

Potarite (Pd-Hg) in thermally metamorphosed dunite from the Inazumi-yama ultramafic complex, southwestern Japan: an implication for the behaviour of mercury in PGE mineralization in peridotite

S. ARAI¹, H. M. PRICHARD², I. MATSUMOTO³ AND P. C. FISHER²

¹ Department of Earth Sciences, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan

² Department of Earth Sciences, Cardiff University, P.O. Box 914, Cardiff, CF1 3YE, UK

³ Dowa Engineering Co., 5-10-5 Shimbashi, Minato-ku, Tokyo 105-0044, Japan

ABSTRACT

Pd-rich PGM (platinum-group minerals) have been found in sulphide-bearing dunites and harzburgites from the Inazumi-yama ultramafic complex in southwestern Japan. In the dunite, potarite (PdHg_{0.85–0.88}) is the most abundant PGM but other associated PGM include stibiopalladinite (Pd₅Sb₂) and rare sperrylite (PtAs₂) and Pd-rich alloys. A Pd telluride has been found in the harzburgite. The PGM are enclosed usually by pentlandite-heazlewoodite composite grains and, rarely, by altered chrome-spinel. These minerals are characteristic of an ultramafic assemblage but they are accompanied by ubiquitous galena and minor sphalerite not usually associated with these ultramafic assemblages. The ultramafic part of this complex has been thermally metamorphosed (olivine-talc zone) within the contact aureole of an adjacent granite. The PGM, sulphides and altered spinel are all intergrown with antigorite and/or chlorite, indicating a metamorphic overprint on the primary igneous mineralogy. The Pd/Pt ratios of 9 suggest a process of hydrothermal concentration for the Pd and it is proposed that the Pd has been remobilized and reconcentrated by hydrothermal solutions derived from the granitic magma which reacted with the Pd concentrated in the primary magmatic sulphides. Mercury may have been leached from surrounding sediments by the hydrothermal solutions. It is possible that potarite and the other PGM formed at temperatures of up to 650°C and are likely to be found in other thermally metamorphosed ultramafic rocks showing a depleted character (spinel Cr/[Cr+Al]>0.7), common in orogenic belts.

KEYWORDS: potarite, stibiopalladinite, metamorphosed dunite, thermal metamorphism, Sangun zone, Japan.

Introduction

THE platinum-group elements (PGE) are concentrated as primary platinum-group minerals (PGM) as well as PGE-bearing sulphides in ultramafic cumulates during early stages of magmatic solidification. They are found in continental layered igneous intrusions (e.g. Wagner, 1929; Cabri and Laflamme, 1976; Naldrett and Cabri, 1976) and to a lesser degree in ultramafic cumulates in ophiolites (Ohnenstetter *et al.*, 1991; Prichard and Lord, 1993; Pedersen *et al.*, 1993). It is well known that primary PGM are easily altered at relatively high temperatures (e.g.

Kinloch, 1982; McLaren and De Villiers, 1982) or at low temperatures (e.g. Prichard and Tarkian, 1988). The PGE, especially Pt and Pd, are theoretically mobile in hydrothermal solutions but their mobility is highly dependent on physicochemical conditions (e.g. Mountain and Wood, 1988*a,b*). On the other hand, the PGE are almost immobile or mobile only for short distances during alteration processes such as serpentinization (e.g. Prichard and Tarkian, 1988; Prichard *et al.*, 1994). However, the formation of secondary PGM during intermediate-temperature geological processes, such as high-grade metamorphism, has not been

investigated in detail. In this article PGM in thermally metamorphosed peridotite are described in order to understand the PGM assemblages present at intermediate temperature conditions (around 500 to 650°C) under the influence of hydrothermal solutions both generated by the progressive dehydration of serpentinite and derived from an adjacent granite magma. This paper discusses for the first time the origin of potarite (PdHg) and the possible mobilization of the PGE, especially Pd, during thermal metamorphism.

Geological background

The Sangun zone, southwestern Japan, is characterized by high-pressure intermediate-type metamorphism (Miyashiro, 1973) and contains numerous ultramafic complexes (Arai, 1980; Matsumoto *et al.*, 1995) (Fig. 1). Harzburgite is

predominant over dunite, and lherzolite is almost absent (Arai, 1980). Podiform chromitites are associated with dunite (Arai, 1980; Matsumoto *et al.*, 1997). The primary harzburgite of the Sangun zone is an homogeneous lithology which is moderately depleted with only a small amount of clinopyroxene. Both the harzburgite and dunite contain olivine with a composition of Fo₉₀₋₉₁ and chromian spinel with Cr# (= Cr/(Cr + Al) atomic ratio) of around 0.5 (Arai, 1980; Matsumoto *et al.*, 1995). The chromitite is of an Al-rich variety; the Cr# of spinel varies from 0.4 to 0.6 (Arai, 1980; Arai and Yurimoto, 1994; Matsumoto *et al.*, 1997). The harzburgite is almost equivalent to the most depleted group of abyssal peridotites obtained from a fast-spreading ridge system (e.g. Dick and Bullen, 1984; Arai and Matsukage, 1996; Niu and Hékinian, 1997).

Many of the ultramafic complexes in the Sangun zone are thermally metamorphosed by

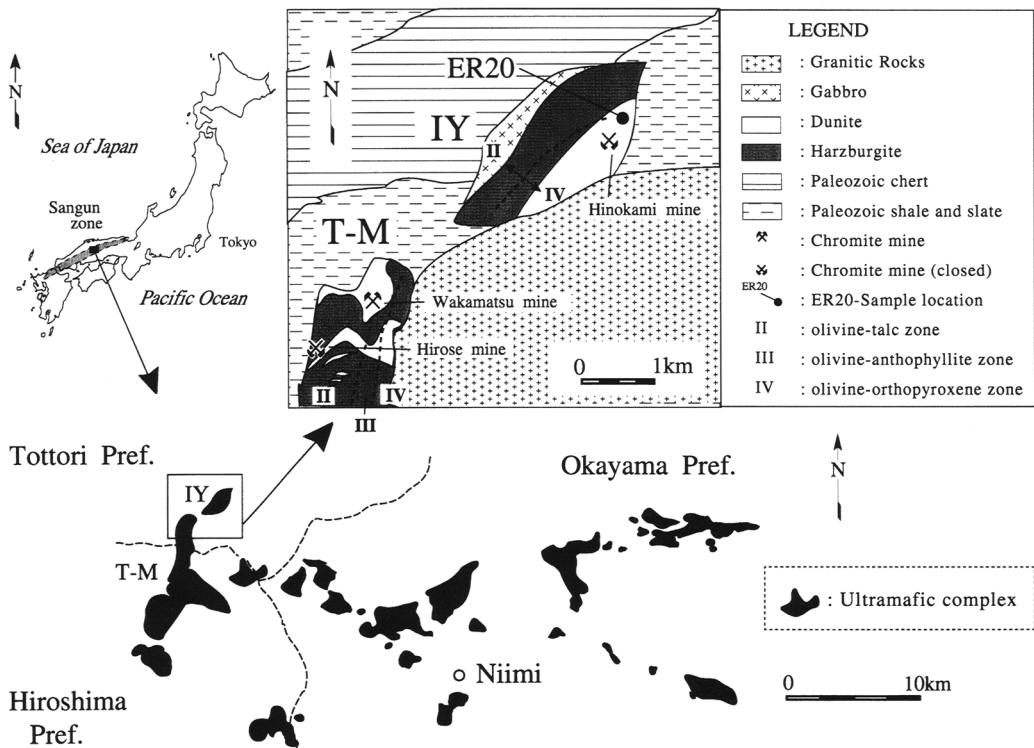


FIG. 1. The Inazumi-yama peridotite complex (IY) in the Sangun zone, southwestern Japan and the location of the meta-dunite, ER 20, within the complex. Both contact metamorphic mineral zones (Arai, 1975; Matsumoto *et al.*, 1995) and primary lithologies (Matsumoto *et al.*, 1995) are shown on the Inazumi-yama complex and the northern part of the Tari-Misaka complex (T-M).

Cretaceous granitic rocks to produce various types of meta-peridotites (Arai, 1975) (Fig. 1). The thermally metamorphic mineral zones for peridotitic rocks were examined by Arai (1975) and Matsumoto *et al.* (1995); five zones toward the granite contact are Zone Ia (chrysotile/lizardite; thermally unmetamorphosed), Zone Ib (antigorite), Zone II (olivine-talc), Zone III (olivine-anthophyllite) and Zone IV (olivine-orthopyroxene). The pressure of metamorphism is estimated to be very low, < 0.3 GPa, because of a stable assemblage of olivine + cordierite in meta-chromitites (Arai, 1975; Frost, 1975).

The Inazumi-yama ultramafic complex (Matsumoto *et al.*, 1995), which is a northern part of the Tari-Misaka ultramafic complex of Arai (1975), is lens-shaped, 3 km x 1 km in plan, and emplaced in Palaeozoic sediments (Fig. 1). The primary lithologies can be identified as dunite for the southeastern third and harzburgite for the rest of the complex as indicated by textures, such as pseudomorphs of orthopyroxene and the morphology of relics of chromian spinel (Matsumoto *et al.*, 1995). Small amounts of podiform chromitites formerly mined at Hinokami mine are associated with the dunite (Arai, 1980; Matsumoto *et al.*, 1995). The complex is thermally metamorphosed by the intrusion of the Cretaceous Inazumi-yama granite to the southeast (Arai, 1975). The complex has two metamorphic mineral zones as defined by Arai (1975) and Matsumoto *et al.* (1995), II and IV, depending on the distance from

the granite. Zone III (anthophyllite zone) is probably absent.

Whole-rock geochemistry

The dunite (ER 20) and other samples (dunite and chromitite) from the ultramafic complexes of the Sangun zone, southwestern Japan, were analysed for all PGE (Fig. 2) using a nickel sulphide fire assay preconcentration method followed by an ICP-MS finish. The dunites and chromitites from the Sangun zone are characteristically barren in PGE, with less than a tenth chondritic values, which is consistent with the intermediately depleted character of these rocks (Cr# of spinel ~0.5). The chromitites have a higher Os-Ir-Ru content than the dunites (Fig. 3) resulting in negative slope chondrite-normalized patterns (Fig. 2). The dunite, ER 20, has an elevated chondrite-normalized Pt and Pd content relative to the other samples giving it a positive slope chondrite-normalized pattern (Fig. 2). It is noteworthy that some of the other dunites exhibit similar but less prominent Pd enrichment relative to the chromitites (Fig. 2). These characteristics appear to be independent of metamorphic grade as the samples analysed belong to various metamorphic grades and as the positive and negative slopes are linked to igneous lithology they are more likely to be due to primary igneous processes.

Petrography

The PGM-bearing sample (No. ER 20) is a metamorphosed dunite, composed of olivine,

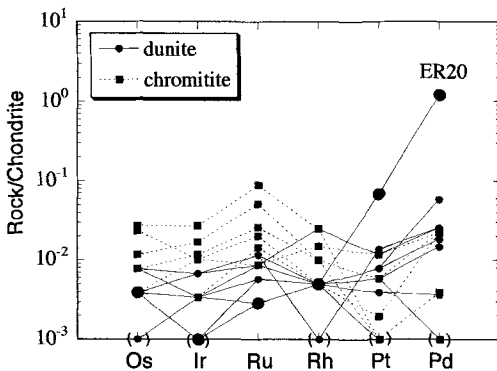


FIG. 2. Whole-rock chondrite normalized PGE distribution patterns of dunites and chromitites in the Inazumi-yama and other ultramafic complexes of the Sangun zone, southwestern Japan. Points in parentheses indicate values below the detection limits.

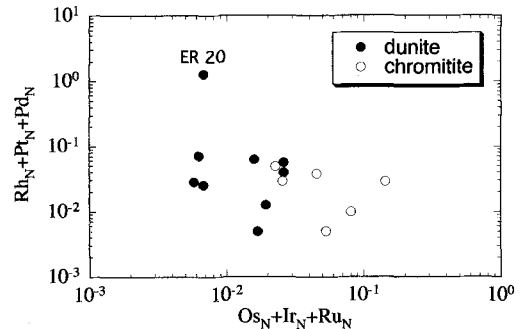


FIG. 3. Relationships between $(Os_N+Ir_N+Ru_N)$ and $(Rh_N+Pt_N+Pd_N)$ in the dunites and chromitites. Subscript N, chondrite-normalized. Note that the dunites are less enriched in Os, Ir and Ru than the chromitites.

antigorite, chlorite, talc, chromian spinel, Fe³⁺-rich chromite ('ferritchromite'), magnetite and sulphides. Chromian spinel or its pseudomorph is rounded in shape, possibly indicating a protolith of dunite (Matsumoto *et al.*, 1995). The sample is from Zone II adjacent to the boundary with Zone IV of Matsumoto *et al.* (1995). The olivine is relatively fine-grained, granular, and has a dusty appearance due to dissemination of minute grains of sulphides and magnetite, which is very similar to the characteristics of metamorphosed olivine in the nearby Tari-Misaka complex, indicating a deserpentinization origin (Arai, 1975). Chromian spinel is a primary mineral and has been partly or completely altered to opaque phases, Fe³⁺-rich chromite and magnetite during the thermal metamorphism and subsequent serpentinization. Chlorite is associated with altered chromian spinel. Talc forms fine-grained aggregates among metamorphic olivine grains, and antigorite has a lath-like morphology and also forms aggregates. The sample, therefore, has the mineral assemblage on the boundary of Zones Ib and II.

The sample is disseminated with sulphide grains which are irregular in shape and less than 0.2 mm across. The pentlandite-heazlewoodite composite grains are intergrown with antigorite laths, indicating their metamorphic origin. Pentlandite and heazlewoodite often demonstrate a complicated intergrowth (Fig. 4A). Pentlandite is sometimes free of heazlewoodite and contains equant magnetite grains (Fig. 4C) rather than magnetite laths characteristic of unmetamorphosed magnetite-pentlandite clusters in ultramafic lithologies (see Prichard *et al.*, 1996a).

Metamorphic olivines in the meta-harzburgite (from Zone IV; 600 to 650 °C) of the Tari-Misaka complex, to the south of Inazumi-yama complex (Fig. 1), sometimes contain chalcopyrite globules (2 µm across). Both the meta-harzburgite and meta-dunite contain ubiquitous galena (PbS), arsenides and sulph-arsenides or As-bearing sulphides associated with Ni-Fe sulphides irrespective of metamorphic grade. Galena forms veinlets in lower-grade rocks and globules in higher-grade rocks. Sphalerite, a Zn-bearing alloy and a Ni-Bi sulphide are rarely found in the metaperidotites of the Tari-Misaka complex.

The most abundant PGM, potarite, occurs as small globules or rods (<3 µm across) in composite grains of pentlandite and heazlewoodite (Fig. 4A,B). Another common PGM is stibiopalladinite (see 'Mineral chemistry' section

below) (<4 µm across), which is also located within composite grains of sulphide and sometimes cuts across pentlandite-heazlewoodite grain boundaries (Fig. 4C). Palladium-rich alloys (<2 µm across) are sometimes associated with potarite. A composite grain of sperrylite (PtAs₂) (5 µm across) and stibiopalladinite was found within a magnetite-Fe³⁺-rich chromite composite grain after chromian spinel (Fig. 4D). These PGM are characteristically arranged near the edge of sulphides, usually in contact with silicates (mainly antigorite), and are very minute, <5 µm across (Fig. 4). The exception is the sperrylite-stibiopalladinite grain which lies within altered chromian spinel.

A metaperidotite, possibly originally a harzburgite, from Zone IV (600 to 650 °C) of the Tari-Misaka complex contains a small (2 µm) globular Pd telluride at the edge of a pentlandite grain.

Mineral chemistry

Potarite and its associated minerals were analysed using a Cambridge 360 SEM with an energy dispersive Link system at the Cardiff University in Wales. Counting time was 100 s, analytical results were calibrated and corrected by a ZAF method and a cobalt standard was used as a reference during analysis. Selected analyses are listed in Table 1. Silicate and oxide mineralogies have been examined extensively by Arai (1975, 1980) and Matsumoto *et al.* (1997) and will not be described further here.

The potarite deviates slightly from stoichiometry; the Pd:Hg atomic ratio varies from 1:0.85 to 1:0.88, i.e. PdHg_{0.85-0.88} (Table 1). Despite the complicated phase relations on the Pd-Sb join at low temperatures (e.g. Kim and Chao, 1996) the Pd-Sb phase in the sample (ER 20) can be identified as stibiopalladinite. It always contains 3–5 at.% of Cu (Table 1). Its (Pd + Cu):Sb atomic ratio is 5:2; the largest grain, for example, has the composition of (Pd_{4.80}Cu_{0.20})Sb_{2.01} (No. 2 of Table 1). The Pd-rich alloys are usually too small to be analysed, but one analysis demonstrates a composition of Pd-Pb-Cu-Hg (Table 1).

The sperrylite also deviates slightly from stoichiometry; the Pt:As atomic ratio is 1:1.84, i.e. PtAs_{1.84} (Table 1). Pentlandite contains ~1% of Co, and Ni:Fe and (Ni + Fe + Co):S atomic ratios are ~1 and ~0.531:0.469 (or ~8:7), respectively (Table 1). Heazlewoodite is almost free of Co and is stoichiometric; the Ni:Fe and (Ni + Fe):S atomic ratios are 0.977:0.023 and ~3:2,

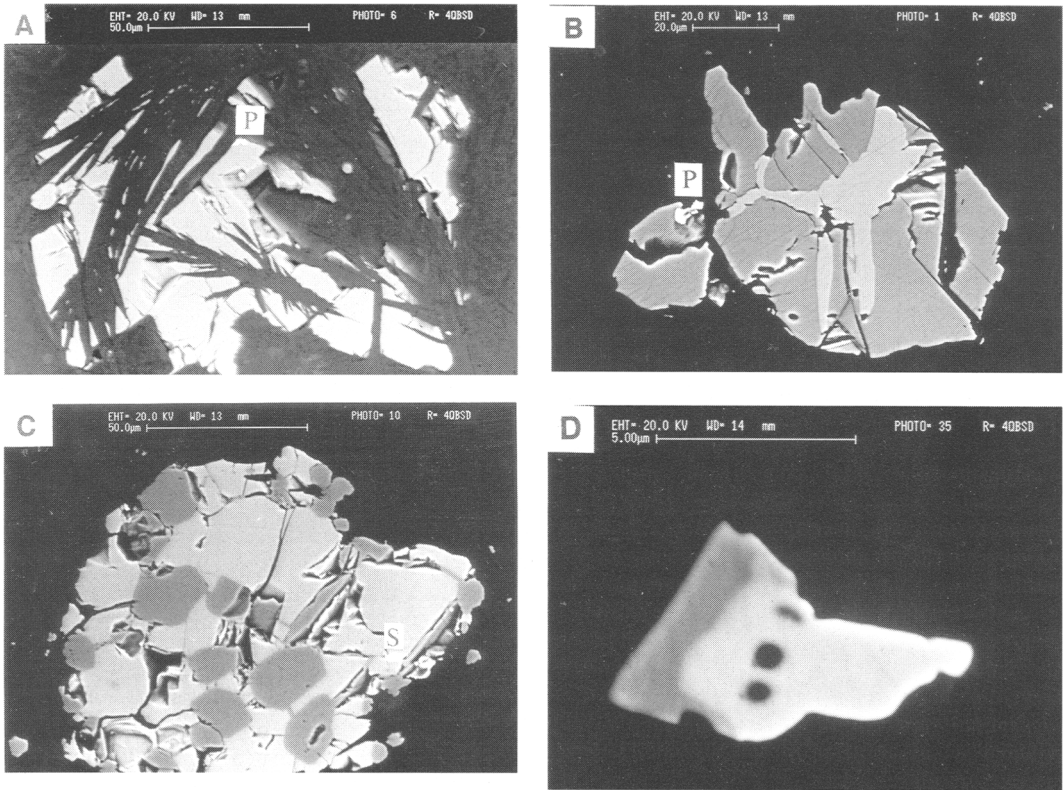


FIG. 4. Scanning electron micrographs of potarite and its associated minerals in the meta-dunite, ER 20. (A) Potarite [P; bright spot] at the edge of pentlandite, which is intergrown with antigorite (dark laths). Scale bar, 50 μm . (B) Potarite [P; bright spot] associated with a composite sulphide grain of pentlandite (darker) and heazlewoodite (brighter). Scale bar, 20 μm . (C) Stibiopalladinite [S; bright spot] in a composite grain of pentlandite (brighter) and magnetite (darker). Note the euhedral shape of the magnetite. Scale bar, 50 μm . (D) A composite grain of stibiopalladinite (darker) and sperrylite (brighter) within pentlandite (dark background). Scale bar, 5 μm .

respectively (Table 1). The chemistry and relative abundances of PGM are consistent with the whole-rock composition for PGE in dunites, i.e. $\text{Pd} > \text{Pt} \gg \text{other PGE}$ (Fig. 2).

Mode of occurrence of potarite: a review

The descriptions of the association of potarite in the literature either state or imply a secondary hydrothermal origin.

In the Merensky Reef and the U-2 chromitite layer, potarite is usually absent or only present as trace amounts and rarely occupies up to 30% of total PGM (Kinloch, 1982; McLaren and De Villiers, 1982). In this latter case potarite is characteristically accompanied by Pt-Fe alloys converted from Pt-Pd sulphides by post-magmatic

hydrothermal activity along conduits (Kinloch, 1982). The Pt-Pd arsenides and tellurides are sometimes associated with potarite (Kinloch, 1982; McLaren and De Villiers, 1982).

Prichard and Tarkian (1988) found one grain of potarite in the Shetland ophiolite. The potarite-bearing sample had a primary magmatic PGE concentration, modified subsequently by hydrothermal solutions resulting in an anomalously high As content (Lord *et al.*, 1994). The hydrothermal activity which produced this anomalous As content is ascribed to the presence of a granite intrusion in the vicinity of the Shetland ophiolite (Lord *et al.*, 1994; Neary and Prichard, 1985). Jedwab (1992) reported potarite from a hydrothermally altered part of the Zabargad peridotite in the Red Sea. Kucha (1982) described

TABLE 1. Selected analyses of PGM and sulphides in the ER 20 dunite

	1	1'	2	3	3'	4	5	6
Pd	34.81	37.22	66.44	47.06	49.98	n.d.	n.d.	n.d.
Pt	n.d.		n.d.	n.d.		56.66	n.d.	n.d.
Fe	1.86		n.d.	2.21		2.89	31.20	1.58
Ni	1.82		n.d.	1.88		n.d.	34.21	71.91
Co	n.d.		n.d.	n.d.		n.d.	1.36	0.02
Cu	1.03	1.10	1.69	7.91	8.40	n.d.	n.d.	n.d.
Pb	n.d.		n.d.	30.98	32.90	n.d.	n.d.	n.d.
Hg	57.69	61.68	n.d.	8.21	8.72	n.d.	n.d.	n.d.
Sb	n.d.		31.83	n.d.		n.d.	n.d.	n.d.
S	1.35		n.d.	2.61		0.83	32.91	26.14
As	n.d.		n.d.	n.d.		40.09	n.d.	n.d.
Total	98.56	100.00	99.96	100.86	100.00	100.47	99.68	99.65
size(μ m)	3		4	2		5	65	65

1, potarite; 2, stibiopalladinite; 3, Pd-Pb-Cu-Hg alloy with stibiopalladinite; 4, sperrylite; 5, pentlandite; 6, heazlewoodite; 5 and 6 make a composite grain and hosts potarite (No. 1); 1' and 3', Fe-Ni-S subtracted and recalculated to 100% from 1 and 3, respectively
n.d., not detected

high concentrations of Pd and Hg in the Kupferschiefer shales of Poland, and Grange (1996) found potarite in these shales. Kucha (1982) interpreted the high PGE content of the Kupferschiefer as a primary sedimentary feature but Mountain and Wood (1988b) suggested the possibility of the addition of PGE from hydrothermal solutions.

Discussion

Genesis of potarite

Mercury is highly incompatible and should be present only in trace amounts in ultramafic rocks. Potarite (Pd-Hg) is actually the main PGM in the meta-dunite (ER 20) from the Inazumi-yama complex. This contrasts with other known occurrences of potarite of low-temperature origin, where it is always subordinate in the PGM assemblages: for example, only one grain of potarite has been found among the abundant secondary arsenic, antimony and tellurium-bearing PGE in the Shetland ophiolite (e.g. Prichard and Tarkian, 1988; Prichard *et al.*, 1994).

Potarite from the Inazumi-yama dunite is always associated with pentlandite-heazlewoodite which is intergrown with antigorite, and thus clearly indicates a metamorphic origin within the granite contact aureole (Arai, 1975; Matsumoto *et al.*, 1995). The metamorphic temperature of the

Inazumi-yama dunite based on the silicate assemblage of olivine + talc + antigorite should be $\sim 500^\circ\text{C}$, nearly equivalent to the boundary temperature between Zones II and Ib at very low pressures (<0.3 GPa) (Berman *et al.*, 1986). This estimate is in accordance with the pentlandite + heazlewoodite assemblage, stable only at low temperatures (e.g. Naldrett, 1989).

Origin of Hg

Mercury may have been provided by the hydrothermal solution during the thermal metamorphism. It is well known that the Hg content in igneous rocks is uniform and low (0.2 ppm or less) and is relatively high in sedimentary rocks, especially in black shales with organic matter (e.g. Rankama and Sahama, 1950; Kucha, 1982; Krupp, 1988). Mercury is expected to be present only as a trace amount in rocks precipitated early from magmas (Rankama and Sahama, 1950). It is likely to be especially low in the mantle peridotite; pyrolitic mantle is estimated to have 0.01 ppm of Hg (McDonough and Sun, 1995). The Hg is highly mobile in hydrothermal solutions and forms mercury ores (e.g. Krupp, 1988; Peabody and Finaudi, 1992). It is possible, therefore, that the hydrothermal solutions passed through the surrounding Palaeozoic shales to leach and concentrate Hg, which reacted with

Pd in the dunite to form potarite (PdHg) (Fig. 5). Note that the hydrothermal solution could have originated from more than one source; it was probably a mixture composed of volatile components released from the granitic magma and produced by dehydration of serpentine and other hydrous minerals and groundwater heated by the granitic magma. The As and Pb in the associated PGM were provided by the granitic magma through hydrothermal solutions (Fig. 5). The frequent occurrence of Pb, As and Zn-bearing minerals in both the dunites and harzburgites supports the interpretation that there has been considerable addition of elements, perhaps including Hg, to the peridotites during the thermal metamorphism associated with the granite.

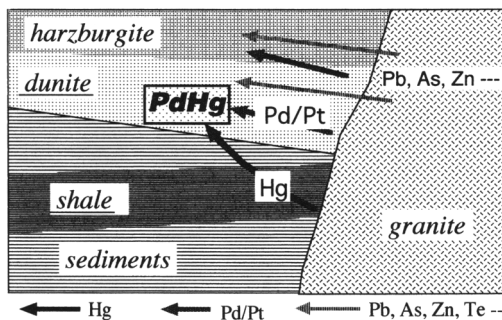


FIG. 5. A schematic illustration of the formation of potarite in metamorphosed dunite of the Inazumi-yama complex within the contact aureole of a granite. Some elements were mobilized by hydrothermal solutions (heated groundwater, magmatic water and released water from dehydrated serpentinite) during the thermal metamorphism. See text.

Remobilization of Pd

The concentration of Pd and Pt in the PGE-enriched dunite (ER 20) is probably in part primary because the dunites of this region tend to be enriched in Pt and Pd relative to the other PGE (Figs 2 and 3). It is well known that the concentration of Pd and Pt relative to Os, Ir and Ru is commonly accomplished by precipitation of magmatic sulphides (e.g. Naldrett, 1989). The notable concentration of Pd in some dunites (Fig. 3) could, therefore, have been caused by precipitation of primary magmatic sulphide(s), because such dunites, including ER 20, also have appreciable amounts of sulphides. The protolith of the meta-dunite ER 20 was initially enriched with sulphide(s), and therefore it is possible that it was also enriched with Pd and Pt. However, the Pd/Pt ratio of the meta-dunite (ER 20) is relatively high, ~9. The Pd/Pt ratio of the UG-2 layer of the Bushveld Complex ranges from 1.2 to 2.8 (McLaren and De Villiers, 1982) and from 0.31 to 4.2 in magmatic sulphides, according to a summary by Naldrett (1989). Therefore, the Pd/Pt ratio may have been modified during metamorphism. Palladium is known to be mobile in relatively low-temperature conditions. Prichard and Lord (1994) demonstrated the mobility of Pd relative to Pt during weathering of PGM-bearing dunite. McCallum *et al.* (1976) showed that Pd-bearing minerals break down in oxidizing conditions and that Pd is mobile under hydrothermal conditions. As well as the high Pd/Pt ratios in the Inazumi-yama complex, the location of a Pd-telluride in the meta-harzburgite is also good evidence for the mobility of Pd as

unmetamorphosed harzburgites rarely contain PGM. This is especially the case where the accompanying dunites are PGE-enriched, as the PGE have been extracted from the harzburgite to be concentrated in the overlying crustal ultramafics (Prichard *et al.*, 1996a). It is possible that Pd was remobilized within the dunite to be selectively added to the meta-dunite (ER 20) and was also introduced into the meta-harzburgite during the thermal metamorphism (Fig. 5).

Implications

Potarite and other PGM may be common in metamorphosed ultramafic rocks within contact aureoles of granitic masses which have yet to be examined for PGE and PGM. Dunites and chromitites from the Sangun zone are primarily barren in terms of PGE because of their depleted character (Cr# of spinel, ~0.5) possibly due to a mid-oceanic origin (Prichard *et al.*, 1996b). Contact metamorphosed ultramafics (especially dunites and chromitites) with a much more depleted character (Cr# of spinel 0.7 or more) of supra-subduction zone origin, which are rich in PGE due to high degrees of partial melting in more hydrous conditions (Prichard *et al.*, 1996), should be searched in future in order to understand more fully the behaviour of PGE and the formation of PGM at these intermediate temperature conditions (up to 650°C). Unmetamorphosed harzburgite is low in PGE, thus the mobility of PGE in these conditions can be checked by

examining metamorphosed harzburgites for PGM introduced during the metamorphism.

Summary and conclusions

(1) Potarite (Pd-Hg) is the main PGM in a dunite which was thermally metamorphosed at ~500°C within the contact aureole of a granitic mass from the Inazumi-yama ultramafic complex, southwestern Japan.

(2) Hg was supplied by the surrounding sedimentary rocks through hydrothermal solutions generated by a granite magma and reacted with primary igneous Pd concentrated with sulphide(s) in the dunite protolith. Palladium was remobilized during metamorphism to concentrate both in the meta-harzburgite and the meta-dunite. The Pd/Pt ratio in the meta-dunite was probably selectively enhanced during metamorphism and Pb, As and Zn were added to the metaperidotites from the granitic magma.

(3) Potarite and other secondary PGM formed at medium-temperatures (500 to 650°C) might be found in other thermally metamorphosed ultramafic rocks, especially in metamorphosed depleted ultramafic rocks of supra-subduction zone origin (the Cr# of spinel = 0.7 or more).

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