PLATINUM-GROUP MINERALS IN THE TIEBAGHI AND VOURINOS OPHIOLITIC COMPLEXES: GENETIC IMPLICATIONS

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ABSTRACT

Platinum-group minerals (PGM) and base-metal sulfides (BMS) have been found included in chromite from dunite and chromitite in the Vourinos (Greece) and Tiébaghi (New Caledonia) ophiolites. The PGM consist of laurite, erlichmanite, xingzhongite, an Ir–Cu sulfide, prassoite and Ir–Os alloys in the Tiébaghi massif, and laurite, Ir–Os alloys and sulfarsenides in the Vourinos massif. In both complexes, the same PGM were found in dunite and in chromitite, an indication of a genetic relationship between these two rock types. BMS inclusions are mainly Ni-rich pentlandite and chalcopyrite. Some grains of pentlandite contain platinum-group elements (PGE) (mainly Rh, Ru and Pd) in solid solution (up to 43.7 wt.%). The PGM and BMS formed early in a magma; their nature and composition depend on the PGE content of the magma and T and aS_2 during crystallization. The PGM and BMS were trapped in chromite crystals. Depending on the further evolution of the magma, this chromite is now found in dunite or, if chromite crystals were concentrated, in chromitite. The PGM from Tiébaghi are enriched in Cu and have crystallized under higher aS_2 than those from Vourinos.

Keywords: platinum-group minerals, platinum-group elements, ophiolitic complex, chromitite, dunite, Vourinos, Greece, Tiébaghi, New Caledonia, inclusions.

SOMMAIRE

Des minéraux du groupe du platine (MGP) et des sulfures de métaux de base (SMB) se trouvent en inclusion dans la chromite de dunite et de chromitite des complexes ophiolitiques du Vourinos (Grèce) et de Tiébaghi (Nouvelle-Calédonie). Les MGP de Tiébaghi sont: laurite, erlichmanite, xingzhongite, un sulfure d'Ir–Cu, prassoïte et des alliages d'Ir–Os. Dans le Vourinos, on ne trouve que de la laurite, des alliages d'Ir–Os et des sulfoarséniures. Dans les deux complexes, les mêmes MGP ont été découverts tant dans les grains de spinelle des dunites que des chromitites, ce qui indique qu'il existe un lien génétique entre ces deux types de roche. Les SMB en inclusion dans le spinelle sont principalement de la pentlandite riche en Ni et de la chalcopyrite. Dans certains cas, la pentlandite contient des éléments du groupe du platine (EGP) en solution solide (essentiellement Rh, Ru et Pd, jusqu'à 43.7% poids). Les MGP et SMB précocement formés dans le magma (leur nature et composition dépendent de la teneur en EGP du magma et des T et aS_2 lors de la cristallisation) ont été piégés dans les cristaux de chromite. Selon l'évolution ultérieure de ce magma, ces grains de spinelle se retrouveront soit dans des dunites, soit dans des chromitites si ils sont concentrés. Les MGP de Tiébaghi, caractérisés par un enrichissement en Cu, se sont formés sous une aS_2 plus élevée que les MGP du Vourinos.

Mots-clés: minéraux du groupe du platine, éléments du groupe du platine, complexe ophiolitique, chromitite, dunite, Vourinos, Grèce, Tiébaghi, Nouvelle-Calédonie, inclusions.

INTRODUCTION

The presence of platinum-group minerals (PGM) in ophiolitic chromitite is now well established. In most cases, the PGM are included in chromite grains (Constantinides *et al.* 1980, Prichard *et al.* 1981, Legendre 1982, Stockman & Hlava 1984, Talkington *et al.* 1984, Augé 1985a, b, 1986, Legendre & Augé 1986). An exception is the Shetland ophiolite where PGM occur also interstitially to chromite (Prichard *et al.* 1986).

This paper provides a description of the PGM in two ophiolite bodies: the Vourinos complex, Greece, and the Tiébaghi massif, New Caledonia. In these complexes, the PGM have been found as inclusions in chromite from massive ore and also in disseminated chromian spinel (the term chromite is used below to describe chrome-bearing spinel) from different types of dunite occurrences. This discovery of PGM in both types of chromite leads to a contribution to the discussion of the origin of dunite bodies in ophiolitic complexes. Base-metal sulfides have also been found included in chromite. Some grains contain large amounts of platinum-group elements in solid solution.

GEOLOGY

Both Vourinos and Tiébaghi are ophiolitic complexes (Fig. 1), but their characteristics (summarized in Table 1) are quite different. The main differences concern the nature of the mantle sequence, which consists of depleted tectonized harzburgite in the Vourinos complex. In the Tiébaghi massif, harzburgite, spinel lherzolite and plagioclase lherzolite form separate units (Moutte 1982), the limits of which are poorly defined. Transitions between the different

TABLE 1. CHARACTERISTICS OF THE VOURINOS AND TIEBAGHI OPHIOLITIC COMPLEXES

Complex	Age of emplacement	Mantle sequence	Crystallization sequence	Lava
Vourinos	Upper Jurassic	Harzburgite	Ol → Cpx → Opx → Plag	Island-arc tholeiite
Tiébaghi	Upper Eocene	Cpx-harzburgite Lherzolite	—	—

rock types at Tiébaghi can be observed on the scale of one meter, and lherzolites have been found in the harzburgite unit (Johan & Augé 1986). In both complexes, different types of dunite occurrences can be distinguished: 1) dunite envelopes to the chromite concentrations, 2) barren dunite bodies of variable extent, and 3) dykes of dunite that may be concordant with the foliation in the harzburgite.

Both complexes are known for their chromite concentrations, and mines are still active. Some deposits contain over 2 million tonnes, and are typically associated with other minor concentrations of chromite.

In the Vourinos complex, cumulates consisting of dunite, grading progressively into wehrlite and gabbro (Jackson et al. 1975) overlie the harzburgite unit. Quartz dolerite, granophyre and plagiogranite, a sheeted dyke complex (Brunn 1956) and pillow lavas of calc-alkaline affinity (Noiret et al. 1981, Bec-

caluva et al. 1984) complete the ophiolitic suite at Vourinos. In contrast, the units that form the crustal components of the ophiolitic suite are missing in the Tiébaghi complex.

ANALYTICAL METHODS

Polished thin sections and polished sections of chromitite were observed under the microscope at 200 times magnification, sufficient to permit a quick but systematic observation of a large number of sections. Thus, from the Tiébaghi massif 70 sections of chromitite (from 14 occurrences) were investigated and 79 PGM grains were discovered; for the Vourinos complex, 38 sections (from 5 main occurrences) were examined and 16 PGM grains were found. Only chromite crystals were examined for PGM since associated silicates are generally highly altered. Where fresh, the poor quality of the polish obtained

laterite   dunite   harzburgite   dunite + harzburgite   lherzolite

plag. lherzolite   serpentinized peridotite   ● chromite deposit
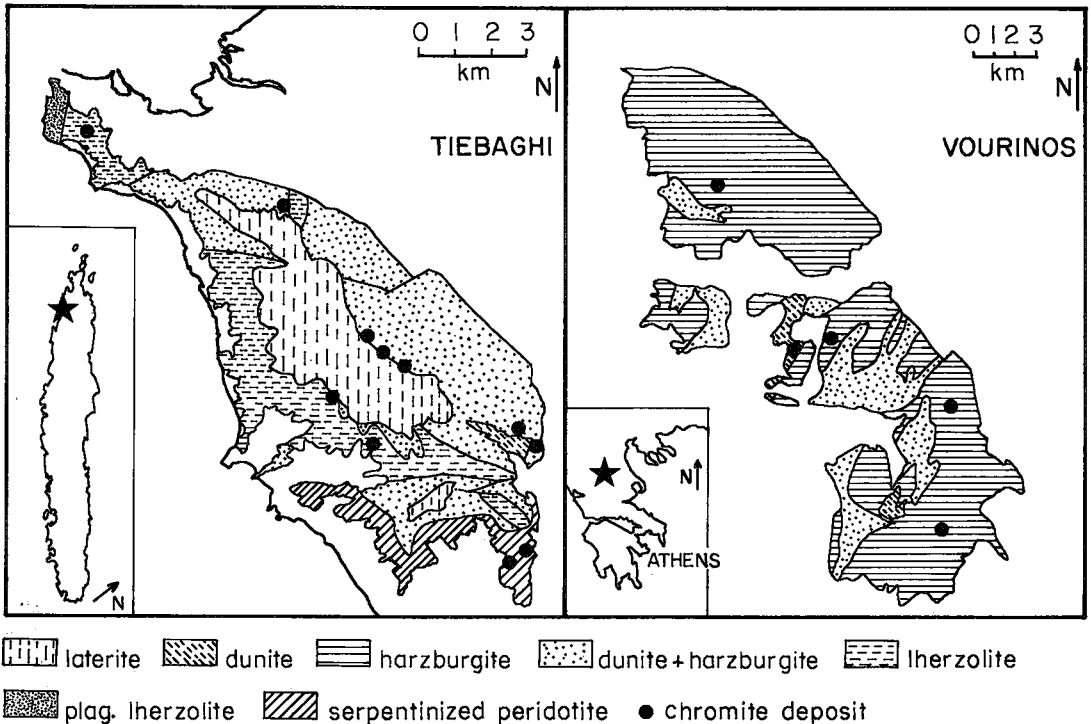
FIG. 1. Schematic geological map of the Tiébaghi (after Moutte 1982) and Vourinos (after Burgath & Weiser 1980) ophiolites, showing location of the complexes (solid star) in New Caledonia and Greece, respectively, and the main chromite deposits.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF PLATINUM-GROUP MINERALS IN CHROMITE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
S (1)	34.16	36.70	32.63	31.14	-	21.70	25.90	28.01	14.91	16.77	20.90	19.15	21.06	11.68		28.84	36.96
As	0.18	0.31	0.06	0.46	0.10	-	0.10	0.12	-	-	-	-	-	-	0.37	0.32	0.20
Os	16.42	0.92	20.52	9.57	37.25	41.85	46.45	40.23	3.34	0.44	-	1.86	-	-	7.21	6.17	3.26
Ru	34.04	52.21	34.37	34.60	0.07	5.65	9.75	18.36	0.52	0.02	-	5.64	0.04	2.49		34.89	51.46
Ir	9.04	3.55	7.65	9.65	56.25	8.84	9.23	5.01	40.03	49.34	57.65	34.99	39.35	0.32	73.49	9.99	4.69
Rh	0.13	1.49	-	1.27	0.03	0.02	0.10	0.05	0.62	0.21	0.20	2.30	9.85	21.24	0.25	0.17	1.10
Pt	-	-	-	-	-	-	-	-	0.38	0.44	1.73	-	0.55	0.17	1.36	-	-
Pd	0.14	-	-	0.18	-	-	0.16	-	-	0.08	0.04	0.02	-	0.24	0.04	0.18	-
Ni	0.20	0.03	0.07	0.25	0.09	0.07	0.24	0.15	0.27	0.09	0.41	1.85	1.21	0.50	1.41	0.15	0.02
Cu	0.51	0.04	0.02	1.91	0.69	-	0.51	-	9.91	12.48	9.58	6.23	9.42	2.08	0.33	-	-
Fe	0.68	0.53	1.08	2.14	0.60	2.18	0.83	0.81	5.77	4.60	1.20	3.09	2.94	10.40	3.77	2.29	0.65
Cr	2.13	1.82	2.24	4.30	2.93	10.42	3.35	2.43	25.95	25.49	6.06	14.41	12.27	20.57	5.68	5.58	1.72
Tot	97.63	97.90	98.65	95.46	98.02	90.73	96.63	95.17	101.70	109.96	97.75	89.54	96.69	69.69	99.43	88.57	100.15
S (2)	36.03	38.41	34.23	34.98	-	27.77	28.01	30.47	21.31	21.00	23.08	26.58	25.85	30.16	2.54	35.73	37.79
As	0.19	0.32	0.06	0.51	0.11	-	0.11	0.13	-	-	-	-	-	-	0.41	0.40	0.20
Os	17.32	0.97	21.52	10.75	39.43	53.56	50.25	43.76	4.77	0.55	-	2.58	-	-	8.02	7.65	3.33
Ru	35.90	54.95	36.06	38.87	0.07	7.23	10.55	19.97	0.74	0.03	-	7.83	0.05	6.44	3.60	43.23	52.62
Ir	9.53	3.71	8.02	10.84	59.53	11.31	9.99	5.45	57.20	61.78	63.70	48.57	48.29	0.83	81.67	12.38	4.80
Rh	0.13	1.56	-	1.43	0.03	0.03	0.11	0.05	0.88	0.26	0.23	3.19	12.09	54.85	0.27	0.21	1.12
Pt	-	-	-	-	-	-	-	-	0.54	0.55	1.91	-	0.68	0.45	1.51	-	-
Pd	0.15	-	-	0.20	-	-	0.17	-	-	0.10	0.04	0.03	-	0.61	0.05	0.22	0.12
Ni	0.21	0.03	0.08	0.28	0.10	0.09	0.26	0.16	0.39	0.11	0.45	2.57	1.49	1.30	1.57	0.19	0.02
Cu	0.54	0.04	0.03	2.15	0.73	-	0.56	-	14.16	15.63	10.58	8.65	11.56	5.36	0.36	-	-
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
S (3)	68.65	67.05	67.50	66.13	-	67.67	66.62	67.33	53.79	53.09	58.16	59.91	58.16	56.80	12.55	67.16	67.09
As	0.15	0.24	0.05	0.42	0.27	-	0.11	0.13	-	-	-	-	-	-	0.86	0.32	0.15
Os	5.56	0.28	7.15	3.43	38.92	22.00	20.14	16.30	2.03	0.23	-	0.98	-	-	6.68	2.42	1.00
Ru	21.70	30.43	22.55	23.31	0.13	5.59	7.96	14.00	0.60	0.02	-	5.60	0.04	3.84	5.65	25.78	29.63
Ir	3.03	1.08	2.64	3.42	58.15	4.60	3.96	2.01	24.09	26.05	26.77	18.26	18.13	0.26	67.39	3.88	1.42
Rh	0.08	0.85	-	0.84	0.05	0.02	0.08	0.04	0.69	0.21	0.18	2.24	8.47	32.18	0.42	0.12	0.62
Pt	-	-	-	-	-	-	-	-	0.23	0.23	0.79	-	0.25	0.14	1.23	-	-
Pd	0.08	-	-	0.11	-	-	0.12	-	-	0.08	0.03	0.02	-	0.35	0.07	0.12	0.06
Ni	0.22	0.03	0.08	0.29	0.31	0.12	0.34	0.19	0.53	0.16	0.62	3.16	1.82	1.33	4.24	0.19	0.02
Cu	0.52	0.04	0.03	2.05	2.17	-	0.67	-	18.04	19.93	13.46	9.83	13.13	5.10	0.90	-	-
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

- element not detected. Laurite: analysis 1, specimen NC 144; 2, NC 136; 3, T 82; 4, NC 280 (associated with a Pt-Pd-Fe alloy); 16, G 98 (associated with iridium 15); 17, G 98. Alloys: 5, osmiridium, NC 300; 15, iridium, G 98 (associated with 16). Erlichmanite: 6, T 8 (associated with xingzhongite 10); 7, NC 300 (associated with Ir-Cu sulfide 11); 8, NC 132. Xingzhongite: 9, T 63 (associated with erlichmanite 10) 10, T 8 (associated with 6). Ir-Cu sulfide: 11, NC 300 (associated with 7); 12, T 70 (associated with laurite); 13, 1001. Prassoite: 14, T 68. PGM 15 to 17 are from Vourinos dunite, 1 to 14 are from Tiébaghi chromitite except 3 and 4, which are from dunite. (1) raw data in weight per cent of the element, (2) composition recalculated, (3) atomic concentration obtained from the corrected analyses.

for interstitial silicates makes pertinent observations very difficult.

The presence of PGM inclusions in chromite from disseminated ore led us to extend the search for PGM to other environments, i.e., to dunite and harzburgite, particularly to their chromite. As chromite represents about 2 modal % of these rocks, concentrates of chromite were prepared to increase the chance of finding PGM. Dunite and harzburgite were crushed and chromite separated in heavy liquids and mounted in resins to prepare polished sections. The resulting chromite concentrate was then studied microscopically under reflected light. Nine dunite (5 from envelopes to chromitite bodies and 4 from unmineralized environments) and 2 harzburgite samples from Tiébaghi and 9 dunite (5 from envelopes and 4 from unmineralized environments) and 4 harzburgite samples from Vourinos were prepared in this manner. PGM were found in 2 barren dunites from Vourinos and 2 from Tiébaghi, and in 5 envelope dunites from Vourinos and in 3 from Tiébaghi. No PGM were found in the chromite from harzburgite.

The presence of inclusions of base-metal sulfides (BMS) in chromitite has been reported by Talkington et al. (1984) and Whittaker & Watkinson (1984). This study of the BMS was undertaken because some appeared to contain PGE. BMS inclusions are common either in chromite from dunite or in chromitite. BMS containing PGE are rarer: only 10 grains were found in the two complexes. The grains seem to be more frequent in dunite, especially in the Vourinos complex, where 5 grains were found in one sample (G 98). PGM and BMS were examined with a scanning-electron microscope using an energy-dispersion Si(Li) detector.

MICROPROBE ANALYSIS

The PGM and BMS were analyzed with a Cameca "Camebax" microprobe under the following operating conditions: acceleration voltage 25 kV, beam current ca. 20 nA, a beam diameter estimated at 0.6 μm. Pure metals were used as standards for Ru, Rh, Pd, Os, Ir, Pt, Cr, Fe, Ni and Cu; pyrite for S, and

TABLE 3. REPRESENTATIVE COMPOSITIONS OF BASE-METAL SULFIDE IN CHROMITE

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
S (1)	35.16	33.35	28.57	20.51	23.25	26.54	27.91	16.28	29.84	32.25	19.99	30.7	31.9	30.1	21.7	29.4
As	0.10	0.17	-	-	-	-	-	-	0.07	0.04	-	-	-	-	-	-
Os	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	-
Ru	-	-	-	2.94	8.96	17.59	13.05	3.33	0.45	0.18	1.84	9.6	-	0.1	-	-
Ir	-	0.04	0.23	0.12	0.09	0.08	0.23	0.14	0.43	0.13	13.40	-	-	18.2	30.9	11.9
Rh	0.02	0.06	0.07	2.00	4.21	13.32	16.75	2.42	3.28	0.09	0.07	4.0	13.3	21.0	9.4	24.5
Pt	-	-	-	0.06	-	0.65	0.18	-	-	-	-	-	-	1.2	5.3	0.1
Pd	0.16	0.11	0.14	-	1.29	0.06	0.15	11.26	0.09	0.06	0.23	-	-	-	-	-
Ni	1.50	44.04	30.11	27.32	19.16	10.12	13.61	13.95	42.32	41.26	17.36	37.6	21.2	10.0	11.7	9.2
Cu	33.28	0.65	-	-	-	-	0.96	9.98	0.21	0.06	2.42	-	-	5.8	4.7	5.7
Co	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	N A	2.1	2.6	-	0.8	0.5
Fe	27.68	19.71	25.73	17.66	17.23	12.20	12.12	15.64	15.86	21.13	11.07	15.4	32.5	16.8	11.3	18.8
Cr	1.50	1.19	14.73	17.87	8.33	13.49	7.51	18.48	2.59	2.74	12.77	-	-	-	-	-
Tot	99.41	99.31	99.58	88.47	82.50	94.05	92.47	91.47	95.15	97.95	79.15	99.4	101.5	103.2	95.8	100.1
S (2)	36.24	34.24	36.62	32.91	33.06	36.59	33.78	25.27	32.53	34.19	32.04					
As	0.11	0.18	-	-	-	-	-	-	0.08	0.05	-					
Os	-	-	-	-	-	-	-	-	-	-	-					
Ru	-	-	-	4.72	12.74	24.25	15.79	5.17	0.49	0.19	2.95					
Ir	-	0.04	0.29	0.18	0.13	0.11	0.22	0.22	0.47	0.13	21.48					
Rh	0.02	0.06	0.09	3.20	5.98	18.36	20.27	3.75	3.56	0.10	0.08					
Pt	-	-	0.01	0.09	-	0.90	0.22	-	-	-	-					
Pd	0.16	0.11	0.08	0.17	-	1.83	0.04	17.47	0.10	0.06	0.37					
Ni	1.54	45.20	38.59	43.83	27.24	13.96	16.48	21.64	46.13	43.75	27.82					
Cu	34.31	0.66	-	-	-	-	1.17	15.49	0.23	0.06	3.88					
Co	-	-	-	-	-	-	-	-	-	-	-					
Fe	27.61	19.51	24.23	15.07	19.01	5.76	11.84	10.99	16.41	21.47	11.38					
S (3)	51.52	48.50	51.05	48.37	50.61	59.87	54.82	42.60	47.37	48.44	53.07	46.9	47.2	54.0	47.0	50.5
As	0.06	0.11	-	-	-	-	-	-	0.05	0.03	-	-	-	-	-	-
Os	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ru	-	-	-	2.20	6.19	12.59	8.13	2.76	0.23	0.09	1.55	4.7	-	-	-	-
Ir	-	0.01	0.07	0.05	0.03	0.03	0.07	0.06	0.11	0.03	5.93	-	-	5.0	11.0	3.5
Rh	0.01	0.03	0.04	1.47	2.85	9.36	10.25	1.97	1.62	0.04	0.04	1.9	6.1	11.0	6.5	13.0
Pt	-	-	-	0.02	-	0.24	0.06	-	-	-	-	-	-	2.0	-	-
Pd	0.07	0.05	0.07	-	0.84	0.04	0.09	8.88	0.04	0.03	0.18	-	-	-	-	-
Ni	1.20	34.97	29.38	35.18	22.77	12.47	14.60	19.92	36.69	33.84	25.17	31.4	17.1	9.0	13.5	8.5
Cu	24.61	0.47	-	-	-	-	0.95	13.17	0.17	0.04	3.24	-	-	5.0	5.0	5.0
Co	-	-	-	-	-	-	-	-	-	-	-	1.8	2.1	-	1.0	0.5
Fe	22.53	15.86	19.39	12.71	16.71	5.41	11.03	10.64	13.72	17.46	10.81	13.5	27.5	16.0	14.0	18.5

- element not detected; NA, not analyzed. Analysis 1, chalcopyrite, specimen G 284 (associated with 2); 2, pentlandite, G 284; 3 to 5, PGE bearing BMS, G 98; 6-7, G 19; 8, G 98; 9, NC 141; 10, NC 365; 11, NC 34 (associated with laurite); 12, analysis from Genkin et al. (1974); 14, Aubut (1979); 13, 15, 16, Cabri et al. (1981). Analyses 1 to 8 are from Vourinos dunite and 9 to 11 are from Tiébaghi chromitite. (1) raw data, (2) composition recalculated, (3) atomic concentration.

GaAs for As. The following lines were used: $SK\alpha$, $AsL\beta$, $OsL\beta$, $RuL\alpha$, $RhL\alpha$, $IrL\alpha$, $PtL\alpha$, $PdL\beta$, $NiK\alpha$, $CuK\alpha$, $FeK\alpha$ and $CrK\alpha$. Corrections were made for a minor interference of $RuL\beta$ and $RhL\alpha$.

The very small size of all the grains analyzed partly explains the low total obtained for most analyses. Representative PGM and BMS compositions are given in Tables 2 and 3. Cr and Fe appear in all compositions; these elements reflect excitation of the matrix (which also explains the low total). Hence, from the raw analytical data, Cr and a proportion of the Fe determined from a knowledge of the Cr/Fe ratio of the host chromite were subtracted. The remaining quantities of elements in the PGM and BMS were recalculated to 100 per cent by weight, and then to atomic per cent. Because of the good approximation to stoichiometry, this procedure seems acceptable. The accuracy is difficult to determine, but ±0.1 wt.% is probably the best obtained.

Hence the second decimal given is not significant. Each composition given in Tables 2 and 3 corresponds to the best result from several point-analyses, i.e., analytical totals nearest 100 wt.%, lowest Cr content, and good stoichiometry.

RESULTS

Chromite

In both complexes the texture of the chromite differs from one chromite occurrence to another, or even within a single deposit. Massive, disseminated, nodular and schlieren ore have commonly been found. Thus the modal ratio of chromite to silicate is variable from one sample to another. Silicate inclusions (olivine, pargasite, pyroxenes) are common in chromite crystals. The interstitial silicate associated with chromitite is olivine, variably transformed to serpentine.

The chromite in dunite is generally small (<1 mm), euhedral, locally showing pull-apart texture, and rimmed by secondary Cr-rich magnetite. Some crystals contain inclusions of clinopyroxene and pargasite. In harzburgite and lherzolite, chromite exhibits diverse forms, from euhedral crystals (<1 mm) to larger "holly leaf" and porphyroclastic crystals.

The compositions of the chromite from chromitite, dunite, harzburgite and lherzolite from the Vourinos and Tiébaghi ophiolite are reported in Figure 2 (Augé 1985b). For both complexes, the composition of the chromite in the ore is similar and very constant, and shows a high Cr/Al ratio. Chromite in dunite from Vourinos plots in the chromitite field, whereas chromite in harzburgite is slightly enriched in Al but has a rather homogeneous composition. In contrast, chromite in the Tiébaghi dunites shows very large variations in the Cr/Al ratio, from a Cr-rich composition similar to that of chromite ore to an Al-rich composition. Cr-rich chromite seems to be restricted to the dunite envelope around the chromite ore with, however, a greater compositional spread, whereas Al-rich chromite is associated with dunite interlayered with lherzolite. Spinel compositions in harzburgite and lherzolite show a very large range in Cr/Al ratio, with a slight shift toward the Al apex compared to coexisting dunite. Note that harzburgite and lherzolite cannot be distinguished on the basis of their spinel composition (Augé 1985b), in contrast to that from other settings (Dick & Bullen 1984).

Platinum-group minerals

All of the BMS and PGM found during this study are within chromite grains, and are remote from large cracks in the host crystal. Hence the BMS and PGM are considered to have been trapped during chromite growth (Constantinides *et al.* 1980, Stockman &

Hlava 1984). The PGM of the Tiébaghi massif occur in any ore type, in any chromite occurrence, independent of the size and type of deposit, or degree of deformation, and the different species found are randomly distributed within a single body. In the Vourinos complex, some chromitite bodies apparently do not contain PGM, but these deposits cannot be distinguished in any way from deposits that contain PGM.

PGM were found in all types of dunite (including barren dunite bodies, dunite dykes, dunite interlayered with harzburgite, and dunite associated with the chromite ore) in both massifs. In the case of Tiébaghi, PGM occur in Al-rich chromite as well as in Cr-rich chromite. Hence, the presence of PGM is not related to composition of the host chromite; this was confirmed by the discovery of PGM in Al-rich ore in the Oman ophiolite (Augé 1986).

The PGM are 1 to 20 μm in their largest dimension, and average approximately 5 μm. They vary in habit from perfect rhombic crystals to rounded forms and occur either as isolated grains or as constituents of a composite inclusion (Fig. 3). These polyphase inclusions may be made of (1) two different PGM (Fig. 3C,D,E), (2) a PGM and a silicate (Fig. 3A,B,E), (3) a PGM and a BMS (Fig. 3F). The morphology of the PGM–PGM or BMS–PGM association does not seem to be compatible with a process of exsolution. Similarly, the presence of PGM in chromite crystals cannot be explained by exsolution from the host (Talkington *et al.* 1984). Note that the PGM occurring in disseminated chromite from dunite do not differ from PGM in chromitite.

Table 4 summarizes the nature and frequency of the PGM found in dunite and chromitite in the two complexes. Three groups of minerals can be distinguished: alloys, sulfides, and sulfarsenides. Their distribution is not the same: 83 grains of sulfides and 4 of alloys have been found in the Tiébaghi massif,
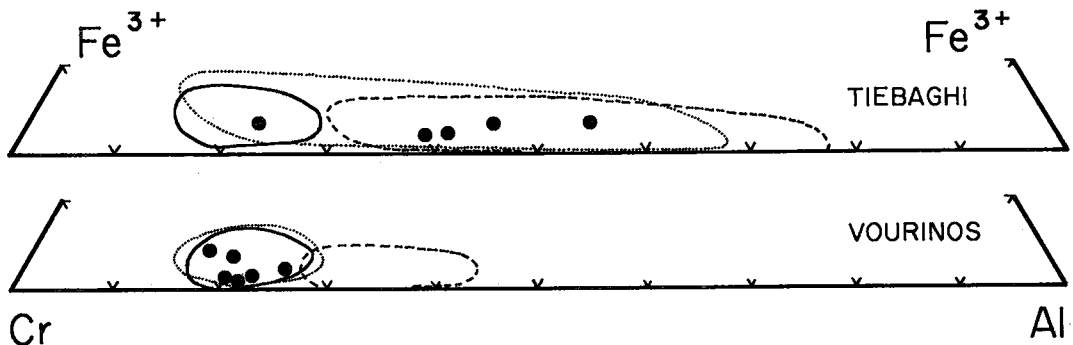

FIG. 2. Chemical composition of spinel (atomic proportion of Cr, Al and Fe^{3+}) from chromitite (solid lines), dunite (dotted lines) and harzburgite and lherzolite (dashed lines). Points correspond to spinel from dunite where PGM have been found.
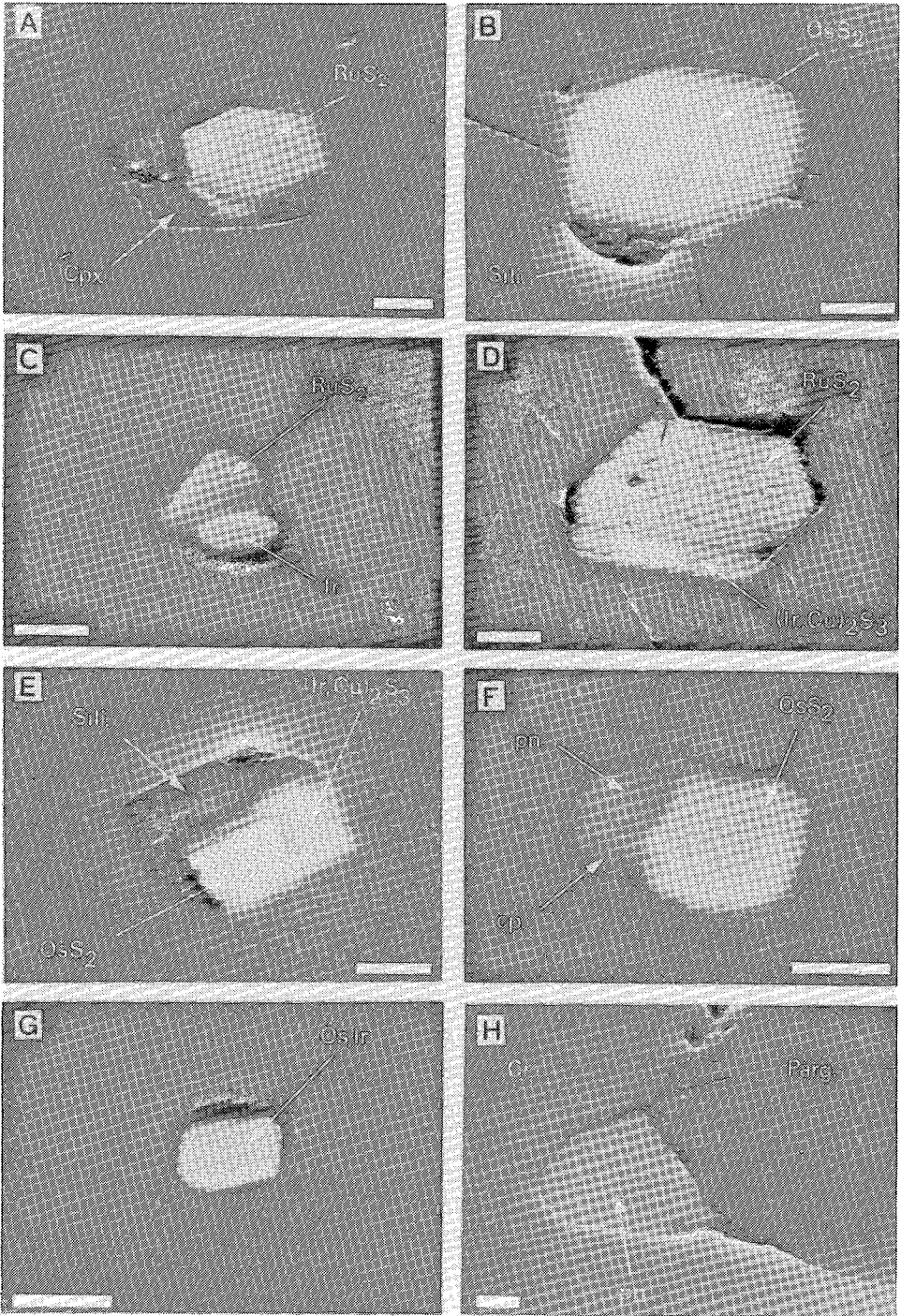
FIG. 3. Scanning electron microscope images of PGM included in chromite crystals. A, laurite with clinopyroxene (NC 144, Tiébaghi); B, erlichmanite with an attached silicate (NC 132, Tiébaghi); C, two-phase grain of laurite and iridium alloy (G 98, Vourinos); D, two-phase grain of laurite and Ir–Cu sulfide (T 70, Tiébaghi); E, two-phase grain of erlichmanite and Ir–Cu sulfide with a silicate (NC 300, Tiébaghi); F, three-phase grain of erlichmanite, chalcopyrite and pentlandite (NC 107, Tiébaghi); G, iridosmine (G 98, Vourinos); H, pentlandite at a grain boundary with chromite and included pargasite (NC 298, Tiébaghi). All samples are chromitite except C and G, which are dunite. Scale bar is 2 μm.

and 15 grains of sulfides, 9 of alloys, and 3 of sulfarsenides in the Vourinos complex. However, it should be emphasized that for a given complex the same proportions of alloy, sulfide, and sulfarsenide are observed in dunite and chromitite (Table 4).

Alloys

With the exception of one sample of Pt–Pd–Fe alloy found in a dunite at Tiébaghi, the remaining alloy samples are ternary Os–Ru–Ir alloys, impoverished in Ru (Fig. 4, Table 2) and characterized by large variations in Ir/Os from one grain to another. They also contain a minor amount of Rh (0.83, $\sigma = 1.56$) and Ni (0.21, $\sigma = 0.40$). The following elements have been observed only in some alloy samples: As (up to 0.41 wt.%), Pd (up to 0.33 wt.%) and Pt (up to 3.07 wt.%). Pt occurs only in Ir-rich samples. Tiébaghi alloys can be distinguished from Vourinos alloys only by the fact that the former systematically contain Cu (up to 4.93 wt.%, average 2.45%, $\sigma = 1.78$). Cu has not been detected in the Vourinos alloys.

The Pt–Pd–Fe alloy mentioned above is part of a three-phase inclusion composed of a Ru sulfide and a Cu sulfide. Its bulk composition includes a small amount of S, Ru and Cu. If these elements are subtracted, assuming that they come from the associated sulfides, the following formula is obtained: $Pt_{0.44}Pd_{0.30}Fe_{0.23}Ni_{0.02}Ir_{<0.01}Rh_{<0.01}$. The formula can also be written $(Pt_{1.76}Pd_{1.21}Ir_{0.02}Rh_{0.01})_3(Fe_{0.93}Ni_{0.07})$, by analogy with isoferroplatinum (Pt_3Fe). However, this phase is enriched in Pd compared to the known isoferroplatinum (Cabri 1981).

Sulfides

Four types of PGE-sulfide have been found (Table 2): laurite RuS_2 (the most abundant and the only

sulfide discovered in the Vourinos complex), erlichmanite OsS_2, Ir–Cu-sulfides, and prassoite RhS (only one grain). The last three have been found only in the samples from Tiébaghi.

TABLE 4. PLATINUM-GROUP MINERALS IN CHROMITE

	TIEBAGHI chromitite	TIEBAGHI dunite	VOURINOS chromitite	VOURINOS dunite
RUTHENIRIDOSMINE (Os,Ir,Ru)			● 1	● 1
IRIDOSMINE (Os,Ir)		● 1	● 3	● 2
RUTHENOSMIRIDIUM (Ir,Os,Ru)	● 1			
OSMIRIDIUM (Ir,Os)	● 1		● 1	
IRIDIUM (Ir)				● 1
LAURITE (RuS₂)	● 61	● 4	● 9	● 6
ERLICHMANITE (OsS₂)	● 10			
XINGZHONGITE (Ir,Cu)S	● 2			
SULFIDE Ir,Cu (Ir,Cu)₂S₃	● 4	● 1		
PRASSOITE (Rh₁₇S₁₅)		● 1		
ALLOY (Pt,Pd,Fe)		● 1		
OSARSITE (OsAsS)			● 1	
IRARSITE (IrAsS)			● 1	
HOLLINGWORTHITE (RhAsS)				● 1

PGM encountered in dunite and chromitite from Vourinos and Tiébaghi complexes. Figures correspond to the number of grains found.
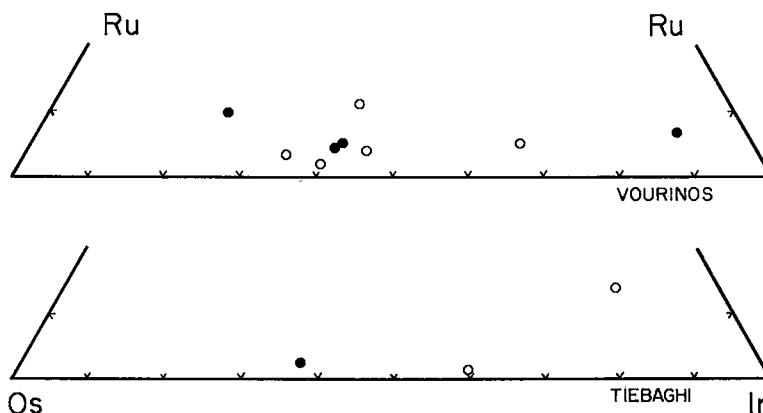

FIG. 4. Results of the electron-microprobe analysis (atomic %) of PGM alloy in the triangular diagram Os, Ru, Ir. Open symbols: PGM occurring in spinel from chromitite; closed symbols: PGM occurring in spinel from dunite.

The *laurite* is characterized by extensive Os–for–Ru substitution (Fig. 5). Its Ir content is low for Ru-rich samples and increases slightly with Os content, but remains constant (at around 3 at.%) where Os exceeds 3 at.%. The composition ranges from $(Ru_{0.95}Ir_{0.03}Os_{0.02})S_2$ to $(Ru_{0.55}Os_{0.29}Ir_{0.16})S_2$. Large variations in composition, within a given grain, similar to those mentioned by Ohnenstetter *et al.* (1986) were not recorded here. The laurite from both complexes typically contains minor elements. Sixty-five grains from Tiébaghi contain 0.38 wt.% As ($\sigma = 0.38$), 1.18 % Rh ($\sigma = 1.53$), 0.22 % Pd ($\sigma = 0.21$), 0.30 % Ni ($\sigma = 0.45$) and 0.83% Cu ($\sigma = 1.41$) and fifteen grains from Vourinos contain 1.07 wt.% As ($\sigma = 0.82$), 0.95 % Rh ($\sigma = 0.41$), 0.20 % Pd ($\sigma = 0.12$), 0.15% Ni ($\sigma = 0.15$), whereas Cu has not been detected.

Ni and Rh are present in all the grains analyzed (Rh reaches 11.1 wt.% in one case). Cu, present in ⅔ of the laurite grains from Tiébaghi (its highest concentration recorded is 6.3 wt.%) has never been detected in laurite from Vourinos. Except for this last point, no significant differences appear in laurite between Tiébaghi and Vourinos ophiolites.

Like laurite, *erlichmanite* is characterized by extensive Ru-for-Os substitution, and its Ir content is constant, similar to Os-rich laurite (Fig. 5). The average composition obtained is $(Os_{0.63,\,\sigma 0.10}Ru_{0.23,\,\sigma 0.11}Ir_{0.14,\,\sigma 0.05})S_2$. From Figure 5, it appears that a composition intermediate between laurite and erlichmanite (*i.e.*, with Os/Ru $\simeq$ 1) is rare. Among 10 grains of erlichmanite, the following elements were detected (concentration in wt.%): As(0.39, $\sigma = 0.38$), Rh(0.26, $\sigma = 0.18$), Pd(0.16, $\sigma = 0.05$), Ni(0.27,
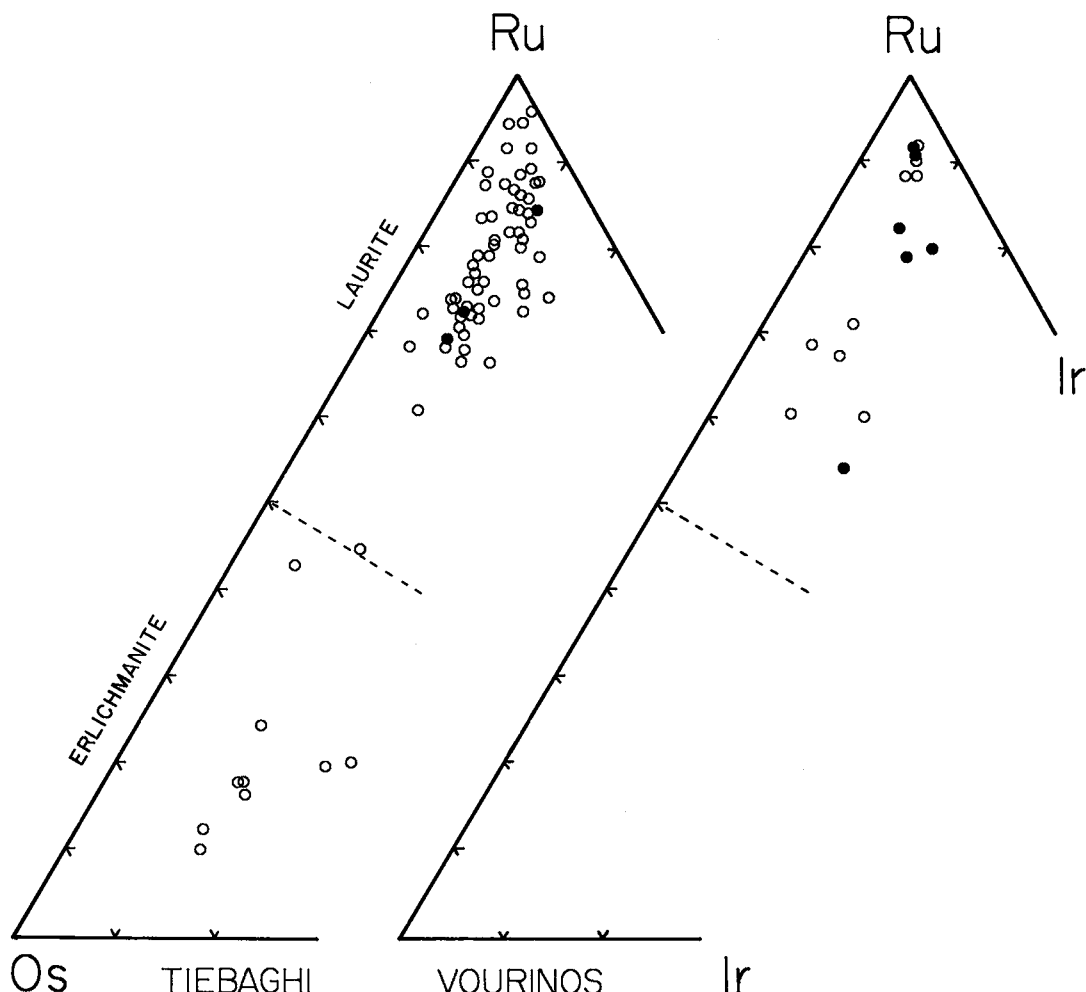
FIG. 5. Results of the electron-microprobe analysis (atomic %) of PGM sulfides (laurite and erlichmanite) in the triangular diagram Os, Ru, Ir. Same symbols as in Figure 4.

$\sigma = 0.26$), Cu(1.28, $\sigma = 0.77$). Ni is the only minor element recorded in all the grains. Note also the presence of Cu.

Two *Ir–Cu-sulfides* have been found in samples from the Tiébaghi massif; one corresponds to xingzhongite (Ir,Cu)S, the other to $(Ir,Cu)_2S_3$, an unnamed phase. *Xingzhongite* was described first by Yu *et al.* (1974). They gave the following formula: $(Ir_{0.43}Cu_{0.28}Rh_{0.13}Fe_{0.08}Pb_{0.07}Pt_{0.04}Os_{0.03})_{1.06}S_{0.94}$. The best analysis obtained here (Table 2) corresponds to $(Ir_{0.52}Cu_{0.40}Rh_{<0.01}Pt_{<0.01}Os_{<0.01}Ni_{<0.01})_{0.94}S_{1.06}$. It differs from that of Yu *et al.* in its high Ir and Cu and lower Rh, Pt and Os contents. Xingzhongite invariably is found in contact with erlichmanite.

(Ir,Cu)$_2$S$_3$ can be distinguished from xingzhongite by an excess of S. Its cation proportion is similar to that in xingzhongite except for one grain, which contains 12 wt.% Rh. This Ir–Cu sulfide has been found either isolated (2 cases) or adjacent to laurite (one case, Fig. 3D) or to erlichmanite (2 cases), with the following composition: $(Ir_{0.91}Cu_{0.66}Rh_{0.42}Ni_{0.09}Pt_{0.01})_{2.09}S_{2.91}$ (isolated grain); $(Ir_{0.91}Cu_{0.49}Ru_{0.28}Ni_{0.16}Rh_{0.11}Os_{0.05})_2S_3$ (laurite-associated); and $(Ir_{1.34}Cu_{0.67}Pt_{0.04}Ni_{0.03}Rh_{0.01})_{2.09}S_{2.91}$ (erlichmanite-associated). A formula comparable to that of the Rh-rich grain has been proposed by Bezigov *et al.* (1975): $(Ir_{0.90}Cu_{0.74}Rh_{0.39})_{2.03}S_3$ for a PGM from ultrabasic rocks from the Urals. Stockman & Hlava (1984) also presented data for an Ir–Cu sulfide associated with laurite. Based on the fact that the atomic proportions are analogous to those in thiospinel, they proposed the following formula: $Ir_2(Cu,Ni,Fe)S_4$. Recalculation of a mean of their analyses on a base of S = 3 gives $(Ir_{1.08}Cu_{0.51}Rh_{0.20}Ni_{0.12}Ru_{0.11}Os_{0.04}Pt_{0.01})_{2.06}S_{2.94}$. This formula is comparable to that obtained here, confirming that the Ir–Cu sulfides analyzed by Stockman & Hlava (1984) are similar to those found in the Tiébaghi massif.

The stoichiometry of *prassoite* is not known exactly (Cabri 1981). It has been found in one chromitite sample from the Tiébaghi massif and is in contact with laurite. The analyses obtained here contain S in excess. The best formula can be written: $(Rh_{2.25}Cu_{0.35}Ru_{0.26}Ni_{0.09}Pd_{0.02}Ir_{0.02}Pt_{0.01})_3S_4$. Note the presence of Pd, Pt, and, as in most PGM from Tiébaghi, Cu (5.4 wt.%).

Sulfarsenides

Three sulfarsenides have been found in the Vourinos complex. *Osarsite,* OsAsS, and *irarsite,* IrAsS, are part of the same inclusion found in a chromitite (Augé 1985a). *Hollingworthite,* RhAsS, has been found included in disseminated chromite from dunite but has only been qualitatively analyzed with the SEM because the grain was lost during a subsequent cleaning of the polished section.

Base-metal sulfides

Like the PGM, base-metal sulfides occur as inclusions within chromite crystals (Fig. 3H), both in massive chromitite and in disseminated spinel in dunite. Because of their optical characteristics, grains greater than 2 μm could be distinguished from PGM under the microscope. Smaller grains were examined by SEM, permitting their identification, but leading also to the discovery that some of them contain PGE in solid solution. PGM exsolutions or very small PGM adjacent to BMS were not observed.

BMS without PGE are mainly Fe–Ni–Cu sulfides (chalcopyrite, pentlandite, and undetermined Cu and Ni–Fe–Cu sulfides: Table 3). Pentlandite is the most common. It is marked by large variations in Ni/Fe, from $(Ni_{5.8}Fe_{3.0})S_{8.2}$ to $(Ni_{8.3}Fe_{0.5})S_{8.2}$. In most cases, the pentlandite is richer in Ni than normal pentlandite (Misra & Fleet 1973). Chalcopyrite, found either isolated or adjacent to pentlandite, is characterized by large variations in Fe/Cu. Grains enriched in Fe are associated with pentlandite with a low Ni/Fe ratio.

Ni–Fe sulfide and Fe–Ni–Cu sulfide containing PGE in solid solution occur either as isolated grains or associated with a PGM. In the latter case, the possibility that the PGE detected are due to X-ray emissions of associated PGM must be ruled out. As with pentlandite, these grains of Ni–Fe sulfide are marked by large variations in Ni/Fe ratio (Table 3) and they have been considered as pentlandite. However, crystallographic data to confirm this hypothesis cannot be obtained because of the small size of the particles.

The PGE concentrations in these grains of pentlandite vary from trace to major amounts (Fig. 6). Two groups have been identified: pentlandite where Σ PGE < 0.5 wt.% and PGE > 4.6 wt.%. For the latter group, the average obtained for Σ PGE is 19.6 wt.%. The relative proportions of the PGE found in BMS are different from those found in PGM: the most common are Ru (up to 24.3 wt.%) and Rh (up to 22.5 wt.%). The Ru/Rh ratio is variable, from 0.1 to 2.1, but the average remains around 1. The Pt content varies between 0 and 0.9 wt.%, and Pd, between 0 and 2.0 wt.% (but reaches 17.5 wt.% in the Fe–Ni–Cu sulfide mentioned above). The Ir content of the BMS is low, around 0.2 wt.%, except in one grain, where it is 21.4 wt.%. An interesting feature is the lack of Os in all the BMS, although it is present in all the PGM. The Ir-rich sulfide, which differs from xingzhongite in its lower Ir content and high Ni content (27.8 wt.% Ni *versus* 0.3 wt.% in xingzhongite), is also impoverished in S and Ir compared to $(Ir,Cu)_2S_3$. Because of its characteristic lack of Os and the fact that its content of PGE is lower than of other metals, this Ir-rich phase has been considered as a PGE-bearing sulfide and not a Ni-bearing PGM.
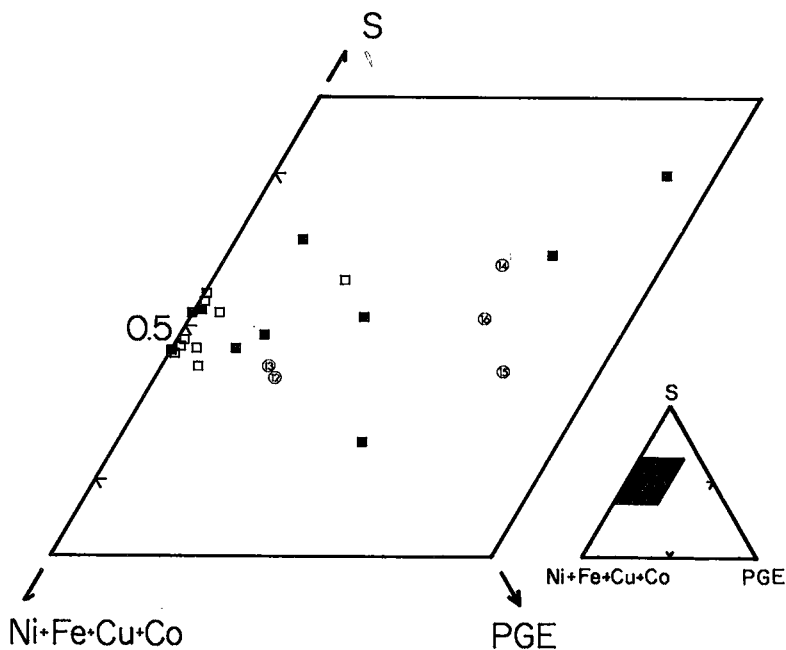
FIG. 6. Compositions of the base-metal sulfides in the S – (Ni + Fe + Cu + Co) – PGE triangular diagram (atomic concentration). Open squares: Tiébaghi; closed squares: Vourinos; circles: data from literature; numbers refer to analyses 12 to 16 given in Table 3.

Compositionally, grain 8 (Table 3) corresponds to a Fe, Ni, Cu sulfide. SEM images indicate that it corresponds to a single crystal. It also contains 17.5 wt.% Pd, 5.2 wt.% Ru and 3.7 wt.% Rh. It is the only BMS containing Pd in major amount. However, its small size has prevented further study. A formula of the type $Cu_2(Fe,Ru)_2(Ni,Pd)_4S_7$ could be proposed.

Polyphase inclusions

As already mentioned, PGM trapped in a chromite crystal can be either isolated or adjacent to another PGM, to a silicate, or to a BMS. Silicates in contact with PGM (included in chromite crystals) have been mentioned in the first description of PGM in ophiolitic chromitite (Constantinides *et al.* 1980). Stockman & Hlava (1984) pointed out the presence of Mg–Al-rich silicates adjacent to many PGM inclusions in peridotite bodies from Oregon, but they failed to obtain quantitative compositional data. Legendre & Augé (1986) also mentioned the presence of silicates associated with PGM and described an occurrence of laurite completely enclosed in orthopyroxene included in a chromite grain. Augé (1986) described silicates attached to most of the PGM from chromitite at Oman and gave the example of laurite enclosed in a two-phase silicate inclu-

sion composed of forsterite and pargasite. In the Oman complex, PGM were found associated with orthopyroxene, clinopyroxene, olivine and amphibole. The compositions of these silicate inclusions in chromite associated with PGM show the same characteristics as those observed for other silicate inclusions (without PGM) trapped in chromitite (Augé 1987). The Oman case seems to indicate that when the silicate inclusions are abundant in chromitite, PGM inclusions are often attached to silicate.

In the Tiébaghi massif, silicates have been found in contact with about one grain of PGM out of 5 (either in dunite or massive chromitite). Clinopyroxene and pargasitic amphibole have been analyzed (Fig. 3A,E). On the other hand, no silicates were found associated with PGM from the Vourinos complex, a fact that can be related to the rarity of silicate inclusions in the chromitite (Augé 1985b).

The association of several PGM as polyphase inclusions is also common. In the Vourinos samples, PGE-alloy grains are often adjacent to laurite. The composition of minerals with this type of association does not differ from that of the same minerals occurring as isolated phases (Augé 1985a). In the Tiébaghi samples, two-phase inclusions have also been found; they consist of two sulfides. The following pairs were found: (1) laurite – $(Ir,Cu)_2S_3$ (Fig. 3D); (2) erlichmanite – $(Ir,Cu)_2S_3$ (Fig. 3E); (3) erlichmanite – xingzhongite (the only occurrence of

xingzhongite is this association). The composition of a phase occurring as an inclusion may differ slightly from that of same mineral in isolation: the composition may be enriched in the elements forming the major constituent of the associated phase. Because of the small size of the grains, this result is considered to be due to the excitation of the the adjacent PGM.

In three cases, PGM have been found in contact with BMS. In one example, the BMS contains PGE that cannot be attributed to the excitation of the associated PGM: an Fe–Ni sulfide with 21.4 wt.% Ir is in contact with laurite. The two other examples are erlichmanite in contact with a pentlandite and chalcopyrite grain (Fig. 3F), and laurite in contact with an undetermined Cu-sulfide.

DISCUSSION

The data in Table 4 and in Figures 4 and 5 confirm differences in the nature and composition of PGM included in chromite from the Vourinos and Tiébaghi ophiolites. These differences are (i) the rarity of Os–Ir alloys in Tiébaghi, whereas they form more than 40% of the PGM occurrences in Vourinos, (ii) the presence of Ir-bearing sulfides in Tiébaghi, (iii) the presence of Os-bearing sulfides in Tiébaghi, and (iv) the presence of Cu as a minor constituent in most PGM in Tiébaghi, and as a major constituent in Ir-bearing sulfides. Cu has never been detected in PGM from Vourinos. Other phases, like prassoite and the sulfarsenides, have been found as isolated grains and cannot be considered as representative. These differences are in contrast to the similarities in the composition of the ores. In both complexes, however, as in most ophiolites, the PGM contain mainly three of the PGE: Ru, Ir and Os. Pt, Pd and Rh enter only in minor amounts or very rarely form discrete minerals.

The similarity in nature and composition of the PGM found in chromite in dunite and chromitite from a given complex contrasts with the differences mentioned above. For example, Ir–Cu-bearing sulfides, characteristic of Tiébaghi chromitite, have also been found in disseminated chromite from the dunite of this complex. These similarities in PGM content in dunite and chromitite on one hand, and the absence of such minerals in harzburgite on the other, lead us to re-evaluate the relationships between these two rock types.

Two hypotheses can be proposed to explain the presence of PGM in chromite grains: (1) the PGM have been exsolved during cooling from the host chromite, the PGE being originally incorporated in chromite as a solid solution (Gijbels et al. 1974, Naldrett & Cabri 1976) and (2) they represent crystals trapped during chromite growth (Constantinides et al. 1980, Talkington et al. 1983, Stockman & Hlava

1984, Augé 1985a). Several points argue against process 1 (e.g., diversity of coexisting phases, presence of two-phase inclusions, association with silicate or PGM enclosed in a silicate crystal, euhedral habit without preferred orientation in the host crystal). Hence mechanism 2 is favored. This implies that the PGM have crystallized before or contemporaneously with chromite. Thus their nature could give information on the conditions of their crystallization. However, several parameters necessary to interpret PGM assemblages are missing, especially knowledge of the initial PGE content of the system. The diagram of aS_2 versus $1/T$ established by Stockman & Hlava (1984) leads to the conclusion that the Tiébaghi PGM have crystallized under a higher activity of S_2 than have the PGM from Vourinos. This is indicated in particular by the presence of erlichmanite and Ir-bearing sulfide at Tiébaghi and the relative abundance of PGE alloys at Vourinos. Moreover, the presence of erlichmanite and Os-poor laurite at Tiébaghi within a given section seems to indicate that the different PGM are not in equilibrium. Also, the Pt–Fe alloy cannot be in equilibrium with erlichmanite. Thus the different PGM found in chromite samples from the same deposit could have crystallized over a large range of T and aS_2. Their coexistence in chromitite can be explained by proposing that they were trapped soon after crystallization and have not had the opportunity re-equilibrate.

The analogy observed between PGM in dunite and in chromitite must indicate that the conditions prevailing during their precipitation were roughly similar. In particular, they seem to have been derived from a compositionally similar liquid. This necessarily indicates, at a certain stage, a genetic relationship between dunite and chromitite. Note that PGM were found in all types of dunite (distinguished only on the basis of field data).

The presence of PGM in disseminated chromite from dunite must be explained by a process similar to the one proposed for chromitite, i.e., trapping during chromite growth, with the PGM possibly acting as nuclei. The proportion of polished sections of chromite concentrates that contain PGM is similar to that for sections of massive chromitite. In addition, the amount of PGM found is similar. Thus we suspect that the quantity of PGE contained in disseminated spinel in dunite is similar to the PGE content of chromitite. This contrasts with the lack of PGM in spinel from harzburgite.

Concerning the origin of the dunite bodies in ophiolitic complexes, two hypotheses are currently proposed: (1) the dunites are the result of transformation of a pyroxene peridotite (harzburgite or lherzolite), or (2) they are the product of accumulation of olivine and chromite formed by fractional crystallization of a magma. Several mechanisms are pro-

posed to account for the transformation invoked in the first case: a) an increase in temperature will cause melting of pyroxenes, dunite being the residue after a high degree of partial melting of the mantle (Dick 1977); b) an interaction between harzburgite and a basaltic magma will cause destabilization of orthopyroxene and leave a dunite "residue" (Hopson *et al.* 1981); c) a metasomatic reaction with an aqueous vapor will transform orthopyroxene from harzburgite into olivine (Dungan & Avé Lallemant 1977, Johan *et al.* 1983).

Difficulties in choosing from these hypotheses are partly due to the absence of chemical criteria able to give a clear answer for a particular dunite occurrence. The sharpness of the dunite–harzburgite contact is a structural argument frequently mentioned in favor of a magmatic origin (by crystal accumulation) of dunite (Harkins *et al.* 1980). However, some authors have proposed the existence of two types of dunites in the same mantle section, one a residue of partial melting and the other "olivine accumulates derived from tholeiitic magma trapped in the mantle sequence" (Boudier & Coleman 1981), or even the existence of two genetic types in the same dunite body, *i.e.*, (1) crystallization from a melt ascending through the mantle, and (2) reaction of this melt with the surrounding harzburgite, which explains the margins of the body (Quick 1981).

Any process leading to the formation of dunite through transformation of a pre-existing pyroxene peridotite must also explain the existence of PGM in chromite in the resulting dunite. Neither a residual origin as proposed in (1) nor a "metasomatic" process is likely to have such an effect (unless the vapor phase carried PGE, which seems improbable since similar PGM occur in dunite and chromitite). However, the problem of the dunite–harzburgite relationship with regard to PGE content is complex. For example, Page & Talkington (1984) obtained similar PGE patterns in dunite and in harzburgite, without significant variations from one ophiolitic complex to another, "the negative sloping PGE patterns of dunite being compatible with a residual origin". On the contrary, as a result of a study of the Thetford mine complex, Oshin & Crocket (1982) showed that harzburgite has a nearly chondritic PGE profile, whereas dunites with similar Ir contents to harzburgite are depleted in Pt and Pd. Oshin & Crocket found that mantle dunites have the same PGE contents as the early dunitic cumulates. Oshin & Crocket concluded that such a difference between harzburgite and dunite cannot be obtained by partial melting; the similarity of the profiles obtained for the two types of dunite led them to the conclusion that the two dunites are genetically related, *i.e.*, both dunites were formed by fractional crystallization. Leaching experiments carried out on grains of spinel separated from dunite and harzburgite led

Oshin & Crocket (1982) to consider that the PGE in harzburgite could be located at chromite–silicate grain boundaries or on the surface of chromite grains; they concluded that most PGE in dunite are located within chromite grains. Oshin & Crocket proposed that PGE in harzburgite, after their incorporation in spinel, will be expelled outside chromite grains during cooling and deformation – recrystallization of the chromite crystals. It was suggested that this phenomenon will be less pronounced in cumulate dunites.

Such explanations cannot be applied to the Vourinos and Tiébaghi complexes, where differences in deformation pattern between dunite and harzburgite cannot be invoked. On the other hand, the PGE occurring in the highest concentrations in the ophiolite environment (Os and Ru) were not determined by Oshin & Crocket.

The hypothesis favored here is that PGM in dunite have been incorporated during spinel crystallization. Two mechanisms are possible: (1) a "purely" magmatic origin, in which dunite (and the included PGM) have crystallized from a magma; and (2) a "semi"-magmatic origin, dunite being the result of transformation of a harzburgite through the action of a percolating magma (from which PGM and new spinel could crystallize). However, the degree of transformation must have been so high that the characteristics of the pre-existing harzburgite were totally obliterated, pointing to a high ratio of liquid to rock and the complete re-equilibration of the residual mineralogy. Hence this process cannot be distinguished from that first invoked for the origin of dunite, *i.e.*, fractional crystallization and segregation from a magma.

The presence of PGM included in disseminated chromite from dunite, analogous to those found in massive chromitite in a given ophiolitic complex, confirms the hypothesis that dunite and chromitite can be formed from a similar liquid. The scenario proposed here is the following: (1) the PGM crystallized from a primitive magma accumulated in an intramantle magma-chamber. The nature and composition of the PGM depended on the initial PGE concentration of the magma and the T and aS_2 of crystallization. (2) Contemporaneously or soon afterward, chromite crystallized, trapping most PGM (because the PGM acted as nuclei for the chromite) and some silicates (that also were able to crystallize on the PGM grains). (3) At this stage, two possibilities must be considered: the first is that normal crystallization of the magma took place and olivine formed. Removal of the residual liquid then gave rise to a dunite with 1 – 2 % chromite containing PGM inclusions. As a second possible mechanism, the concentration of chromite crystals could occur through processes similar to those proposed by Lago *et al.* (1982). This mechanism requires a continuous injec-

tion of fresh magma into the chamber from which new PGM and chromite crystallize. The result will be the formation of chromitite containing PGM. Hence, the enrichment of PGE in chromitite observed for numerous ophiolites reflects the fact that individual chromite crystals containing PGM are concentrated. This confirms the hypothesis that chromite is a "mechanical" concentrator for PGM and that PGM crystallization and formation of chromite bodies are not necessarily related (Augé 1985a).

The association of PGE with BMS (pyrrhotite, pentlandite, chalcopyrite) is well known in intrusive ultramafic bodies (Naldrett & Cabri 1976). Several authors have proposed that PGM in these associations could result from the crystallization of an immiscible sulfide liquid enriched in PGE (*e.g.,* Cabri & Laflamme 1976) or exsolve from BMS containing PGE. The presence of PGE in solid solution in BMS has been proposed by Vermaak & Hendricks (1976), and Mostert *et al.* (1982) described laurite exsolution in pyrrhotite. Some PGE have been detected in BMS. Ross & Keays (1979) described the presence of Pd in pentlandite. Cabri (1981) mentioned up to 0.65 wt.% Pd in pentlandite from Lac des Iles, Ontario; Bow *et al.* (1982) reported 2 wt.% Pd and Todd *et al.* (1982) 3.3 wt.% Pd in pentlandite from the Stillwater Complex. As far as we know, this value is the highest recorded in this context, which is much lower than the values reported in this study.

However, PGE in high concentrations have been detected in Fe–Ni sulfides from Alaskan-type ultramafic complexes [Lower Tagil'sk dunite, USSR: Genkin *et al.* (1974); the Tulameen Complex, British Columbia: Aubut (1979); the Yubdo Complex, Ethiopia: Cabri *et al.* (1981)]. Compositions from these studies are given in Table 3 and are plotted as Figure 6. The total PGE content varies between 13.6 and 45.3 wt.%. Amongst these sulfides, one pentlandite has been identified by X-ray diffraction (Genkin *et al.* 1974). Like the phases described here, it contains Ru (9.6 wt.%) and Rh (4.0 wt.%). The other sulfides contain various PGE but none contains Pd or Os, similar to the BMS containing PGE reported here. The Ru–Rh-bearing pentlandite described by Genkin *et al.* (1974) occurs in serpentinized dunite, associated with irarsite, heazlewoodite, millerite and platinum. The pentlandite fills interstices between chromite grains, and is interpreted as having formed during serpentinization, with the PGE derived from primary PGM. Its composition is very similar to compositions given here, in particular, its Ni/Fe ratio is very high (Fig. 6).

Experimental work on the solubility of PGE in pentlandite by Makovicky *et al.* (1986) has shown that up to 10.9 wt.% Pd, 12.4 wt.% Rh and 12.9 wt.% Ru can be incorporated in pentlandite in solid solution and still be retained at low temperature. On the contrary they found that no Pt enters pentlandite. These results seem to confirm that the grains of PGE-bearing Fe–Ni sulfide found in this study are pentlandite (their small size does not permit us to confirm this). Nevertheless, the consequences of their presence as inclusions in chromite crystals are interesting. The inclusions indicate that minor sulfides can be formed in the early stage of the crystallization and, like PGM, can be trapped by chromite growth (either from dunite or chromitite). Similarly, BMS together with laurite and "some other platinum-group minerals" are described as inclusions in chromite from the UG-2 chromitite of the Bushveld Complex by McLaren & De Villiers (1982).

Hence it is suggested that these sulfides can act as collectors of the PGE dissolved in the magma (mainly Ru, Rh and Pd). The very low quantity of the sulfides formed can explain the abnormally high concentration of PGE that they incorporate. The presence of Pd and Rh in these sulfides, which are elements found in very low concentrations in whole-rock analysis of chromitites for PGE, indicates that these elements were present in the system (probably together with Pt, also found in Ir-rich alloys). Hence, the well-known negatively sloping PGE pattern for ophiolitic chromitite (Page *et al.* 1982a,b, 1983, 1984, Page & Talkington 1984) implies that conditions for concentration of Pt, Pd and Rh during the early stages of crystallization (*i.e.,* the segregation of BMS, which could then act as a "chemical" collector for these PGE) were rarely obtained (Talkington & Watkinson 1986), and does not indicate that these three PGE were absent from the magma in ophiolitic complexes.

CONCLUSION

Vourinos and Tiébaghi are two ophiolites with very different mantle sequences but with chromite deposits of similar composition. In both complexes, the PGM occur as inclusions in chromite from dunite and chromitite. Whereas the PGM assemblages are quite different in the two ophiolites, the same phases were found in dunite and chromitite in a given complex, indicating that both rock types have crystallized from a chemically similar magma.

The composition of PGM is a function not only of the PGE content of the magma, but also of the T and aS_2 during crystallization, parameters that do not influence chromite composition to a large extent. It appears that the PGM from Tiébaghi have been formed under higher aS_2 than PGM from Vourinos. Moreover, the characteristic presence of Cu in the PGM from Tiébaghi probably reflects an enrichment of Cu in the magma. The enrichment in PGM observed in massive chromitite has been related to the process of chromite concentration, chromite crystals playing the role of a "mechanical" collec-

tor for Os-, Ir- and Ru-bearing PGM formed in the magma. The discovery of BMS containing platinum-group elements in solid solution, trapped, like PGM, in chromite crystals indicates that these sulfides can act as "chemical" collectors for Pd, Rh and Ru.

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