

IN SITU ALTERATION OF PLATINUM-GROUP MINERALS AT LOW TEMPERATURE: EVIDENCE FROM SERPENTINIZED AND WEATHERED CHROMITITE OF THE VOURINOS COMPLEX, GREECE

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ABSTRACT

Chromitite samples from the Vourinos ophiolite complex, in northwestern Greece, are found to contain platinum-group minerals (PGM) derived from the *in situ* alteration of primary (magmatic) PGM at low temperature. Primary laurite and ruthenian pentlandite located adjacent to cracks in partially serpentinized chromitite are replaced along their rim by metallic Ru and awaruite. Laurite in serpentine displays a rim depleted in S, Ir, and Os, and enriched in Fe and Ni. Several PGE alloys enriched in Ir, Pt, and Pd (Ir–Rh–Fe–Ni–Cu, Ni–Fe–Pt, Cu–Pt–Pd), and an unknown Ru–Os–Ir–Fe compound, were discovered in strongly weathered chromitite from Agriates, usually associated with chlorite, ferrian chromite, and abundant limonite. Experimental monitoring of the fluorescence effect due to chromite in the analysis of various PGM leads to the inference that the Ru–Os–Ir–Fe compound contains oxygen. It was not possible to establish if the mineral is an intergrowth of Ru-rich alloy with Fe-hydroxide (goethite or limonite) or a true PGE oxide. On the basis of the restricted occurrence of these PGM to weathered chromitite, as well as paragenetic and compositional considerations, the secondary assemblage seems to have formed at low temperatures by *in situ* desulfurization of a PGM sulfide precursor, during serpentinization, followed by oxidation of the desulfurized PGM, under conditions of weathering.

Keywords: platinum-group minerals, alteration, serpentinized chromitite, weathered chromitite, Vourinos, Greece.

SOMMAIRE

Des échantillons de chromitite provenant du complexe ophiolitique de Vourinos, dans le secteur nord-ouest de la Grèce, contiennent des minéraux du groupe du platine (MGP) dérivés par l'altération *in situ* à faible température de minéraux primaires (magmatiques). La laurite et la pentlandite ruthénifère se trouvant le long de fissures dans la chromitite partiellement serpentinisée sont remplacées à leur bordure par le Ru natif et l'awaruite. La laurite piégée dans la serpentine a une bordure appauvrie en S, Ir, et Os, et enrichie en Fe et Ni. Plusieurs alliages des éléments du groupe du platine enrichis en Ir, Pt, et Pd (Ir–Rh–Fe–Ni–Cu, Ni–Fe–Pt, Cu–Pt–Pd), et un composé à Ru–Os–Ir–Fe méconnu ont été découverts dans des échantillons de chromitite fortement météorisés d'Agriates, généralement en association avec chlorite, chromite enrichie en Fe³⁺, et limonite abondante. Un contrôle expérimental de l'effet de fluorescence dû à la chromite dans l'analyse des particules de MGP nous fait penser que le composé à Ru–Os–Ir–Fe contient de l'oxygène. Par contre, il n'a pas été possible d'établir si le minéral est en fait une intercroissance d'un alliage riche en Ru et d'hydroxyde de fer (goéthite ou limonite), ou bien vraiment un oxyde de Ru. D'après la distribution de ces MGP limitée aux échantillons de chromitite météorisés, ainsi que les considérations de paragenèse et de composition, l'assemblage de minéraux secondaires se serait formé à faible température, par perte de soufre *in situ* d'un minéral primaire précurseur, au cours de la serpentinisation, suivie d'une oxydation du minéral néoformé dans un milieu de météorisation active.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, altération, chromitite serpentinisée, chromitite météorisée, Vourinos, Grèce.

INTRODUCTION

It is commonly held that platinum-group minerals (PGM) associated with chromitites are magmatic in origin. They generally consist of alloys, sulfides and sulfarsenides that are believed to have crystallized before and during the precipitation of chromite. Paragenetic and textural relationships among different phases

are generally consistent with magmatic conditions involving the increase of sulfur fugacity with decreasing temperature (Stockman & Hlava 1984), leading, in some case, to the appearance of an immiscible sulfide liquid in the chromite-forming system. On the other hand, there is now convincing evidence that primary PGM may become unstable during postmagmatic, supergene evolution of the ultramafic host (Bowles 1986, 1987,

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Bowles *et al.* 1994). Several recent studies have confirmed that *PGM* can be in some way modified or altered as a result of the mobility of the platinum-group elements (*PGE*) at a relatively low temperature. Inversion of the $f(S_2)$ magmatic trend can take place during serpentinization, and formation of native *PGE* instead of sulfides is generally favored. Stockman & Hlava (1984) argued that Ru-rich alloys in chromitites of southwestern Oregon may have originated by desulfurization of primary laurite during serpentinization, the process involving addition of Fe – Ni to the reduced *PGM*. Formation of native *PGE* and alloys as a result of low-temperature secondary alteration was subsequently reported from a number of *PGM*-mineralized chromitites (Prichard & Tarkian 1988, McElduff & Stumpfl 1990, Nilsson 1990, Kieser 1994, Prichard *et al.* 1994). In particular, the alteration of laurite to form native Ru at low temperature was conclusively

demonstrated in chromitites of Ronda, Spain (Torres-Ruiz *et al.* 1996).

As part of a comparative study of chromite-related *PGE* mineralization in upper-mantle orogenic massifs, an overview of *PGM* mineralization in the Vourinos chromitites was undertaken. The results of the previous investigations were generally confirmed; they show the existence of primary Ru – Os – Ir *PGM* (laurite, irarsite, Os – Ir alloys) as inclusions in fresh chromite (Augé 1985, 1988, Legendre & Augé 1986, Augé & Johan 1988). A distinctive paragenetic assemblage of *PGM* in apparent disequilibrium with magmatic conditions was also discovered. The assemblage suggests an origin at low temperature, by *in situ* desulfurization of pre-existing *PGM* sulfides. In this paper, we describe the mineralogy, textural relations and composition of these *PGM* and their associated minerals, and discuss genetic aspects of the mineralization.

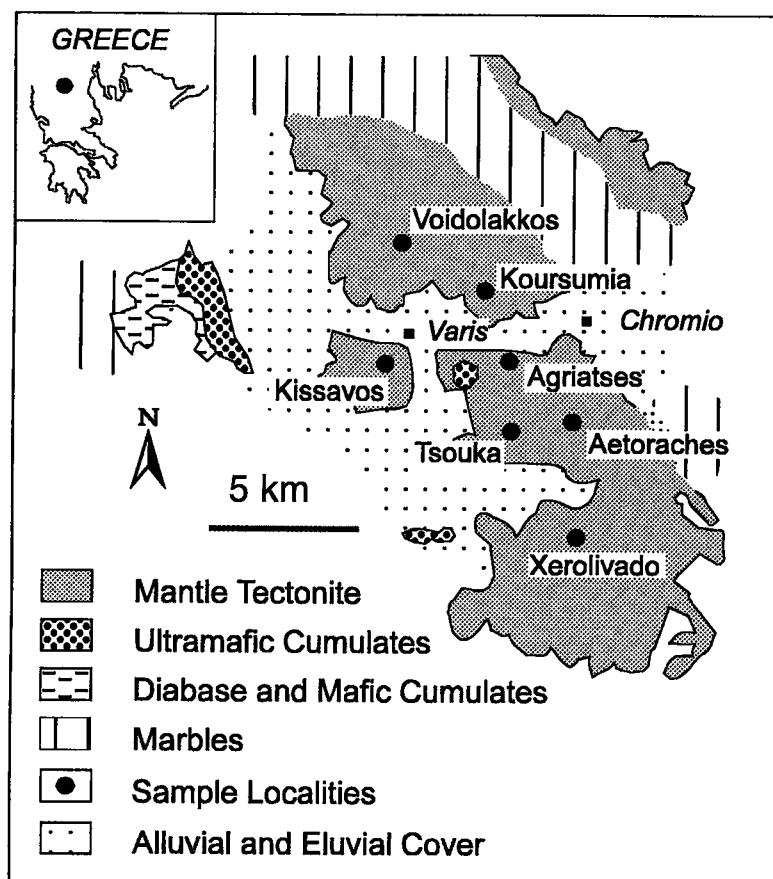


FIG. 1. Geological sketch-map of the Vourinos ophiolite complex, showing location of the chromite mines and chromitite occurrences examined in the present work.

TABLE 1. MINERALOGY AND FREQUENCY OF PGM GRAINS IN THE SAMPLES INVESTIGATED

Sample	Locality	Source	Ore type	Degree of serpentinization	PGM	No. of grains
VS 1	Kissavos	In place	Massive	Strong	Laurite	2
VS 2	Kissavos	Dump	Massive	Strong	Laurite	1
VS 3	Kissavos	In place	Leopard	Strong	Laurite	2
VS 5	Agriatses	Dump	Massive	Strong	Laurite	2
					Irarsite	1
VS 6	Agriatses	Dump	Massive	Strong	Secondary PGM	16
					Laurite	1
					Secondary PGM	4
VS 11	Voidolakkos	Dump	Leopard	Weak	Laurite	1
VS 12	Voidolakkos	Dump	Massive	Weak	Os-Ir-Ru alloy	1
					Ruthenian pentlandite	1
VS 13	Voidolakkos	Dump	Schlieren	Weak	Laurite	1
					Secondary PGM	1
VS 14	Koursoumia	Dump	Massive	Strong	Laurite	2
VS 15	Aetoraches	In place	Schlieren	Medium	Laurite	1
VS 16	Aetoraches	In place	Schlieren	Strong	Laurite	1
VS 18	Xerolivado	Stock pile	Schlieren	Medium	Os-Ir-Ru alloy	1
					Cupro-iridsite	1
VS 19	Xerolivado	Stock pile	Schlieren	Medium	Laurite	1
VCR 2	Xerolivado	Stock pile	Schlieren	Medium	Laurite	1

GEOLOGICAL SETTING AND THE MATERIAL INVESTIGATED

The Vourinos ophiolite complex (Fig. 1) extends over about 400 km² in northwestern Greece. Although tectonically disrupted and affected by serpentinization, the complex constitutes an almost complete ophiolite suite of early to middle Jurassic age. More than 700 occurrences of chromitite ore, including some of the largest producing chromium mines in the country, are found in the complex, mostly in the mantle tectonite unit. Size, morphology, and textures typical of ophiolitic chromitite, disseminated, schlieren, leopard, and massive ore, have been described (Economou *et al.* 1986, Roberts *et al.* 1988).

During this investigation, a total of 20 chromitite samples were collected in place or from stockpiles and dumps in mining operations at Kissavos, Agriatses, Voidolakkos, Koursoumia, Aetoraches, Xerolivado, and Tsouka (Fig. 1). The samples containing PGM are listed in Table 1. The samples are representatives of different types of ore and exhibit partial (<10%) to almost complete serpentinization. In the less-altered samples from Voidolakkos, Aetoraches, and Xerolivado, pseudomorphic serpentine develops on olivine relics, and serpentine veins are rare. In the most intensely serpentinized samples (Kissavos, Agriatses), relics of olivine are absent, and serpentine displays a felted texture, with abundant cross-cutting veins (of serpentine). The samples from Agriatses were collected in the old mine

dump, and exhibit evidence of long exposure to weathering, resulting in clay-rich and ferruginous crusts.

The chromite locally shows pull-apart textures and brecciation, and invariably is transformed into Mg-Al-poor and Cr-Fe³⁺-rich "ferritchromit" (hereafter referred to as ferrian chromite) along the rim and cracks, whereas the core of grains is usually free of such alteration. Primary inclusions in fresh chromite consist of Ni-Fe-Cu sulfides (pentlandite, pyrrhotite, chalcopyrite, bornite), silicates (olivine, pyroxenes), and the PGM (Table 1). Serpentine and chromian clinoclase constitute the most common filling of cracks and fissures in the chromite, usually associated with the ferrian chromite alteration and, in some cases, accompanied by Cr-rich magnetite. The secondary opaque-mineral assemblage also comprises pentlandite, millerite, heazlewoodite, Ni-Fe alloys (awaruite) and native copper occurring in the ferrian chromite alteration zones or in the silicate matrix to the chromite. Abundant limonite developed along cracks as minute botryoidal aggregates in the weathered samples of Agriatses. Several PGM were discovered as part of the secondary paragenesis (Table 1).

EXPERIMENTAL

Methods of investigation

Two polished sections were prepared from each sample of chromitite and examined by reflected-light

microscopy at 250–800 $\times$ magnification, which allowed the detection of more than 50 grains of *PGM*. Observation of optical properties was limited to the estimate of color, anisotropy, and reflectance, the latter by comparison with associated *PGM* and base-metal sulfides. The *PGM* grains were investigated *in situ* by scanning electron microscopy (SEM) and electron-microprobe analysis. Back-scattered electron (BSE) images were obtained at the University of Parma using a JEOL instrument operated at 15 kV and 20 nA. Electron-microprobe analyses were carried out at the University of Modena using an ARL-SEMQ instrument operated at an accelerating voltage in the range 25–15 kV and a beam current in the range 20–10 nA, with a beam diameter of about 1 μm . Pure metals and natural chromite were the standards for *PGE* and Cr, respectively, whereas counts of S, As, and the base metals (Fe, Ni, Co, and Cu) were

calibrated with synthetic NiAs, FeS₂, CoAsS, and CuFeS₂. The following X-ray lines were used: $K\alpha$ for S, Cr, Fe, Cu, Co and Ni, $L\alpha$ for Ir, Ru, Rh, Pt, Pd and As, and $M\alpha$ for Os. Automatic corrections were made to take care of the interferences Ru – Rh, Ir – Cu, and Rh – Pd.

Electron-microprobe analytical problems

It is well known from the literature that electron-microprobe analysis of *PGM* poses a serious challenge owing to the small size of grains, usually close to the limits for quantitative determination, and because of the common presence of pores or small-scale intergrowths with other phases. The main problems involved are: i) low analytical totals, and ii) spurious fluorescence from direct or secondary excitation of the adjacent

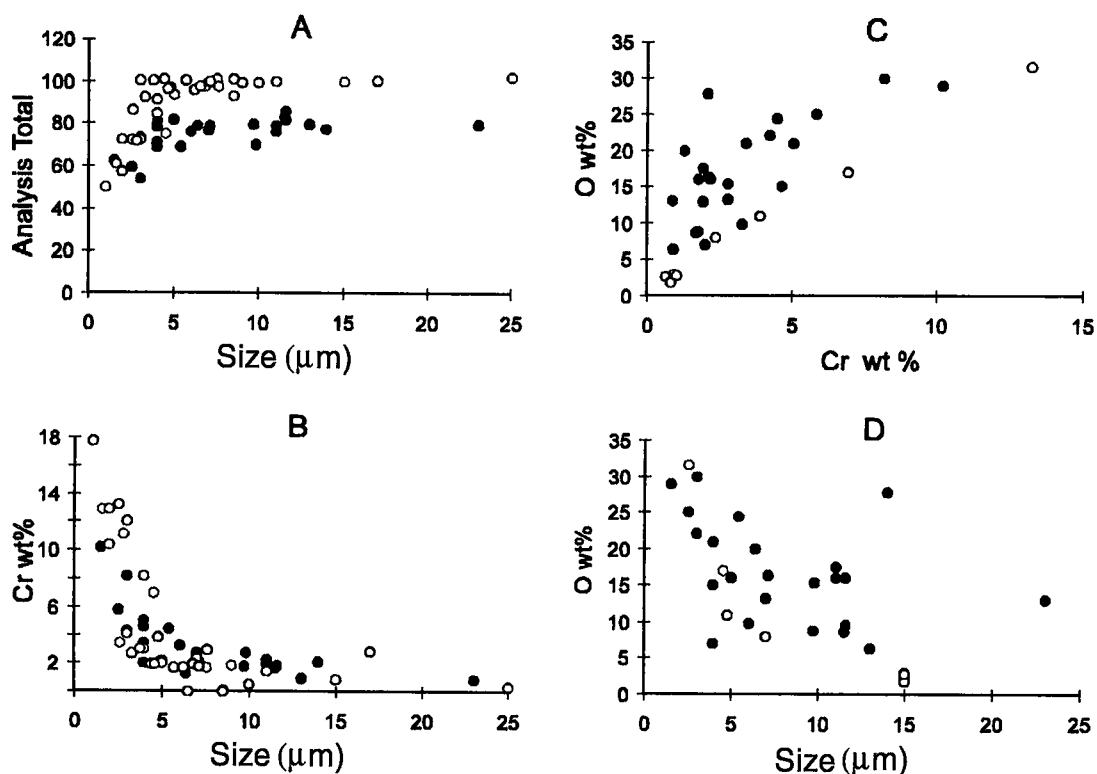


FIG. 2. A and B. Monitoring of the matrix-fluorescence effect on the total (after correction for chromite) and the apparent Cr content of *PGM* as function of grain size. The size of 5 μm appears to be a critical limit, under which matrix effects become dramatic because of direct excitation of the surroundings. Open circles: grains of laurite and Os – Ir alloy included in chromite (the two grains between 5 and 10 μm having 0 wt% Cr are included in silicate); filled circles: grains of oxygen-bearing Ru – Os – Ir – Fe compound. C and D. Variation of oxygen content as function of chromium and grain size in chromite-hosted laurite (open circles) and oxygen-bearing Ru – Os – Ir – Fe compound (filled circles). The high content of oxygen in the compound is unrelated to grain size in grains larger than about 7 μm .

phases, which can be efficiently minimized by the choice of appropriate analytical conditions (accelerating potential, beam current and diameter, takeoff angle of the instrument). In the present case, the analyzed *PGM* vary in size from 1 to 25 μm , and are mostly enclosed in chromite. The effects of these features were experimentally monitored by plotting the variation in analytical total and Cr content as function of grain size for various types of *PGM* (Figs. 2A, B). Size was measured in surface sections of grains, which does not take into account the third dimension, whereas totals and Cr contents refer to the grain core; we assumed that in this zone, the analytical results were as close to ideal as possible. Substantial Cr was found in all the analytical results, except for *PGM* grains included in silicate (laurite and Os – Ir alloy), as a result of fluorescence from the chromite matrix. The Cr amount dramatically increases for size values smaller than 5 μm , suggesting that direct excitation of the chromite probably occurred. The analytical results were therefore recalculated by subtracting all Cr and proportional amounts of Fe according to Cr/Fe in the host chromite. A diameter of 5 μm appears to be a critical limit (with the instrumental conditions adopted) even to the total amount of elements after Cr subtraction, which rapidly drops down to 50% as a consequence of the drastic reduction of the *PGM* volume excited by the electron beam.

Qualitative determination of oxygen content

Figure 2A shows that the Ru – Os – Ir – Fe compounds systematically have analytical totals in the range 75–85 wt%, in spite of the relatively large size of the grains (>10 μm) and lack of porosity. This feature was ascribed to the presence of an undetected light element in the phases investigated. Oxygen was then sought in a separate run at 10 kV and 40 nA, using the $K\alpha$ line, a RAP analyzer crystal, and a flow-counter detector. The grains were analyzed for chromium at the same time, in order to evaluate the influence of fluorescence from the chromite. Analyses were calibrated with pure Cr_2O_3 as reference material, with 30- and 5-s counting times for peak and background, yielding an average peak-to-background ratio for oxygen of about 35, and a detection limit of 0.38 wt%. The detection limit climbs to about 1.2 wt% on average in the investigated *PGM* owing to the increased absorption-coefficient of the matrix. A strong fluorescence effect from the chromite host was recorded in the analysis for oxygen. Repeated analyses of a 15- μm grain of laurite gave 0.66 wt% Cr and only 2.6 wt% O, whereas increasing amounts of oxygen, up to 30 wt%, were detected in grains of laurite ranging from 7 to 2.5 μm across, being positively correlated with Cr as a function of decreasing grain-size (Figs. 2C, D). The oxygen content of the Ru – Os – Ir – Fe compounds also correlates with both Cr content and grain size, suggesting a strong matrix-effect. Nevertheless, O concentrations are apparently

very high, even in grains larger than 10 μm ; these results are ascribed to the presence of the element as a constituent of the grains, although the determination has only qualitative significance.

THE PRIMARY ASSEMBLAGE OF *PGM*

The first studies of *PGM* in chromite deposits of the Vourinos complex (Augé 1985, 1988, Legendre & Augé 1986, Augé & Johan 1988) revealed assemblages dominated by alloys, sulfides, and minor sulfarsenides in the ternary system Ru – Os – Ir, accompanied by a (Ru,Rh)-bearing base-metal sulfide. The minerals were found included in fresh chromite (Fig. 3A) and were interpreted as crystals formed in the early magmatic stage and mechanically trapped in the spinel at a high temperature. On the basis of morphological relationships, including epitaxial growth among coexisting alloys and sulfides and theoretical predictions based on relative stabilities of the *PGM*, those authors were able to recognize that alloys formed before sulfides, and thus deduced that the minerals crystallized under conditions of continuously increasing $f(\text{S}_2)$ and decreasing T. In the course of the present investigation, laurite, irarsite, and hexagonal Os – Ir alloy were encountered as primary magmatic inclusions in chromite; these have morphological and compositional characters in agreement with the results of previous studies. Representative results of analyses of these *PGM* are presented in Table 2. In addition, the same *PGM* are also located in the silicate matrix of the chromitite samples, included in olivine or serpentine. The inclusion of the *PGM* in olivine provides conclusive evidence that they were not exsolved from the chromite at a subsolidus temperature, as suggested for other occurrences (Gijbels *et al.* 1974, Naldrett & Cabri 1976, Cousins & Vermaak 1976), but instead crystallized at a high temperature from the magma. The fact that some of these *PGM* were found also in contact with secondary phases such as ferrian chromite, chromian chlorite, and serpentine only means that they could survive the low-temperature alteration of the host. As an example, the *PGM* aggregate entirely surrounded by serpentine (Fig. 3B) consists of $\text{Os}_{0.5}\text{Ir}_{0.35}\text{Ru}_{0.15}$ and an Ir sulfide with a cupro-iridsite-type stoichiometry $(\text{Fe}_{0.48}\text{Cu}_{0.35}\text{Ni}_{0.16})_{20.99}(\text{Ir}_{1.31}\text{Rh}_{0.41}\text{Os}_{0.25}\text{Pt}_{0.05})_{22.01}\text{S}_4$, but having $\text{Fe} > \text{Cu}$ (Table 2, anal. VS18a-1-1 and VS18a-1-4). The alloy is similar in composition and habit to the primary Os – Ir inclusions in chromite (Augé 1985, 1988), consistent with a magmatic origin. The association with cupro-iridsite can be interpreted as a case of epitaxial growth of the sulfide over the pre-existing alloy, in agreement with the relative stabilities of the two phases under increasing $f(\text{S}_2)$ and decreasing T at the magmatic stage. Clearly, the grain is not in equilibrium with the enclosing serpentine-rich matrix, and was apparently preserved from alteration.

THE ASSEMBLAGE OF SECONDARY PGM

The PGM of this group may coexist with primary PGM at the scale of a polished section, but are typically

located in the altered zones of chromite crystals, close to fractures, or within the serpentine matrix. They never are found encased in unfractured, fresh chromite. In some cases, they are observed to replace primary magmatic

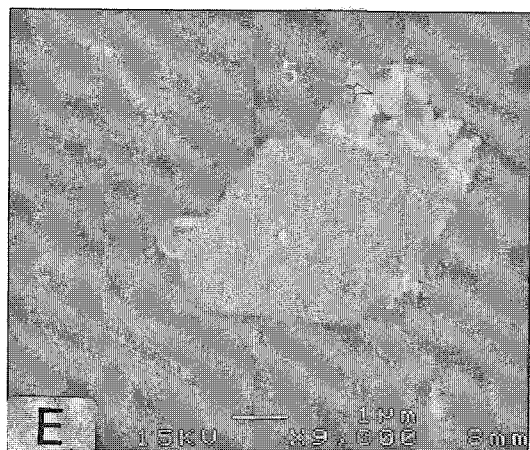
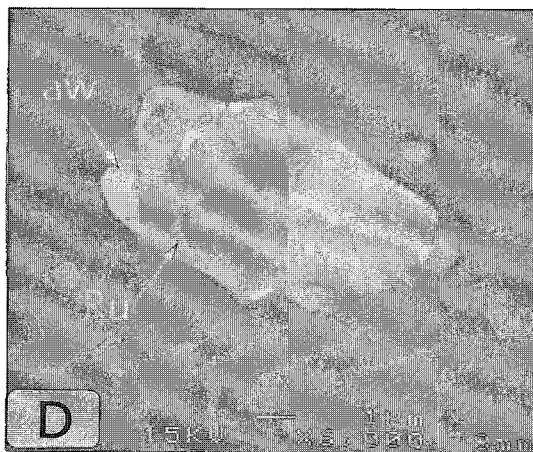
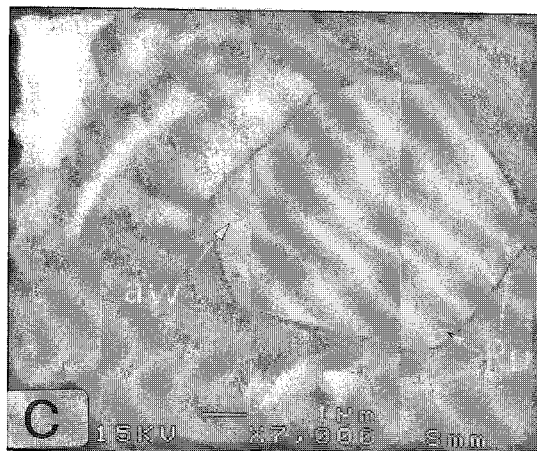
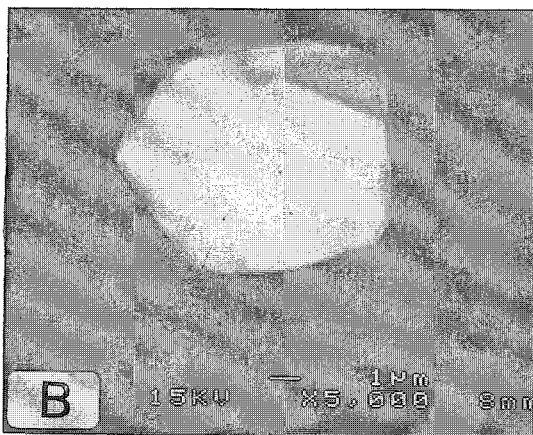
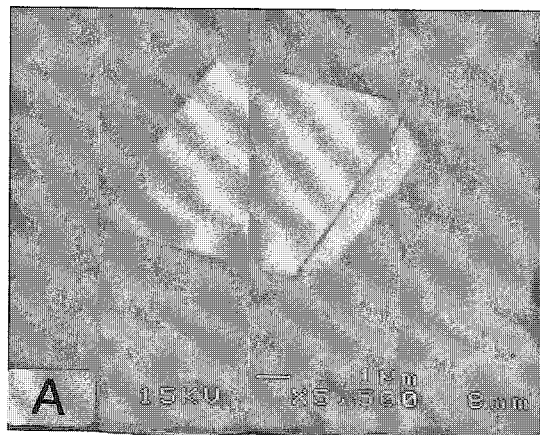


TABLE 2. REPRESENTATIVE COMPOSITIONS OF PRIMARY PGM FROM THE VOURINOS CHROMITITES

Wt%		Cr	Fe	Fe*	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	Tot*
Laurite														
VS1-1	Fig.	4.14	1.21	0.03	0.15	0.00	11.84	7.63	45.04	0.89	0.00	0.34	34.65	100.57
VS1a-1	3-A	1.82	0.55	0.01	0.11	0.00	8.41	6.21	45.75	2.01	0.04	0.06	36.08	98.68
VS3a-2		1.62	0.42	0.00	0.18	0.00	2.85	1.95	56.82	0.74	0.00	0.88	35.62	99.04
VS3a-6	3-C	1.58	0.55	0.10	0.19	0.05	2.80	1.86	55.52	0.70	0.27	0.72	36.46	98.67
VS6a-2		3.07	1.42	0.30	0.09	0.04	21.34	8.41	36.84	0.07	0.00	0.42	32.98	100.49
VS11a-1		0.00	0.29	0.29	0.06	0.05	0.78	1.59	56.74	1.47	0.00	0.57	37.45	99.00
VS13a-1-1	3-E	1.93	0.50	0.00	0.00	0.00	0.33	59.34	2.11	0.11	0.84	36.37	99.13	
VS14a-1		1.97	0.56	0.02	0.05	0.00	6.56	3.51	52.78	0.00	0.00	0.61	37.21	100.74
VS15-4		1.95	0.65	0.00	0.09	0.00	8.23	8.61	46.01	0.21	0.00	0.42	36.20	99.77
VCR2-1		4.31	2.34	0.96	1.64	3.41	24.25	5.28	32.44	0.00	0.00	0.30	32.37	100.66
Ruthenian pentlandite														
VS12-1	3-D	3.01	17.44	16.55	26.16	0.00	3.94	3.44	16.92	0.00	0.09	0.12	27.03	94.25
Cupro-iridsite														
VS18a-1-4	3-B	0.00	3.90	3.90	1.32	3.18	7.01	36.3	20.00	6.05	1.32	0.00	18.55	77.65
Os-Ir alloy														
VS12a-1		11.23	3.27	0.00	0.05	0.00	39.32	22.42	5.67	0.58	0.00	0.23	0.08	68.35
VS18a-1-1	3-B	0.00	0.49	0.49	0.02	0.00	49.18	39.93	8.07	0.00	0.00	0.14	0.09	97.92
Atomic percent (calculated from corrected data)														
Laurite														
VS1-1		0.04	0.15	0.00	3.79	2.42	27.12	0.53	0.00	0.19	65.76			
VS1a-1		0.01	0.12	0.00	2.64	1.93	27.00	1.16	0.01	0.04	67.10			
VS3a-2		0.00	0.18	0.00	0.87	0.59	32.75	0.42	0.00	0.48	64.71			
VS3a-6		0.10	0.18	0.04	0.85	0.56	31.73	0.39	0.08	0.39	65.67			
VS6a-2		0.35	0.10	0.04	7.19	2.80	23.35	0.04	0.00	0.25	65.88			
VS11a-1		0.30	0.06	0.05	0.23	0.47	31.74	0.81	0.00	0.30	66.04			
VS13a-1-1		0.00	0.00	0.00	0.01	0.10	33.51	1.17	0.03	0.45	64.74			
VS14a-1		0.02	0.05	0.00	1.98	1.05	29.97	0.00	0.00	0.33	66.60			
VS15-4		0.00	0.09	0.00	2.58	2.67	27.10	0.12	0.00	0.24	67.21			
VCR2-1		1.09	1.76	3.38	8.03	1.73	20.22	0.00	0.00	0.18	63.61			
Ruthenian pentlandite														
VS12-1		16.53	24.86	0.00	1.15	1.00	9.34	0.00	0.03	0.06	47.03			
Cupro-iridsite														
VS18a-1-4		6.90	2.22	4.95	3.64	18.67	0.00	5.81	0.67	0.00	57.14			
Os-Ir alloy														
VS12a-1		0.00	0.20	0.00	52.93	29.86	14.36	1.45	0.00	0.55	0.65			
VS18a-1-1		1.55	0.06	0.00	46.25	37.15	14.27	0.00	0.00	0.24	0.47			

Fe*: Amount of Fe corrected for the chromite matrix effect. Tot*: total of corrected data.

or even secondary *PGM* along the external boundary; in others, they are found as independent grains having no replacement relation with primary *PGE* phases. In this instance, their secondary nature was established indirectly, on the basis of distinctive features such as extremely variable morphology, irregularly zoned internal texture, rugged surface, intimate intergrowth with products of low-temperature alteration, such as chlorite, ferrian chromite, limonite, and chemical compositions characterized by low to absent S, and a high content of Fe, Ni, and Cu. Some of these grains may be classified as *PGE*-bearing alloys, although others were found to systematically contain oxygen in amounts not attributable to the matrix effect.

Replacement associations: evidence for desulfurization of *PGM*

These associations were found in partially serpentinized samples collected *in situ* and from dumps at all of the localities investigated. They are characterized by decrease or disappearance of sulfur in the replacing phases, indicating desulfurization reactions. Significant examples are described below.

One grain of primary laurite (Table 2, anal. VS3a-6) associated with pentlandite is located in chromite close to a large fracture filled with serpentine (Fig. 3C). The laurite is corroded along its rim, and is replaced by the following metallic phases, reflecting desulfurization: i) a highly reflective Ru-rich alloy, and ii) a less highly reflective Fe-Ni alloy (awaruite?), which also replaces the adjacent pentlandite. Minor concentrations of S in the altered rim are ascribed to fluorescence from the sulfide. One grain of pentlandite from Voidolakkos is located at the intersection of fractures, in the altered portion of a chromite crystal, where its transformation into ferrian chromite is apparent (Fig. 3D). Results of the electron-microprobe analysis (Table 2, anal. VS12-1) confirm the pentlandite-type stoichiometry, but show a relatively high content of Ru ($\text{Ni}_{4.23}\text{Fe}_{2.81}\text{Ru}_{1.59}\text{Os}_{0.2}\text{Ir}_{0.17}\text{S}_{2.9}\text{S}_8$), suggesting ruthenian pentlandite (Genkin *et al.* 1976). The grain is rimmed almost continuously with metallic Ru. Laths of Ru-free pentlandite are attached to the external border, and appear to be partially replaced by Ni-Fe alloy, possibly awaruite. Further evidence for desulfurization is given by a single grain of laurite included in serpentine irregularly replaced by a S-poor Ru-Os-Ir sulfide (Fig. 3F). A small crystal of irarsite in contact with the sulfide exhibits a polygonal shape and a homogeneous surface, suggesting that it did not suffer alteration. A series of four spot-analyses across the *PGM* sulfide (Fig. 4) shows that the sulfur/metal ratio decreases from 2 in the laurite to 0.75 and 0.53 in the rim sulfide (Table 3, anal. VS2a-1-2 and VS2a-1-3). The proportion of Ru, Os and Ir, and the Fe content, also are modified; there is an increase in Ru/Ir and also, to a lesser extent, Ru/Os; at the same time, there is a significant increase in Fe, along with a minor increase

FIG. 3. BSE images of unaltered and partially desulfurized, primary *PGM*. A. Laurite (anal. VS1a-1, Table 2) associated with silicate (probably pargasite), included in unfractured fresh chromite from Kissavos. B. Os-Ir alloy (anal. VS18a-1-1, Table 2), with epitaxial overgrowth of Fe-rich cupro-iridsite (anal. VS18a-1-4, Table 2) included in serpentine (Xerolivado). C. Composite grain, from Kissavos, of laurite (anal. VS3a-6, Table 2) and pentlandite partially replaced with metallic Ru and awaruite (aw). D. Composite grain of normal pentlandite and ruthenian pentlandite (anal. VS12-1, Table 2) replaced with awaruite (aw) and metallic Ru (Voidolakkos). E. Primary laurite (anal. VS13a-1-1, Table 2) associated with Ir-Rh-Fe-Cu-Ni (anal. VS13a-1-5, Table 4), from Voidolakkos, intergrown with chlorite (black). F. Corroded grain of laurite associated with irarsite (I) in serpentine (Agriatses). Laurite is replaced along the rim by S-poor Ru-Os-Ir sulfide. Numbers refer to entries in Table 3 (anal. VS2a-1-1 to VS2a-1-4), the data being illustrated as profiles in Figure 4.

in Ni and Co. One grain (Fig. 5B) displays a core zone characterized by a Ru:Os:Ir proportion similar to that in laurite, but with a sulfur/metal ratio of about 0.5–0.3 (Table 3, anal. VS5-1-1 and VS5-1-2), possibly representing partially desulfurized laurite. The rim in contact with ferrian chromite gave sulfur/metal values as low as 0.18–0.07 (Table 3, anal. VS5-1-3 and VS5-1-4), indicating progressive loss of sulfur, and corresponding increase of Fe, Ni, and even Pt. The above data suggest that laurite may undergo almost complete desulfurization, probably during serpentinization. The process involves formation of low-S Ru – Os – Ir sulfides which, in turn, seem to be unstable with continuing alteration. Progressive loss of S was apparently counterbalanced by introduction of Fe and Ni. The PGE underwent some

remobilization: Ir was removed during the first step of desulfurization, and some Pt had to be added to the system in the last stage, if we accept that the grain in Figure 5B is desulfurized laurite.

Secondary Pt-, Pd-, Ir-, Rh-bearing alloys and arsenides

Several PGM, containing Pt, Pd, Ir, and Rh as major elements, were encountered in the secondary assemblage of partially to totally altered samples of chromite from Voidolakkos, Kissavos, and Agriatses.

Figure 3E shows an idiomorphic grain of unaltered laurite (Table 2, anal. VS13a-1-1) overgrown by a

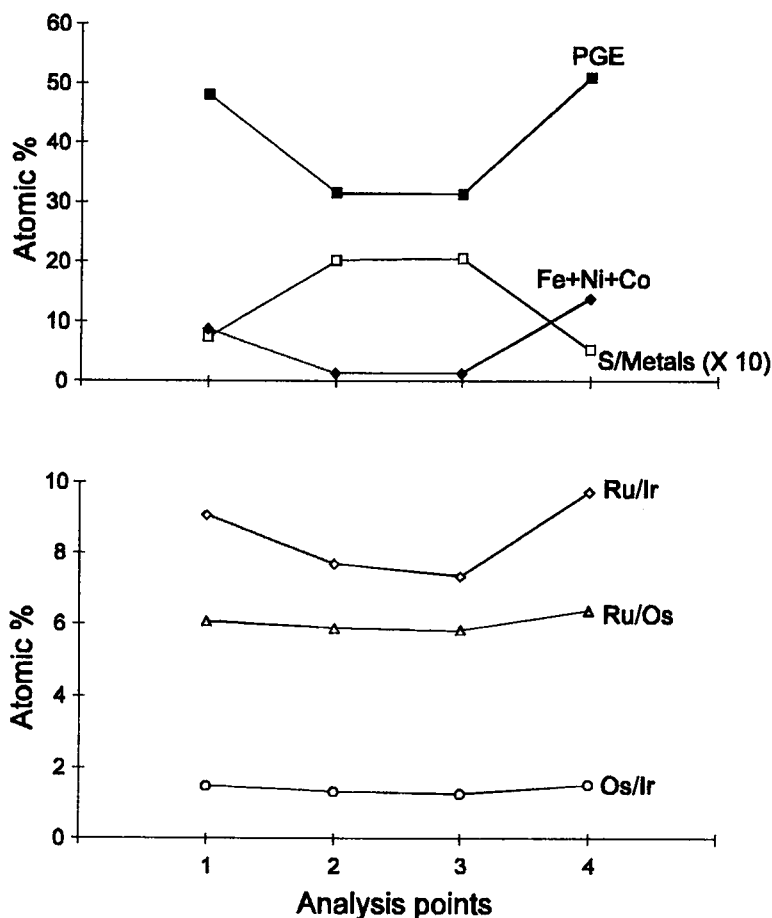


FIG. 4. Compositional variations in partially desulfurized laurite, obtained from the four points analyzed (anal. VS2a-1-1 to VS2a-1-4, Table 3) in the PGM grain in Figure 3F. Total PGE and the sum Fe + Ni + Co are expressed in atom%, whereas the sulfur/metal ratio has been multiplied ten times. The rim phase is depleted in S, Os, and Ir with respect to the laurite core because of desulfurization and loss of PGE during the serpentinization.

speck of Ni – Fe sulfide, less than 1 μm across, rimmed by Ru, and a large grain of a *PGM* having an approximately polygonal boundary and consisting of a complex intergrowth of at least two phases: Ir – Rh – Fe – Cu – Ni alloy (Table 4, anal. VS13a–1–5), and silicate. Another grain of this type (Table 5, anal. VS5–5–1) is shown in Figure 6F, associated with the Ru – Os – Ir – Fe compound (Table 4, anal. VS5–5–6). In both cases, only apparent bulk-compositions were obtained by electron-microprobe analysis, which were characterized by strong matrix-effects and very low totals. A qualitative energy-dispersion (EDS) analysis shows that the silicate consists of Si, Al, and Mg in similar proportion as in the chlorite filling the cracks in the chromite. A relatively high amount of As (6.17%) was detected in the grain of Figure 6F. We believe, therefore, that the intergrowth might have formed at a relatively low temperature by reduction of an original Ir – Rh chalcogenide (irarsite?), with introduction of chlorite and possibly also Fe – Cu – Ni.

The grain of partially desulfurized laurite in Figure 5B is in contact with an intergrowth consisting of Cu – Pt – Pd and Ni – Fe – Pt (Table 4, anal. VS5–1–10, VS5–1–7), chlorite and ferrian chromite encased within a polygonal cavity that probably was formerly occupied by an unknown *PGM*. Optically, both minerals are characterized by high reflectance and isotropy. Oxygen was detected in the analysis of Cu – Pt – Pd and Ni – Fe – Pt. It was, however, clearly due to secondary fluorescence from the associated O-bearing phases, the low totals of the electron-microprobe analyses being due to the small grain-size ($<5 \mu\text{m}$). Compositions are not consistent with common Pt – Fe alloys known from the literature (Bowles 1990), but exhibit prevalence of the base metals over the *PGE*, suggesting *PGE*-rich awaruite and copper. On the basis of their mode of

occurrence, these alloys are interpreted as having formed by secondary deposition of *PGE*. An origin by *in situ* reduction of specific Pt – Pd sulfides is unlikely on account of the absence of such minerals in the primary *PGM* assemblage of the Vourinos chromitites (Augé 1985, 1988, Legendre & Augé 1986, Augé & Johan 1988, and this work).

Another (Ir, Pt)-bearing Ni – Fe alloy, possibly *PGE*-rich awaruite (Table 4, anal. VS5a–3–1 and VS5a–3–4), occurs as colloform, botryoidal particles associated with an unknown (Rh,Ni) arsenide (Fig. 5D) in brecciated altered chromite cemented by chlorite and limonite. The (Rh,Ni) arsenide (Table 4, anal. VS5a–3–3) corresponds to the general formula (Rh,Ir,Pt,Pd)NiAs, which may possibly be referred to as the rhodian analogue of majakite (ideally PdNiAs). It is difficult to establish the origin (primary or secondary) of this phase. It might be a relic of an original interstitial *PGE* arsenide involved in the low-temperature alteration of the silicate matrix of the chromite. However, small specks of the same mineral associated with the Pt-rich alloy were observed disseminated in cracks cross-cutting the chromite breccia, suggesting formation by deposition of the *PGE* at low temperature.

The oxygen-bearing Ru – Os – Ir – Fe compounds

These *PGM* were found exclusively in two samples of weathered chromite from the mine dump of Agriates, a locality not investigated in previous studies. BSE images of the grains are shown in Figures 5A, C, 6A to F, whereas representative electron-microprobe analytical data are listed in Table 5. A number of grains (21) were encountered, but most of them were not readily recognized during initial examination of polished sections because of their relatively low reflectance. They

TABLE 3. REPRESENTATIVE COMPOSITIONS OF PARTIALLY DESULFURIZED LAURITE FROM THE VOURINOS CHROMITITES

Wt%	Fig.	Cr	Fe	Fe*	Co	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	Tot*
VS2a-1-1	3-F	0.53	4.56	4.56	0.08	0.53	0.00	13.47	9.15	43.60	0.16	0.32	0.49	16.03	88.39
VS2a-1-2	3-F	0.46	0.52	0.52	0.01	0.22	0.00	12.57	9.71	39.25	0.22	0.47	0.38	34.91	98.26
VS2a-1-3	3-F	0.45	0.52	0.52	0.00	0.19	0.00	12.66	10.16	39.13	0.50	0.38	0.46	35.52	99.52
VS2a-1-4	3-F	0.47	7.05	7.05	0.11	1.28	0.00	13.36	8.85	45.13	1.35	0.00	0.44	12.61	90.18
VS5-1-1	5-B	1.28	5.12	4.33	2.17	11.87	0.75	16.95	7.54	31.84	0.51	0.88	1.37	12.04	90.25
VS5-1-2	5-B	2.36	9.74	8.28	3.10	10.52	0.78	14.06	6.90	35.15	0.29	2.52	2.19	10.65	94.44
VS5-1-3	5-B	1.26	3.94	3.16	0.64	9.00	0.44	15.82	8.27	35.03	0.18	0.50	2.10	3.79	78.93
VS5-1-4	5-B	1.93	12.39	11.20	1.18	15.64	0.56	10.35	5.48	24.25	0.23	14.28	1.55	1.90	86.62
Atomic percent (calculated from corrected data)															
VS2a-1-1			7.11	0.12		0.79	0.00	6.16	4.14	37.52	0.13	0.14	0.40		43.48
VS2a-1-2			0.58	0.01	0.23	0.00	4.09	3.13	24.05	0.13	0.15	0.22	0.27		67.41
VS2a-1-3			0.57	0.00	0.20	0.00	4.06	3.23	23.63	0.30	0.12	0.27	0.62		67.62
VS2a-1-4			11.24	0.17	1.94	0.00	6.25	4.10	39.76	1.17	0.00	0.37	35.01		
VS5-1-1			6.63	3.14	17.28	1.01	7.62	3.35	26.94	0.42	0.39	1.10	32.12		
VS5-1-2			12.17	4.32	14.70	1.00	6.07	2.94	28.54	0.23	1.06	1.69	27.27		
VS5-1-3			6.71	1.29	18.20	0.82	9.87	5.10	41.13	0.20	0.30	2.34	14.03		
VS5-1-4			20.72	2.07	27.52	0.90	5.62	2.95	24.79	0.23	7.56	1.50	6.13		

Fe*: Amount of Fe corrected for the chromite matrix effect. Tot*: total of corrected data).

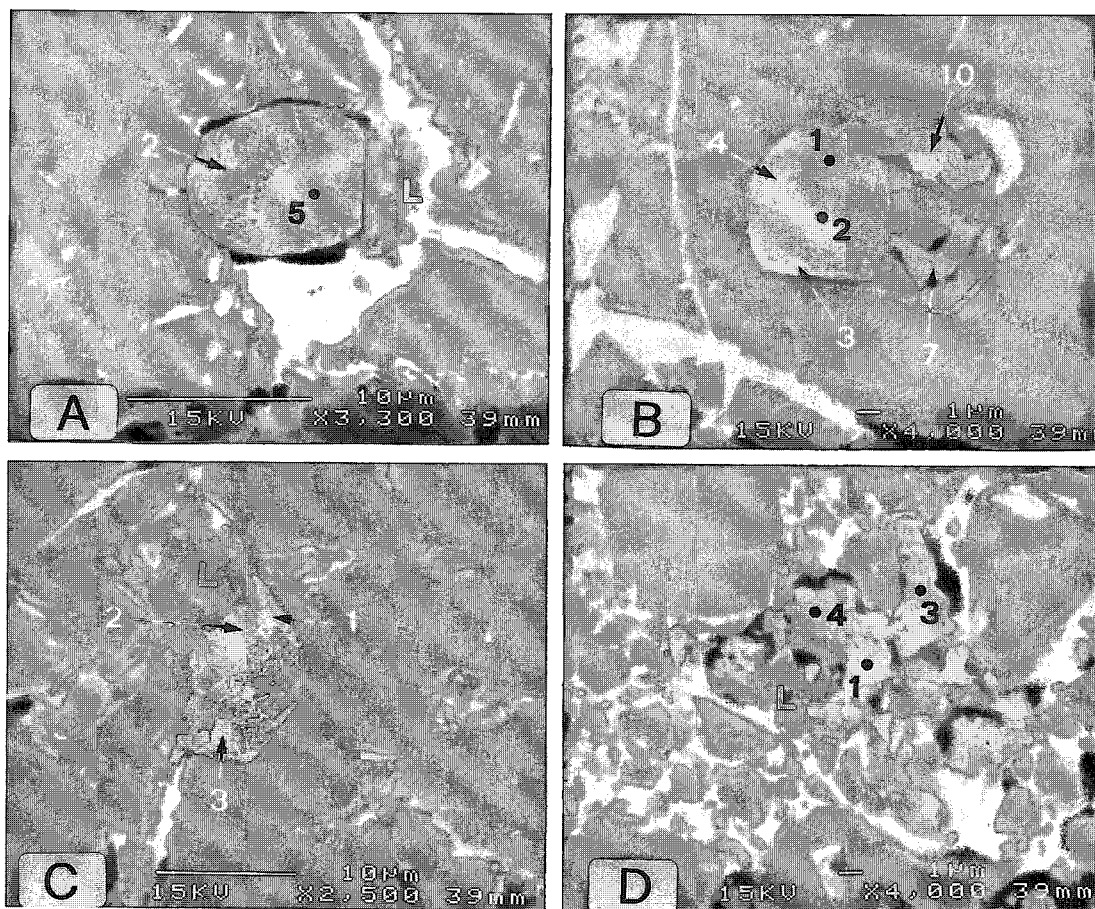


FIG. 5. BSE images of secondary PGM from the weathered samples of chromitite from Agriatses, showing the effects of low-temperature mobilization of the PGE. A. Zoned grain of oxygen-bearing Ru – Os – Ir – Fe associated with chlorite and limonite (L) in crack. The altered portion of the grain (point 5) is depleted in Pt, Ir, Pd with respect to point 2 (anal. VS6-2-2 and VS6-2-5, Table 5). B. Grains of partially desulfurized laurite displays rim depleted in S and enriched in Pt (anal. VS5-1-1 to VS5-1-4, Table 3). Ni – Fe – Pt and Cu – Pt – Pd alloys (anal. VS5-1-7 and VS5-1-10, Table 4) are intergrown with chlorite (black) and ferrian chromite (f) within a cavity with a polygonal shape. C. Zoned grain of oxygen-bearing Ru – Os – Ir – Fe, intergrown with abundant limonite (L), having Pt- and Pd-enriched areas (anal. VS5a-2-1 to VS5a-2-3, Table 5). D. Botryoidal aggregate of Ir – Pt – Ni – Fe alloy (anal. VS5a-3-1 and VS5a-3-4, Table 4) associated with Rh arsenide (anal. VS5a-3-3, Table 4) in ferrian chromite breccia cemented by chlorite and limonite (L).

attracted our attention only under the electron microscope owing to their brightness with respect to other sulfides, and were proven to contain PGE by qualitative EDS analysis. The grains range 2.5 to 23 µm in diameter and vary from distinctly polygonal to roundish to extremely irregular. They may occur as single grains, associated with chlorite, limonite, ferrian chromite, or with other secondary PGM. They are noticeably less reflectant than laurite, and vary in color from yellowish white to pinkish grey. At high magnification (800×) and oil immersion, the grains exhibit a typically patchy extinction, that in the case of the grain in Figure 6D has

a characteristic hourglass zoning (not visible in the BSE image). The internal texture of grains becomes conspicuous under partially crossed nicols; it varies from mosaic-like to radial-fibrous, with strong anisotropy that gives the effect of iridescence, similar to graphite. It was impossible to establish by means of optical observation whether the grains consist of one or more phases. Back-scattered electron images show rugged, spotted surfaces (Figs. 6A, B), which would appear to be a result of chemical heterogeneity, *i.e.*, mixtures of two phases with different average atomic number, rather than porosity. The surface of some grains appears as a

TABLE 4. REPRESENTATIVE COMPOSITIONS OF Pt-, Ir-, Pd-, AND Rh-BEARING ALLOYS AND ARSENIDES FROM THE VOURINOS CHROMITITES

Wt%		Cr	Fe	Fe*	Co	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	As	Tot*
<i>Alloys</i>																
VS5-1-7	5-B	2.84	20.05	17.94	1.18	22.91	1.52	0.36	0.48	4.08	0.20	44.27	0.60	0.02	0.00	93.56
VS5-1-10	5-B	6.53	11.95	4.83	1.72	9.97	37.45	0.33	0.04	2.17	0.37	23.42	10.76	0.02	0.00	91.08
VS5a-3-1	5-D	5.54	19.63	16.26	1.64	34.73	0.00	0.00	22.43	0.04	8.98	12.22	1.33	0.00	0.00	97.63
VS5a-3-4	5-D	5.04	14.00	10.94	0.18	22.05	0.00	0.12	28.52	0.00	1.00	10.99	0.10	0.11	0.27	74.28
VS13a-1-5	3-E	16.05	11.97	7.41	0.00	1.42	1.97	3.02	31.96	2.35	8.17	0.14	0.06	0.35	0.27	57.12
<i>Arsenides</i>																
VS5-5-1	6-F	2.18	18.98	17.36	0.07	11.72	0.09	0.00	34.19	0.54	8.27	0.98	0.78	0.04	6.17	80.21
VS5a-3-3	5-D	11.02	7.73	1.01	0.05	19.93	0.00	0.03	10.53	0.08	25.36	7.33	3.30	0.08	27.89	95.59
Atomic percent (calculated from corrected data)																
<i>Alloys</i>																
VS5-1-7				31.03	1.93	37.70	2.31	0.18	0.24	3.90	0.19	21.92	0.54	0.05	0.00	
VS5-1-10				7.70	2.60	15.12	52.44	0.15	0.02	1.91	0.32	10.68	9.00	0.07	0.00	
VS5a-3-1				24.47	2.34	49.71	0.00	0.00	9.81	0.03	7.33	5.26	1.05	0.00	0.00	
VS5a-3-4				24.56	0.38	47.09	0.00	0.08	18.60	0.00	1.22	7.06	0.12	0.43	0.45	
VS13a-1-5				27.16	0.00	4.95	6.35	3.25	34.03	4.76	16.24	0.14	0.12	2.26	0.73	
<i>Arsenides</i>																
VS5-5-1				35.62	0.14	22.88	0.16	0.00	20.38	0.61	9.21	0.58	0.84	0.14	9.44	
VS5a-3-3				1.64	0.08	30.75	0.00	0.02	4.96	0.07	22.33	3.41	2.81	0.22	33.72	

Fe*: Fe corrected for the chromite matrix effect; Tot*: total of corrected data.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF OXYGEN-BEARING Ru-Os-Ir-Fe COMPOUNDS IN WEATHERED CHROMITITES OF AGRIATSES, VOURINOS

Wt%	Fig.	Cr	Fe	Fe*	Co	Ni	Cu	Os	Ir	Ru	Rh	Pt	Pd	S	Tot*
VS5-2-4	6-D	1.56	6.61	5.66	0.27	2.65	0.00	31.13	9.63	32.95	0.41	0.09	0.43	0.06	83.28
VS5-3-2		0.88	8.12	7.58	0.20	1.13	0.20	19.24	11.80	37.33	0.68	0.43	0.75	0.00	79.34
VS5-4-1		5.83	13.46	9.90	0.08	1.79	0.00	33.35	6.15	7.77	0.35	0.14	0.12	0.02	59.67
VS5-5-6	6-F	2.95	10.62	8.82	0.10	3.40	0.28	18.89	12.77	32.76	0.57	3.03	0.65	0.00	81.27
VS5-5a-2		5.07	7.49	4.40	0.08	4.59	0.00	13.85	11.81	40.03	0.69	0.52	0.19	0.00	76.16
VS5-6-3		2.62	19.21	17.61	0.06	1.51	0.00	24.74	9.58	22.21	0.50	0.23	0.40	0.03	76.87
VS5-8-1	6-C	1.77	9.22	8.13	0.22	1.77	0.00	24.03	12.43	31.86	0.69	0.02	0.37	0.00	79.52
VS5-9-5		1.71	5.53	4.48	0.13	1.13	20.29	16.50	10.07	27.94	1.23	0.66	1.96	0.00	84.39
VS5-10-1		4.25	19.52	16.93	0.17	1.51	0.00	6.10	8.00	39.47	0.75	0.08	0.51	0.00	73.52
VS5-11-1		10.18	8.30	2.09	0.14	0.16	16.39	11.14	6.77	25.30	0.60	0.02	0.26	0.00	62.87
VS5-13-1		5.06	7.33	4.25	0.67	6.36	0.00	1.79	8.22	46.09	0.51	0.14	0.50	0.09	68.62
VS5-13-5		4.18	10.43	6.65	2.10	12.84	0.00	2.07	7.83	37.71	0.20	0.21	0.60	11.54	81.75
VS5a-1-1	6-E	0.94	8.31	7.74	0.44	6.57	0.33	21.56	13.84	25.62	1.04	1.06	0.93	0.07	79.20
VS5a-1-4	6-E	1.47	9.60	7.00	0.31	9.48	1.23	19.81	8.16	18.74	0.16	14.00	2.01	0.07	80.97
VS5a-2-1	5-C	2.50	11.53	10.01	0.07	3.74	0.20	9.87	18.23	16.08	0.11	27.99	1.13	0.09	87.52
VS5a-2-2	5-C	1.81	15.43	14.33	0.00	0.79	0.40	11.87	18.64	27.22	0.38	0.64	3.36	0.00	77.63
VS5a-2-3	5-C	1.91	11.46	10.28	0.00	1.18	2.28	11.40	13.07	16.55	0.00	3.37	19.85	0.00	77.98
VS6-2-2	5-A	2.27	16.15	15.36	0.16	1.18	0.00	16.40	11.89	28.63	0.33	3.68	0.46	0.02	78.11
VS6-2-5	5-A	1.78	19.17	18.54	0.08	0.89	0.00	16.98	6.64	32.25	0.39	0.15	0.24	0.00	76.16
VS6a-1-2	6-A	2.36	20.85	20.02	0.00	0.82	0.00	19.90	6.95	30.59	0.40	0.00	0.20	0.00	78.88
VS6a-3-3	6-B	5.55	16.99	15.05	0.00	0.27	0.00	11.17	5.53	37.74	0.32	0.00	0.29	0.00	70.37
VS6a-4-2		2.18	18.63	17.86	0.00	0.49	0.00	21.41	7.13	33.89	0.93	0.00	0.16	0.00	81.87
VS6a-5-1		3.43	19.33	18.14	0.15	0.89	0.01	16.61	11.80	22.65	0.44	0.17	0.36	0.00	71.22

Fe*: Fe corrected for the chromite matrix effect; Tot*: total of corrected data.

vermicular intergrowth of different phases (Figs. 6C, D, F), although X-ray maps showing the distribution of elements could not reveal the nature of the intergrowths because of their low resolution relative to the small size of the aggregate of particles.

Electron-microprobe-derived compositions display (Ru > Os > Ir) > (Fe > Ni > Co), with the ratio of the *PGE* to the base metals in the range 3.6–1.07. Ru and Fe are usually predominant, although composition VS5-4-1 exhibits Os > Ru, and analyses VS5-13-5, VS5-9-5 and VS5-11-1 reveal Ni > Fe or Cu > Fe. Variable amounts of Rh, Pt and Pd were detected in some grains. Three grains (Figs. 5A, C, 6E) contain Pt-

and Pd-enriched zones (Table 5, anal. VS5a-2-1, VS5a-2-3, VS5a-1-4, VS6-2-2), usually associated with an increase in the concentration of Ni or Cu or both. These areas do not differ substantially in optical character from the remainder of the grain, and would appear to reflect compositional zoning. The presence of oxygen was qualitatively ascertained in the largest grains, but failure to obtain quantitative determinations prevents any conclusive interpretation of the nature of these minerals. Nevertheless, following the arguments of Augé & Legendre (1994), who described *PGE* oxides and hydroxides in placer deposits from New Caledonia, at least two hypotheses can be envisaged to explain the

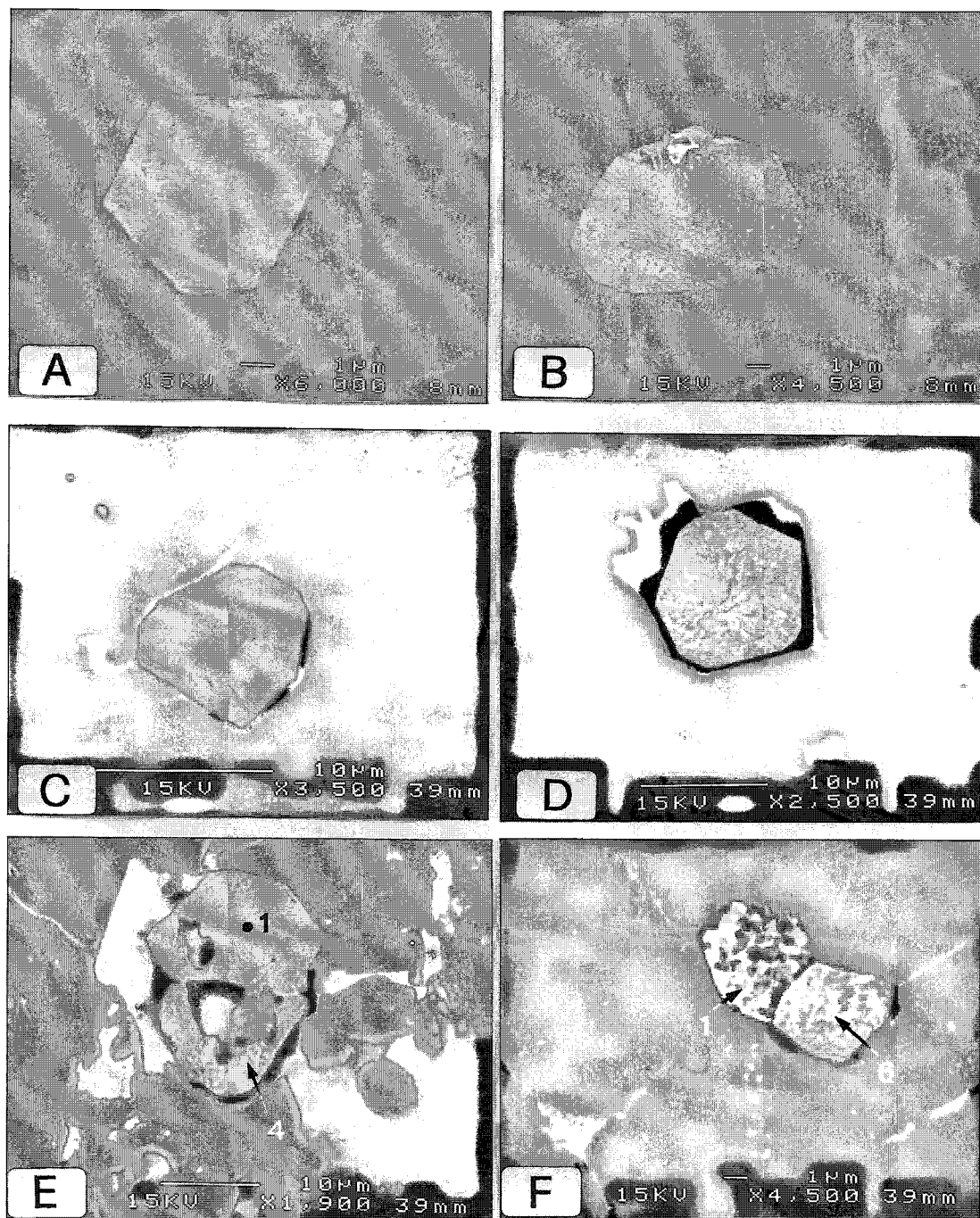


FIG. 6. BSE images of oxygen-bearing Ru – Os – Ir – Fe compound associated with altered chromite and chlorite in the samples of weathered chromitite of Agriatsets. Grains from A to D refer to compositions VS6a-1-2, VS6a-3-3 and VS5-6-3, VS5-2-4 (Table 5). E. Zoned grain of Ru – Os – Ir – Fe, showing enrichment in Pt and Pd at point 4 (anal. VS5a-1-1 and VS5a-1-4, Table 5). F. Ru – Os – Ir – Fe grain (anal. VS5-5-6, Table 5) associated with Ir – Rh – Fe – Cu – Ni alloy (anal. VS5-5-1, Table 4) intergrown with chlorite (black) analogous to the grain in Fig. 3E.

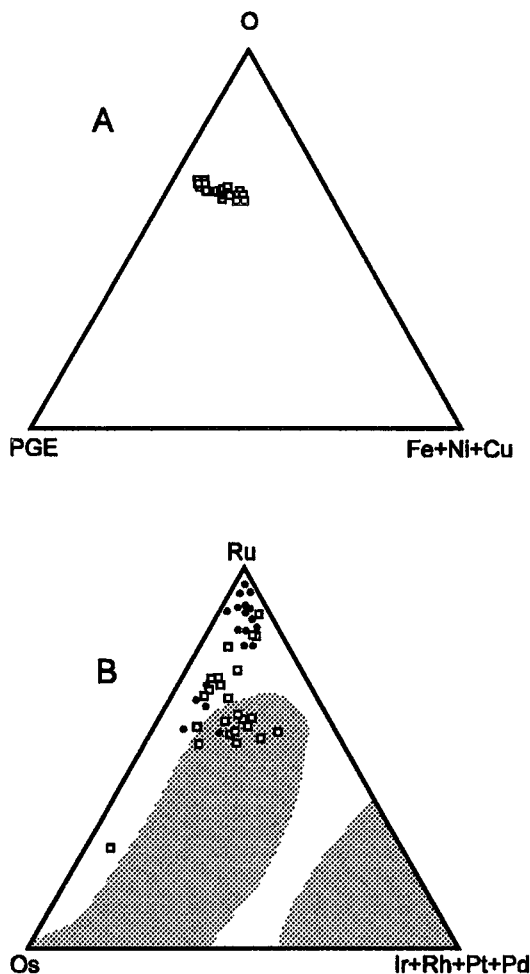


FIG. 7. A. Plot of the composition of the Ru – Os – Ir – Fe oxygen-bearing compound in terms of O – *PGE* – (Fe + Ni + Cu), in atomic %, after recalculation of metals as ideal oxides considering (*PGE*)O₂, Fe₂O₃, NiO, and CuO. B. Plot of the composition of laurite (filled circles) and oxygen-bearing Ru – Os – Ir – Fe compound (open squares), in terms of Ru – Os – Ir, in atomic %, with minor amounts of Rh, Pt, and Pd added to Ir. Compositional fields of previously reported terrestrial Os – Ir – Ru alloys (Harris & Cabri 1991) are shown, as shaded areas, for comparison. Some of the data points for the Ru – Os – Ir – Fe compound overlap the field of primary laurite, and some display enrichment in Ir + Rh + Pt + Pd, which is unusual for natural laurite.

origin of oxygen in the *PGM*: 1) There is some evidence that some of these grains actually consists of submicroscopic associations of native *PGE* with Fe-hydroxides. This conclusion is supported by optical and

SEM investigations, indicating that a number of these minerals are visibly heterogeneous, and commonly in contact with limonite. 2) Alternatively, the compounds could be “true” oxides. The existence of *PGE* – O chemical bonding cannot be demonstrated in the absence of structural data, although it should not be ruled out in principle. Hypothetical compositions of the Ru – Os – Ir – Fe compounds in the ternary diagram O – *PGE* – (Fe + Ni + Cu) are presented in Figure 7A. They were obtained by recalculation of all metals as ideal oxides, considering a constant valence of 4+ for *PGE*, and the oxides Fe₂O₃, NiO, and CuO. Recalculation yielded totals between 96 and 104 wt% in grains larger than 5 µm, the deviation from 100% possibly being due to either the presence of OH or the presence of other valence states of the *PGE*, between 2+ and 6+ in oxygen-bearing compounds (Brookins 1987).

Some grains contain traces of sulfur, whereas others display S-enriched zones (Table 5, anal. VS5–13–5) in which the sulfur/metal value is as low as 0.47 and approaches that of partially desulfurized laurite. This observation suggests that the oxygen-bearing compounds may have had sulfide precursors, and possibly represent the last stage of laurite desulfurization, analogous to the porous Ru – Fe alloy described by Stockman & Hlava (1984). However, the Ru – Os – (Ir + Rh + Pt + Pd) diagram (Fig. 7B) shows two distinct groups of compositions. One group plots close to the Ru – Os join, is clearly distinct from previously reported terrestrial alloys (Harris & Cabri 1991) because of a higher Ru content, and overlaps the compositional field of the Vourinos laurite, confirming a possible genetic relation. The other group plots in the Ru-rich field of the terrestrial alloys, and displays enrichment in Ir, having Ir > Os in some cases. These compositions also have relatively high Pt and Pd that is quite unusual for the Vourinos laurite. Therefore, if laurite was the sulfide precursor of this group of *PGM* also, enrichment in Ir, Pt and Pd must have occurred at some stage during or after desulfurization.

There is also evidence that the Ru – Os – Ir – Fe compounds are unstable during low-temperature evolution of the host chromitite. The zoned grain located in a crack in contact with ferrian chromite, chlorite and limonite (Fig. 5A) consists of two parts separated by a sharp boundary that clearly appears to be in physical continuity with the left border of the crack. An electron-microprobe analysis shows that Ir, Pt, Pd, and Ni are depleted, whereas Ru and Fe are enriched in the portion of the grain inside the crack (Table 5, anal. VS6–2–2 and VS6–2–5). The presence of abundant limonite in this fissure and adjacent to the grain suggests that Fe may have been added by reaction with a circulating aqueous fluid, whereas grain zonation demonstrates that these solutions were able to remove Ir, Pt, and Pd, preferentially; these elements were redistributed in the chromitite alteration-system, thus resulting in a relative increase of the less mobile Ru and Os in the relict *PGM*.

CONCLUDING REMARKS

Examination of chromitite samples from the Vourinos ophiolite complex has revealed that primary-magmatic laurite and ruthenian pentlandite are replaced along their rim by low-S Ru – Os – Ir sulfide or metallic Ru and Cu – Ni alloys. These minerals are in apparent disequilibrium with the conditions inferred for precipitation of magmatic PGM at Vourinos, involving progressive increase of $f(S_2)$ at decreasing T (Legendre & Augé 1986). On the contrary, they are interpreted to have formed in response to decrease of $f(S_2)$ during postmagmatic evolution of the chromitite at relatively low temperatures.

The Ru – Os – Ir – Fe oxygen-bearing compounds of Vourinos are similar in composition to the porous Ru – Fe alloy from ophiolitic chromitites of Oregon (Stockman & Hlava 1984), but they differ in optical properties, probably indicating a distinct mineral species. Nevertheless, we believe that, similarly to the Oregon alloy, it represents the last stage of *in situ* desulfurization of crystals of primary laurite under the influence of chemically active solutions. This is supported by detection of S in some of the grains, indicating origin by reduction of a sulfide precursor, and argues against direct deposition of these PGM from circulating solutions. Porosity produced by reducing reactions, typical of the Oregon alloy, was not observed in the samples described here. External morphology and apparent lack of voids indicate that there was no significant change in volume, and the loss of S was presumably compensated by gains in Fe, Ni, and Cu. Incorporation of oxygen, not reported from the Oregon alloy, was qualitatively demonstrated in some grains from Vourinos, although it was not possible to establish the chemical bonding with PGE and with Fe.

Paragenetic and compositional observations suggest that the assemblage of secondary PGM was not formed in a single step of alteration, but is the result of complex reworking of the primary PGM involving important variations of the physical and chemical parameters. Serpentinization, which is easily visible in all of the samples examined, has produced important modifications to the assemblage of opaque minerals in the chromitites. Secondary sulfides (pentlandite, millerite, heazlewoodite), alloys (awaruite, native copper), and oxides (magnetite, ferrian chromite) were formed during this event, reflecting the establishment of reducing conditions (relatively low Eh and pH) determined by release of H_2 during hydration of olivine (Eckstrand 1975). At this stage, chromite was little affected, and protected the included PGM from alteration. Only those

grains in contact with fractures or within the silicate matrix may undergo partial desulfurization along their rim because of the marked drop of $f(S_2)$. Precipitation of abundant Fe hydroxides and formation of oxygen-bearing PGM are confined to samples from Agriates. The Fe hydroxides (goethite, lepidocrocite, and limonite) are not expected as product of serpentinization (Filippidis 1982, 1985), but they are very common as weathering products after iron-bearing minerals in various types of gossans. Their crystallization must, therefore, postdate the main event of serpentinization. The samples collected in old mine dumps have probably been exposed to present-day weathering for a long time, which involved increase of $f(O_2)$ and shifting of pH toward basic values. Under these conditions, Fe-hydroxides become stable, desulfurization proceeds by oxidation of S to SO_4 ion in aqueous solution, and at the same time reduced metals present in the PGM grains can be oxidized. Theoretical Eh–pH diagrams (Brookins 1987) suggest that oxides of Ru and Os might coexist with $Fe(OH)_3$ in a relatively wide range of conditions, supporting the possible existence of PGE – O bonding in the Ru – Os – Ir – Fe compounds of Agriates.

Several lines of evidence indicate movement of the PGE during the formation of the secondary PGM assemblage at low temperature: 1) laurite loses some Ir and probably Os during early stages of desulfurization, 2) oxidized compounds of Ru – Os – Ir – Fe are unstable, releasing $Ir < Pd < Pt$, 3) variable amounts of Ir, Pt, and Pd were probably added to some desulfurized grains, together with Fe, Ni, Cu, and O, and 4) anhedral to colloform and botryoidal Ir-, Pt- and Pd-bearing alloys probably formed by redeposition from aqueous solutions. It seems clear that the PGE display differential mobility, approximately in the order $Ru < Os < Rh < Ir < Pd < Pt$. This sequence is in broad agreement with i) theoretical predictions on Eh–pH conditions of stability of PGE species in aqueous systems (Westland 1981, Wood *et al.* 1992), and ii) the higher mobility of Pt and Pd with respect to the other PGE observed in many natural occurrences (Bowles 1986, Bowles *et al.* 1994, Prichard & Lord 1994). The absence of specific Pt- and Pd-bearing PGM in the magmatic assemblage implies that these metals were originally provided to the solutions by alteration of primary laurite, irarsite and cuproiridsite containing Pt and Pd in trace amounts. Because of their higher mobility in comparison with the rest of the PGE, Pt and Pd were progressively and selectively concentrated during advancing alteration, until the precipitation of specific phases. The process should act as a sort of chemical refining as a result of repeated cycles of dissolution and redeposition at low temperature, in response to appropriate changes of Eh and pH (Bowles 1987).

The extent of PGE mobilization is difficult to determine on the basis of mineralogical observations. It has been suggested that Pt may be mobilized into soils over distances of several tens of meters (Bowles 1987, Cook &

Fletcher 1992, Cook *et al.* 1992, Prichard & Lord 1994). However, we believe that in the example described here, there probably was redistribution of the more mobile metals (Ir, Pt, Pd) only at a small scale (centimetric). Furthermore, this evidence is limited to strongly weathered samples, as the mutual relations of PGE in normally serpentized chromitites of the Vourinos complex actually reflect magmatic processes (Economou *et al.* 1986, Kostantopoulou & Economou-Eliopoulos 1991).

ACKNOWLEDGEMENTS

The authors express their appreciation to Drs. Elias Grivas and Anna Rassios of the IGME (Kozani, Greece) for their help and useful suggestions during the field work. Special thanks are due to Dr. Stelio Gavrilidis, who was our guide in the field and provided substantial support in collecting samples. Prof. Giam-piero Venturelli and Dr. Emma Salvioli are gratefully acknowledged for their assistance during the work at the SEM laboratory of the Dipartimento di Scienze della Terra, University of Parma. Comments by Drs. Stephen L. Chrysosoulis, Nigel J. Cook, Prof. Maria Economou and Robert F. Martin greatly improved the quality of the paper. The present investigation was in part financed by the Italian MURST (grant 1990).

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Received July 10, 1996, revised manuscript accepted December 29, 1996.