

## Palladium oxides in ultramafic complexes near Lavatrafo, Western Andriamena, Madagascar

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### ABSTRACT

Small (<2 km diameter), ultramafic intrusive complexes in the Andriamena region of Madagascar contain zones with disseminated chromite and sulphides which carry high concentrations of platinum-group elements (PGE). Assay of drill core from one complex, designated UM2, revealed three zones showing consistently high PGE grades. Mineralogical investigation of the UM2 core reveals that a small number of low reflecting, Pd-bearing platinum-group minerals (PGM) are present — always in association with a poorly characterized Pd stibio-arsenide [Pd<sub>3</sub>(Sb,As)] phase — in the shallowest of the three zones. Electron microprobe analysis of these PGM indicates the presence of oxygen and that at least two species exist. The resulting stoichiometries suggest that at least one species could be a hydrated form of palladinite [PdO.(H<sub>2</sub>O)<sub>n</sub>]. The other phase could be a hydroxide [Pd(OH)<sub>2</sub>] or a less strongly hydrated form of palladinite. Textural evidence suggests that the Pd-O species formed via the replacement of a precursor Pd-rich PGM, with only a limited removal of Pd, rather than via precipitation of a Pd-O PGM from a fluid that was Pd-bearing. The limited thermal stability of hydrated Pd oxides and the apparent restriction of the Pd-O phases to a shallow zone which is affected by the seasonal movement of groundwater, suggests that they may have formed at low temperatures via the leaching and replacement of other elements from a precursor Pd-rich PGM by oxygen and water during alternating water-saturated and dry conditions. If this is the case, the water table interface might be another environment, in addition to the surface, in which to look for the development of PGE oxides.

**KEYWORDS:** platinum-group elements, palladium, oxygen, hydrated oxides, Andriamena, Madagascar.

### Introduction

GEOCHEMICAL exploration carried out by workers at the BRGM (Salpéteur and Jezequel, 1992; Salpéteur *et al.*, 1995) has indicated that some mafic intrusive complexes near Lavatrafo in the Andriamena region of Madagascar (Fig. 1) contain high concentrations of the platinum-group elements (PGE). The complexes appear relatively small (<2 km across in surface outcrop), were emplaced into Archaean lower crustal granulites and amphibolites during a period of

crustal extension (Ohnenstetter *et al.*, 1991), and were subsequently re-equilibrated under greenschist facies conditions. Zircons recovered from apparently co-magmatic plagiogranites indicate ages of between 0.78–0.77 Ga. Guerrot *et al.* (1993) have indicated that these ages could be related to Pan African rifting between 0.80–0.75 Ga, but this interpretation has recently been questioned by Salpéteur *et al.* (1995) who suggest that the complexes are older and that the zircons might reflect a later post-tectonic granitic event.

Trenching and drilling have shown that dunites within the Lavatrafo UM2 and UM3 ultramafic complexes defined by Salpéteur and Jezequel (1992) contain zones of PGE mineralization. Since 1993 we have been studying the miner-

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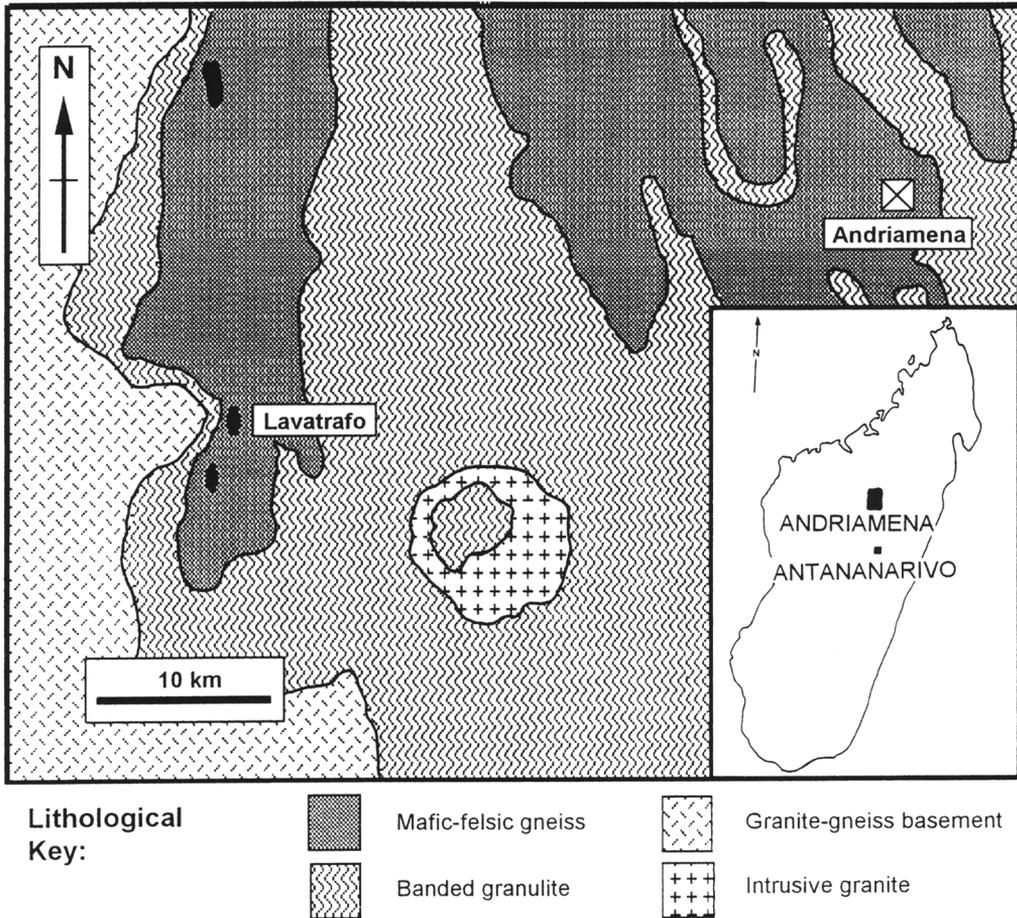


FIG. 1. Map of Madagascar showing the Andriamena area. Mafic-ultramafic intrusive complexes are shown in solid black.

alogical and geochemical characteristics of this mineralization as part of a European Union BRITE-EURAM project. More comprehensive papers dealing with all aspects of the work are currently in preparation but the style of the mineralization is unusual in that PGE enrichment is not associated with obvious enrichment in either Ni-Cu sulphides or chromite, as occurs in other deposits (Ohnenstetter and Johan, 1993; Ohnenstetter, 1996). Palladium phases showing low reflectance were found associated with aggregates of altered sulphides and other platinum-group minerals (PGM) in samples from the UM2 drill core.

Since the first account of a natural compound of palladium, iron and oxygen from Brazil, by

Johnson and Lampadius (1837), the existence of PGE oxides — marked by low reflectance in comparison to other PGM — has been suspected (Cabri *et al.*, 1981; Nixon *et al.*, 1990; Milliotti and Stumpfl, 1993; Jedwab *et al.*, 1993; Prichard *et al.*, 1994). Most reports of PGE oxides derive from alluvial occurrences (e.g. Cabri *et al.*, 1981; Weiser, 1990; Jedwab *et al.*, 1993; Jedwab, 1995; Augé *et al.*, 1995). *In situ* PGE oxides or hydroxides are known to occur within chromitites (e.g. Nixon *et al.*, 1990; Milliotti and Stumpfl, 1993; Prichard *et al.*, 1994; Augé and Legendre, 1994; Augé and Maurizot, 1994) but these are principally Ru and Ir species which are associated with altered laurite [RuS<sub>2</sub>] crystals in replacement zones and may themselves have formed as a result

of lateritization (Milliotti and Stumpfl, 1993; Augé and Legendre, 1994). Rare Pt-Fe oxides have also been observed as small grains associated with Ru-Mn-Fe oxide-hydroxides included in altered chromite from New Caledonia (Augé and Legendre, 1994). Finally, in Shetland, a low reflectance Pt-oxide and Pd ochres resulting from the alteration of Pd antimonides occur in chromite-rich dunite and may result from the present-day weathering of pre-existent PGM (Prichard *et al.*, 1994).

Despite the early account given by Johnson and Lampadius (1837), the existence of definite Pd oxide minerals has only very recently been confirmed. An apparent Pd-Hg oxide, which appeared to consist of ~90% PdO and 10% HgO, was reported in heavy mineral concentrates from Itabira in Brazil by Clark *et al.* (1974) and the mineral palladinite (PdO) was firmly identified for the first time in the Itabira concentrates by Jedwab *et al.* (1993). The material is more extensively described in Jedwab (1995). Palladinite, as well as Ce-rich palladinite and Pt and Ru oxygenated compounds, have more recently also been reported from various localities in the former Zaïre (Jedwab, 1995; 1997).

Nevertheless, PGE oxides, and many Pd-O species in particular, remain poorly characterized. Prior to this study, Salpéteur *et al.* (1995) described a possible mixture of palladinite and a Pd-Cu alloy associated with what they interpreted as a relic of vincentite [Pd<sub>3</sub>(As,Sb,Te)] in Fe-rich sulphide boxworks from the ferralitic soils covering some of the PGE-rich ultramafic complexes at Lavatrafu. With this in mind, the aim of this study was to try to locate and characterize any poorly reflecting Pd-rich PGM in bedrock beneath the weathered horizon in the same area. These species may have formed in a different manner to oxides generated by lateritization and are therefore important to an understanding of the environments in which PGE oxides might occur.

### Description of the mineralization

Assay of core from the UM2 complex shows that consistently high PGE concentrations are found in three main zones, including an upper dunite zone (designated 2C) 40.0–41.5 m down the core (Fig. 2) which contains dull, Pd-rich PGM. All of these enriched zones are located below the supergene lateritic alteration described by Salpéteur *et al.* (1995). In hand specimen, the

2C zone dunites are medium grained and relatively fresh although small veins filled with serpentine and magnesite are also present. In thin section, the dunites comprise >90% olivine (Fo<sub>84–87</sub>), with <1% phlogopite and ~1% each of interstitial Cr-spinel and sulphides. The remaining volume is occupied by veins and cracks filled with serpentine, chlorite and magnesite. Development of secondary hydrosilicates is uneven and, on a millimetre-scale, the extent of replacement varies between 5 and 20%.

The PGM assemblage throughout the whole complex is dominated by Pt and Pd arsenides and stibio-arsenides, while sulphides and sulpharsenides are rare (Table 1). The most common textural association in which PGM are found is on the margins of interstitial sulphide (pyrrhotite, pentlandite and chalcopyrite) aggregates with one or more faces of the PGM in contact with olivine or secondary hydrosilicates. The anhedral sulphide aggregates show variable degrees of alteration, including replacement by Fe-rich carbonates and hydroxides. The most extensive replacement of sulphides is strongly correlated with the development of secondary hydrosilicates and may be linked to the action of serpentinizing fluids. Platinum-rich PGM and most Pd-rich phases remain unaltered by secondary fluids but five low reflecting Pd-rich PGM have been positively identified by optical and scanning electron microscopy in the 2C zone. To date, similar minerals have not been found in the other PGE-rich zones of the complex.

### Analytical methodology

All of the PGM were initially examined and qualitatively characterized by energy-dispersive X-ray spectrometry (EDS) using a Jeol JSM 6400 scanning electron microscope at the University of Manchester (operating conditions in McDonald *et al.*, 1995). The PGM in aggregates containing dull, Pd-rich phases were subjected to quantitative analysis by wavelength dispersive X-ray spectrometry (WDS) using a Cameca CAMEBAX microprobe at Manchester. Operating conditions and standards are given in a footnote to Table 2. The dull, Pd-rich phases always gave low totals and were subsequently analysed for oxygen and other major elements by WDS using a Cameca SX50 microprobe at the BRGM in Orleans. Operating conditions and standard procedures for oxygen analyses were as reported in Augé and Legendre (1994). Agreement between the two

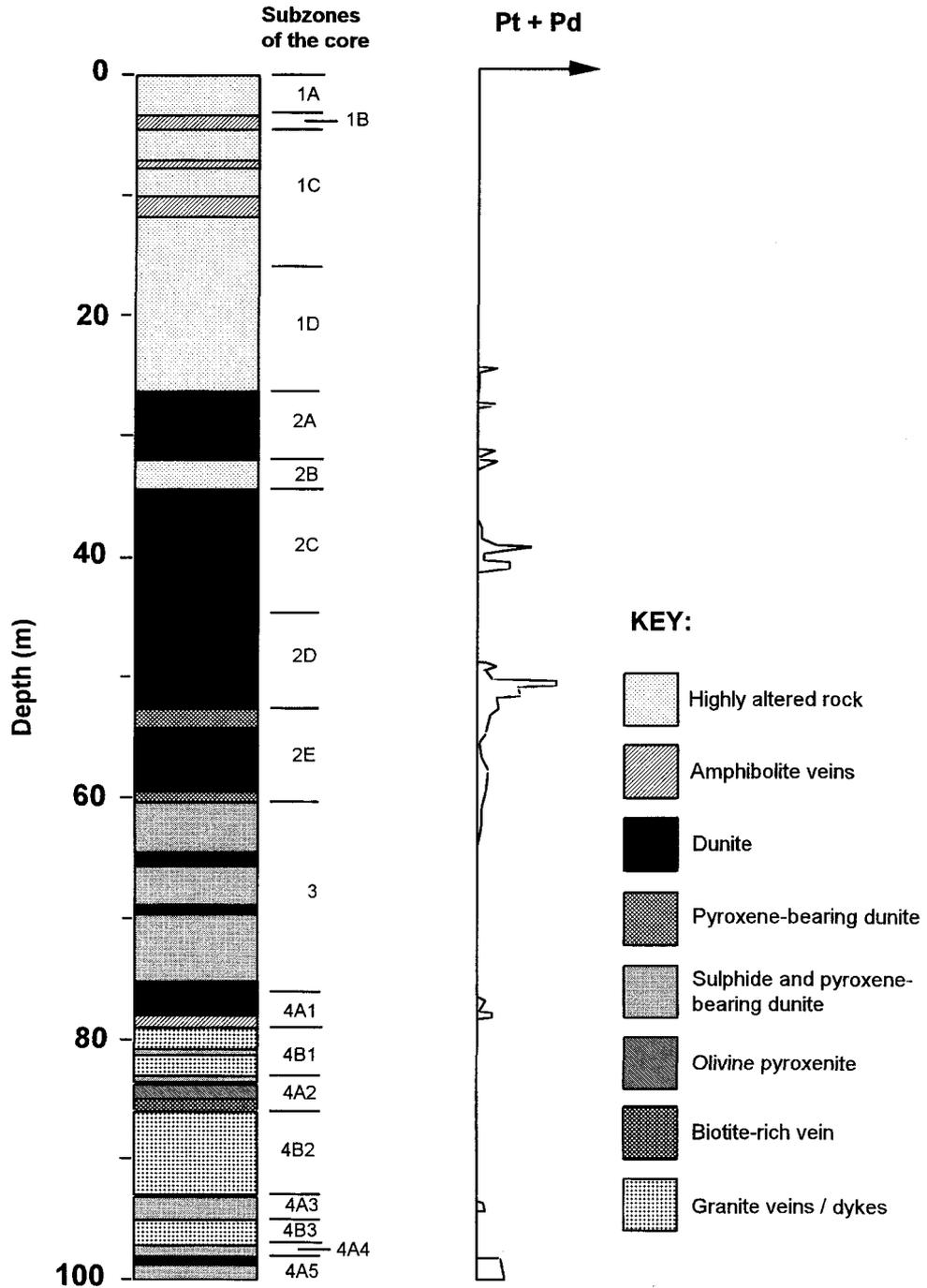


FIG. 2. Lithological summary of the LVF-C8 drill core from the UM2 complex (from Ohnenstetter *et al.*, 1996; and in prep.). Subzones and the relative tenor of PGE mineralization are indicated. Modified from Ohnenstetter *et al.* (1994).

TABLE 1. Relative amounts of different PGM identified in the LVFC8 drill core.  $N_{\text{obs}}$  indicates the number of crystals of that PGM observed. The other columns show the number of PGM associated with sulphides alone (BMS), at the margin between sulphides and silicates (SMR) and in the silicates (SIL)

Platinum-Group Mineral	$N_{\text{obs}}$	BMS	SMR	SIL
Sperrylite [PtAs <sub>2</sub> ]	20	2	8	10
Pd stibio-arsenide [Pd <sub>3</sub> (Sb,As)]	6	0	6	0
Guanglinitite [Pd <sub>3</sub> (As,Sb)]	4	1	3	0
Pd-oxide phases	5	0	5	0
Palladoarsenide [(Pd, Pt) <sub>2</sub> As]	2	0	2	0
Unknown [(Pd, Fe,Cu) <sub>21</sub> (AsS) <sub>5</sub> ] phase	2	0	2	0
Michenerite [PdBiTe]	2	0	1	1
Irarsite [IrAsS]	2	0	1	1
Palladium Telluride	1	0	0	1
Hollingworthite [RhAsS]	1	0	0	1
Unknown [(Pd,Cu) <sub>13</sub> As <sub>2</sub> ] phase	1	0	1	0
Unknown [(Pd,Cu) <sub>9</sub> (AsS) <sub>2</sub> ] phase	1	0	1	0
Unknown [(Pd <sub>11</sub> Ni <sub>12</sub> )As <sub>11</sub> ] phase	1	1	0	0
Total	48	4	30	14

microprobes for the concentrations of Pd, Fe, Ni, Cu, As and Sb in the same crystal was generally very good. Relative differences varied between 0.3–2.0% for major cations and between 2–6% for minor cations.

## Results

A PGM aggregate from a dunite within the UM2 complex is shown in Fig. 3 and analyses of the phases present are given in Table 2. The large crystal is sperrylite [PtAs<sub>2</sub>], and the three smaller crystals to the right of it appear to be an ill-defined Pd-Sb-As species. Based on simple stoichiometry, the phase is roughly [Pd<sub>3</sub>(Sb,As)] and resembles the 'vincentite'-like Pd stibio-arsenide reported by Salpéteur *et al.* (1995; see their Table 3). The composition is unusual in that the preliminary EDS analysis showed that the material contains no Te (cf. type locality vincentite [Pd<sub>3</sub>(Sb,As,Te)] as defined by Stumpfl and Tarkian, 1974) and that on the basis of the WDS analyses it commonly has a small excess of Sb over As (Table 2). Table 1 shows that As occurs in many other PGM, while the Pd stibio-arsenide is the principal host for Sb and the Sb enrichment in this phase may simply reflect competition for As with the other PGM.

The three Pd stibio-arsenide crystals are in contact with a fractured, dull grey phase designated O1. The fractures are filled with

goethite and were deliberately avoided. The O1 phase contains 23.3 and 67.9 wt.% of O and Pd respectively and has the best-fit stoichiometric formula [Pd<sub>0.86</sub>Fe<sub>0.03</sub>Ni<sub>0.04</sub>Cu<sub>0.11</sub>]<sub>1.04</sub>O<sub>1.96</sub> (based on 3 atoms). The two Pd stibio-arsenide crystals (V1 and V2) on the right of the aggregate are also in contact with a different Pd phase (designated O2) which has a lower average atomic number than O1. The WDS analysis indicates that it contains 50.4 wt.% Pd and 40.0 wt.% oxygen, with a stoichiometry of [Pd<sub>0.78</sub>Fe<sub>0.07</sub>Ni<sub>0.04</sub>Cu<sub>0.07</sub>]<sub>1.06</sub>O<sub>4.04</sub> (based on 5 atoms).

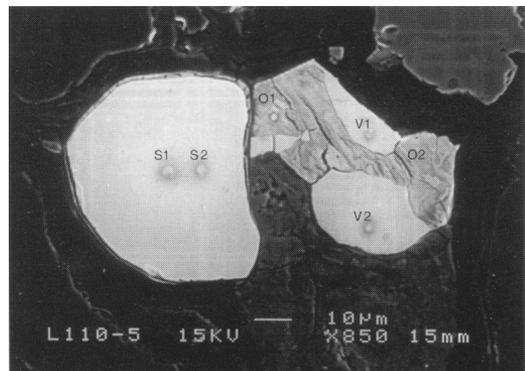


FIG. 3. Secondary electron image of a PGM aggregate from a dunite in the 2C subzone of the UM2 complex. Annotated points mark analysis points for the data in Table 2.

TABLE 2. Microprobe analyses (wt.%) of Pt and Pd phases in the PGM aggregate. S1, S2, V1 and V2 by the CAMEBAX. O1 and O2 by the SX50. Corresponding atomic percent are shown in brackets. Positions of the analysis points are indicated in Fig. 3

	Pt	Pd	Fe	Ni	Cu	As	Sb	Bi	S	O	Total
S1	59.23 (34.90)	0.00 (0.00)	0.10 (0.20)	0.00 (0.00)	0.00 (0.00)	41.00 (63.61)	0.13 (0.10)	0.00 (0.00)	0.31 (1.19)	0.00 (0.00)	100.67
S2	59.20 (34.84)	0.00 (0.00)	0.08 (0.17)	0.00 (0.00)	0.00 (0.00)	41.11 (63.83)	0.13 (0.10)	0.00 (0.00)	0.28 (1.06)	0.00 (0.00)	100.80
V1	0.00 (0.00)	74.68 (72.01)	0.14 (0.44)	0.00 (0.00)	0.81 (1.35)	8.92 (12.24)	16.35 (13.96)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	100.90
V2	0.00 (0.00)	73.80 (70.26)	0.41 (0.76)	0.00 (0.00)	1.70 (2.85)	8.90 (12.09)	16.76 (14.04)	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	101.57
O1	0.78 (0.18)	67.85 (28.52)	1.36 (1.09)	1.60 (1.22)	4.84 (3.41)	0.00 (0.00)	0.00 (0.00)	1.41 (0.30)	0.13 (0.18)	23.29 (65.10)	101.26
O2	0.00 (0.00)	50.42 (15.33)	2.23 (1.29)	1.51 (0.83)	2.83 (1.44)	0.00 (0.00)	0.00 (0.00)	0.89 (0.14)	0.06 (0.06)	40.02 (80.91)	97.96

Key: S1, S2 = sperrylite; V1, V2 = 'vincentite-like' Pd stibio-arsenide; O1, O2 = Pd oxide.

#### CAMEBAX Operating Conditions:

Accelerating voltage, 20 kV; Incident beam current, 3 nA (Faraday Cage); Focused beam size, 2–4  $\mu\text{m}$ ; Count time, 30 s (Pt, Pd) 100 s (other elements); Detector system, Link Analytical AN10855; Spectrum processing, ZAF-4 FLS; X-ray lines and standards - Pt- $L\alpha$ , Pd- $L\alpha$ , Fe- $K\alpha$ , Ni- $K\alpha$ , Bi- $M\alpha$  (pure metals), Cu- $K\alpha$ , Sb- $L\beta$  (chalcostibite), As- $L\alpha$  (arsenopyrite), S- $K\alpha$  (sphalerite). Detection limits (wt.%): Pt (0.22), Pd (0.09), Fe (0.07), Ni (0.04), Cu (0.06), As (0.08), Sb (0.21), Bi (0.14), S (0.03).

Three other dull PGM crystals found to date (but not yet analysed for oxygen) show similar features to the O1 phase shown in Fig. 3: namely, a low total with 64–66 wt.% Pd, a shared grain boundary with a Pd stibio-arsenide similar to V1 or V2, and an overall shape which follows the margins of the larger mineral (PGM + altered sulphide) aggregate as if it originally formed a component of it.

#### Discussion and conclusions

There is apparently an excess of oxygen in the O1 and O2 phases compared with PdO. This cannot be accounted for by oxides of Fe, Ni or Cu and must be a feature of the O1 and O2 materials. Higher oxides such as PdO<sub>2</sub> are unstable (Westland, 1981; Cotton and Wilkinson, 1988), but the presence of hydrogen in the structure could permit a number of possible species. Given the analytical uncertainty it is possible that the O1 species could be related to Pd(OH)<sub>2</sub> (Wood, 1991) or the hydrated monoxide PdO.H<sub>2</sub>O. Both are known to form solids within the stability field of water (Westland, 1981; Wood, 1991). The simple

hydroxide Pd(OH)<sub>4</sub> and the hydrated dioxide PdO<sub>2</sub>.2H<sub>2</sub>O are only stable outside the stability field of water (Westland, 1981; Wood, 1991) and are unlikely candidates for the O2 species. Therefore a strongly hydrated monoxide species approaching PdO.3H<sub>2</sub>O seems the most likely means of accounting for both the oxygen excess and the slightly low total found in O2 (c.f. the Ru oxides reported by Augé and Legendre, 1994).

While recognising the restricted nature of the dataset at present, it is nonetheless difficult to explain the textural features observed in the Pd-O phases via precipitation of oxides or hydroxides into open space from some secondary fluid which was Pd-bearing. Based on the textural association, it seems more likely that there was an unidentified precursor Pd mineral that initially grew in association with the Pd stibio-arsenide and which may have been subsequently converted to either Pd(OH)<sub>2</sub> or hydrated PdO with only limited removal of Pd. If so, this implies that Pd may not be significantly remobilized by the fluids which affected the UM2 dunites. These include greenschist facies fluids and those associated with the early stages of serpentinization. However, this

may not preclude Pd becoming mobile during very extensive serpentinization (cf. Wood, 1991).

There is no clear evidence at present for what the suggested precursor Pd species was. Jedwab (1997) found palladinite in association with keithconnite  $[Pd_{3-x}Te]$ , oosterboschite  $[(Pd,Cu)_7Se_5]$  and potarite  $[Pd(Hg,Au)]$  in strata-bound copper deposits at Shaba and suggested that palladinite formed from these precursors. None of the possible Pd-binding elements (Au, Hg, Se and Te) was quantitatively analysed in this study but bearing in mind the close proximity to 100% of the O1 and O2 analyses and the absence of X-ray peaks for these elements in the qualitative EDS analysis, it seems unlikely that they are currently present at significant concentrations in the two Pd-O species.

Given the location of the Pd-O species beneath the weathering horizon; two possible mechanisms for complexing Pd with O and H suggest themselves: (a) replacement of the precursor PGM during serpentinization; or (b) replacement during seasonal fluctuations in the local water table which produce alternating water saturated and moderately aerated conditions within the rock during the wet and dry seasons of the year (see Salpéteur and Jezequel, 1992). If the Pd-O species formed as a result of serpentinization, one might expect to find them throughout the complex, whereas, even after an extensive search of the other PGE-rich zones, they have only been found to date in the 2C zone. This zone is located approximately 20 m beneath the current land surface (Martel Jantin *et al.*, 1991) and is very likely to be subjected to seasonal variations in water content.

If the stoichiometry of the O2 species establishes it as a very probable hydrated oxide, then, given the limited thermal stability of such compounds (typically  $\ll 100^\circ\text{C}$ ; Cotton and Wilkinson 1988), it must have formed under relatively low temperature conditions. This does not completely exclude serpentinization processes (reactions generally take place between 85 and  $500^\circ\text{C}$ ; Wenner and Taylor, 1974) but places the possible reaction conditions firmly within the region typified by groundwater. Furthermore, seasonal lowering of the water-table and drying of the rock would promote the incorporation of water of crystallization within the material whereas serpentinization is a process in which the rock is constantly wet and would not necessarily produce this. For these reasons we suggest that the Pd-O phases probably developed

in a dunite zone which was subject to the seasonal movement of air and groundwater. This type of process at the water-table interface, and particularly the removal of non-PGE components of the precursor mineral, might also explain the development of other PGE oxides in other parts of the world, which also appear along with secondary minerals, but are not clearly associated with either weathering or lateritization.

Furthermore, following erosion and the introduction of the minerals into the soil profile, hydrated oxides may become repeatedly baked during the tropical dry season. Hydrated Pd oxides can be dehydrated with heating to produce  $PdO.(H_2O)_{1-x}$  or eventually Pd (Cotton and Wilkinson, 1988). These products closely resemble the palladinite and Pd(Cu) alloy associated with Pd stibio-arsenide which were found in the overlying ferralitic soil by Salpéteur *et al.* (1995).

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