PLATINUM-GROUP-MINERAL INCLUSIONS IN OPHIOLITIC CHROMITITE FROM THE VOURINOS COMPLEX, GREECE

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ABSTRACT

Several types of platinum-group-mineral (PGM) inclusions have been found in chromitite from the Vourinos ophiolite complex, Greece. They contain three platinumgroup elements, Os, Ir and Ru, occurring as sulfide (Oslaurite and laurite), sulfarsenide (osarsite and irarsite) and alloy (rutheniridosmine, iridosmine and osmiridium). Some PGM contain minor quantities of Pt, Pd, Rh and Ni, In spite of their small size (< 10 μ m), two-phase euhedral inclusions (alloy - sulfide) have been successfully analyzed. PGM inclusions have been identified in massive and disseminated chromite, and some have also been observed in accessory spinel from dunite. All the PGM, including the sulfarsenides, are primary. PGM-rich and PGM-free deposits have been distinguished within the massif, but there is no systematic distribution of the PGM in chromite since all the phases may coexist in any one deposit. The role of chromite as a collector of platinum-group elements appears to be restricted to a mechanical trapping of the PGM. It has not been possible to establish a genetic link between the crystallization of PGM and that of chromite.

Keywords: platinum-group minerals, platinum-group elements, ophiolitic complex, chromitite, Vourinos complex, Greece, inclusion, ultramafic rocks.

SOMMAIRE

On trouve différents types de minéraux du groupe du platine (MGP) en inclusion dans des échantillons de chromitite du complexe ophiolitique du Vourinos (Grèce). Tous ces minéraux comprennent trois éléments du groupe du platine: Os, Ir et Ru. Ce sont des sulfures (laurite à Os et laurite sensu stricto), des sulfarséniures (osarsite et irarsite) et des alliages (rutheniridosmine, iridosmine et osmiridium). Certains contiennent Pt, Pd, Rh et Ni en quantités mineures. Malgré leur petite taille ($< 10 \mu m$), des inclusions biphasées automorphes (sulfure - alliage) ont pu être analysées. On a identifié des inclusions de MGP dans la chromite massive et disséminée. On en signale également dans le spinelle d'une dunite. Tous les MGP, y compris les sulfarséniures. sont primaires. A l'échelle du massif, on a pu distinguer des gisements riches en MGP et d'autres sans MGP, mais on n'a observé aucune distribution définie des différents MGP dans la chromite puisque toutes les phases peuvent coexister dans un seul et même gisement. Le rôle de la chromite comme collecteur des éléments du groupe du platine semble réduit à un simple piégeage mécanique des MGP. On n'a pas pu établir de lien génétique entre la cristallisation des MGP et celle de la chromite.

Mots-clés: minéraux du groupe du platine, éléments du groupe du platine, complexe ophiolitique, chromitite, Vourinos, Grèce, inclusion, roches ultramafiques.

INTRODUCTION

Particular attention has recently been paid to the geochemistry of platinum-group elements (PGE), in part owing to improvements in analytical techniques. Previous studies have been devoted mainly to stratiform complexes, as many contain economic concentrations of PGE (Page & Jackson 1967, Page 1971, Crocket et al. 1976). The discovery of platinumgroup minerals (PGM) as discrete inclusions in massive chromitite in ophiolitic complexes (Constantinides et al. 1980, Johan & Legendre 1980, Prichard et al. 1981, Legendre 1982, Stockman & Hlava 1984) has led to studies of PGE in ophiolitic chromitite (Page et al. 1982a, b, 1984, Legendre 1982, Page & Talkington 1984). The study of PGE distribution is of great interest in theoretical models of magmatic processes (Page et al. 1983, 1984).

Detailed investigations of chromite mineralization in the Vourinos ophiolitic massif provide a framework for a systematic study of PGM in massive and disseminated chromite. Inclusions in chromite grains in chromitite have often been described in the literature, e.g., silicate inclusions (McDonald 1965, in the Bushveld complex), fluid inclusions (Anthonioz & Viana Correa 1974) or PGM inclusions (Page & Jackson 1967). Because of the systematic association of such inclusions with chromite, their presence must be considered in any genetic model of chromite crystallization. The aim of this paper is to contribute to our understanding of the concentration processes of PGE in chromium-rich environments. New chemical data of PGM in chromitite of the Vourinos ophiolite complex are presented.

LOCATION AND GEOLOGY OF CHROMITE DEPOSITS

The Vourinos ophiolite complex, located in northwestern Greece (Fig. 1), is about 30 km long and 15 km wide. Tectonized harzburgite interlayered with dunite constitutes about 80% of the complex (Moores 1969, Harkins *et al.* 1980). This unit, corresponding to the mantle sequence, contains several types of chromite occurrences associated with dunite bodies (Zachos 1969, Burgath & Weiser 1980, Apostolidis *et al.* 1981). Overlying this harzburgite unit is a thick massive layer of dunite, corresponding to the base of the cumulate section (Fig. 1) and grading progressively into wehrlite and gabbro. A few occurrences of chromite are located within the basal dunite (Augé, in prep.). Above the gabbro unit, quartz dolerite, granophyre and plagiogranite or dolerite, locally arranged in a sheeted dyke complex, complete the succession (Brunn 1956). Pillow lavas of calcalkaline affinity have also been recognized (Noiret *et al.* 1981, Beccaluva *et al.* 1984).

Five chromite zones (forming one or several layers commonly associated with minor chromite seams) have been sampled in detail. One of the characteristics of the Vourinos chromitite is the diversity in ore textures: schlieren (most common), banded, massive, disseminated and nodular types of chromite are all present. In some cases, the different types occur within the same body; otherwise, a single textural type dominates. Cumulus textures have been recognized (Burgath & Weiser 1980), but a hightemperature deformation fabric is superimposed and makes it difficult to interpret magmatic features. For example, "crescumulate" textures, commonly observed in the Aetorache deposit, have been recently reinterpreted as the result of metamorphic processes (Christiansen & Roberts, in prep.). Olivine, forming the main gangue mineral, has a deformation fabric that has obliterated primary features. Orthopyroxene and clinopyroxene grains (poikilitically enclosing chromite or interstitial to chromite crystals) have also been observed. Most of the textures observed are recrystallized to varying degrees.

The degree of alteration of the gangue minerals is highly variable from fresh to completely transformed, and it is estimated that the average degree of serpentinization is no more than 50%. It should



FIG. 1. Location map of the chromite deposits studied in the Vourinos complex, Greece: 1 Tsouka, 2 Aetorache, 3 Voidolakkos, 4 Konivoy, 5 Xerolivado (after Burgath & Weiser 1980).

be noted that only the least altered samples were collected. Another characteristic of the Vourinos chromite deposits is their location in extremely large bodies of dunite.

The chemical composition of the chromite is constant. All the chromitites, regardless of their positions in the series and the type of ore, have the same relative proportions of trivalent elements (microprobe analyses, average of 35 samples of chromitite from the 5 ores zones: Cr_2O_3 57.6 wt.%, σ 1.7; Al_2O_3 11.5 wt.%, σ 1.1; Fe_2O_3 3.0 wt.%, σ 0.9). The observed variations of the Mg/(Mg + Fe²⁺) ratio (between 0.68 and 0.72) are related to the chromite/olivine ratio of the rock. It has been established (Lehmann 1983) that during cooling of an olivinespinel assemblage, Mg migrates from spinel to oli-



FIG. 2. Scanning-electron-microscope images of PGM included in chromite crystals. A-B, same two-phase grain (A, secondary electron; B, back-scattered electron images); rounded crystal, iridosmine; crystal on left, laurite (specimen G 274). C-D, laurite (G 141 and G 97 b). E, two-phase grain of irarsite and osarsite (G 229). F, iridosmine and laurite (distinguishable on the left) in a cavity (G 133). Scale bar is 2 μm.

vine whereas Fe migrates from olivine to spinel. The Fe/Mg ratio of the mineral pair results from diffusive processes during subsolidus re-equilibration (at a temperature lower than that of the metamorphic recrystallization). Hence the composition of the two phases is a function of their relative proportion.

METHODS

Polished thin sections were systematically studied in reflected light at a magnification of $400 \times$. Thirtyeight sections of chromitite, chromitiferous dunite and a few dunites were investigated. Only the chromite grains were examined for PGM; associated silicates were not studied because of their high degree of alteration and the poor quality of the polish.

Five chromite zones have been studied (Fig. 1): Tsouka (6 sections investigated, no PGM found), Aetorache (12 sections, PGM in 6), Voidolakkos (5 sections, PGM in 2), Konivoy (10 sections, no PGM found), Xerolivado (5 sections, PGM in 2). Each section corresponds to a different sample collected from different parts of the ore zones. The samples are taken to be representative of the deposits.

From the above data, the distribution of PGM in the different ore-zones appears to be highly heterogeneous. Moreover, two sections from Aetorache contain two PGM grains and one section three PGM grains, and all the grains are in massive or disseminated ore except one, which is in a grain of spinel from a dunite in the vicinity of chromitite.

PGM were studied with a scanning-electron microscope (Fig. 2) and analyzed using a Camebax electron microprobe using the following operating conditions: acceleration voltage 25 kV, reference current 20 nA, beam diameter 0.6 μ m, counting time 10 s. The following X-ray lines were used: SK α , AsL β , OsL β , RuL α , RhL α , IrL α , PtL α , PdL β , NiK α , CuL α , FeK α , CrK α . A pure-metal phase was used as a standard for all the elements, except for S, where pyrite was employed. A minor interference exists between RuL β and RhL α . This interference was corrected (100% Ru corresponding to 2.3% Rh). Matrix-absorption errors were not estimated here.

The PGM analyses total to much less than 100% and typically have significant concentrations of Fe and Cr (Table 1). These deficiencies are attributed to the very fine grain-size of the PGM; the Fe and Cr values are either due to fluorescence of the host chromite or to its direct X-ray emission. Because of the good approximation to stoichiometry, the analytical results are presumed acceptable. The raw data in weight percent after the Rh correction are given in Table 1 together with compositions recalculated

TABLE 1. COMPOSITION OF PLATINUM-GROUP MINERALS IN CHROMITE FROM THE VOURINOS OPHIOLITE COMPLEX, GREECE

	1	2	3	4a	5	6b	7	8c	9	10	11c	12	13a	14b	15	16
S (1) As	30.55	37.58	28.25 1.15	21.26	30.53 2.09	23.62	32.28 0.03	10.90 24.44	9.11 24.23	10.60 24.14	11.04 23.32	0.03	0.14	0.92	-	-
Os Ru Ir Ph	2.59 42.88 3.90 1.27	4.03 48.49 5.37	4.15 40.11 5.21	14.14 21.25 3.41	19.22 27.16 13.05	21.59 22.81 5.28	17.32 33.28 7.51	31.15 7.90 13.10	34.30 8.61 4.29	6.42 3.00 40.62	7.60 1.93 45.66	49.19 5.89 39.43	55.66 0.97 37.15	61.00 1.09 31.91	44.70 1.96 37.41	27.47 2.55 56.46
Pt Pd Ni	0.15	0.10	0.06	0.30	0.08	0.03	0.14	1.14	0.01	0.38 0.77 0.18 1.38	0.14 0.75 0.99	0.24	0.31	0.01	0.18	2.03 0.28 0.15
Cu Fe Cr Tot.	1.05 4.33 86.77	0.41 1.54 98.21	1.45 5.51 87.32	8.74 24.29 94.23	1.08 2.72 96.56	- 1.38 5.43 80.74	1.03 4.40 96.87	1.61 2.97 93.72	2.22 5.48 88.65	1.40 4.19 93.08	0.85 2.35 94.94	0.93 2.85 99.39	1.20 2.80 99.12	0.71 2.21 98.62	2.56 10.50 97.74	2.34 9.51 101.03
S (2) As Os	,37.54 3.18	39.04 4.19	35.15 1.43 5.16	34.74 23.10	32.91 2.25 20.72	31,96	35.30 0.03 18.94	12.23 27.42 34.95	11.25 29.93 42.36	12.12 27.59 7.34	12.03 25.42 8.28	0.03 51.45	0.15 58.52	0.96 0.25 63.74	52.79	- 30.71
Ru Ir Rh Pt	52.68 4.79 1.56	50.37 5.58 0.72	49.91 6.48 1.78	34.72 5.57 1.21	29.28 14.07 0.68	30.85 7.14 0.72	36.40 8.21 0.89	8.86 14.70 0.57	10.64 5.30 0.17	3.43 46.43 0.43	2.10 49.77 0.34	6.16 41.24 0.82	1.02 39.06 0.85	1.14 33.34 0.49	2.31 44.18 0.41	2.85 63.12 0.57
Pd Ni Cu	0.18	0.10	0.07	0.49 0.16	0.09	0.12	0.15	1.28	0.01 0.33	0.21	0.82	0.25	0.33	0.01	0.21	0.31
S (3) As Os	66.84	68.57	64.92 1.13	67.86	66.81 1.96 7.09	66.38	68.16 0.03	33.98 32.61	31.52 35.88 20.00	34.42 33.55	35.14 31.77	0.08	0.37	5.36 0.60	-	-
Ru Ir Rh	29.76 1.42 0.87	28.07 1.63 0.39	29.24 2.00 1.02	21.52 1.82 0.74	18.85 4.76 0.43	20.32 2.48 0.46	22.29 2.65 0.53	7.81 6.81 0.50	9.45 2.48 0.15	3.09 22.00 0.38	1.95 24.24 0.31	10.93 38.48 1.42	1.88 37.93 1.54	2.02 31.03 0.85	4.26 42.73 0.75	5.21 60.70 1.02
Pt Pd Ni	0.10 0.06	0.10	- 0.07	0.29 0.17	 0.10	0.14	0.09	- 1.94	0.01 0.51	0.42 0.18 2.45	0.07 0.72 1.72	0.42 0.16	0.57 0.27	0.02 0.19	0.37 0.30	2.15 0.54 0.53

- element not detected. Laurite: analysis 1, specimen 6 141, chromite deposit: Aetorache; 2, 6 302, Voidolakkos; 3, 6 94, Xerolivado. <u>Os-laurite</u>: 4, 6 133, Aetorache; 5, 6 137, Aetorache; 6, 6 274, Voidolakkos; 7, 6 97 b, Xerolivado. <u>Osarsite</u>: 8 & 9, 6 229, Aetorache. <u>Irarsite</u>: 10 & 11, 6 229, Aetorache. <u>Rutheniridosmine</u>: 12, 6 134, Aetorache. <u>Iridosmine</u>: 13, 6 133, Aetorache; 14, 6 274, Voidolakkos; 15, 6 231, Aetorache. <u>Osmiridium</u>: 16, 6 231, Aetorache. Superscripts (a-c) correspond to analyses of the same biphase grain. (1): raw analyses in weight percent of the element (after Rh correction). (2): analyses recalculated after subtraction of Fe and Cr. (3): atomic concentration calculated from the corrected analyses. to 100% after the subtraction of Fe and Cr, and atomic proportions calculated from the corrected compositions. This correction seems reasonable since the Fe/Cr ratio of the PGM grains is approximately constant and identical to that of the host chromite. Each analysis in Table 1 represents the best results of several point-analyses, on the basis of analytical totals nearest 100 wt.% and low Cr content.

PGM DESCRIPTION AND ANALYTICAL RESULTS

The PGM in these grains of ophiolitic chromite are very fine grained (2–9 μ m, mean 4.5 μ m). All of them are likely to be magmatic since they are 1) included in chromite (always remote from crystal fractures in spinel), 2) never interstitial (associated with other sulfides), in contrast to PGM in the Bushveld complex (Vermaak & Hendriks 1976) and in the Shetland ophiolitic chromite (H.M. Prichard, pers. comm.) and 3) never found within intercumulus silicates (as in the Bird River sill, Manitoba; D.H. Watkinson, pers. comm.). Crystals vary in habit from perfect rhombic crystals with rounded apices (Fig. 2C, D) to ellipsoidal grains (Fig. 2A). However, polyhedral crystals are the most common, and some of the grains appear to consist of two phases (Fig. 2A, B, F). Although no silicate has been found in contact with the PGM (as described by Legendre 1982, Stockman & Hlava 1984), a two-phase grain has been found in a cavity (Fig. 2F).

No relationships have been established among composition, textural type and paragenesis of the chromite, and the mineralogy of the PGM inclusions. Six different phases have been identified. Using the nomenclature of Harris & Cabri (1973) and Cabri (1981), these are Ru-Ir-Os alloys (rutheniridosmine, iridosmine and osmiridium), sulfides and sulfarsenides (laurite, osarsite and irarsite) (Fig. 3). All occur in a single chromite zone (i.e., Aetorache). Iridosmine and laurite coexist in the Voidolakkos area, whereas laurite is the only phase observed in the Xerolivado mine. It is difficult to draw conclusions from this distribution. The diversity of the phases occurring within the Aetorache orebody is notable. In a comprehensive study of eight different complexes, Legendre (1982) never mentioned more than three different primary phases in the same massif.

Another interesting point is the coexistence of sulfide and alloy not only in the same section but also within the same grain. In this latter case, the proportion of the alloy is markedly larger than that of sulfide (Fig. 2A, B, F).

Laurite

Laurite (ideally, RuS_2) accounts for 50% of the PGM occurrences. Table 1 and Figure 3A show that

two compositional ranges can be distinguished: (i) laurite senso stricto, in which Ru/(Ru + Os + Ir) > 0.9, and (ii) Os-bearing laurite, in which 0.60 < Ru/(Ru + Os + Ir) < 0.7. The Ir content is constant for both types. For other ophiolitic complexes, however, Os-for-Ru substitution is continuous between RuS₂ and Ru_{0.7}Os_{0.3}S₂ (Constantinides et al. 1980, Legendre 1982). Minor elements have also been detected in significant concentrations; in addition to Rh, which is still present after correction, As exceeds 1.0 wt. % in two grains, whereas it is below the detection limits in other grains. Ni and Pd contents are less than 0.1 wt. %.

Sulfarsenides

Two phases have been analyzed in this study. They are part of the same inclusion (Fig. 2E). Intermediate compositions (Os,Ir)AsS have also been obtained, but they correspond to compositions of the interface between the two phases of the inclusion. Os and Ir X-ray images show the existence of two distinct phases. Moreover, important crystal-structure differences between osarsite (monoclinic) and irarsite (cubic) dictate a miscibility gap between these phases.



Fic. 3. Results of electron-microprobe analyses (at. %) of PGM alloys and sulfides (A) and sulfarsenides (B) in the triangular diagram Os-Ir-Ru. Symbols: ● alloys O sulfide and □ sulfarsenide. Tie lines: --- links PGM occurring in the same section, — links PGM occurring in the same grain.

However, Feather (1976) reported an osarsite containing 20 wt. % Ir (but only 8.2 atomic % S instead of 33.3).

Osarsite is richer in Ru than irarsite (Fig. 3B). This can be explained by a structural analogy between irarsite and ruarsite, RuAsS, involving a solid solution, whereas there probably is a miscibility gap between irarsite (cubic) and ruarsite (monoclinic). Furthermore, Snetsinger (1972) described a sample of osarsite containing 18 wt. % Ru. The Ru content determined here, 8 wt. %, is the same as that given for an osarsite by Distler & Laputina (1979, in Cabri & Laflamme 1981).

Osarsite and irarsite contain equal amounts of Rh (0.3 wt. %) and Ni (1.0 wt. %), whereas Pd and Pt occur only in irarsite (Table 1). A wide range of irarsite compositions is given by Cabri & Laflamme (1981); the present compositions fall within this range (Table 1).

Alloys

In contrast to the sulfides, the Ru content of the alloys is very low (Fig. 3A); the rutheniridosmine compositions are very close to those of iridosmine, according to Harris & Cabri (1973). Iridosmine is the most common. All the grains of alloy contain minor Rh, Pd and Ni, whereas osmiridium is significantly enriched in Pt (up to 2.5 wt. %). The same feature is reported by Legendre (1982) in osmiridium from New Caledonia.

PGE sulfide – alloy associations

The grains of alloys associated with a sulfide and those that occur alone do not differ in composition. Similarly, sulfides associated with alloys are not specific (Table 1, Fig. 3A), *i.e.*, the same composition can be found in isolated inclusions. This suggests that the alloy – sulfide association is primary and not the result of a late transformation.

DISCUSSION

From Figure 3A, it appears that there are both Rurich and Os-Ir-rich minerals. The former are sulfides and the latter are alloys; sulfides and alloys may or may not coexist in the same inclusion. Where a sulfide and alloy coexist, the proportion of sulfide is always low, and its texture (Fig. 2A, B) suggests that it crystallized after the alloy. Furthermore, Legendre (1982) has described an epitactic growth of sulfide on a grain of alloy, confirming the order of crystallization: (1) alloy (\pm sulfide), (2) sulfide alone. This is not consistent with the hypothesis of sulfurization of an alloy. Legendre (1982) and Talkington *et al.* (1983) have shown that alloy and sulfide can coexist at fixed T and $f(S_2)$, the $f(S_2)$ required for the formation of RuS₂ being lower than that for the formation of Os – Ir sulfides.

The existence of two sulfide compositional groups could be explained by the fact that the Os content of laurite is a function of T and $f(S_2)$ during crystallization (Legendre 1982). Local variations of either T or $f(S_2)$ (or both) could explain variations in the Os content of laurite.

Except for one crystal of osmiridium, the composition of alloy is rather constant compared with that of the sulfides (Fig. 3A). This osmiridium coexists in the same section with iridosmine. The compositions of these two alloys plot exactly on both sides of the miscibility gap defined by Harris & Cabri (1973).

The presence and composition of sulfarsenides are more difficult to explain. Feather (1976) studied mixtures of erlichmanite, irarsite and osarsite resulting from partial or complete alteration of Ir-Ru-Os alloys, and Stumpfl & Tarkian (1976) described reaction rims of pure irarsite; the reaction is characterized by the introduction of As and S. This study does not provide any indication that the sulfarsenides are products of transformation. They are not associated with other types of PGM, are included in the chromite and are remote from any fractures (Fig. 2E). It is more likely that they are primary, unaffected by secondary processes such as those described by Stockman & Hlava (1984), *i.e.*, they crystallized before being trapped in chromite crystals.

Although the systematic association of PGE concentrated in chromite is well established (e.g., Page et al. 1976, Wolf & Agiorgitis 1978), its significance is still a problem under debate. Naldrett & Cabri (1976) mentioned the possibility that the spinel structure could act as a collector for PGE that are later exsolved as inclusions during cooling. Gijbels et al. (1974) considered that in the Bushveld complex, cumulus chromite concentrates PGE very efficiently before expelling up to 25% PGM into surrounding silicates during cooling. In Greek chromitites, a correlation between the Cr content of the chromite and its PGE content has been observed (Agiorgitis & Wolf 1978), which might indicate a PGE-for-Cr substitution in chromite. However, this correlation (of the Cr₂O₃ content of the ore and not of the chromite crystals) only means that the PGE are located in chromite grains and not in the silicate gangue. Cousins & Vermaak (1976) questioned the possibility of solid solution of PGE in chromite and favored the existence of discrete inclusions in chromite grains, although such were never observed.

It is now well established that PGE form discrete mineral phases in chromite (Constantinides *et al.* 1980, Talkington *et al.* 1983, Stockman & Hlava 1984). Their euhedral habit (without particular orientation in the host crystal) and their irregular distribution from one deposit to another are not compatible with an exsolution process, nor is the diversity of their composition. The implication is that the PGE are not incorporated in chromite as a solid solution.

Hiemstra (1979) proposed a possible collection of PGE through droplets of metallic iron existing under certain conditions in a magma. Because of their physical properties, droplets will be concentrated. An increase in $f(O_2)$ would cause a dissolution of the iron and the formation of PGM that will then be carried down, included in chromite crystals.

Legendre (1982) proposed two mechanisms for the preconcentration of PGE. The first is similar to that invoked by Hiemstra (1979) but, in this case, PGE are collected in nickel metal droplets and would then be expelled because of an increase in $f(O_2)$ that would promote a redissolution of Ni. The second model implies collection of PGE related to clinopyroxene crystals since this phase is systematically associated with PGM inclusions in chromite (Legendre 1982). None of those processes seems likely to account for the occurrences described here. Neither Ni-Fe alloy nor clinopyroxene has been observed associated with the PGM inclusions, and whatever the process involved, the PGM will be expelled before chromite crystallization.

The problem, therefore, is to determine whether and why there is a genetic correlation between the formation of chromite bodies and the crystallization of PGM, as has been recently suggested by Talkington et al. (1983). A partial answer is provided in this study. Firstly, PGM crystallization is not only associated with chromite concentration, since PGM have been found in disseminated spinel from one dunite. At least 50 thin sections would have to be investigated to have the same chance of finding a PGM as in a massive chromite. Secondly, within the same ophiolite complex, PGM-rich and PGM-free chromite deposits exist. Finally, the compositional diversity of PGM occurring within the same body noted here cannot simply be explained by modification in magmatic conditions during chromite crystallization, as indicated by Talkington et al. (1983) in the example of the Bird River sill. The close association of PGM and chromite crystals does not necessarily imply that the crystallization of the PGM is due to the same conditions as the crystallization of the chromite.

In ophiolitic complexes, most of the chromite and its included PGM crystallized in magma pockets in the mantle sequence, before the magma entered the main overlying chamber (Neary & Brown 1979, Brown 1980, Lago *et al.* 1982). However, it is not known whether PGM precipitate in the same horizon as the chromite and are then trapped (acting as nuclei) or whether they precipitate before and are carried in the upwelling magma into pockets or conduits where chromite would then crystallize. If PGE are not collected in chromite as solid solution, chromite crystallization will provoke a mechanical trapping of the PGM, as for other solid inclusions (*i.e.*, silicates).

CONCLUSIONS

Platinum-group-mineral inclusions in chromite are small (< 10 μ m) and commonly euhedral. In ophiolitic chromitites, the inclusions mainly contain Os, Ir and Ru. Sulfides (laurite), sulfarsenides (osarsite and irarsite) and alloys (rutheniridosmine, iridosmine and osmiridium) have been found in the same deposit (Aetorache) of the Vourinos complex. Such a diversity in composition of the coexisting primary PGM had not been described in ophiolitic complexes. Hence, a statistical distribution of the PGM in chromite deposits cannot be established. PGM are not only associated with chromite orebodies since one inclusion has been found in a spinel grain from a dunite.

Although this study has emphasized the diversity of the PGM occurring within a single complex, the chemical composition of the PGM has not, however, been interpreted in detail because of the lack of experimental data concerning PGE in appropriate magmatic systems, especially their degree of solubility.

The problem of whether a chemical collector for the PGE exists or not is still debatable. However, if there is such a collector, the PGM will be expelled before chromite crystallizes. Thus, although chromite crystals and PGM are closely related, it has not been possible to establish a genetic relationship between the conditions of crystallization of the two nor with the formation of the chromite orebodies.

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REFERENCES

- AGIORGITIS, G. & WOLF, R. (1978): Aspects of osmium, ruthenium and iridium contents in some Greek chromites. *Chem. Geol.* 23, 267-272.
- ANTHONIOZ, P.M. & VIANA CORREA, A. (1974): Inclusions fluides dans la chromite. Cas des chromites podiformes d'âge précambrien en Portugal du Nord-Est. C.R. Acad. Sci. Paris 278, 3271-3273.
- APOSTOLIDIS, G., MASTORIS, K. & VGENOPOULOS, A.G. (1981): Exploration of the Xerolivado chromite deposits and their chemical, mineralogical and physical properties. *In* International Symposium on Metallogeny of Mafic and Ultramafic Complexes (S.S. Augustithis, ed.). UNESCO, Athens, 1, 1-20.
- BECCALUVA, L., OHNENSTETTER, D., OHNENSTETTER, M. & PAUPY, A. (1984): Two magmatic series with island arc affinities within the Vourinos ophiolite. *Contr. Mineral. Petrology* 85, 253-271.
- BROWN, M. (1980): Textural and geochemical evidence for the origin of some chromite deposits in the Oman ophiolite. *In* Ophiolites, Proc. Int. Ophiolite Symp. (Cyprus) (A. Panayiotou, ed.). Geol. Surv. Dep., Nicosia, 714-721.
- BRUNN, J.H. (1956): Étude géologique du Pinde septentrional et de la Macédoine occidentale. Ann. Géol. Pays Hellén. 7, 358 p.
- BURGATH, K. & WEISER, T. (1980): Primary features and genesis of Greek podiform chromite deposits. In Ophiolites, Proc. Int. Ophiolite Symp. (Cyprus) (A. Panayiotou, ed.). Geol. Surv. Dep., Nicosia, 675-690.
- CABRI, L.J. (1981): The platinum-group minerals. In Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). Can. Inst. Mining Metall., Spec. Vol. 23, 83-150.
 - & LAFLAMME, J.H.G. (1981): Analyses of minerals containing platinum-group elements. *In* Platinum-Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* 23, 151-173.
- CONSTANTINIDES, C.C., KINGSTON, G.A. & FISHER, P.C. (1980): The occurrence of platinum group minerals in the chromitites of the Kokkinorotsos chrome mine, Cyprus. *In* Ophiolites, Proc. Int. Ophiolite Symp. (Cyprus) (A. Panayiotou, ed.). Geol. Surv. Dep., Nicosia, 93-101.
- COUSINS, C.A. & VERMAAK, C.F. (1976): The contribution of Southern African ore deposits to the geochemistry of the platinum group metals. *Econ. Geol.* 71, 287-305.
- CROCKET, J.H., TERUTA, Y. & GARTH, J. (1976): The relative importance of sulfides, spinels and platinoid

minerals as carriers of Pt, Pd, Ir and Au in the Merensky Reef at Western Platinum Limited, near Marikana, South Africa. *Econ. Geol.* **71**, 1308-1323.

- DISTLER, V.V. & LAPUTINA, I.L. (1979): Nickel and cobalt sulpharsenides containing platinum metals. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* 248, 718-721.
- FEATHER, C.E. (1976): Mineralogy of platinum-group minerals in the Witwatersrand, South Africa. *Econ. Geol.* 71, 1399-1428.
- GIJBELS, R.H., MILLARD, H.T., JR., DESBOROUGH, G.A. & BARTEL, A.J. (1974): Osmium, ruthenium, iridium and uranium in silicates and chromite from the eastern Bushveld Complex, South Africa. *Geochim. Cosmochim. Acta* 38, 319-337.
- HARKINS, M.E., GREEN, H.W., II & MOORES, E.H. (1980): Multiple intrusive events documented from the Vourinos ophiolite complex, northern Greece. *Amer. J. Sci.* 280A, 284-295.
- HARRIS, D.C. & CABRI, L.J. (1973): The nomenclature of the natural alloys of osmium, iridium and ruthenium based on new compositional data of alloys from world-wide occurrences. *Can. Mineral.* 12, 104-112.
- HIEMSTRA, S.A. (1979): The role of collectors in the formation of the platinum deposits in the Bushveld complex. *Can. Mineral.* 17, 469-482.
- JOHAN, Z. & LEGENDRE, O. (1980): Minéralogie des platinoïdes dans les chromites massives du feuillet ophiolitique de la Nouvelle Calédonie. *In* Résumés des Principaux Résultats Scientifiques et Techniques du Service Géologique National, BRGM, Orléans (résumé).
- LAGO, B.L., RABINOWICZ, M. & NICOLAS, A. (1982): Podiform chromite ore bodies: a genetic model. J. Petrology 23, 103-125.
- LEGENDRE, O. (1982): Minéralogie et Géochimie des Platinoïdes dans les Chromitites Ophiolitiques. Comparaison avec d'autres Types de Concentrations en Platinoïdes. Thèse de troisième cycle, Université de Paris, France.
- LEHMANN, J. (1983): Diffusion between olivine and spinel: application to geothermometry. *Earth Planet*. *Sci. Lett.* 64, 123-138.
- McDonald, J.A. (1965): Liquid immiscibility as one factor in chromitite seam formation in the Bushveld Igneous Complex. *Econ. Geol.* **60**, 1674-1685.
- MOORES, E.M. (1969): Petrology and structure of the Vourinos ophiolitic complex of northern Greece. Geol. Soc. Amer. Spec. Pap. 118.

NALDRETT, A.J. & CABRI, L.J. (1976): Ultramafic and

related mafic rocks: their classification and genesis with special reference to the concentration of nickel sulfides and platinum-group elements. *Econ. Geol.* **71**, 1131-1158.

- NEARY, C.R. & BROWN, M. (1979): Chromites from Al Ays Complex, Saudi Arabia and the Semail Complex, Oman. In Evolution and Mineralisation of the Arabian Shield (A.M.S. Al Shanti, ed.). Inst. Appl. Geol. Bull. 2, 193-205.
- NOIRET, G., MONTIGNY, R. & ALLEGRE, C.J. (1981): Is the Vourinos complex an island arc ophiolite? *Earth Planet. Sci Lett.* 56, 375-386.
- PAGE, N.J (1971): Sulfide minerals in the G and H chromitite zones of the Stillwater Complex, Montana. U.S. Geol. Surv. Prof. Pap. 694.
 - ____, ARUSCAVAGE, P.J. & HAFFTY, J. (1983): Platinum-group elements in rocks from the Voikar-Syninsky ophiolite complex, Polar Urals, USSR. *Mineral. Deposita* 18, 443-455.
 - ____, CASSARD, D. & HAFFTY, J. (1982a): Palladium, platinum, rhodium, ruthenium, and iridium in chromitites from the Massif du Sud and Tiébaghi Massif, New Caledonia. *Econ. Geol.* 77, 1571-1577.
 - _____, ENGIN, T., SINGER, D.A. & HAFFTY, J. (1984): Distribution of platinum-group elements in the Bati Kef chromite deposit, Guleman-Elazig area, eastern Turkey. *Econ. Geol.* **79**, 177-184.
 - & JACKSON, E.D. (1967): Preliminary report on sulfide and platinum-group minerals in the chromitites of the Stillwater Complex, Montana. U.S. Geol. Surv. Prof. Pap. 575-D, 123-126.
 - PALLISTER, J.S., BROWN, M.A., SMEWING, J.D. & HAFFTY, J. (1982b): Palladium, platinum, rhodium, iridium and ruthenium in chromite-rich rocks from the Samail ophiolite, Oman. *Can. Mineral.* 20, 537-548.
 - ____, Rowe, J.J. & HAFFTY, J. (1976): Platinum metals in the Stillwater Complex, Montana. *Econ. Geol.* 71, 1352-1363.

& TALKINGTON, R.W. (1984): Palladium, platinum, rhodium, ruthenium and iridium in peridotites and chromitites from ophiolite complexes in Newfoundland. *Can. Mineral.* 22, 137-149.

- PRICHARD, H.M., POTTS, P.J. & NEARY, C.R. (1981): Platinum-group element minerals in the Unst chromite, Shetland Isles. *Trans. Inst. Mining Metall.* 90, B186-B188.
- SNETSINGER, K.G. (1972): Osarsite, a new osmiumruthenium sulfarsenide from California. Amer. Mineral. 57, 1029-1036.
- STOCKMAN, H.W. & HLAVA, P.F. (1984): Platinumgroup minerals in alpine chromitites from southwestern Oregon. *Econ. Geol.* 79, 491-508.
- STUMPFL, E.F. & TARKIAN, M. (1976): Platinum genesis: new mineralogical evidence. *Econ. Geol.* 71, 1451-1460.
- TALKINGTON, R.W., WATKINSON, D.H., WHITTAKER, P.J. & JONES, P.C. (1983): Platinum-group-mineral inclusions in chromite from the Bird River sill, Manitoba. *Mineral. Deposita* 18, 245-255.
- VERMAAK, C.F. & HENDRIKS, L.P. (1976): A review of the mineralogy of the Merensky Reef, with specific reference to new data on the precious metal mineralogy. *Econ. Geol.* 71, 1244-1269.
- WOLF, R. & AGIORGITIS, G. (1978): On an unusual platinum element enrichment in chromites from Skyros Island, Greece. Neues Jahrb. Mineral. Monatsh., 39-41.
- ZACHOS, K. (1969): The chromite mineralization of the Vourinos ophiolite complex, northern Greece. In Magmatic Ore Deposits (H.D.B. Wilson, ed.). Econ. Geol., Mon. 4, 147-153.
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