their formation in the northern Oman ophiolite. PGE-poor chromitites were produced around the MTZ and, to a lesser extent, in the deeper part of the mantle section in the first stage. Fig. 9A, B. Cartoon showing two stages of magma generation in the northern Oman ophiolite. A The first stage was relatively low degrees of partial melting in a mid-ocean ridge setting. Magma precipitated the MTZ chromitites and PGE-poor ones in deeper levels of the mantle section by assimilation of ophiolitic lower crust and spinel-rich orthopyroxenite respectively. **B** In the second stage, the PGE-rich chromitite was produced in the deeper mantle section from a magma possibly formed under a high degree of partial melting in a supra-subduction zone environment

This was linked to the formation of residual harzburgite with unfractionated PGE patterns and tholeiitic melt under relatively low degrees of partial melting, possibly in a fast spreading, mid-ocean ridge setting (Nicolas 1989; Fig. 9A). Olivine is the only silicate mineral inclusion in spinel of this type of chromitite which is consistent with the almost anhydrous nature of the mantle section beneath the mid-ocean ridge. Also, the gently negative slope of the PGE pattern in the PGEpoor chromitite from Ru to Pd with slight PPGE depletion may reflect the low degree of partial melting for the involved magma beneath the mid-ocean ridge environment (Barnes et al. 1985; Prichard et al. 1996a, 1996b). The primary MORB may have partially removed Pt and Pd from the residual mantle peridotite (Prichard and Tarkian 1988; Edwards 1990).

The PGE-rich chromitites in the deeper part of the mantle section, which have dike-like occurrence, were formed during the second stage of magma generation, possibly linked to arc-type magmatism by a higher degree of partial melting of peridotite in a supra-subduction zone setting (Fig. 9B). This PGE-rich chromitite has chemical characteristics distinctive from the PGEpoor chromitites. Apart from its unusually high PGE concentrations, it has high-Cr# (>0.7) spinel and a very low PPGE/IPGE ratio (Pd/Ir=0.007). This strongly implies that the PGE-rich chromitite was formed either from a high-degree partial melt or from melting of already depleted peridotite. This kind of second-stage magma is most easily formed in the supra-subduction zone environment, where H_2O is supplied as a flux from the slab. This kind of magma may facilitate the removal of PGEs from the mantle (Prichard et al. 1996a, 1996b). The dike-like discordant occurrence of the PGE-rich chromitite most probably indicates a younger generation than the concordant chromitites which are always PGEpoor (Figs. 2E, 3).

This means that the upper mantle of the Oman ophiolite has been modified by a substantial amount of supra-subduction zone components after initially being formed in a mid-ocean ridge setting. A similar sequence of magma activity has been described in the Troodos ophiolite, Cyprus (Mehegan and Robinson 1991), and the Luobusa ophiolite, southern Tibet (Zhou et al. 1996), where early tholeiite magmas were followed by depleted tholeiites and boninites.

Economic importance

To judge the economic importance of the high PGE concentrations in chromitite of the northern Oman ophiolite, further investigations are urgently needed to estimate to which extent the PGE-rich chromitite is distributed in the deeper mantle section. If the PGE-rich chromitite is common in the deeper mantle of the Oman ophiolite, then this high-grade chromitite may become a potential source of Os, Ir and Ru. On the other hand, there have been no studies carried out on the placer deposits of the Oman ophiolite with respect to the PGE source. Wadi sediments, which are so common in the deeper part of the northern Oman ophiolite, would be enriched in PGM, especially Os–Ir–Ru alloys, as well as in chromite. Moreover, Pt and Pd, which tend to be retained in the residual melt, are expected to be concentrated somewhere at a higher level in the Oman ophiolite, since they are highly depleted in the deeper mantle section where the conditions are favourable to concentrate IPGEs. Hence, further investigations in the deeper mantle section as well as in shallower levels of the Oman ophiolite are needed to estimate the possibility of finding exploitable resources or grades of PGE concentrations.

Summary and conclusions

- 1. Podiform chromitites occur either at a shallow level around the MTZ or at a deeper level within the mantle section of the northern Oman ophiolite. Matrix silicate minerals are different between the two types: clinopyroxene and amphibole in the former and olivine in the latter. The disseminated, nodular and anti-nodular chromitites associated with the massive chromitite in both types have only olivine as matrix silicate.
- 2. Massive MTZ chromitites have relatively low-Cr# spinel (~ 0.5) , whereas the associated disseminated, nodular and anti-nodular ones have relatively high- $Cr#$ spinel (> 0.6). In terms of spinel chemistry and inclusion mineralogy, chromitite in the deeper part of the mantle section has two distinctive types. One type

contains chromian spinel with intermediate Cr# (~ 0.6) which has olivine inclusions. The other type has high-Cr# (>0.7) spinel with inclusions of clinopyroxene and hydrous silicates (amphiboles and phlogopites). The latter type from the deeper mantle section is PGE-rich, containing up to 1.5 ppm in total PGE contents.

- 3. All chromitite pods display a negative PGE slope from Ru to Pt, more or less a characteristic ophiolite PGE pattern. The flat, unfractionated PGE patterns of harzburgite reflect its undepleted nature with respect to the PGEs, and the slightly negative PGE slopes of some dunite envelopes around chromitites suggest the presence of chromite grains with high IPGE/PPGE ratios.
- 4. The diversity of chromitite types in the Oman ophiolite suggests the presence of two stages of magma generation. The first stage produced the residual peridotite with unfractionated PGE patterns and melt by a relatively low degree of partial melting, possibly in a fast spreading, mid-ocean ridge setting. The magma precipitated low-Cr#, PGE-poor chromitites at the MTZ and in the mantle section. The second stage produced refractory magma by a high degree of partial melting, possibly in a supra-subduction zone environment. The magma formed the high-Cr#, PGE-rich chromitite in the deeper mantle section.
- 5. Gabbroic rocks and mantle orthopyroxene were assimilated by olivine-spinel-saturated magmas to form chromitites at the MTZ and in the upper mantle respectively.

Acknowledgements This study was supported by the Japanese research project of the Oman ophiolite. We wish to acknowledge the geological staff in the Ministry of Commerce and Industry, Sultanate of Oman, for their help to facilitate field research in the northern Oman mountains. We also thank Mr. K. Kadoshima and J. Uesugi for their assistance in the fieldwork and laboratory analyses. We are greatly indebted to S. Miyashita, T. Mizuta and S. Umino for helpful discussion. We have greatly benefited by the support of H. Kusaba and Y. Shibata. The Embassy of Japan in Oman helped our fieldwork. Critical comments by Dr. Jean Bedard, Dr. R.J. Arculus, and Dr. T. Grove greatly improved the manuscript.

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