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NEW OCCURRENCES OF ANDUOITE, $(Ru,Os)As_2$, FROM CHROMITE DEPOSITS OF UKRAINE AND ALBANIA

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Abstract

Two new occurrences of anduoite, $(Ru,Os)As_2$, a rare platinum-group mineral (PGM), are reported from chromitites, one from the Kapitanov deposit, Ukrainian Shield, Ukraine, and the other from the Maja e Sukës deposit, Tropoja ophiolitic massif, Albania. At Kapitanov, anduoite occurs as discrete, homogeneous, euhedral crystals (6–9 and 1–2 μm) enclosed in two chromian spinel grains devoid of fractures. At Maja e Sukës, one crystal of anduoite (3 μm in diameter) belongs to a complex polyphase assemblage of PGM comprising sperrylite, hollingworthite and an unnamed sulfarsenide of Rh, Ir, Pd and Ni. The chemical composition of anduoite is comparable in both deposits: $(Ru_{0.79–0.80}Os_{0.10–0.11}Ir_{0–0.03}Rh_{0.03–0.04}Pt_{0–0.01}Pd_{0.01–0.02}Ni_{0–0.04})_{\Sigma 0.98–1.01}(As_{1.98–2.01}S_{0.01–0.02})_{\Sigma 1.99–2.03}$. These examples of anduoite have a lower content of Ru than that described from the type locality in Tibet. A magmatic origin is proposed.

Keywords: anduoite, platinum-group mineral, arsenides, chromitite, chromian spinel, ophiolites, Albania, Ukraine.

Sommaire

Deux nouveaux exemples d'anduoïte, $(Ru,Os)As_2$, minéral rare du groupe du platine (MGP), sont signalés dans des chromitites, l'une dans le gisement de Kapitanov, situé dans le bouclier ukrainien en Ukraine, et l'autre dans le gisement de Maja e Sukës, appartenant au massif ophiolitique de Tropoja, en Albanie. A Kapitanov, l'anduoïte se présente sous forme de cristaux isolés, homogènes et automorphes (6–9 et 1–2 μm) inclus dans deux grains de chromite dépourvus de fractures. A Maja e Sukës, un cristal d'anduoïte (3 μm de diamètre) appartient à un assemblage complexe et polyphasé de MGP comprenant sperrylite,

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hollingworthite et un sulfoarséniure innommé de Rh, Ir, Pd et Ni. La composition chimique de l'anduoïte est semblable dans les deux gisements: $(Ru_{0.79–0.80}Os_{0.10–0.11}Ir_{0–0.03}Rh_{0.03–0.04}Pt_{0–0.01}Pd_{0.01–0.02}Ni_{0–0.04})_{\Sigma 0.98–1.01}(As_{1.98–2.01}S_{0.01–0.02})_{\Sigma 1.99–2.03}$. Ces exemples d'anduoïte ont des teneurs de Ru plus faibles que l'anduoïte de la localité-type au Tibet. Une origine magmatique est privilégiée.

Mots-clés: anduoïte, minéral du groupe du platine, arséniures, chromitite, spinelle chromifère, ophiolites, Albanie, Ukraine.

INTRODUCTION

Anduoite, $(Ru,Os)As_2$, of orthorhombic symmetry, is considered to have the marcasite structure. It is isostructural with omeiite $(Os,Ru)As_2$ (Ren *et al*. 1978) and iridarsenite $(Ir,Ru)As_2$ (Harris 1974). Anduoite was discovered in a chromite deposit enclosed by augite peridotite and dunite in Anduo, Tibet, China (Yu & Chou 1979). It occurs there as massive grains or granular aggregates (60–100 μm) in association with other platinum-group minerals (PGM). There, anduoite and other arsenides and sulfarsenides generally are found near grains of Os–Ir–Ru alloy; anduoite locally replaces irarsite. This occurrence is the only one mentioned in the literature (*e.g.,* Chao 1980, Cabri 1981, Anthony *et al*. 1990, Daltry & Wilson 1997, Mandarino 1999).

In this paper, we present results of our investigations of two new occurrences of anduoite. One is associated with massive chromitite from the Kapitanov deposit, Ukrainian Shield, Ukraine, and the other is from the Maja e Sukës chromite deposit, Tropoja ophiolitic massif, Albania. The primary *versus* secondary origin of anduoite is discussed. In our opinion, anduoite could have precipitated as a very refractory phase from a mafic silicate melt with an As:S ratio higher than that necessary to stabilize laurite, or precipitated directly from an As-rich melt, as chromite was deposited.

THE KAPITANOV DEPOSIT

The Kapitanov chromite deposit is hosted by a 1.96–2.1 Ga differentiated fault-bounded massif 2500 m in

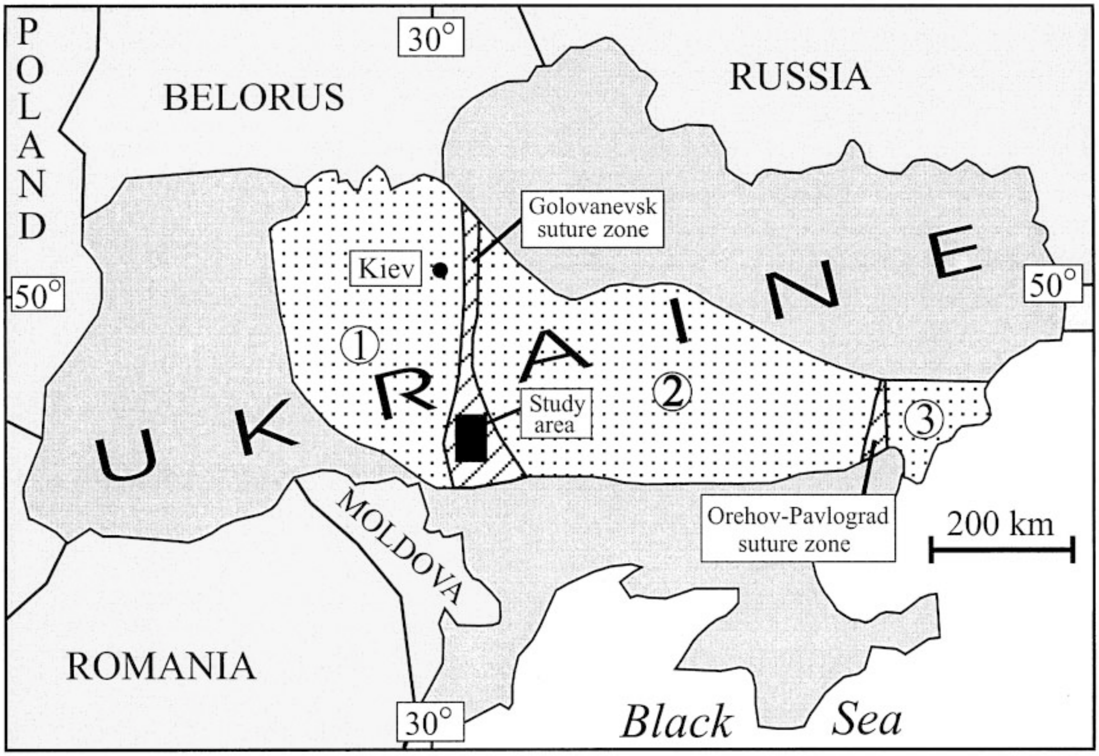

FIG. 1. Location of the study area in the Ukrainian Shield (stippled). Major blocks of the Shield: 1 Volyno–Podolsky (western), 2 Central, 3 Priazovsky (eastern). Simplified after Dagelaysky (1997).

length and 260 m in width containing dunite–peridotite (with minor pyroxenite) (Fomin 1979, Kanevskii 1981, 1991). The massif is located in the Golovanevsk suture zone, which separates the Western and Central blocks of the Ukrainian Shield (Fig. 1). This zone hosts several ultramafic massifs of ophiolitic nature (Nalivkina 1977, Gornostayev *et al.* 2000a). In the Ukrainian Shield, economic deposits of chromite (*s.l.*) are known only in this area (Kanevskii 1981, 1991, Gornostayev *et al.* 2000a). The Kapitanov deposit includes lenses and veins (Fomin 1979) of massive and disseminated varieties of chromite ores hosted by serpentinized and carbonatized dunite, harzburgite and, rarely, by pyroxenite. The chromitite bodies are 2–16 m thick and 40–250 m long. Grains of chromian spinel are of variable size (0.002–1 mm) and composition. Other minerals observed are ilmenite (euhedral to subhedral grains in a silicate matrix and lamellae in chromian spinel), magnetite (ferrian chromite rims around chromian spinel), serpentine, forsterite (Fo$_{80-90}$), orthopyroxene and clinopyroxene. Opaque minerals in the serpentine matrix and in some cases within the grains of chromian spinel comprise millerite, nickeline, gersdorffite, maucherite, pentlandite, violarite, As-bearing tučekite, chalcopyrite and galena (Gornostayev *et al.* 2000c). The ores also carry PGM represented by anduoite, irarsite, laurite, ruarsite, minor sperrylite and unidentified Ru–Rh–Ir–As, Ru–Os–As, Pd–Sb and Pd–As phases (Gornostayev *et al.* 2000b). The PGM observed in chromitites of the Kapitanov deposit occur as small irregular grains (mostly 1–5 μm in longest dimension) attached to edges of chromian spinel or within interstitial silicates and discrete grains in fresh chromian spinel. The PGM included in chromian spinel are represented by single-phase inclusions of irarsite, laurite and Os–Ir–Ru alloy and, in one case, by a two-phase inclusion of Os$_{0.74}$Ir$_{0.35}$Ru$_{0.29}$ and an undefined Ru–Os–As phase (Gornostayev *et al.* 2000b). The chromitites of the Kapitanov deposit possess PGE characteristics similar to those found in chromitites from ophiolitic mantle tectonites, including a high ratio of Ir-group PGE to Pd-group PGE (Gornostayev *et al.* 2000a).

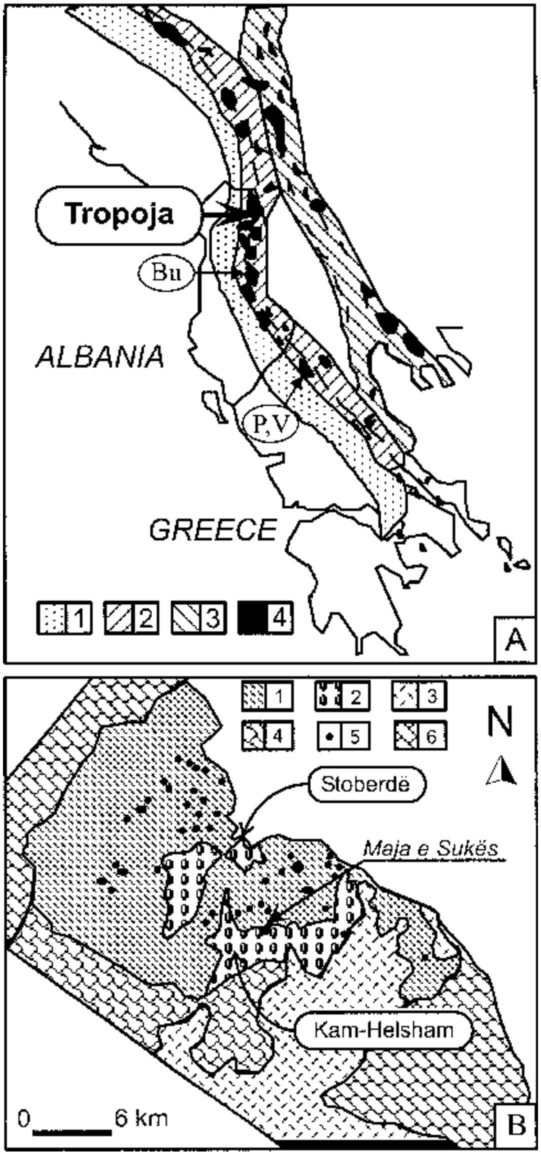

FIG. 2. The Tropoja ophiolitic massif, Albania. A. Location of the Tropoja ophiolitic massif along the Dinarides–Hellenides belt. 1 Mirdita zone with Mesozoic sediments, 2 Mirdita ophiolitic zone, with a dashed line separating the western and eastern belts, 3 Vardar ophiolitic zone, 4 ophiolitic massifs. The location of the Bulqiza massif (Bu), Albania and of the Pindos and Vourinos massifs (P,V), in Greece is also indicated. B. Geological map of the Tropoja massif, simplified from Neziraj (1992). 1 mantle sequence, 2 ultramafic cumulates, 3 mafic cumulates, 4 volcanic rocks, 5 chromite deposits, 6 sedimentary rocks. The location of the two types of cumulate sequences (Stoberdë and Kam–Helshan) is shown.

The Maja e Sukës Deposit, Tropoja Ophiolitic Massif

The Tropoja massif occurs in the northern part of a double ophiolitic belt trending NW–SE in Albania (Fig. 2). The western and eastern ophiolitic belts show contrasting petrological and metallogenic characteristics (Çina *et al.* 1987) related to their formation in distinct geotectonic environments during Jurassic time. The Tropoja massif belongs to the eastern ophiolitic belt, which hosts all the economically important deposits, mostly of metallurgical-type (high-Cr) chromite ore.

The Tropoja massif comprises mantle rocks, 2.5–3 km thick, covered by cumulates and lavas in the southwest. Chromite deposits are concentrated at three major stratigraphic levels: 1) in the deep part of the mantle sequence, 2) in the transition zone at the top of the mantle sequence, and 3) in the cumulate sequence. Chromitites locally contain Pt and Pd (Ohnenstetter *et al*. 1991b, Neziraj 1992, Çina *et al*. 1995). Two main types are defined: Pd-rich mineralization with a low Pt:Pd ratio (0.3) locally occurs in podiform mantle-derived chromitite hosting accessory base-metal sulfide (BMS); Pt-rich mineralization with a high Pt:Pd ratio (>3; up to 100) is defined in dykes of chromitite cutting basal cumulates in the Stoberdë area. The Stoberdë sequence of cumulates comprises, from base to top, dunite, orthopyroxenite with dykes of chromitite, pyroxenites, and gabbronorite. The high Pt:Pd ratio is due to the predominance of Pt–Fe alloys. PGM recovered in the Bregu i Bibës deposit are composed of 88% alloys (mostly Pt–Fe alloy and locally Ir–Os–Ru alloy), 10% sulfides and sulfarsenides (mainly laurite and hollingworthite), and 2% arsenides or tellurides.

The Maja e Sukës deposit, where the anduoite was found, occurs south of the Stoberdë area, in a body of serpentinized dunite at the transition between the harzburgitic mantle and the Kam–Helshan sequence of cumulates. The latter is distinct from the Stoberdë sequence, and consists, from base to top, of plagioclase-bearing harzburgite, wehrlite, lherzolite, olivine gabbro and gabbronorite. The chromitite deposit is tabular to lenticular (170 × 80 m); it was dismembered by late faulting. Its thickness varies between 1.2 and 3.7 m. Layered, disseminated and schlieren ores are recognized in the deposit. Disseminated ore is prevalent at the rim of the chromite deposit, in the contact zone with the host dunite. Only one sample of disseminated chromitite (33A) was taken from this deposit during prospecting for platinum in chromite deposits of the Tropoja massif. A platinum-group element (PGE) anomaly was found in this sample; it contains 540 ppb Pt and 13 ppb Pd, and a correspondingly high Pt:Pd ratio (42), as in the Pt-rich mineralization defined in cumulate chromitites from the Bregu i Bibës area.

OCCURRENCE OF ANDUOITE

Two inclusions of anduoite were observed in massive chromitites of the Kapitanov deposit. One (sample KAP18) is represented by a 6–9 μm euhedral crystal enclosed in a grain of chromian spinel (Table 1, anal. 1) that is free of fractures and contains numerous lamellae (10–12 μm long and 0.5–1 μm wide) of ilmenite (Figs. 3a, b). Another crystal of anduoite is small (1–2 μm) and euhedral. It occurs in a grain of chromian spinel (Table 1, anal. 2) that is also free of cracks or other inclusions (Figs. 3e, f; sample 3541/369–1).

In the sample of Pt-rich chromitite from the Maja e Sukës deposit, a grain of anduoite was found during an investigation to determine the platinum carrier (Neziraj 1992, Ohnenstetter *et al*. 1999). Anduoite belongs to a complex polymineralic arsenide-rich assemblage (20 × 16 μm) included in a grain of chromian spinel (Fig. 4, Table 1, anal. 18). This assemblage is composed of sperrylite, which forms a wide discontinuous rim (up to 6 μm thick) around PGM of finer grain-size, filling the space between these PGM and the host chromian spinel (Table 2, anal. 8–12). Anduoite (3 μm in diameter) occurs in the fine-grained PGM assemblage with hollingworthite, which is intergrown with a complexly zoned sulfarsenide of Rh, Ir, Pd and Ni. These are the only PGM found in the sample.

ANALYTICAL RESULTS

Analytical techniques

Analyses of anduoite and associated chromian spinel from the Kapitanov deposit were done at the Institute of Electron Optics, University of Oulu, Finland, using a JEOL JSM–6400 scanning electron microscope (SEM) equipped with a LINK eXL energy-dispersion spectrometer (EDS method, analyses of anduoite) and JEOL JCXA–733 electron microprobe (WDS method, analyses of chromian spinel). In the case of anduoite, the analyses were performed at 15 kV, with a beam current of 1.2 nA and 100 s counting time. The following lines (and standards) were used: Pt$M\alpha$, Pd$L\alpha$, Ru$L\alpha$, Rh$L\alpha$, Ir$M\alpha$, Os$M\alpha$ (pure elements), S$K\alpha$ (pyrite) and As$L\alpha$ (sperrylite, $PtAs_2$). Analyses of chromian spinel were carried out at 15 kV, with a beam current of approximately 13 nA using the following X-ray lines (and standards): Ni$K\alpha$, Co$K\alpha$, Fe$K\alpha$, Zn$K\alpha$, Mn$K\alpha$, Ti$K\alpha$, V$K\alpha$ (pure elements), Al$K\alpha$ (Al_2O_3), Si$K\alpha$ (wollastonite), Mg$K\alpha$ (MgO), K$K\alpha$ (orthoclase), Na$K\alpha$ (jadeite), Ca$K\alpha$ (wollastonite) and Cr$K\alpha$ (pure element and chromite).

Quantitative electron-microprobe analyses of PGM from Albania were performed with the CNRS – BRGM – Université d'Orléans Camebax electron microprobe equipped with wavelength-dispersion spectrometers and LiF, TAP, and PET analyzing crystals. The operating conditions were: accelerating voltage 25 kV, reference current 30nA, beam diameter 0.5 μm, counting time 6 s (10 s for iron). Lines used were: S$K\alpha$, As$L\beta$, Sb$L\alpha$, Os$L\beta$, Ru$L\alpha$, Ir$L\alpha$, Rh$L\alpha$, Pt$L\alpha$, Pd$L\beta$, Fe$K\alpha$, Ni$K\alpha$, Cu$L\alpha$, Co$K\alpha$ and Cr$K\alpha$. Standards were pure metals and pyrite for S$K\alpha$, $PtAs_2$ for As$L\beta$, and stibnite for Sb$L\alpha$. Low totals are due to the small size of PGM and to the subtraction of Cr and corresponding Fe attributed to fluorescence of the host chromian spinel. The correction of the overlap of Ru$L\alpha$ and Rh$L\alpha$ was done for all Ru-rich minerals; pure Ru gave about 2.5% Rh (Ohnenstetter *et al*. 1986). Routine analyses for major elements of the spinel were made at 15 kV, 10 nA, and 10 s counting time. All data were corrected with the ZAF program MBXCOR of Henoc & Tong (1978). Backscattered images were obtained with a Cambridge Stereoscan 200 scanning electron microscope at the BRGM, Orléans, France.

TABLE 1. ELECTRON-MICROPROBE DATA ON CHROMIAN SPINEL, KAPITANOV AND MAJA E SUKËS DEPOSITS

	Sample	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	V_2O_3	FeO	MnO	MgO	ZnO	NiO	CoO	total
1	**KAP18**	0.19	36.18	26.57	3.66	0.55	22.34	0.29	9.72	0.27	0.22	0.08	100.10
2	3541/369-1	0.33	27.07	36.44	2.64	0.12	24.77	0.70	6.84	0.26	0.01	0.03	99.21
3	3533/148.5	0.40	21.42	36.78	9.96	0.12	22.42	0.66	7.98	0.18	0.17	0.10	100.19
4	3533/178.5	0.21	21.56	46.46	5.14	0.10	12.89	0.30	14.83	0.04	0.18	0.06	101.77
5	3533/182.0	0.60	22.99	30.82	13.22	0.03	25.35	0.60	6.42	0.13	0.15	0.15	100.46
6	3533/187.8	0.28	16.94	44.41	6.54	0.16	24.34	0.52	6.28	0.25	0.09	0.08	99.89
7	3533/195.0	0.25	18.64	36.22	13.26	0.14	23.44	0.94	6.57	0.17	0.39	0.12	100.14
8	3533/197.5	0.30	20.92	43.25	6.52	0.08	13.28	0.49	13.80	0.06	0.21	0.01	98.92
9	3533/218.7	0.39	23.80	42.59	3.22	0.16	21.97	0.44	9.19	0.00	0.21	0.13	102.10
10	3533/222.4	0.30	23.95	42.48	3.46	0.21	20.20	0.42	10.28	0.00	0.18	0.03	101.51
11	3535/274.0	0.16	23.68	44.12	2.26	0.25	19.96	0.18	10.36	0.04	0.29	0.00	101.30
12	3507/179.0	0.21	21.55	36.10	11.14	0.09	18.39	0.65	9.96	0.46	0.39	0.10	99.04
13	3507/188.3	0.28	21.27	35.45	13.22	0.03	21.48	0.44	8.78	0.19	0.37	0.11	101.62
14	3507/287.2	0.33	17.45	37.08	14.89	0.07	23.02	0.68	7.34	0.20	0.10	0.09	101.25
15	3536/194.0	0.23	20.51	43.97	4.74	0.09	17.28	0.35	11.33	0.00	0.14	0.00	98.64
16	3541/405-1	0.10	38.41	22.27	5.56	0.10	23.67	0.47	8.84	0.18	0.16	0.06	99.82
17	3536/195.0	0.15	36.11	26.28	3.30	0.45	22.04	0.22	9.59	0.17	0.27	0.07	98.65
18	33A	0.04	6.88	59.71	3.87	0.00	16.98	0.35	10.66	0.00	0.03	0.00	99.05

Cation proportions (*apfu*)

	Sample	Ti	Al	Cr	Fe^{3+}	V	Fe^{2+}	Mn	Mg	Zn	Ni	Co	*Y*Cr	*X*Mg
1	KAP18	0.01	1.27	0.63	0.08	0.01	0.56	0.01	0.43	0.01	0.01	0.00	31.82	43.43
2	3541/369-1	0.01	1.01	0.91	0.06	0.00	0.66	0.02	0.32	0.01	0.00	0.00	45.95	32.65
3	3533-148.5	0.01	0.81	0.93	0.24	0.00	0.60	0.02	0.38	0.00	0.01	0.00	46.97	38.78
4	3533-178.5	0.01	0.77	1.11	0.12	0.00	0.33	0.01	0.66	0.00	0.01	0.00	55.50	66.67
5	3533-182.0	0.01	0.87	0.78	0.32	0.00	0.68	0.02	0.31	0.00	0.01	0.00	39.59	31.31
6	3533-187.8	0.01	0.66	1.16	0.16	0.00	0.67	0.02	0.31	0.01	0.01	0.00	58.59	31.63
7	3533-195.0	0.01	0.72	0.94	0.33	0.00	0.64	0.03	0.32	0.00	0.01	0.00	47.24	33.33
8	3533-197.5	0.01	0.77	1.07	0.15	0.00	0.35	0.01	0.64	0.00	0.01	0.00	53.77	64.65
9	3533-218.7	0.01	0.87	1.04	0.08	0.00	0.57	0.01	0.42	0.00	0.01	0.00	52.26	42.42
10	3533-222.4	0.01	0.87	1.03	0.08	0.01	0.52	0.01	0.47	0.00	0.01	0.00	52.02	47.47
11	3535-274.0	0.00	0.86	1.07	0.05	0.01	0.51	0.01	0.48	0.00	0.01	0.00	54.04	48.48
12	3507-179.0	0.01	0.81	0.91	0.27	0.00	0.49	0.02	0.47	0.01	0.01	0.00	45.73	48.96
13	3507-188.3	0.01	0.79	0.88	0.31	0.00	0.57	0.01	0.41	0.00	0.01	0.00	44.44	41.84
14	3507-287.2	0.01	0.67	0.95	0.36	0.00	0.63	0.02	0.36	0.01	0.01	0.00	47.98	36.36
15	3536-194.0	0.01	0.77	1.11	0.11	0.00	0.46	0.01	0.54	0.00	0.00	0.00	55.78	54.00
16	3541/405-1	0.00	1.35	0.53	0.12	0.00	0.59	0.01	0.39	0.00	0.01	0.00	26.50	39.80
17	3536-195.0	0.00	1.28	0.64	0.08	0.00	0.56	0.01	0.43	0.00	0.01	0.00	32.00	43.43
18	33A	0.00	0.27	1.59	0.10	0.00	0.48	0.10	0.53	0.00	0.00	0.00	81.07	52.72

Note: 1-17: Kapitanov deposit, with datasets 16–17 from Gornostayev *et al.* (2000a); 18: Maja e Sukës deposit (composition includes 0.53 wt.% SiO_2). *apfu*: atoms per formula unit. The proportion of Fe_2O_3 is calculated. The electron-microprobe data are reported in weight %.

Anduoite

Anduoite in sample KAP18 from the Kapitanov deposit does not show any features indicative of compositional zoning or alteration (X-ray mapping for As and Ru; Figs. 3C, D). The chemical formula can be written (Table 2, average of four analyses) as: $(Ru_{0.80}Os_{0.10}Ir_{0.03}Rh_{0.03}Pd_{0.01}Pt_{0.01})_{\Sigma 0.98}(As_{2.01}S_{0.02})_{\Sigma 2.03}$.

The small size (1–2 µm) of the second euhedral crystal from Kapitanov (sample 3541/369–1; Fig. 3) does not allow one to obtain a good quantitative analysis (Table 2, anal. 5). However, its stoichiometry is close to that of the first crystal (sample KAP18).

In the Maja e Sukës specimen, only one analysis (Table 2, anal. 7) was obtained because of the small size of the crystal, which approaches that of the diameter of the electron beam. The chemical formula of this crystal of anduoite is: $(Ru_{0.79}Os_{0.11}Rh_{0.04}Ni_{0.04}Pd_{0.02}Ir_{0.01})_{\Sigma 1.01}(As_{1.98}S_{0.01})_{\Sigma 1.99}$.

The chemical composition of the Tropoja anduoite is quite similar to that from Kapitanov (Table 2, Fig. 5) with respect to the proportion of the anduoite end-mem-

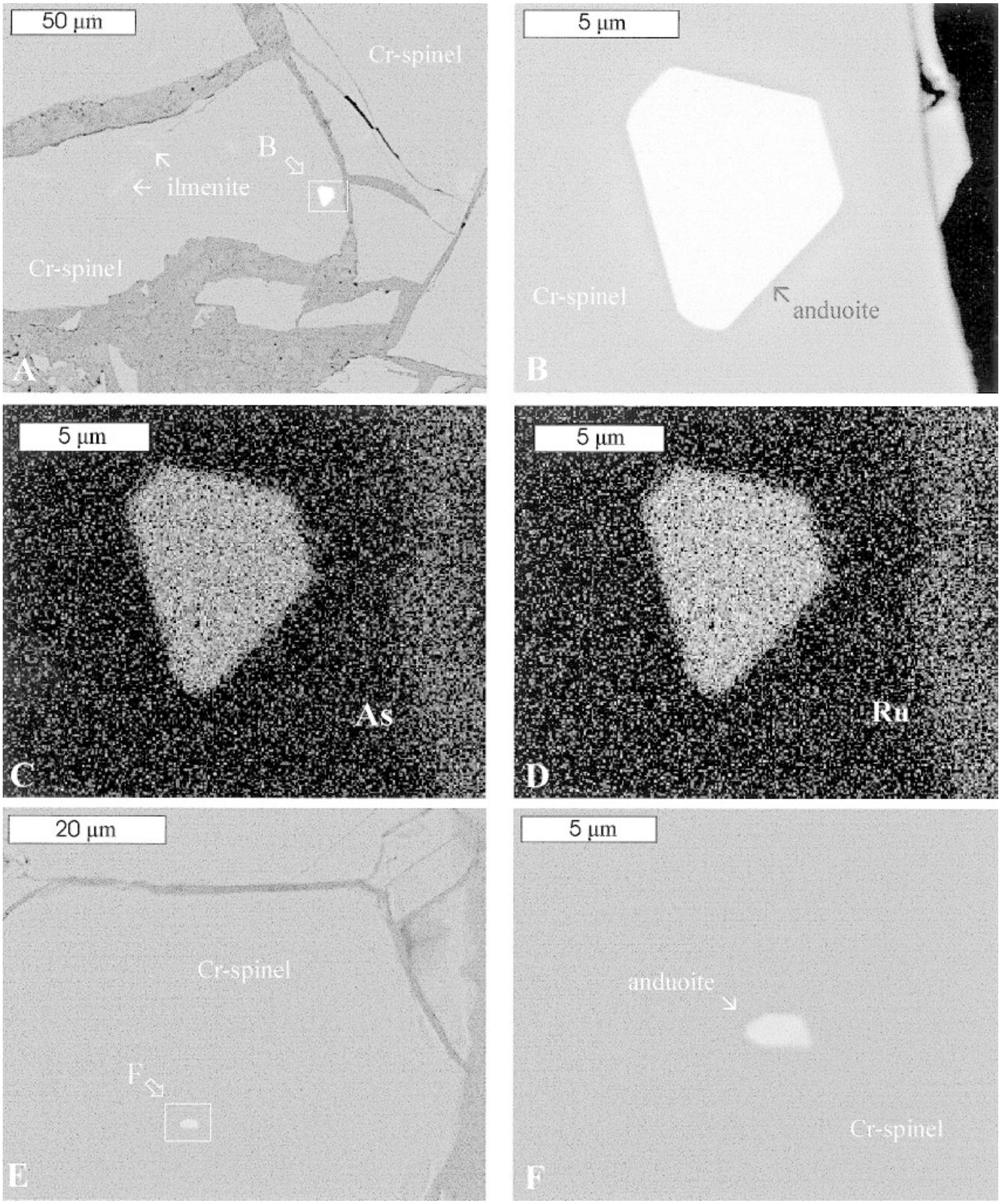

FIG. 3. Anduoite from the Kapitanov deposit. A and B. Euhedral crystal enclosed in chromian spinel containing lamellae of ilmenite, sample KAP18. C and D. X-ray maps of the euhedral crystal in sample KAP18 for As and Ru. E and F. Euhedral crystal enclosed in a chromian spinel grain, sample 3541/369–1; see Table 2 for analytical data.

TABLE 2. ELECTRON-MICROPROBE DATA ON ANDUOITE AND ASSOCIATED PGM

	1	2	3	4	5	6	7	8	9	10	11	12
S wt.%	0.32	0.29	0.27	0.14	0.26	0.09	0.12	0.22	13.97	13.67	8.93	9.84
As	57.58	56.65	56.28	56.56	55.47	56.65	56.91	41.15	27.65	30.94	31.21	31.85
Sb	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.06	0.05	0.41	0.14	0.00
Os	6.75	8.13	6.98	7.22	2.96	6.20	8.37	0.06	1.44	1.30	1.87	0.83
Ir	2.20	1.62	1.68	1.96	2.35	2.08	0.54	0.65	30.71	10.67	19.17	4.99
Ru	30.92	30.04	30.41	30.07	31.86	34.47	30.65	0.00	0.64	0.57	2.72	1.20
Rh	1.01	0.83	1.15	1.11	0.00	0.00	1.54	0.17	20.72	32.64	13.03	22.88
Pt	0.83	0.87	0.85	0.74	0.00	0.00	0.65	54.85	1.66	3.06	6.36	3.98
Pd	0.16	0.71	0.50	0.69	0.00	0.00	0.61	0.01	0.00	3.95	10.33	13.26
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.89	0.94
Cu	0.00	0.00	0.00	0.00	0.00	0.10	0.00	0.02	0.47	0.18	0.33	0.10
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.95	0.03	0.07	2.19	7.14	9.28
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.10	0.04	0.00	0.00
total	99.77	99.14	98.12	98.49	92.90	99.60	100.34	97.25	97.49	99.80	102.12	99.15
	Formula based on 3 atoms per formula unit								Formula based on 7 atoms per formula unit			
S *apfu*	0.026	0.024	0.022	0.012	0.022	0.007	0.010	0.024	1.090	0.966	1.583	1.630
As	2.010	2.003	2.001	2.011	2.035	1.981	1.975	1.951	0.923	0.935	2.367	2.258
Sb	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.001	0.008	0.007	0.000
Os	0.093	0.113	0.098	0.101	0.043	0.085	0.114	0.001	0.019	0.015	0.056	0.023
Ir	0.030	0.022	0.023	0.027	0.034	0.028	0.007	0.012	0.400	0.126	0.567	0.138
Ru	0.800	0.787	0.802	0.793	0.866	0.894	0.789	0.000	0.016	0.013	0.153	0.063
Rh	0.026	0.021	0.030	0.029	0.000	0.000	0.039	0.006	0.504	0.718	0.720	1.181
Pt	0.011	0.012	0.012	0.010	0.000	0.000	0.009	0.999	0.021	0.036	0.185	0.108
Pd	0.004	0.018	0.013	0.017	0.000	0.000	0.015	0.000	0.000	0.084	0.552	0.662
Fe	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.091	0.089
Cu	0.000	0.000	0.000	0.000	0.000	0.004	0.000	0.001	0.019	0.006	0.030	0.008
Ni	0.000	0.000	0.000	0.000	0.000	0.000	0.042	0.002	0.003	0.084	0.691	0.839
Co	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.004	0.002	0.000	0.000

Colums 1–5: anduoite, Kapitanov deposit (1–4: KAP18, 5: 3541/369-1); 6: anduoite, Tibet (average result of six analyses: Yu & Chou (1979), calculated from Fleischer *et al.* (1980); 7–12: Maja e Sukës deposit; 7: anduoite; 8: sperrylite; 9, 10: hollingworthite; 11, 12: unnamed Rh–Pd–Ir–Ni arsenide.

ber (79 to 80 mole %) or that of omeiite (10–11 mole %). Anduoite from Tropoja has a higher content of Ni (0.95%) than that from Kapitanov. Minor compositional differences also exist with respect to the contents of minor PGE (Ir, Rh, Pt and Pd). The Ru content is significantly lower in anduoite from Kapitanov and Tropoja than in anduoite described from Tibet (Yu & Chou 1979) (Table 2, anal. 6, Fig. 5), whereas that of Os is slightly higher. In all the examples of anduoite, the S content invariably is low (<0.3 wt%), *i.e.*, the extent of S-for-As substitution is insignificant.

Associated PGM from the Maja e Sukës deposit

The chemical composition of sperrylite is rather close to the end member, with minor amounts of Os, Ir, Rh, Ni and Fe (Table 2, anal. 8). Two compositions of hollingworthite (Table 2, anal. 9, 10) show large variations of Rh and Ir, which reflect an irarsite–hollingworthite solid-solution series (Ohnenstetter *et al.* 1991a). The molar proportion of hollingworthite decreases from 72.4 to 52.5% as the irarsite proportion increases from 12.7 to 41.7%. The Rh-rich hollingworthite contains significant amounts of Pd (3.95 wt.%) and nickel (2.19 wt.%), and is richer in As than the Ir-rich hollingworthite.

The other phase analyzed in the polymineralic assemblage is a complex, mixed PGE – base metal (BM) species with a low S:As ratio (about 0.7) and a high PGE:BM ratio (2.3 < PGE/BM < 2.7) (Table 2, anal. 11, 12). The (S + As):(BM + PGE) ratio is greater than 1 (1.25 and 1.30, respectively), and deviates considerably from the 2:1 stoichiometry of PGE sulfarsenides such as hollingworthite. It corresponds rather to a thiospinel-type stoichiometry. In this case, the tetrahedral site is occupied by Ni rather than by Cu or Fe (5.8 < Ni/BM < 8.6), in contrast to previous published compositions of "cuprorhodsite" (Johan *et al.* 1991). The existence of nickeloan malanite is reported by Barkov *et al.* (1997), but that mineral displays a Ni-for-PGE type of substitution. Ir, Rh, Pd and, to a lesser extent, Pt are the predominant PGE in the two compositions ob-

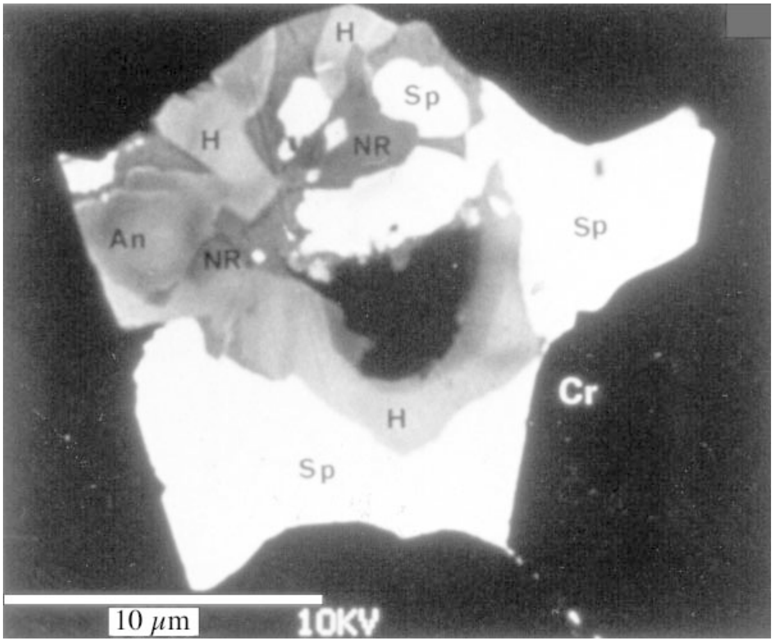

FIG. 4. Complex polymineralic inclusion of arsenides and sulfarsenides within chromian spinel from the Maja e Sukës deposit. Symbols: Cr: chromian spinel, An: anduoite, H: hollingworthite, Sp: sperrylite, NR: unknown sulfarsenide of Rh, Ir, Pd and Ni; see Table 2 for analytical data.

tained from the unnamed PGM. Comparison of the two compositions indicates little variation in level of S, As and BM, but major variation in the proportion of Ir and Rh, as in the adjacent hollingworthite. Extensive solid-solution between PGE and BM, and between S and As, is commonly reported in sulfarsenides of platinum-group elements and base metals (Distler & Laputina 1979, Gervilla *et al.* 1997, Melcher *et al.* 1997).

Chromian spinel

The chemical compositions of chromian spinel hosting anduoite are reported in Figure 6, together with the fields of chromite deposits from the Kapitanov and Tropoja massifs. Contrasting compositions are shown by the chromian spinel that hosts anduoite in the Maja e Sukës and Kapitanov deposits. In Maja e Sukës, it is a magnesiochromite, which falls in the compositional field of ophiolitic deposits at a very high *Y*Cr ratio (81) (*Y*Cr = 100 Cr/ΣR^{3+}) (Neziraj 1992), whereas in Kapitanov, it is a chromian hercynite, which falls outside the fields of ophiolites and layered complexes owing to relatively low *Y*Cr and *X*Mg (*X*Mg = 100 Mg/ΣR^{2+}) ratios (Table 1).

In the Tropoja massif, the chemical evolution of chromian spinel is controlled by two major trends. The

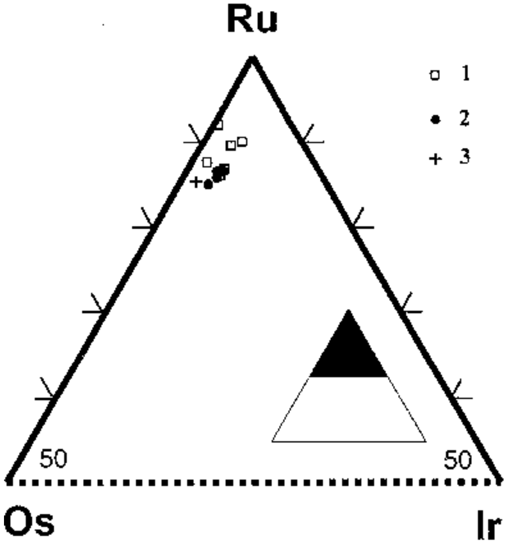

FIG. 5. Ru–Os–Ir plot of anduoite compositions. 1 Tibet (Yu & Chou 1979), 2 Kapitanov deposit, 3 Maja e Sukës deposit.

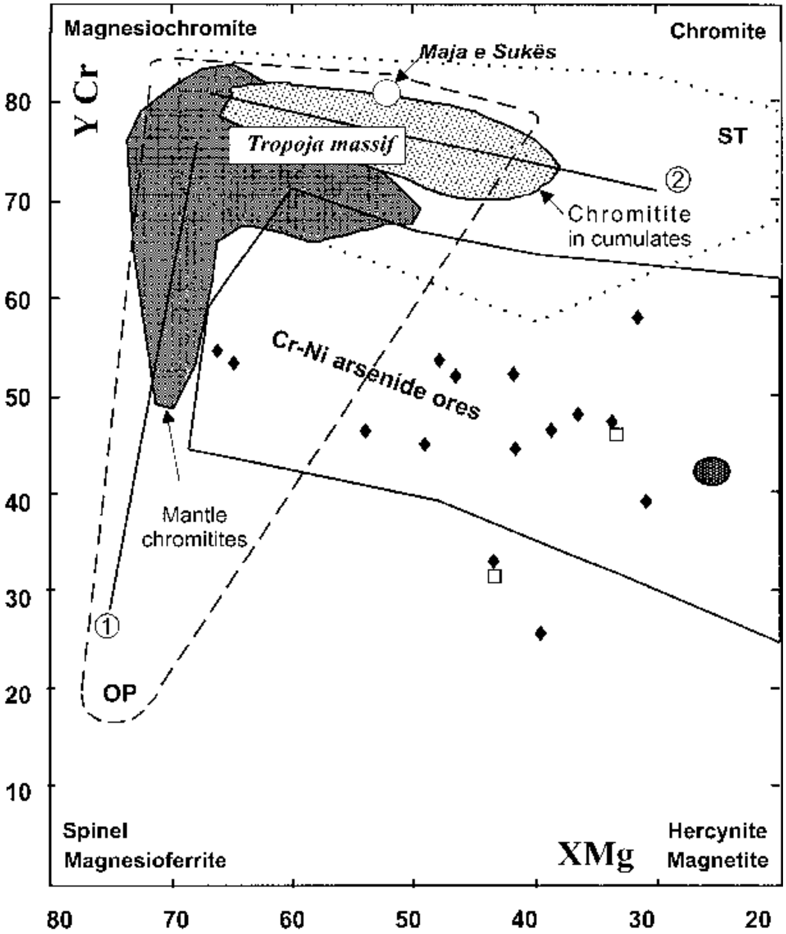

FIG. 6. XMg (= 100 Mg/ΣR^{2+}) *versus* YCr (= 100 Cr/ΣR^{3+}) diagram for chromian spinel hosting anduoite (open square: Kapitanov, open circle: Maja e Sukës). These data are compared with compositions from chromite deposits at Kapitanov (black diamonds), a PGE-rich chromitite from the Tropoja massif (full circle), and with fields for chromite ore from the mantle and cumulate sequence of the Tropoja massif (Neziraj 1992). The two trends (1, 2) illustrate the major substitutions in the mantle and cumulate deposits (see text). The field of Cr–Ni arsenide ores is from Oen *et al*. (1979) and Gervilla & Leblanc (1990). The field of podiform ophiolitic chromitites (OP) and that of stratiform chromitites (ST) are taken from Gervilla & Leblanc (1990).

first trend, recorded by most mantle deposits, involves substitution of the spinel and magnesiochromite components. A variation in the YCr ratio of chromian spinel accompanied by little variation in the XMg ratio is generally related to the composition of the parental melts. Cr-rich magnesiochromite would derive from boninitic-type magmas produced from hydrous melting of a severely depleted mantle. Spinel and Al-rich magnesiochromite would derive from less depleted melts, such as those produced in mid-oceanic ridges and back-arc basins (Dick & Bullen 1984, Ohnenstetter 1985, Roberts 1988). The second trend, shown by chromite deposits from cumulates and by some deposits in the mantle, is characterized by an increase of magnetite or hercynite components (or both) at the expense of spinel or magnesiochromite components (or both). Decrease of Cr and Mg with Al, Fe^{3+} and Fe^{2+} increase is considered to result from crystal fractionation, which may occur in magma chambers in the crust. However, an increase in the proportion of the magnetite component could also be achieved by metamorphism and late-stage serpentinization (Evans & Frost 1975). Because the Maja e Sukës deposit plots in the field of cumulate chromite deposits from Tropoja, at high *Y*Cr and relatively low *X*Mg, such a deposit could have been derived from a boninitic-type magma after fractionation occurred to some extent.

Chromian spinel from the Kapitanov massif plots within the fields of magnesiochromite, chromite and chromian hercynite. Because a low *Y*Cr ratio coupled with a low *X*Mg ratio is observed, the Kapitanov deposit may have been derived from melts richer in Al and Fe than those parental to the Tropoja deposits. On the other hand, considerable variation in the *X*Mg ratio in the Kapitanov samples indicates that significant fractionation of magma occurred, which involved a decrease in concentration of Cr and Mg and an increase in that of Al and Fe^{2+}. Magma fractionation probably occurred under low $f(O_2)$, as deduced from the low Fe^{3+} content and the high Fe^{2+}:Fe^{3+} ratio, even in crystals with a low *X*Mg ratio. A low *X*Mg coupled with low Ti and Fe^{3+}, as shown by the chromian hercynite from Kapitanov, is unusual in ophiolitic chromite deposits. For example, a PGE-rich chromite deposit from Tropoja, which plots close to the chromian hercynite from Kapitanov, is composed of chromian magnetite with a high Ti content (up to 4.2 wt.%).

Characteristics similar to those from the Kapitanov deposit (high Al:Cr ratio, low *X*Mg ratio and Fe_2O_3 contents), are shared by chromian spinel at the Malaga deposits (Spain) despite their different setting. At Kapitanov, arsenides are accessory phases, whereas at Malaga, chromite is locally associated with Ni–Co–PGE-rich arsenide ores located in interstices between chromite grains (Oen *et al.* 1979, Gervilla & Leblanc 1990). In addition, trace-element contents are distinct in chromian hercynite from Kapitanov and Malaga. Chromian spinel from the chromite – Ni arsenide ores of Malaga is much richer in Ti (up to 0.8 wt.% TiO_2), V (up to 2.7 wt.% V_2O_3) and in Zn (up to 1.5 wt.% ZnO) than that reported from Kapitanov. In the latter case, the concentrations of TiO_2, V_2O_3 and ZnO, which are respectively 0.19–0.33, 0.12–0.55 and 0.26–0.27 wt.%, are in the range of chromian spinel from ophiolitic complexes (Paktunc & Cabri 1995). The content of Zn is especially important because its abundance in chromian spinel is considered to be related to the precipitation of this mineral from silicate melt coexisting with S- and As-rich melt (Gervilla & Leblanc 1990) or to metasomatism related to the formation of large amounts of Cu–Co–Zn–Au ore (Liipo *et al.* 1995) or, more generally, to sulfide ores (Paktunc & Cabri 1995).

Discussion and Conclusions

In podiform chromitites from ophiolites, two different modes of occurrence of PGM are defined, relative to chromian spinel: 1) inclusions in chromian spinel of Os–Ir–Ru alloys or sulfides (or both) with accessory PGE sulfarsenides and base-metal sulfides; a particular case exists for the alloy type of Pt mineralization with Pt–Fe alloys included in chromite (Ohnenstetter 1996); 2) interstitial PGM found between chromite grains; these PGM comprise diverse mineral species, mostly Pt, Rh and Pd sulfarsenides and arsenides, antimonides, bismuthides and tellurides (Talkington & Watkinson 1986, Prichard & Tarkian 1988), one or two of these mineral species being predominant in each deposit. Those PGM included in chromite precipitate before or contemporaneously with chromite, whereas the interstitial PGM crystallized later. A purely magmatic origin, based on the similarity with PGM occurrences in layered complexes (Talkington *et al.* 1984), would indicate early entrapment of the more refractory PGE (Ir, Os and Ru), which precipitated from silicate melts or sulfide melts (or both) during the growth of chromite (Stockman & Hlava 1984), and late-stage intercumulus deposition of the more incompatible PGE (Rh, Pt and Pd) (Prichard *et al.* 1986). An other point of view would suggest that the two distinct groups of PGM might have a different origin, and those included in chromite could be genetically related to chromite deposition, whereas PGM in altered interstitial silicates would be the products of hydrothermal processes that accompanied serpentinization (Tarkian *et al.* 1991, Prichard *et al.* 1994). In addition, where the PGM are located in the ferrian rim of a homogeneous chromian spinel grain, it is generally admitted that the PGM assemblage is secondary, as well as those occurring in cracks (Thalhammer *et al.* 1990).

The secondary origin of the interstitial PGM, which are composed mainly of the Pd group (Pd, Pt, Rh) of PGE (PPGE), raises not only the question of the origin of enrichment in As and Sb, Bi, and Te, but also that of the mobility of the most incompatible PGE. Exploration studies on rocks and soils (Prichard & Lord 1993), and careful examination of PGE distribution in bulk-rock and PGM assemblages (Garuti *et al.* 1999a), generally indicate only small-scale mobility of the PGE, such that PGE distribution in moderately serpentinized bulk-rocks may be considered to be primary (Economou 1986). In such a case, the extraction of PGE from primary sulfides or alloys by hydrous fluids is later followed by redeposition of low-temperature PGM assemblages in proximity.

The present anduoite-hosting assemblage contrasts with the common association of PGM found within chromite grains in podiform chromitites (Talkington *et al.* 1984) in the significant development of As-bearing minerals formed with the Ir group of PGE (IPGE), Ni and also Pt, instead of alloys and sulfides. It is generally assumed that laurite or Os–Ir alloys (or both) represent 70 to 80% of the PGM observed (Legendre & Augé 1986, Tarkian *et al.* 1991). The occurrence of sulfarsenides and arsenides within chromite is not exceptional, but their origin is highly controversial, considering either their setting or their composition. Discrete inclusions of PGM in chromian spinel, either alloys or sulfides and arsenides, may be considered as evidence for primary mineralization (*e.g.,* Garuti *et al*. 1999b, and references therein). For example, all the IPGE minerals, alloys, sulfides and sulfarsenides are considered to be primary in the Vourinos complex (Augé 1985). Similarly, irarsite, ruarsite and osarsite found in Bulgarian ophiolitic chromitites also are considered primary, because of their similar occurrence as the associated Ru–Os–Ir alloys and laurite within homogeneous chromian spinel grains (Tarkian *et al*. 1991). In contrast, because of the presence of As in sulfarsenides, notably irarsite and hollingworthite, these minerals are considered to be secondary in podiform chromitites (Thalhammer & Stumpfl 1988, Thalhammer *et al*. 1990, McElduff & Stumpfl 1990, Nilsson 1990, Prichard & Lord 1993, Prichard *et al*. 1994, Melcher *et al*. 1997). Similar reasoning holds for sperrylite. According to Stockman & Hlava (1984), the small anhedral Pt–As grain partly rimming laurite in a polyphase inclusion is considered to belong to the primary PGM assemblage. The presence of significant amounts of sperrylite in PPGE-mineralized chromitites is notably reported from Cliff, Shetlands (Prichard *et al*. 1986) and from Hochgrössen, Austria (Thalhammer & Stumpfl 1988, Thalhammer *et al*. 1990), but their origin is controversial. The sperrylite-bearing PGM assemblage, which is located either within or between chromite grains in the two massifs, is interpreted to be original in the former case and secondary in the latter case.

Considering the setting of the discrete and polyphase inclusions of anduoite observed within chromite in our study, this Ru–As mineral could be considered as primary. In addition, no evidence for late-stage recrystallization, *i.e.,* annealing and sintering in the presence of fluid, was found in grains of chromian spinel near the inclusions. At Kapitanov, anduoite occurs as euhedral discrete grains randomly distributed within homogeneous chromian spinel devoid of cracks, providing good evidence for its early entrapment. Consequently, anduoite is considered to have the same origin as the other discrete single-phase inclusions of irarsite, laurite and Os–Ir–Ru alloy and, in one case, a two-phase inclusion of Os–Ir–Ru alloy and undefined Ru–Os–As phase (Gornostayev *et al*. 2000b).

At Maja e Sukës, the zoned PGM assemblage with diarsenides (sperrylite + anduoite) rimming sulfarsenides, forming the polyphase inclusion, as well as the presence of cracks, ending in the inclusion bordered by irregular walls, may be interpreted in terms of progressive replacement of early alloys or sulfides (or both), which have reacted with As-rich fluids during serpentinization. Because of the low content of Pd in the bulk rock, corroborated by the absence of Pd minerals, one may ask if the arsenide-bearing inclusion results from the alteration of Pt-rich chromitite related to the Pt-alloy type of PGE mineralization, which is located to the north in the Bregu i Bibës area. In such a case, the Maja e Sukës assemblage would have been derived from the alteration of the sparse chromitites hosting polyphase inclusions with Pt–Fe and Os–Ir–Ru alloys and laurite. However, reaction between this primary assemblage and As-rich fluids would have involved considerable change in the inter-element ratio of PGE and base metals within the inclusion, as Fe was lost, and Ni together with most of Ir and Rh were gained from the fluids. This process contrasts with the results of Tolstykh *et al*. (1997), who showed that the proportions of Ir, Os and Ru minerals in secondary assemblages (in this case arsenotellurides and telluroarsenides) are inherited from the composition of primary alloys (Os–Ir–Ru and Pt–Fe alloys). In addition, two types of secondary assemblages do exist at Bregu i Bibës. The more common type comprises diverse complex Fe–Ni–Cu–Pt–Pd-bearing alloys, which may have formed during serpentinization. Such a process involves reduction and locally desulfidation of early-formed PGE-bearing sulfides, as in Oregon (Stockman & Hlava 1984) and Greece (Garuti & Zaccarini 1997), in a manner similar to that producing Fe–Ni alloy (awaruite) and low-S sulfide (Chamberlain 1966). The second type of assemblage comprises sulfarsenides (mostly hollingworthite) locally associated with the primary alloys and occasionally with the secondary complex alloys. Sperrylite, which is related to this second type of assemblage, was only observed once in interstices among chromite grains (47 PGM grains were analyzed in the Bregu i Bibës deposit) (Neziraj 1992). Late-stage As-bearing phases may have crystallized during serpentinization with the complex base-metal and PGE alloys as in the Pt-mineralized rocks in Quebec (Gauthier *et al*. 1990). However, we cannot rule out the possibility that these As-bearing phases represent relict magmatic minerals rimming the early alloys or forming discrete phases in interstices, which were later involved in low-temperature alteration.

Characteristic PGE and Au hydrothermal deposits exist in ophiolites. They occur along basal thrust planes and shear zones leading to the formation of talc–carbonate–silica-bearing serpentinites (*e.g.,* review by Leblanc 1991). In these deposits, noble metals occur as sulfides and arsenides, but the distribution of PGE and Au (high contents of Au and, to some extent, Pd, low contents of Ir-group PGE and Pt) contrast with that deduced from the mineral assemblage observed in the chromite deposits studied, characterized by high contents of Ir-group PGE and Pt, and rather low contents of Au and Pd.

A primary origin for the inclusions of anduoite

At Kapitanov, the euhedral shape of the anduoite grains suggests that they grew in a melt-rich milieu and were trapped in chromian spinel as solid, well-formed crystals. Anduoite could have precipitated directly from a mafic silicate magma under relatively high fugacity of As, as suggested, for example, by Merkle (1992) and Torres-Ruiz *et al*. (1996). According to Merkle (1992), arsenide saturation in the silicate melt during crystallization of the UG2 Pt- and Pd-rich chromitites could have taken place before sulfide saturation, leading to the crystallization of refractory arsenides. This hypothesis is compatible with the formation of PGE- and As-rich clusters within a silicate magma, which may lead to significant concentration of the PGE (Tredoux *et al*. 1995). Nevertheless, taking into account that Ru is the most chalcophile PGE (Fleet *et al*. 1999), it could be that this element has a very high affinity for As as well (there are no experimental data). Consequently, the origin of anduoite from Kapitanov could be similar to that of laurite: a very refractory phase segregated from a mafic silicate melt with an As:S ratio higher than that necessary to stabilize laurite. The other plausible alternative is that As-bearing minerals precipitated from an As-rich melt available as chromitite was deposited in veins cutting a lherzolitic mantle massif (Oen 1973). A mantle origin for arsenic is also accepted for the disseminated Ni arsenides associated with Fe–Ni–Cu sulfides in garnet peridotites from the Beni–Bousera lherzolitic body (Lorand 1987). In such conditions, enrichment in S as well as As would derive from partial melting of lherzolitic mantle massifs, such as those occurring in Spain and Morocco, before being redeposited. Saturation of the resulting silicate melt in arsenides and sulfides after significant crystallization of chromite is a well-known process (Buchanan & Nolan 1979) that finally leads to the formation of an immiscible As- and S-rich melt gathering PGE, which coexisted with the chromite-producing silicate melt. During cooling, PGE arsenides could be formed from this S- and As-rich melt, which may have been trapped within chromian spinel as it crystallized from the coexisting silicate magma, or among grains of chromian spinel. The existence of an As-rich melt carrying PGE was demonstrated experimentally (Skinner *et al*. 1976) and also in nature, in view of the presence of As-rich globules trapped in alloys (Johan *et al*. 1990) and in sulfides (Gervilla *et al*. 1996). In fact, an As-rich melt could be an important collector of noble metals, even in the presence of an immiscible sulfide melt. In the As-rich portion of the experimental system Pd–Pt–As–S, Makovicky *et al*. (1990) found evidence of two melts at 850°C, a Pd–As-enriched melt that dissolves between 0.2 and 33 at.% Pt, and a Pt–As-enriched melt that can dissolve no more than 10% Pd. A sulfur-free Pt–As-enriched melt was also found in the As-rich part of the system Pt–Fe–As–S at 850°C (Makovicky *et al*. 1992).

At Maja e Sukës, the resulting bulk composition of the polymineralic assemblage is characterized by high As (38.7 wt.%) and PGE (54.2 wt.%) contents, and low S (4.4 wt.%) and base-metal (2.6 wt.%) contents, notably Fe. The high Pt:Pd ratio (10) of the polyphase assemblage may be original, and may correspond to that of a Pd-poor Pt–As-enriched melt trapped during crystallization of the chromian spinel. The scarcity of S-bearing phases in the PGM assemblage and the low S content of sperrylite are also indicative of the existence of a S-poor melt (Makovicky *et al*. 1990). Despite the lack of similar experiments involving the Ir-group of PGE, we contend that these compatible PGE, notably Ru, could form their own discrete phases from a PGE- and As-rich melt.

The zoned assemblages observed in Maja e Sukës and Tibet could be explained in terms of crystal growth from a fractionating S- and As-rich melt during cooling. The sequence of crystallization deduced from the different styles of zonation [*i.e*., 1) Ru–Os–Ir alloy or laurite, 2) sulfarsenide, 3) monoarsenide, 4) diarsenide], indicates that from the early to the late stage, the proportion of As was increasing in the successively formed minerals. The residual S- and As-rich magma may thus have become progressively enriched in As as early alloys and sulfides were deposited with cooling. As an alternative, reaction of these early-formed PGM with a trapped As-rich melt could also take place as crystallization was proceeding.

Concluding remarks

Anduoite, $(Ru,Os)As_2$, was found in chromitite from two distinct massifs, where it occurs either as discrete grains or as polyphase inclusion within chromian spinel. These two new occurrences, following the discovery site in Tibet, permit an interpretation of the origin of this mineral, primary *versus* secondary, considering its setting and the mineral assemblage closely associated with anduoite or found within the deposit. A magmatic origin is preferred, whether anduoite crystallized directly from a silicate melt, locally saturated in As, or from an immiscible As-rich melt formed as chromite was crystallizing.

The fact that As forms compounds with IPGE instead of S is relevant to the existence of a S-poor system in ophiolites that underwent at an early stage of accumulation of chromitites. According to Hamlyn & Keays (1986), progressive depletion of the residual peridotite during partial melting will lead to successive batches of magma more and more S-poor and PGE-rich. Consequently, PGE mineralization poorest in S is expected to be found in mantle rocks and crustal sequences associated with a boninitic type of magma.

The Tropoja massif illustrates the fact that a boninitic-type liquid could lead to S-poor mineralization characterized either by the presence of alloys (Bregu i Bibës) or arsenides (Maja e Sukës). However, the chemical composition of the chromian spinel hosting anduoite in the two deposits studied (Kapitanov and Maja e Sukës) indicates that S-poor, As-rich magma could be derived from various types of silicate melts, from MORB to boninitic-type parental melts. PGE mineralization in Kapitanov, considered to be formed from a MORB-type magma, is compatible with the fact that arsenide ore from Malaga (Oen 1973, Gervilla & Leblanc 1990) is hosted by slightly depleted mantle peridotites and associated crustal complexes possibly related to a rifting event.

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