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Review

On the diversity of the PGE content in chromitites hosted in ophiolites and in porphyry-Cu systems: Controlling factors

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ABSTRACT

The present study on the diversity of the platinum-group elements (PGE) content in chromitites and porphyry-Cu deposits from Greece and everywhere (literature data) aims to define factors controlling precious metal enrichment in ophiolite complexes and the unknown Pd and Pt potential in porphyry Cu systems, through an integrated set of mineralogical and geochemical approaches. The PGE content in chromitites associated with ophiolite complexes is commonly low (a few 100 s of ppb). However, a significant PGE-enrichment (up to 10 s of ppm) is a feature of relatively small chromite occurrences, regardless their major element composition. Plots of the Pd/Ir *versus* normalized Pt/Pt* ratios defined separate fields corresponding to various chromitite types. Large chromite deposits exhibit low Pd/Ir values, reflecting low degree of fractionation (primitive magmas), negative (Pt/Pt* < 1) Pt/Pt* (partial melting of already depleted mantle) and increasing partial melting trend from high-Al towards to high-Cr deposits. The association with hydrous silicates (Cr-bearing hydrogrossular, chlorite and serpentine) and texture features of Os, Ir, Ru-rich (compatible) or IPGE-minerals, coupled with very low Pd/Ir and negative Pt/Pt* values were attributed to an origin by partial melting of already depleted mantle and increased partial melting degree, during a subsequent crustal/mantle recycling stage, via fluid-driven processes. Assuming that the increasing Pd/Ir reflects a fractionation trend of parent magma, a significant enrichment in Pt and Pd (incompatible) or PPGE, occurring in small occurrences (either high-Cr or high-Al type) may be a sensitive fingerprint for the orientation in the mantle sequence of the ophiolites and exploration for chromite.

Commonly the PGE content in porphyry Cu-Mo-Au deposits is less than 10 ppb. However, elevated (Pd + Pt) contents (over 6 ppm in sulfide-rich samples) are a characteristic feature of certain porphyry Cu-Au alkaline intrusions. Evidence of a favorable tectonic setting (post-collisional) for the origin of porphyry Cu-Au-Pd-Pt-elevated porphyry deposits include elevated (up to hundreds of ppm) contents in Cr, Co, Ni and Re, and elevated $^{187}Os/^{188}Os$ ratios, reflecting mixing and contribution to the magma composition. The oxidized nature of parent magmas (abundant magnetite) and the evolved mineralized fluid system in porphyry deposits are considered to be critical requirements for the transportation and deposition of sufficient Au and PGE. Elevated Pd, Pt and Au contents in porphyry deposits combined with the association of the major Pd-mineral (merenskyite) with bornite and chalcopyrite (major Cu-minerals) are encouraging economic factors for the contribution to the global (Pd + Pt) production.

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1. Introduction

Traditionally the platinum-group elements (Os, Ir, Ru, Rh, Pt and Pd) or PGE are associated with mafic-ultramafic complexes and have been described in a wide range of geotectonic settings. The majority of the PGE supply worldwide is produced from magmatic ores hosted in well-defined stratiform reefs of large layered intrusions, such as the Bushveld Complex (South Africa), the Great Dyke (Zimbabwe) and the Stillwater Complex (USA). The PGE mineralization has also been described and investigated in ophiolites and zoned Alaskan-Ural type (targets of exploration and sources of significant economic platinum placer deposits) emplaced in orogenic zones (Cowden et al., 1986; Barnes and Campell, 1988; Barnes and Maier, 2002; Tolstykh et al., 2005; Naldrett, 2010). Platinum-group elements can be classified into two subgroups: the Os, Ir, Ru-rich (IPGE or Ir-group, compatible) and (Rh, Pt, Pd)-rich group (PPGE, incompatible), with Pd/Ir ratio as an indicator of the fractionation degree of the parent magma (Barnes et al., 1985).

Although the PGE content in ophiolite complexes is relatively low (a few hundreds of ppb) in large chromite deposits, a significant PGE-enrichment is a common feature of disseminated chromite and/or relatively small chromite occurrences in the transitional zone between the upper mantle and the lower crust (Prichard et al., 1986; Economou-Eliopoulos, 1996; Tarkian et al., 1996; Ohnenstetter et al., 1999; Proenza et al., 1999, 2008; Prichard and Brough, 2009; Kapsiotis et al., 2009a,b; Economou-Eliopoulos et al., 2013; O'Driscoll and González-Jiménez, 2016). Also, during the last decades, elevated Pd and Pt contents in certain porphyry Cu-Au deposits, such as in Mt Milligan, British Columbia (over 6 ppm were measured in high grade ores) (Thompson et al., 2001) and Late Cretaceous to Miocene porphyry Cu deposits, extending from Romania, Serbia and Bulgaria, (up to 4 ppm in in high grade ores) from the Elatsite deposit (Augé et al., 2005) to Greece, up to 3 ppm measured in sulfide-concentrates (Economou-Eliopoulos, 2005). The Pd-telluride merenskyite occurs as inclusions or/and at margins of chalcopyrite and bornite or forms intergrowths with Pd-Pt-Bi- and Ag-tellurides in Greece (Tarkian et al., 1992a,b), in Philippines (Tarkian and Koopmann, 1995), in Bulgaria (Augé et al., 2005). Although the potential for PGE mineralization associated with such large Cu and Au-Cu porphyry deposits is still unknown, the elevated (Pd + Pt) values in the above examples of porphyry-Cu deposits, and the recovery results (Kiousis, 2005; Kiousis and Papavasiliou, 2005) are considered to be encouraging for Pd and Pt exploitation as by-products.

The present study is an approach on the formation and stability of PGE-minerals (PGM) and the characteristics of the PGE-depleted and PGE-enriched ores (a) in chromitites hosted in ophiolite complexes and (b) porphyry-Cu deposits, aiming at providing a better understanding of the genesis and exploration of that type of ore deposits. Different petrogenetic processes are reviewed in the light of magmatic and post-magmatic processes towards defining factors which control precious metal enrichment of PGE in ophiolite complexes and the Pd and Pt potential in porphyry Cu systems.

2. Analytical methods

Polished sections from chromite deposits of Greece and the Kempirsai (Urals) deposits (Table 2), and porphyry-Cu-Mo deposits from Greece (Skouries), Bulgaria (Elatsite, Medet, Assarel and Trar Asen), Russia (Aksug, Sora and Zhireken) and Mongolia (Erdenetuin-Obo), were carbon coated and examined by reflected light microscopy and with a scanning electron microscope (SEM) using energy-dispersive spectroscopy (EDS). SEM images and EDS analyses were carried out at the University of Athens (Department of Geology and Geoenvironment) using a JEOL JSM 5600 scanning electron microscope, equipped with automated energy-dispersive analysis system ISIS 300 OXFORD, with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, time of measurement 50 s and beam diameter 1–2 μm. The following X-ray lines were used: OsMα, PtMα, IrMβ, AuMα, AgLα, AsLα, FeKα, NiKα, CoKa, CuKα, CrKα, AlKα, TiKα, CaKα, SiKα, MnKα, MgKα, ClKα. Standards used were pure metals for the elements Os, Ir, Ru, Rh, Pt, Pd, Cu, Ni, Co and Cr, indium arsenide for As and pyrite for S and Fe.

Major and trace elements on mineralized porphyry samples were measured by inductively coupled plasma mass spectroscopy (ICP/MS) after hot aqua regia digestion at the ACME Analytical Laboratories Ltd., Vancouver, BC, Canada. Detection limits are 0.1 ppm for Ag, Cu, Pb, Ni, and Mo, 0.2 ppm for Co and 1 ppm for Zn and Cr. PGE were determined by ICP-MS analysis after pre-concentration using the nickel fire assay technique from large (30 g) samples, at the Acme Laboratories Ltd, Canada. This method allows for complete dissolution of samples. Detection limits are 5 ppb for Ru,

2 ppb for Os, Ir, Pt, Pd and 1 ppb for Rh and Au. Oxygen isotopic and hydrogen compositions presented herein were determined on quartz veinlets containing Cu–Fe-minerals, magnetite and precious metal-minerals, at the Geochron Laboratories, in Cambridge, Massachusetts. The hydrogen (δD) and oxygen ($\delta^{18}O$) data were normalized to the SMOW (Standard Mean Ocean Water) standard (Sheppard, 1986).

3. Characteristic features of chromitites associated with ophiolite complexes

The origin of major Jurassic ophiolite complexes of Greece (Vourinos, Pindos and Othrys) (Fig. 1) in an hydrous Supra Subduction Zone (SSZ) environment (Pearce et al., 1984; Konstantopoulou, 1990; Mansolas, 1991; Economou-Eliopoulos and Vacondios,

Table 1
Trace element contents in orthopyroxenes (opx) and clinopyroxenes (cpx) from harxburgites.

VOURINOS			wt%						ppm				
			Al_2O_3	Cr#sp	Ti	La	Ce	Nd	Sm	Eu	Dy	Er	Yb
Kokkinodromos	kok2	opx	1.51	0.58	90	0.668	0.145	0.169	0.01	0.007	0.013	0.012	0.038
Kissavos	Kis1	opx	1.68	0.64	41	0.222	0.083	0.083	0.006	0.002	0.06	0.005	0.004
Kissavos	Kis2	opx	0.91	0.67	120	2.891	0.545	0.076	0.035	0.043	0.074	0.016	0.028
OTHRYS	Eretria	opx	1.95	0.52	80	0.331	0.58	0.526	0.107	0.064	0.171	0.128	0.159
PINDOS													
Dramala	NIC	cpx	1.71	0.57	100	0.018	0.025	0.012	0.02	0.001	0.046	0.069	0.12
Trygona	T10C	cpx	1.83	0.64	81	0.05	0.035	0.03	0.916	0.009	0.025	0.04	0.08
Kambos Despoti	DIB	cpx	1.73	0.62	36	0.013	0.072	0.046	0.06	0.01	0.039	0.03	0.043

Symbol Cr#sp = Cr/(Cr + Al) in spinel.
Data: Economou-Eliopoulos and Vacondios (1995), Bizimis et al. (2000).

Table 2
Geochemical characteristics of PGE-poor and PGE-rich chromite ores.

Location	Sample	ppb											ppm					
		Os	Ir	Ru	Rh	Pt	Pd	ΣPGE	Pd/Ir	Pt/Pt*	Cr #	Mg#	Ni	Co	V	Zn	Ti	Ga
Large chromite deposits																		
Vourinos, high-Cr																		
Average	n = 30	23	19	58	12	6	3	121	0.16	0.32	0.81	0.63	1400	190	400	200	310	
Othrys, high-Al																		
Average	n = 10	35	13	38	3	6	2	97	0.15	0.78	0.57	0.7	1500	210	980	340	420	
S. Kempirsai,XL Let KazakhUrals, high-Cr																		
Average	n = 8	44	40	82	9	4	2	181	0.05	0.30	0.81	0.73	1640	130	490	230	660	
N. Kempirsai, Urals, Batamshinskoe, high-Al																		
Average	n = 4	30	12	35	3	4	1	85	0.08	0.74	0.56	0.7	1730	160	890	380	1500	
Chromite occurrences																		
Pindos, high-Cr																		
Trygona	AH107	25	21	50	10	152	36	294	1.71	0.74	0.82	0.62	2050	180	260	390	240	18
Trygona	AH1011	13	9	47	8	40	11	128	1.22	2.56	0.81	0.63	1340	190	310	340	300	13
Pefki	MP123	124	46	280	8	63	14	535	0.3	1.36	0.79	0.61	960	220	820	410	240	14
Pindos, high-Al										1.90								
Dako's mine	D.49A	5	12	42	1	34	68	162	5.8	1.32	0.56	0.51	1000	350	650	510	1200	33
Dako's mine	D.49B	3	4	16	1	6	16	46	0.6	0.48	0.6	0.5	1800	290	700	530	2600	42
Dako's mine	DM49C	4	6	30	1	4	6	51	1	0.52	0.52	0.63	1280	210	450	460	660	30
Koziakas	KOZ-1	20	22	48	2	18	8	118	0.36	1.44	0.53	0.66	1700	230	800	470	1300	32
Koziakas	KOZ-2	18	16	48	1	8	4	95	0.25	1.28	0.5	0.66	1510	260	710	520	1200	34
Korydallos	K-158	8	3	11	1	75	19	117	6.33	5.50	0.42	0.71	1500	260	710	520	1200	34
PPGE-elevated																		
Pindos																		
Korydallos	KG.170	47	49	55	104	3020	600	3875	12.2	3.86	0.67	0.57	750	270	760	500	780	16
Korydallos	KG.174	62	47	80	112	1460	337	2098	7.2	2.40	0.69	0.49	720	240	760	620	840	23
Korydallos	KG.191	14	11	57	13	3460	1660	5215	151	7.53	0.68	0.57	1550	230	510	450	720	30
Korydallos	KG.193	50	55	110	98	2220	766	3300	14	2.59	0.42	0.73	1600	200	500	360	720	28
Korydallos	KG.182	66	34	107	94	4420	2145	6866	63	3.15	0.41	0.73	1450	270	620	530	720	32
Korydallos	KG.165	88	74	130	142	1720	525	2679	7.1	2.01	0.4	0.72	630	240	790	510	1080	25
IPGE-elevated																		
Milia	M2	150	320	350	82	150	7	1059	0.22	2.00	0.82	0.42	1900	370	980	1180	300	15
Skyros																		
Achladones	Ax2.Sk	140	480	1200	160	280	39	2300	0.08	1.13	0.61	0.64	950	300	890	510	420	34
Veria																		
Galaktos	G.79	7400	6020	9700	310	760	750	24,940	0.1	0.50	0.67	0.61						
Galaktos	G.80	1520	3900	2300	510	1360	250	9840	0.06	1.22	0.77	0.58						
Galaktos	G65	170	440	620	30	1	2	1263	0.005	0.04	0.76	0.56						
Vourinos																		
Voidolakkos	940	830	1401	749	35	11	3	3032	0.002	0.34	0.78	0.66						
Rizo	957	998	763	234	6	23	3	2028	0.003	1.73	0.8	0.69						
Koursouma	200	217	131	237	27	18	9	640	0.07	0.37	0.66	0.66						

Symbol Cr# = Cr/(Cr + Al); Mg# = Mg/(Mg + Fe^{2+}).
Data from Tarkian and Stribrny (1999), Economou-Eliopoulos and Eliopoulos (1999), Economou-Eliopoulos et al. (1999).

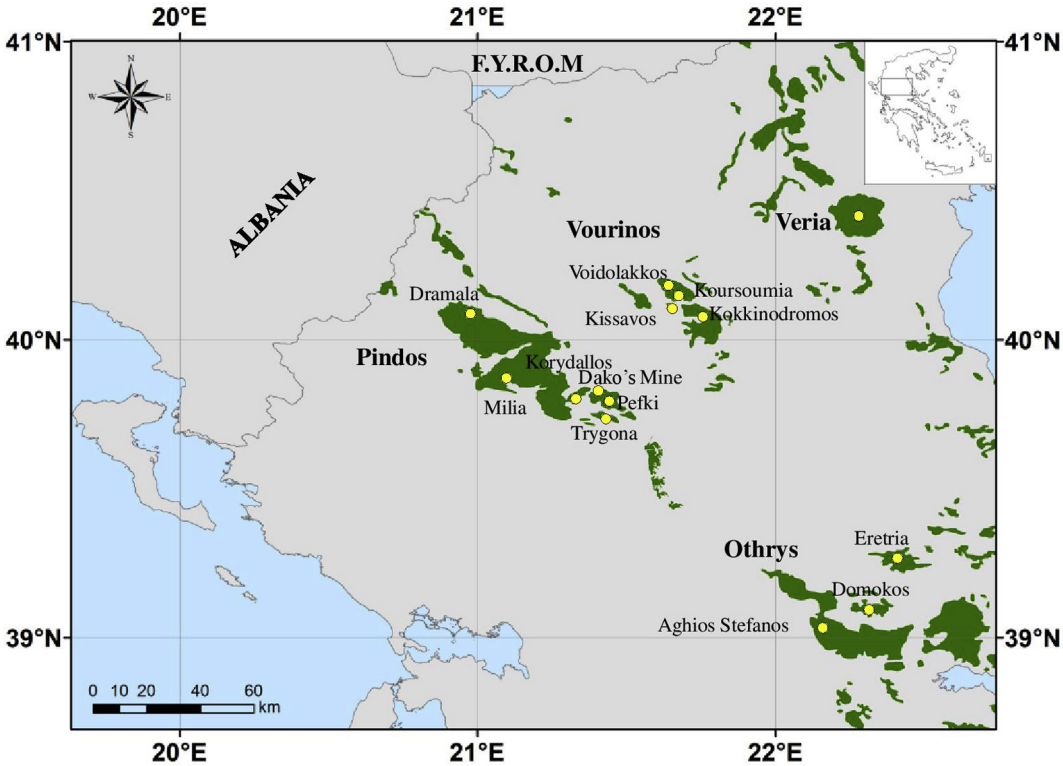

Fig. 1. Sketch map of the Pindos, Vourinos and Othrys ophiolite complexes, showing the location of the studied chromitites.

1995; Beccaluva et al., 2005; Rassios and Moores, 2006; Rassios and Dilek, 2009) has been evidenced by (1) the presence of hydrous silicate inclusions such as amphibole and phlogopite, in the Vourinos high-Cr chromitites, (2) the trace and REE data on separated orthopyroxenes and clinopyroxenes from harzburgites of these ophiolites, despite the high degree of alteration and serpentinization (Bizimis et al., 2000) and (3) the $\Delta\log fO2$ *versus* Cr/(Cr + Al) diagram and $Ti/Fe^{3+}/(Fe^{3+} + Al + Cr)$ *versus* $Ga/(Fe^{3+} + Al + Cr)$ ratios for chromites from the Vourinos complex (Dare et al., 2009). Additionally, structural and paleomagnetic studies on those ophiolites have revealed widespread heterogeneous deformation and rotation during their original displacement and subsequent tectonic incorporation into continental margins (Rassios and Dilek, 2009).

Sometimes, chromite in chromite ores contains fine inclusions (of often globular shape) of Na-rich pargasite, clinopyroxene, phlogopite and Cu-Ni sulfides, as is exemplified in the Othrys, Skyros and Veria ophiolites (Tarkian et al., 1992a,b; Garuti et al., 1999a; Tsoupas and Economou-Eliopoulos, 2008). Furthermore, although all of the above ophiolite complexes of Greece are SSZ ophiolites, the location of the harzburgite samples in the ophiolite complex and additional mineral chemistry data (Table 1) may be of genetic significance for the mineralogical and chemical variations of chromite and PGE. More specifically, the harzburgite samples coming from Central Vourinos (Kissavos) differ compared to those of the main complex by: (1) the presence of gradational zones (low pyroxene harzburgite) between dunite and enclosing harzburgite, (2) having clinopyroxenes and amphiboles with a wide major element compositional variation, (3) the presence of only small chromitite occurrences of both high-Cr and -Al type, in a spatial association, even in the same chromitite body and (4) a wide range in their PGE content, in contrast to the chromitite ores in the whole complex (Konstantopoulou, 1990; Rassios and Moores, 2006).

The mantle sequence of the Pindos ophiolite complex resembles that of Vourinos in the presence of extensive and highly depleted harzburgite, but in contrast to Vourinos, there is only a limited number of small chromite occurrences (low potential for exploitation) in the Pindos complex (Economou et al., 1986; Economou-Eliopoulos and Vacondios, 1995). Also, clinopyroxenes from harzburgite samples of the Pindos ophiolite complex (Table 1) differ compared to orthopyroxenes from the Vourinos complex, as far as the higher depletion degree in light rare earth elements (LREE) and lower depletion in heavy rare earth elements (HREE), while orthopyroxenes from the Othrys (Eretria) harzburgite exhibit the lowest depletion in both LREE and HREE (Table 1; Fig. 2).

Apart from large individual chromite deposits, dominated by metallurgical (Vourinos) or refractory type (Othrys complex), small chromite occurrences, ranging in composition from high-Cr to high-Al, are often found in a close spatial association, such as in the Pindos, Skyros and Evia islands, Rhodope massif, central part of the Vourinos complex and elsewhere (Fig. 3; Konstantopoulou, 1990; Economou-Eliopoulos and Vacondios, 1995; Economou-Eliopoulos and Eliopoulos, 1999).

3.1. Variation in the PGE and other trace elements in chromite deposits

The PGE content in chromitites related to ophiolite complexes is relatively low (a few hundreds of ppb) in large chromite deposits, as is exemplified in the Vourinos and Othrys deposits in Greece and elsewhere like the Kempirsai (Urals) deposit, with the PGE content in high-Al ores being lower than in high-Cr ones (Table 2). However, small chromitite occurrences, ranging in composition from high-Cr to high-Al, exhibit a significant PGE-enrichment, which may be dominated by (a) IPGE such as in the Skyros, Veria, Pindos (Milia area) and the central part of the Vourinos complex (Kissavos area) and (b) PPGE, such as in the Pindos (Korydallos area) (Table 2). In addition, the chondrite-normalized PGE patterns show a negative slope for chromitite from large deposits (Fig. 4a) and IPGE-elevated ores (Fig. 4c, d), which is typical for chromitites

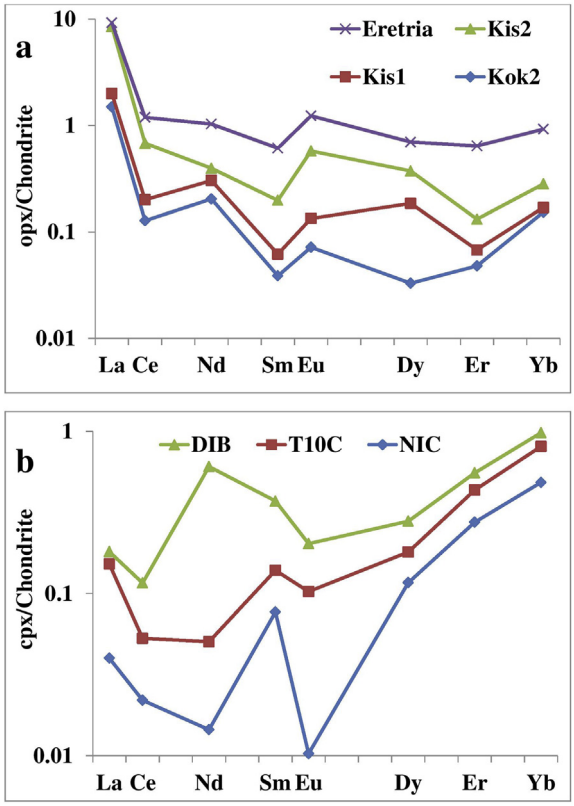

Fig. 2. Chondrite-normalized REE patterns (after Anders and Grevesse, 1989) for the orthopyroxenes (opx) from harzburgite of the Vourinos (Kok2 = Kokkinodromos area; Kis1 and Kis2 = Kissavos area) Othrys (Eretria) ophiolites, and clinopyroxene (cpx) from the areas of Dramala (NIC), Trygona (T10C and Kampos Despoti (DIB) of the Pindos ophiolite complex. Data from Bizimis et al. (2000).

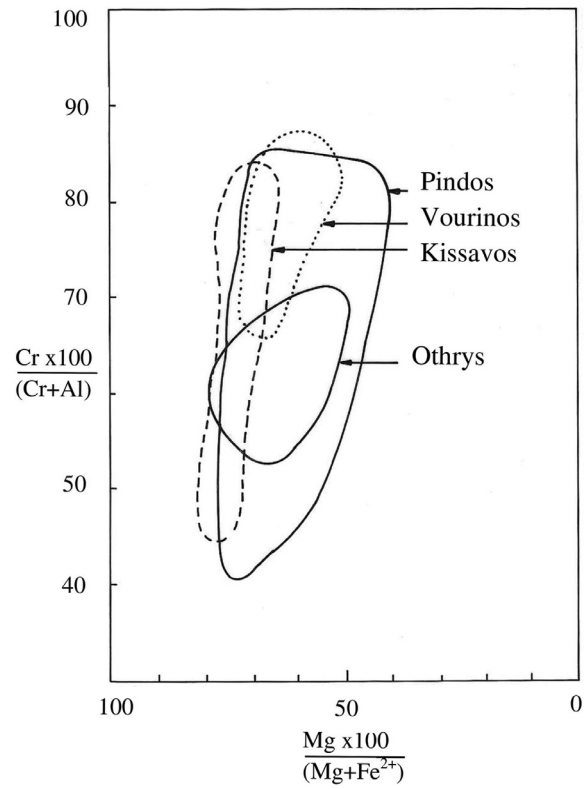

Fig. 3. Plot of Cr/(Cr + Al) *vs* Mg/(Mg + Fe^{2+}) for chromite ores from the Vourinos, including the Kissavos area (central part), the Othrys and Pindos ophiolites complexes (after Economou-Eliopoulos, 1996).

related to ophiolites, and a positive slope for PPGE-elevated ores from the Pindos ophiolite (Fig. 4b; Konstantopoulou, 1990; Economou-Eliopoulos and Vacondios, 1995; Tarkian et al., 1992a, b; Tsoupas and Economou-Eliopoulos, 2008) and elsewhere (Prichard et al., 1986; Melcher et al., 1997; González-Jiménez et al., 2014; O'Driscoll and González-Jiménez, 2016).

3.1.1. PPGE-enrichment

An unusually high PPGE content (up to tens of ppm) is commonly measured in relatively small chromite occurrences (thousands tons), such as in the Korydallos area of the Pindos ophiolite complex (Economou-Eliopoulos and Vacondios, 1995; Tarkian et al., 1996; Economou-Eliopoulos et al., 1999; Kapsiotis et al., 2009a,b) and only occasionally observed in large (million tons) chromite deposits (Table 2; Konstantopoulou and Economou-Eliopoulos, 1991).

3.1.2. IPGE-enrichment

The IPGE enrichment (up to tens of ppm) has been recorded in small chromite occurrences, such as in the Skyros island in the Aegean sea, the Veria, 20 km east–northeast of Pindos, the Milia area of the Pindos complex and only occasionally in the Vourinos complex (Table 2 (Konstantopoulou and Economou-Eliopoulos, 1991; Tsoupas and Economou-Eliopoulos, 2008; Kapsiotis et al., 2009a,b) and elsewhere (Melcher et al., 1997; González-Jiménez et al., 2014). The chondrite-normalized PGE-patterns for the latter chromitites are similarly shaped as those for common chromite ores in ophiolites, but the IPGE level is up to 100 orders of magnitude higher (Table 2; Fig. 4c, d). In addition, PGE data on chromite ores from the Vourinos, Pindos, Othrys, Veria and Skyros ophiolites (Konstantopoulou, 1990; Economou-Eliopoulos et al., 1999; Tsoupas and Economou-Eliopoulos, 2008) were normalized to the asthenospheric mantle (Barnes and Campell, 1988). The Pd/Ir values were plotted *versus* normalized values [(Pt/Pt* = Pt/8.3/√(Rh/1.6)(Pd/4.4) and data from chromite deposits and occurrences from Greece were compared to other ophiolites (Fig. 5). The plots of the Pt/Pt* and Pd/Ir ratios for chromite ores define separate fields corresponding to PGE-elevated ores (either PPGE or IPGE), PGE-poor, high-Cr or high-Al chromitites (Fig. 5).

Trace elements (PGE, Ni, Cu, Co, V, Zn, and Ga) content (whole rock samples) in high-Cr and high-Al chromitites indicated higher Ga, Ti, V and Zn in high-Al ores than high-Cr ores (Table 2).

3.1.3. PGE in Fe-Ni-Cu sulfides associated with chromitites

A salient feature of certain ophiolite complexes, such as the Othrys (Eretria or Tsagli) in Greece, Lemesos (Pefka), Cyprus, Shetland, U.K., Bulqiza (Ceruja, Krasta) in Albania, Oregon, USA, Moa-Baracoa ophiolitic massif, Cuba and elsewhere is the occurrence of Fe-Ni-Cu-sulfide mineralization with dominant minerals pyrrhotite, chalcopyrite and minor pentlandite, hosted in mantle serpentinized peridotites and mafic to ultramafic rocks of the cumulate sequence of the ophiolite complexes (Economou and Naldrett, 1984; Foose et al., 1985; Foose, 1985; Prichard et al., 1994; Proenza et al., 2001; Cina, 2010). In the Othrys complex massive sulfide mineralization occurs at the peripheral parts of podiform chromite bodies in association with chromitite and magnetite, having average (n = 12) PGE contents in 100% sulfide of 106 ppb Os, 31 ppb Ir, 162 ppb Ru, 16 ppb Rh, 193 ppb Pt and 8 ppb Pd (Economou and Naldrett, 1984). Texture and geochemical characteristics, including PGE-contents, flat chondrite-normalized PGE-patterns, and very low partition coefficient for Ni and Fe between olivine and sulfides are inconsistent with sulfides having equilibrium with Ni-rich host rocks, at magmatic temperature

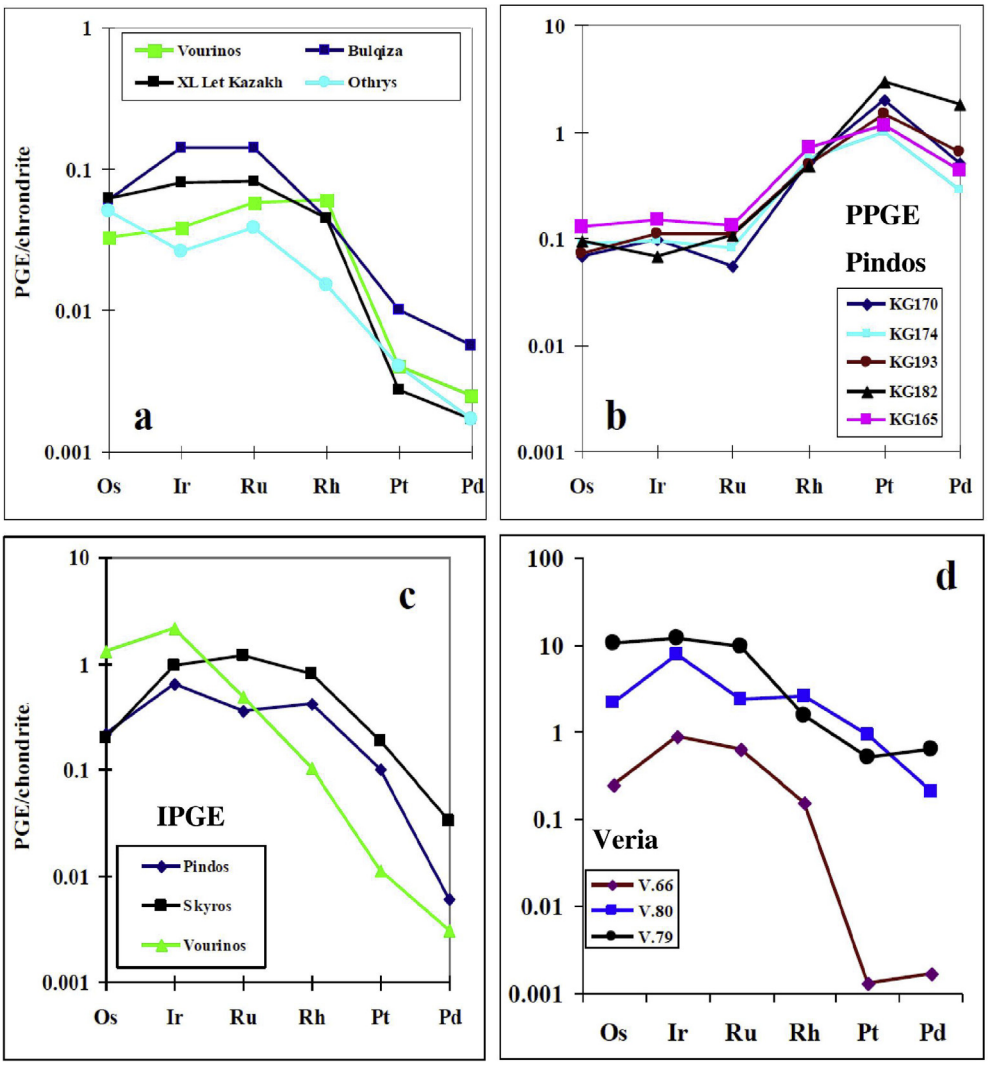

Fig. 4. Chondrite-normalized PGE-patterns (sample/C1 chondrite, after Naldrett and Duke, 1980) for chromite ores (average values) from large chromite deposits hosted in the Vourinos, Bulqiza, Othrys and Urals (XL Let Kazakz) large chromite deposits (4a), PPGE-enriched ores from the Pindos (Korydallos, labeled as KG) chromitites (4b) and IPGE-enriched ores from the Pindos (Milia), Skyros and Vourinos ores (4c) and extremely IPGE-enriched from the Veria chromitites (4d). Data from Table 2.

(Economou and Naldrett, 1984; Foose et al., 1985). Although the initial magmatic origin is not precluded, present characteristics of the highly transformed ore may indicate that the magmatic features have been lost or metals were released from the host rocks by a low level hydrothermal circulation process (Economou and Naldrett, 1984).

However, the Fe-Ni-Cu-sulfide mineralization occurring in the magmatic sequence of ophiolites exhibits magmatic texture features, an enrichment in PPGE over IPGE and steep positive chondrite-normalized PGE patterns, which have been interpreted as reflecting immiscible segregation of sulfide melts (Foose, 1985; Prichard et al., 1994; Proenza et al., 2001). Pentlandite-bearing mineralization, accompanied by chromite, olivine, pyrrhotite, chalcopyrite, cubanite, magnetite, native copper, valleriite, mackinawite and PGM, occurs in chromitites hosted in the cumulate sequence of the Bulqiza (Ceruja, Krasta) ophiolitic complex (Karaj, 1992; Cina, 2010).

The chromite mineralization occurring within the mantle–crust transition zone in the Moa-Baracoa ophiolitic massif (Cuba) is associated with sulfides (pyrrhotite, pentlandite, cubanite, and chalcopyrite) in a varying proportion. Brecciated chromite ores occurring within pegmatitic gabbro dikes, are associated with chromian diopside and plagioclase, containing droplet-like sulfide aggregates. The sulfide-rich ores with elevated PGE content (up to 1113 ppb ΣPGE) showing flat chondrite normalized PGE-patterns, have been interpreted as the result of the crystallization of immiscible sulfide melt segregated from the volatile-rich silicate melt (Proenza et al., 2001).

The Pd/Ir values for the unusual sulfide mineralization associated with chromitites, were plotted *versus* normalized Pt/Pt* (Fig. 5f). The defined field for sulfides from the magmatic sequence of the Bulqiza ophiolitic complex (Karaj, 1992; Cina, 2010) is separated from that for sulfides from the Eretria (Greece), Lemesol (Cyprus) and Cuba ophiolites, while it is comparable to that for the PPGE-elevated chromitites from the Pindos ophiolites, in terms of the high Pt/Pt∗ and Pd/Ir ratios (Fig. 5b).

3.2. Platinum-group minerals in Greek ophiolites

The presence of platinum-group minerals (PGM) in the chromite deposits of Greece has been recorded by several authors. Laurite (RuS_2) constitutes more than 75% of the PGM population, accounting for the Ru-Os-Ir dominated composition of the chromitite host, but sometimes Ir-Os alloys and sulfarsenides are dominant PGM (Augé, 1985; Tarkian and Stribrny, 1999; Garuti and Zaccarini, 1997; Prichard et al., 2008; Kapsiotis et al., 2009a,b). The PGM in

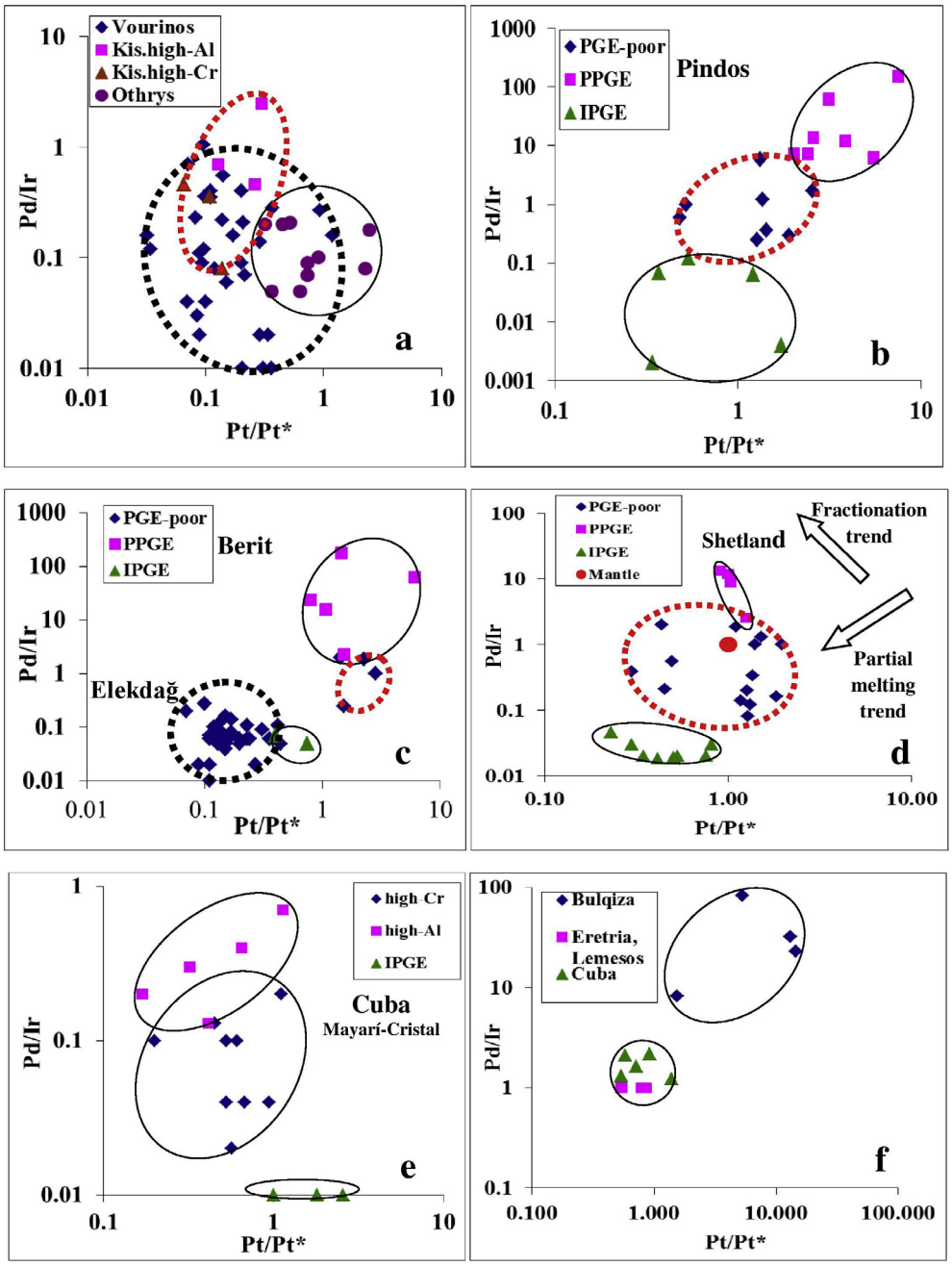

Fig. 5. Plots of the Pd/Ir *versus* Pt/Pt* normalized values [(Pt/Pt* = Pt/8.3/√(Rh/1.6)x(Pd/4.4)] for chromitites from (a) Vourinos (high-Cr), including the Kissavos area, with a spatial association of high-Cr and high-Al ores (Fig. 5a, red cycle), (b) the Pindos complex (Fig. 5b), (c) the Elekdağ (black cycle) and Berit ophiolites (Turkey), (d) the Shetland complex, (e) The Cuba high-Cr and high-Al chromitites in a spatial association, and (f) for Fe-Ni-Cu sulfides hosted in mafic-ultramafic rocks of ophiolite complexes. Data from Konstantopoulou (1990), Economou-Eliopoulos et al. (1997, 1999); Kozlu et al. (2014), Proenza et al. (2001), and Cina (2010). Red circle = Asthenospheric mantle, calculated by Barnes and Campell (1988). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the Pindos ophiolite complex consist of Os-rich laurite as inclusion in chromite, sperrylite, exclusively in the serpentinized matrix of chromitite; IPGE-alloys and sulfarsenides are dominated in the Milia area, while in the area of Korydallos the dominated assemblages are PGE-arsenides and sulfarsenides (Tarkian et al., 1992a, b; Prichard et al., 2008). The PGM are irregular in shape and are located almost exclusively in the altered silicate matrix interstitial to the chromite grains, at the edges of chromite grains, and in veins of silicate cross-cutting chromite (Tarkian et al., 1996; Kapsiotis et al., 2009a,b). In addition, Ru-rich alloys in chromitites from the Milia area, with relatively high Rh and Pt abundances, have been described as well (Kapsiotis et al., 2009b).

Apart from the common occurrence of laurite inclusions within unaltered chromite grains (25 μm diameter in average), a salient feature is the existence of extremely large PGM grains, up to 1.3 mm in size and extremely abundant solitary fragmented PGM (more than 100 grains) were identified within sheared massive chromite samples (Fig. 6e–g; Tsoupas and Economou-Eliopoulos, 2008). Also, the sulfarsenide irarsite occurs as an inclusion in laurite and at the periphery or along cracks of large IPGM grains from Veria (Fig. 6e). Pentlandite, awaruite, heazlewoodite, maucherite, PGE- arsenides and antimonides have been reported in chromitites from Veria. The composition of the laurite is rather constant, whereas the Os–Ru–Ir–Fe alloys exhibit a

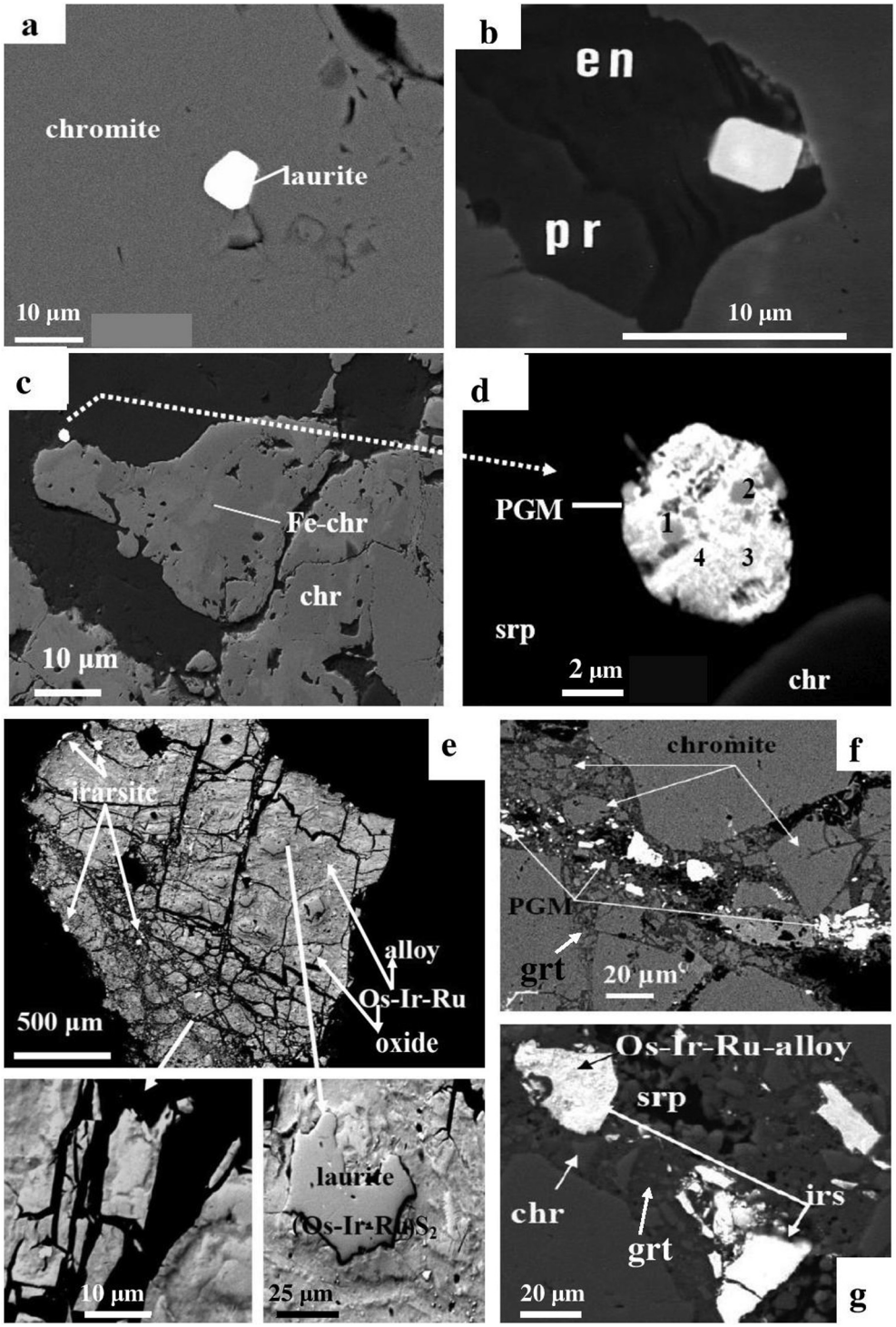

Fig. 6. Back-scattered electron images of an euhedral shaped fine laurite inclusion within unaltered chromite (6a), euhedral laurite crystal (white) associated with enstatite (en) and pargasite (pr), all included in fresh chromite (6b) from the Othrys ophiolite complex, IPGM in a matrix of serpentine (srp) associated with chromite/Fe-chromite (Fe-chr) from the Skyros island (6c and 6d, Table 3), an extremely coarse PGM-grain composed by laurite remnants, (Ru-Ir-Os) alloys and oxides (6e), dismembered–fragmented abundant PGM in a matrix of garnet (grt) and lesser amounts of serpentine, and extremely abundant IPGM grains (6f, g) from the Veria area. After Garuti et al. (1999a); Tsoupas and Economou-Eliopoulos (2008; Table 3).

wider variation (Table 3). Similarly, Ru-Ir-Os alloys and sulfides exhibiting significant Fe, Ni, Cr, Sb and As contents were identified in Skyros (Fig. 6c, d; Table 3). Although the analyses given in the Table 3 are coming from the large PGM crystal from Veria and PGM from Skyros found in the silicate matrix, the influence of chromite is not precluded.

3.3. Discussion on PGE in chromitites

The preferential concentration of the extracted PPGE in silicate melts during partial melting, while the mantle residue is enriched in IPGE, may explain the decrease of the Pd/Ir ratio with increasing partial melting degree in the mantle peridotites of ophiolites

Table 3
Representative SEM-EDS analyses of IPGM from PGE-rich chromitites of the Skyros and Veria ophiolites.

SKYROS						VERIA			
wt%	laurite*	Fig. 6a,1	Fig. 6a.2	Fig. 6a.3	Fig. 6a.4	laurite*	Fig. 6e	Fig. 6f	Fig. 6f
Os	14.1	5.9	8.1	15.5	13.1	22.2	2.2	6.2	n.d.
Ir	7.8	6.3	5.7	18.5	27.2	6.6	52.1	81.2	59.7
Ru	43.4	53.4	48.5	38.2	27.2	36.4	4.7	2.8	7.2
Rh	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	n.d.
Pt	n.d.	2.7	0.7	3.6	4.6	n.d.	n.d.	6.2	n.d.
Ni	n.d.	0.7	0.2	1.2	1.1	n.d.	n.d.	n.d.	6.5
Fe	n.d.	0.9	0.6	0.5	0.5	0.3	0.8	1.4	22.1
Cr	n.d.	0.4	5.8	0.4	0.4	n.d.	n.d.	n.d.	0.9
Sb	n.d.	n.d.	0.5	0.6	1.1	n.d.	n.d.	n.d.	n.d.
As	n.d.	2.1	2.8	5.8	10.1	n.d.	27.6	n.d.	1.2
S	34.8	26.7	27.2	14.8	11.8	34.8	11.5	n.d.	n.d.
	100.1	99.1	100.1	99.1	97.1	100.3	98.9	100.1	97.6

Symbols: n.d. = below detection limit; * = typical composition.

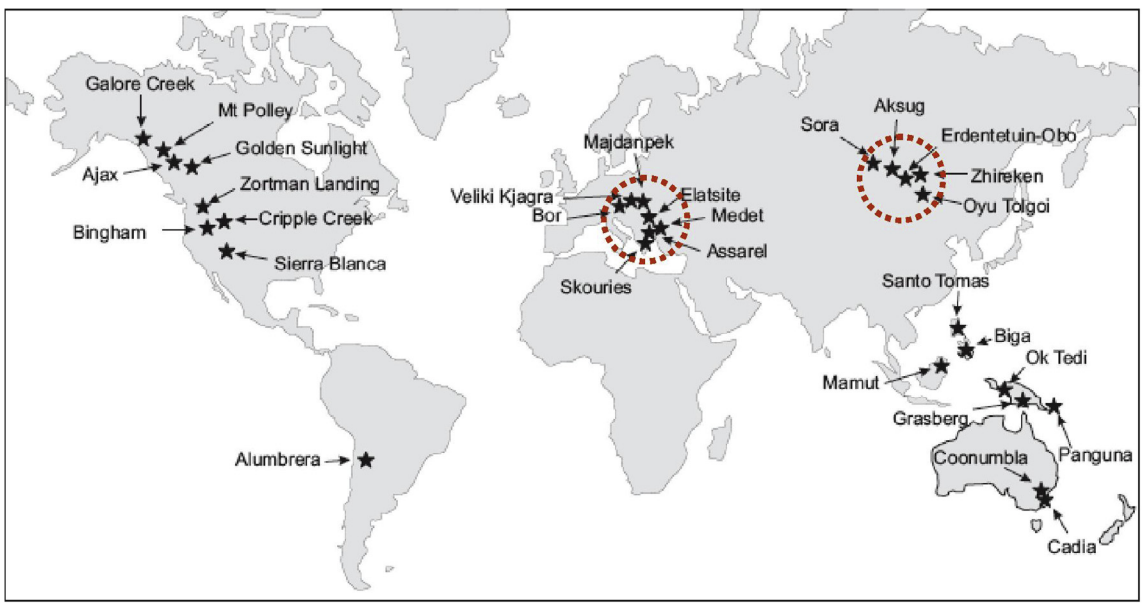

Fig. 7. Location map of porphyry Cu ± Mo ± Au ± Pd ± Pt deposits. Symbol: Red circles = deposits studied by the described methods. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Garuti et al., 1997; Melcher et al., 1997; Uysal et al., 2009; Zhou et al., 2014). However, magma fluxing through the lithospheric mantle may change the initial PGE content inherited from the melting events, depending on the melt/rock ratios (Lorand et al., 2013; and references therein). Complexities of peridotite structure, geochemistry and mineral chemistry of the mantle wedge above a subduction zone and heterogeneity of the convective mantle have been well established in thorough reviews (Arai, 2010; Liou et al., 2010, 2014 and references herein). Thus, the PGE content in chromitites hosted in ophiolites may have been affected by several mantle and crustal processes, such as partial melting, fractional crystallization, post magmatic processes and crust-mantle recycling. The factors controlling the extreme variability of the PPGE and IPGE contents in small chromite occurrences hosted in certain ophiolite complexes, such as the Pindos complex and Veria (Table 2; Fig. 7) during subduction-related crustal and mantle recycling are discussed.

3.3.1. Magmatic processes on PGE mineralization

Some authors have proposed that PGE can be dissolved in the lattice of the chromite at high temperature and subsequently may be exsolved and form discrete PGE-rich minerals during cooling (Naldrett and Duke, 1980; Capobianco and Drake, 1990; Capobianco et al., 1994; Righter et al., 2004). However, experimental data under appropriate conditions of T, P, $fO2$ and $fS2$, have shown that laurite can be formed in equilibrium with Os–Ir alloys in mafic magmas, being stable up to the temperature less than 1300 °C (Brenan and Andrews, 2001; Andrews and Brenan, 2002; Mungall, 2005) and that it may be the first sulfide mineral to crystallize directly out of a sulfide-undersaturated silicate melt (Bockrath et al., 2004).

The possible origin of PGE-clusters and the formation of the submicroscopic PGM has been suggested (Tredoux et al., 1995; Helmy et al., 2013) in S-poor environments (boninitic magmas). In addition, the identified PGE-alloys (Pagé et al., 2012) were considered to be consistent with experimental data (Finnigan et al., 2008) showing that the local reduction of fO_2 in the melt at the faces of growing chromite crystals may cause the formation of metallic "micro-nuggets" of these elements (Borisov and Palme, 1997). Thus, Os may be transported as submicroscopic Os-bearing alloys which could subsequently react with S to form sulfides, in volatile-rich melts at high temperature, low pressure and

low fS_2 (Bockrath et al., 2004; González-Jiménez et al., 2014; O'Driscoll and González-Jiménez, 2016). Also, it has been suggested that the possibility of formation of IPGE-minerals from the direct reaction of free metals with sulfur would be inconsistent with the estimated entropy of activation values, being approximately zero (−1.8 and −0.5 $mol^{-1} K^{-1}$, at 1250 °C and 1000 °C, respectively, after Petrou and Economou-Eliopoulos, 2009a,b). In other words, it has been proposed that, at magmatic temperatures, an outer-sphere "complex" is initially formed and then, the leaving ligand (for example oxygen) moves from the inner to the outer coordination sphere, while simultaneously the entering ligand (sulfur) moves from the outer to the inner coordination sphere (Petrou and Economou-Eliopoulos, 2009b).

Given that the composition of parental melts is strongly dependent on the mantle source (geotectonic setting), the composition of chromitites, including the PGE, is probably the consequence of the composition of parental melts (Zhou and Robinson, 1997; Garuti et al., 1997; Proenza et al., 1999; Gervilla et al., 2005; Zhou et al., 2014; O'Driscoll and González-Jiménez, 2016). According to these authors Cr-rich chromitites are formed from magmas of boninitic affinity, whereas high-Al chromitites could be the products of the fractionation or they could be derived from tholeiitic partial melts in a back-arc basin setting. The coexistence of high-Cr and high-Al, and/or PGE-rich and PGE-poor chromitites also suggests that different parental melts and/or formation of chromitites from fractionated to some extent magmas.

Considering the plot Pd/Ir *versus* Pt/Pt* for chromite deposits and occurrences (Fig. 5) it appears that large chromite deposits in Greece (Vourinos of metallurgical and Othrys of refractory type) and Turkey (Elekdag ophiolite) exhibit Pd/Ir < 1 and negative (Pt/Pt* < 1) Pt/Pt* values, suggesting partial melting of already depleted mantle (Barnes and Campell, 1988; Garuti et al., 1997), and an increasing partial melting trend from high-Al toward to high-Cr deposits (Fig. 5a). The difference in the Pd/Ir ratio, that is considered as index of fractionation degree of the PGE during petrological processes (Barnes et al., 1985) provide evidence for discrimination between ores derived from primitive magmas (low Pd/Ir values) and fractionated to some extent (high Pd/Ir values). Thus, the occurrence of both high-Cr and high-Al chromitites with low Pd/Ir ratios in the Pindos ophiolite complex suggests that they are derived from different parental melts, while the existence of both types with relatively high values of the Pd/Ir ratios reflects a fractionation trend (Barnes et al., 1985) in both chromitite-groups, regardless their major element composition (Table 2).

Also, assuming that IPGM as inclusions in chromite (Fig. 6a, b) are primary phases, they are controlled by fS_2 and temperature of the magma, and may exhibit a significant variation on the Os/Ru ratios, particularly in the Othrys, due to the fractionation between these two elements (Garuti et al., 1999a). More specifically, the restriction of the laurite composition, in the range of Ru_{100}-Ru_{72} to Os_{28}, corresponding to the Ru:Os atomic ratio in the Cl chondrite, has been attributed to the low fS_2 (and high temperature), whereas the $(Ru,Os)S_2 + OsS_2$ (erlichmanite) assemblage recorded in Othrys chomitites suggests that fS_2 was initially sufficiently high to crystallize laurite and subsequently the fS_2 increased to attain the Os-OsS_2 buffer (Garuti et al., 1999a, 1999b; Ahmed and Arai, 2003).

3.3.2. Post magmatic versus magmatic processes

Although the dominant PGE-contents and PGE-bearing minerals remain characteristic features of individual chromite deposit, the effect of post magmatic processes, such as melt–rock reactions, subduction-related crustal recycling and metasomatism on the PGM and accompanying chromitites has been well documented. The presence of exsolution lamellae of diopside and coesite in some chromite grains together with numerous highly reduced minerals and alloys have been interpreted as evidence of their formation near the mantle transition zone (Walker et al., 1996; Ahmed and Arai, 2003; González-Jiménez et al., 2014; Pearson et al., 2007; Borisova et al., 2012; Zhou et al., 2014).

Recently, the occurrence of diamonds and other ultrahigh-pressure (UHP) minerals in ophiolitic mantle peridotites and podiform chromitites of both high-Cr and high-Al type from different orogenic belts has been well documented (Yang et al., 2014, 2015). Carbon and other recycled crustal materials, characterized by exceptionally light $\delta^{13}C$ values (Sobolev and Sobolev, 1980; Cartigny et al., 2001), have been transported to shallow mantle and incorporated as trace assemblages in subsequently exhumed UHP metamorphic complexes. These relict phases and rocks provide evidence for the recycling of crustal lithosphere into the deep Earth, and the circulating mantle (Yang et al., 2014, 2015).

Highly heterogeneous Os isotopic composition at Cuba, Bulgaria (Rhodope massif), China and everywhere suggest different episodes of partial melting, subduction-related crustal recycling and metasomatism (Ohnestetter, 1992; Walker et al., 1996; Borisov and Palme, 1997; Ahmed and Arai, 2003; Gervilla et al., 2005; Pearson et al., 2007; Fonseca et al., 2012; González-Jiménez et al., 2014; Zhou et al., 2014; Kozlu et al., 2014; Brouch et al., 2015). The analysis of laurite grains entirely enclosed in unaltered chromite (magmatic chromite) has $^{187}Os/^{188}Os$ compositions very distinct from the laurite in highly metamorphosed chromitites of Central Rhodope peridotite (Bulgaria) (González-Jiménez et al., 2011, 2013, 2014). Alternatively, the heterogeneity in the $^{187}Os/^{188}Os$ signatures of PGM has been attributed to small-scale events of melt extraction and melt-rock reaction that could cause a decrease in fS_2 in the mantle, promoting the breakdown of PGE-bearing base-metal sulfides into 'residual' laurites (Parkinson and Pearce, 1998; González-Jiménez et al., 2014).

3.3.3. PPGE-enrichment in chromite occurrences

Considering the PPGE-elevated chromitites, such as those from the Pindos, Shetland, Beri and Cuba, they are characterized by high Pd/Ir ratios at a level comparable to that for the Fe-Ni-Cu-sulfide mineralization hosted in the cumulate sequence of the Bulqiza (Ceruja and Kresta) ophiolite complex (Fig. 5). Despite the potential re-mobilization and re-deposition of PGE along with base metals during the deformation of ophiolites (Economou and Naldrett, 1984; Foose et al., 1985) they have interpreted to reflect a fractionation trend due to a magmatic process (Foose, 1985; Prichard et al., 2008; Cina, 2010). Thus, the similarity between the PPGE-enriched chromitites and Fe-Ni-Cu-sulfide mineralization on the plot Pd/Ir *versus* Pt/Pt*, may reflect immiscible segregation of sulfide melts (Tarkian and Prichard, 1987; Prichard et al., 1994; Ohnenstetter et al., 1999; Prichard and Brough, 2009; Brough et al., 2015) and suggest that the PPGE-enrichment in chromitites is a result of sulfide crystallization with the proximity towards the petrological Moho of ophiolite complexes.

3.3.4. IPGE-enrichment in chromite occurrences

A common feature of IPGE-elevated chromitites from Greece (Veria, Pindos, Vourinos) (Fig. 5b), Turkey (Fig. 5c) and Shetland (Fig. 5d) chromitites are the lowest Pd/Ir and Pt/Pt* values compared to those for other chromite ores in each of these ophiolites, suggesting probably that the parent magma exhibits a very low fractionation degree and was derived by an increasing partial melting degree. The IPGE enrichment (up to tens of ppm) and the presence of extremely large (up to 1.5 mm) IPGM grains and extremely abundant PGM small grains/fragments (>100) dispersed along a highly fragmented chromitite zone of the Veria chromitites (Fig. 6e, f) appears to be unique among chromite ores associated with ophiolites (Tsoupas and Economou-Eliopoulos, 2008). The cataclastic texture shown by large PGM grains along with the

occurrence of Os-Ir-Ru-bearing PGM assemblages interstitial to strongly fragmented chromite grains (Fig. 6e, f), suggest an emplacement of these PGM post-dated that of chromite. The brittle structures in chromite ores were probably initiated at conditions overlapping those of mylonite formation, as semi-ductile structures, and continued during a subsequent stage of the transformation of laurite into oxides/hydroxides (Fig. 6e).

Although PGE are generally considered to be relatively resistant to geochemical processes (Barin et al., 1977; Valero and Vieillard, 2012) the occurrence of the IPGE minerals between chromite grains, in a matrix of Cr-bearing garnet in chromitite from Veria, Skyros (Fig. 6f, g) and elsewhere (Garuti et al., 2012) suggest mobility and redistribution of PGE, under conditions different from that of their formation, and transformation to secondary PGM. A differential stress driving the deformation of ores associated with ophiolite complexes along with the changes in temperature, pressure, surface energies, solubility and the diffusion process (Van der Weijden, 2007) can also impact the PGM reactions.

The application of basic thermodynamic parameters may contribute to a better understanding of the formation and stability of PGE-phases (Cabri, 1981; Ezzouia et al., 1984; Sassani and Shock, 1998; Barnes and Liu, 2012; Olivotos and Economou-Eliopoulos, 2016). Although experimental data on the activation energy values for IPGM are not available, since chemical processes follow the minimum energy pathways, the Arrhenius equation has been used as a new approach for the IPGE mineralization (Petrou and Economou-Eliopoulos, 2009a). The estimated minimum activation energy required for the formation of IPGM found to be approximately 450 kJ/ mol (Petrou and Economou-Eliopoulos, 2009a,b). Applying the plot of ln(r) *versus* 1/T (straight line) to PGM grains of known r, the formation temperature was estimated for large IPGE in chromite from Veria area (Fig. 6c–f) at approximately 750 °C.

Therefore, texture and mineralogical characteristics of the IPGE-minerals, coupled with the low Pd/Ir and Pt/Pt∗ values may suggest an origin by partial melting of already depleted mantle and increased partial melting degree (Barnes and Campell, 1988; Garuti et al., 1997), probably during a subsequent stage of polymetamorphic evolution of the geotectonic environment (ophiolite), under appropriate physico/chemical conditions and an increased H_2O content (Ohnestetter, 1992; Walker et al., 1996; Ahmed and Arai, 2003; Gervilla et al., 2005; Pearson et al., 2007; Borisova et al., 2012; Zhou et al., 2014; González-Jiménez et al., 2014).

4. PGE mineralization in Porphyry-Cu-Au±Pd±Pt systems

The mobility of PGE has been well documented in a compositional spectrum from ophiolite complexes, komatiites to alkanine intrusions associated with porphyry-Cu-Au deposits. The solubility data on PGE (Sassani and Shock, 1998; Xiong and Wood, 2000; Wood, 2002; Simon and Pettke, 2009), and a thermodynamic modelling (Barnes and Liu, 2012) are in a good agreement with their occurrence in nature and suggest that Pd and Pt can be readily transported as bisulfide complexes in acidic-neutral solutions under reduced and moderate oxidation conditions at 300° C, and chloride complexes are only important under extremely acidic/oxidized conditions.

The majority of giant Au-rich porphyry deposits are generated at convergent margins during or following subduction of lithosphere, varying from compressional to tensional and shearing (Sillitoe, 2000, 2010; Richards, 2009, 2011; Simon et al., 2008). Many important porphyry Cu–Au, Cu–Mo, Mo–W deposits are located around the Pacific rim, in Mediterranean and Carpathian regions of Europe, and in the Alpine-Himalayan system, extending from western Europe through Iran and the Himalaya to China and Malaysia (Fig. 7). Parental magmas are considered to be moderately water-rich as indicated by the presence of hydrous minerals (amphibole, biotite), whose stability requires at least 3 wt% H_2O in the melt. Such hydrous melts may contain metals and ligands of critical significance to the formation of Au-rich porphyry deposits (Sillitoe, 2000, 2010). The Au-rich porphyry deposits are mostly linked to alkaline magmatic systems and may grade upward and/or outward into telluride-rich epithermal deposits, both characterized by high halogen (chlorine, fluorine) contents and by high oxygen fugacity (Sillitoe, 2000, 2010; Richards, 2009, 2011 and references herein).

Significant Pd and Pt contents have been reported in high-grade bornite-chalcopyrite and/or flotation concentrates from porphyry deposits, associated mostly with alkaline type intrusions, including those in British Columbia, Colorado (Mutschler et al., 1985) in the Santo Tomas II deposit, Philippines (Tarkian and Koopmann, 1995), the Skouries porphyry deposit, Greece, Elatsite, Bulgaria (Eliopoulos and Economou-Eliopoulos, 1991; Eliopoulos et al., 1995, 2014), the Kalmakyr deposit, Uzbekistan (Pašava et al., 2010) the Sora, Aksug and Zhirenken deposits, Russia, the Erdenetiun-Obo deposit, Mongolia (Sotnikov et al., 2000), Grasberg deposit, Indonesia Ok Tedi, Papua New Guinea, the Mamut deposit, Malaysia the Bajo de la Alumbrera, Argentina (Tarkian and Stribrny, 1999).

4.1. The Skouries deposit: a case study

The Skouries subvolcanic-porphyritic stocks and volcanic complexes at the Chalkidiki Peninsula, northern Greece, of Miocene age (18 Ma), are related to porphyry-Cu deposits (Kockel et al., 1977). At least four monzonite porphyries have been described (Tobey et al., 2001; Frei, 1995): (1) pink monzonite, (2) main monzonite, (3) intra-mineral monzonite, and (4) late-stage porphyry. High grade ore is directly associated with the main and intra-mineral monzonite phases. Two mineral assemblages of mineralization, occurring as veinlets/disseminations, can be distinguished: (a) magnetite- (reaching up to 10 vol%, average 6 vol%) bornite-chalcopyrite, linked to pervasive potassic and propylitic alteration type, in the central parts of the deposit, and (b) chalcopyrite-pyrite, which dominate at the peripheral parts of the deposit. Magnetite is Cr-bearing (0.65–2.26 wt% Cr_2O_3 in the matrix, to 0.29 wt% Cr_2O_3 in magnetite of vein type), in contrast to the Cr-free magnetite of the main porphyry. Chalcopyrite and pyrite contain 0.45–2.4 wt% Ni and 0.64–4.18 wt% Co. Ti-magnetite, with titanium content ranging from 17.5 to 23.5 wt%, is commonly associated with rutile, both postdating the main stage of the magnetite deposition. The Skouries porphyry is characterized by high values of the ratios Ce/Lu (>225), relatively high Th and U contents (up to 63 ppm and 9 ppm, respectively), Ba (up to 2260 ppm) and Sr (up to 1230 ppm) contents, reflecting probably a strong fractionation of parental magmas (Eliopoulos and Economou-Eliopoulos, 1991). The Ce/La ratio is relatively high (average = 2.1), ranging from 1.8 to 2.5 (Table 4). Also, the Pd/Pt ratio is relatively high, ranging from 0.76 (sample from a depth of 525 m) to 7.2 (sample from the surface of the deposit), Table 4, exhibiting overall a good negative correlation (r = −0.78).

The defined reserves in the porphyry Cu–Au deposit of Skouries are approximately 206 Mt at 0.54% Cu, and 0.80 ppm Au. An investigation of slag from prehistoric Macedonian gold production in Greece revealed a significant Pd content (40 ppb Pd). The subsequent analysis of representative ore samples showed a significant Pd-enrichment in mineralized samples, up to 490 ppb Pd in oxidized ore samples (Eliopoulos and Economou-Eliopoulos, 1991). Subsequently, a more detailed study in the Skouries and other deposits of the Balkan Peninsula was carried out to define relation-

Table 4
Geochemical characteristics of the Skouries porphyry Cu-Au-Pd-Pt deposit.

Samples depth (m)	Sku99 Surface	SOP18 142	GS09 251	SOP1 328	SOP06 365	GS06 525	Detection limit
wt%							
Cu	2.08	1.52	1.1	1.47	1.27	0.68	0.001
Fe	4.89	3.17	4.74	5.56	8.01	7.34	0.01
Al	4.75	5.64	3.30	5.63	4.11	6.14	0.01
Ti	0.05	0.11	0.19	0.25	0.08	0.27	0.001
Ca	0.21	0.76	3.78	1.74	0.50	4.50	0.01
Mg	0.29	0.60	4.31	1.87	0.49	3.00	0.01
Na	1.87	1.65	0.67	1.19	0.95	1.50	0.01
K	2.39	4.43	2.51	3.42	3.30	0.52	0.01
P	0.03	0.14	0.06	0.13	0.03	0.07	0.01
S	1.51	1.25	0.80	2.02	0.68	0.83	0.05
ppm							
Mo	1.3	2.5	0.8	1.0	1.6	1.2	0.5
Pb	84	100	30	50	80	45	0.5
Zn	40	53	120	55	50	110	5
Ag	1.4	2.4	0.8	6.9	18	1.3	0.5
Ni	57	48	400	300	19	370	0.5
Co	32	25	44	28	29	71	1
Mn	76	190	480	330	270	790	5
U	4.8	8.4	1.5	0.8	7.3	1.2	0.5
Th	42	60	15	11	37	8.4	0.5
Sr	340	460	44	120	330	150	5
Bi	5.2	18	4.9	53	150	1.4	0.5
V	33	32	68	76	74	110	10
Cr	10	4	8	110	10	260	1
Ba	770	1230	58	230	960	44	5
W	580	540	410	400	600	420	0.5
Zr	7.5	8.3	1.7	<0.5	5.8	5.3	0.5
La	13	18	28	13	6.6	53	0.5
Ce	24	42	67	32	13	93	5
Sn	7.4	5.5	7.0	10	2.2	6.7	0.5
Y	5.9	16	24	19	3.2	29	0.5
Nb	3.2	7.0	15	12	4.5	7.1	0.5
Ta	0.7	1.0	0.9	1.0	0.9	0.9	0.5
Sc	1	2	8	12	4	18	1
Li	10	14	35	18	8.2	7.8	0.5
Rb	90	180	290	220	120	50	0.5
Hf	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5
Se	16	19	11	29	18	<5	5
ppb							
Au	5280	3850	1410	4930	3880	549	2
Pd	290	42	31	53	49	29	2
Pt	40	64	33	42	49	22	<10
Pd/Pt	7.2	1.52	1.06	0.8	1	0.76	

Table 5
Stable isotope analyses of quartz in mineralized veinlets from the Skouries porphyry deposit.

Samples	Depth meters	Cr ppm	(Pd + Pt) ppb	Pd/Pt	Mineral (measured) $\delta^{18}O_{(V\text{-}SMOW)}$	Mineral (measured) $\delta D_{(V\text{-}SMOW)}$	Water (calculated) $\delta^{18}O_{(V\text{-}SMOW)}$ per mil
A-group							
SOP06	525	260	51	0.76	9.7	−73	4.33–6.53
SOP43	200	480	24	1.6	9.6	−110	4.33–6.43
SOP01	326	130	55	0.96	9.7	−96	4.43–6.53
Average		*290*	*43*	*1.1*	*9.7*	*−93*	*5.43*
B-group							
SOP09	479	8	64	1.1	12.6	−74	7.33–9.45
SOP18	178	4	42	1.6	11.3	−99	6.03–8.13
SG-6	465	7	436	16	9.6	−100	4.33–6.43
SOP06	367	10	98	1	9.6	−89	4.33–6.43
SOP39	446	10	679	8.3	10.9	−99	5.63–7.73
SKU99	60	10	328	7.2	11.5	−101	6.23–8.33
Average		*8.2*	*274*	*5.9*	*10.9*	*−94*	*6.7*

Water compositions calculated using the min (350 °C)/max (440 °C) temperatures (after Tarkian et al., 1991).

ships between the Pd–Pt and vein-type Cu mineralization, various alteration types or redistribution by leaching from an early-stage. A relatively high Pd content, was documented by analysis of a composite drill hole sample (~15 kg) showing 76 ppb Pd and 5000 ppm Cu (Table 4; Economou-Eliopoulos and Eliopoulos, 2000). An intergrowth between merenskyite (Pd,Pt,Bi)Te_2, which

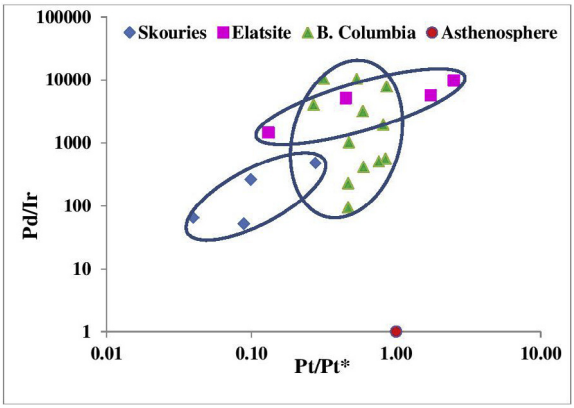

Fig. 8. Plots of Pd/Ir *versus* Pt/Pt* normalized values [(Pt/Pt* = Pt/8.3/√(Rh/1.6)x(Pd/4.4)] for porphyry-Cu-Au-Pd-Pt deposits. Data from Eliopoulos and Economou-Eliopoulos (1991), Thompson et al. (2001) and Augé et al. (2005).

is the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, hessite (Ag_2Te), electrum with Cu-bornite or chalcopyrite (Tarkian et al., 1992a,b) is considered to be an important factor for the recovery of Pd and Pt as by-products.

Stable isotope analyses of oxygen and hydrogen for quartz veins from various drill holes and depths were performed and varying chromium content have been provided in order to constrain the origin of fluids trapped in quartz veins (Table 5, after Eliopoulos et al., 2014). These data were used to calculate the isotopic composition of the fluids in equilibrium with quartz, at crystallization temperature to be minimum 350 °C and maximum 440 °C, based on the intergrowth of Cu–Fe sulfides and precious metal tellurides (Tarkian et al., 1992a,b). Isotopic trends of fluids, co-existing with quartz from various depths and drill holes in the Skouries porphyry Cu deposit are characterized by relatively high ($\delta^{18}O$ = 4.33‰–9.45‰) equilibrium fluid compositions (Table 5), which are comparable to those given in previous publications (Frei, 1995).

In addition, on the basis of PGE database on porphyry-Cu-Au-Pd-Pt deposits (Eliopoulos and Economou-Eliopoulos, 1991; Thompson et al., 2001; Augé et al., 2005) the Pd/Ir values were plotted *versus* normalized Pt/Pt* values [(Pt/Pt* = Pt/8.3/√(Rh/1.6)(Pd/4.4) (Fig. 8), which may provide evidence with respect to the source(s) of Pd, Pt ± Rh in porphyry-Cu deposits.

4.2. Discussion on the PGE content in porphyry Cu deposits

4.2.1. Evaluation of Pd and Pt as an economic factor for porphyry Cu–Au systems

The preferential enrichment of precious metals, particularly Pd, in porphyry Cu–Au deposits seems to be consistent with the thermodynamic database (Sassani and Shock, 1998; Liu Xiong and Wood, 2000; Wood, 2002; Barnes and Liu, 2012; Tagirov et al., 2013), the precious metal endowment and the physico/chemical conditions of parent magmas, responsible for scavenging the metals in evolved hydrothermal systems (Eliopoulos et al., 2014; Park et al., 2015; Delibaş et al., 2016). Based on the average Pd and Pt contents and reserves in certain porphyry-Cu deposits, such as the, Skouries porphyry deposit (Greece), Santo Tomas II (Philippines), the Elatsite porphyry deposit (Bulgaria), the approximately tonnage has been estimated to be 15 tons Pd and 3.5 tons Pt, the Elatsite deposit about 13 tons Pd and 3.7 tons Pt, the Santo Tomas II, Philippines deposit, 10.5 tons Pd, respectively (Economou-Eliopoulos, 2005) and the Kalmakyr, giant Cu–Au–Mo porphyry deposit in eastern Uzbekistan, approximately 17 tons Pd and 1.7 tons Pt (Pašava et al., 2010). A recovery method applied on chalcopyrite concentrates from the Skouries and other porphyry Cu-Au deposits (Kiousis et al., 2005) coupled with data of the technico-economical approach (Kiousis and Papavasiliou, 2005) and the estimated precious metal tonnage suggest that in addition to Au these deposits can be considered as important source of Pd and Pt.

4.3. Sources of metals and sulfur in porphyry Cu deposits

Porphyry Cu deposits have all been formed in a supra-subduction geotectonic environment, moderately chalcophile elements such as Cu (and perhaps Mo), have the potential to form porphyry Cu ± Mo deposits, and all porphyry Sn–W deposits are derived primarily from melting of metasomatized mantle wedge and continental crust; the Au-Pd-Pt-rich porphyry deposits may be derived by partial melting in post-collisional tectonic settings modified sources, which has a high potential for a significant modification during the previous subduction cycling. (McInnes and Cameron, 1994; Keith et al., 1997; Richards, 2009; Park et al., 2015). More specifically, these authors have emphasized that on the basis of geological, mineralogical, geochemical and isotopic data from xenoliths in porphyry Cu deposits major metals (Cu, Mo, Au, Sn, and W) may be derived predominantly from four main sources in convergent and collisional plate margins: (a) the asthenospheric mantle wedge between the subducting and overriding plates, (b) the upper plate lithosphere, (c) the subducting oceanic plate basaltic crust and (d) the subducted seafloor sediments. At the metasomatized mantle wedge, a relatively high abundance of sulfides is often thought to be typical of active arcs, where fS_2 is high, and highly siderophile elements such as Au and PGE will be retained in the source, but magmas may be relatively undepleted in abundant, moderately chalcophile elements such as Cu (and perhaps Mo), having the potential to form porphyry Cu ± Mo deposits. In contrast, some porphyry Mo and all porphyry Sn–W deposits are associated with felsic granitoids, derived primarily from melting of continental crust; while Au-rich porphyry deposits would only form where residual sulfide abundance was very low, due probably to unusually high oxidation states. More specifically, partial melting in post-collisional tectonic settings modified sources (upper plate lithosphere, which may have undergone significant modification during the previous subduction cycling), may generate calc-alkaline to alkaline magmas, which have the potential to form Au-Pd-Pt-rich porphyry deposits (Richards, 2009; Park et al., 2015).

Assuming mantle-crust interactions and transfer of PGE from the mantle into the crust an additional evidence may be provided by the plots of the Pd/Ir *versus* Pt/Pt* normalized values for porphyry-Cu-Au-Pd-Pt deposits of the Skouries, Elatsite (Bulgaria) and British Columbia (Fig. 8). The calculated ratio Pt/Pt* = 1 in the reference material (primitive asthenosphere, after Barnes and Campell, 1988) is negative (Pt/Pt* < 1) in the presented samples (Fig. 8). Since the Ir content is <0.5 ppb in the presented samples the extremely high Pd/Ir ratios, particularly in the Elatsite deposit (Augé et al., 2005) appears to be the result of a remarkable enrichment in Pd. In addition to a negative trend between decreasing Pt/Pt* and increasing Pd/Ir, reflecting a strong fractionation, the Pd enrichment compared to primitive mantle may suggest a contribution to the parent magma of porphyry Cu-Au-Pd-Pt deposits from a metasomatized upper plate lithosphere rather than primitive asthenospheric mantle.

Recently, on the basis of U–Pb zircon ages, lithogeochemical and radiogenic isotopic data of the host rocks associated with the porphyry-intrusions it was concluded that high-K calc-alkaline to shoshonitic magmas at Emeksen and Elbeyli, located in the Eastern Pontides, Turkey, were derived from a metasomatized, heterogeneous and enriched lithospheric mantle, with variable degrees of partial melting of the mantle wedge and variable crustal contamination (Delibaş et al., 2016). These authors suggested that mixing

processes between mafic magmas derived from the lower crust and acidic magmas at upper crustal levels played an important role in the formation of Cu–Mo porphyry-type mineralization in the Eastern Pontides. The incorporation of mafic material within the crust, prior to the final emplacement of porphyry-intrusions, is supported by the presence of mafic fragments (xenoliths) within porphyries, such as those at the Skouries porphyry (Economou-Eliopoulos, 2005), the elevated $^{87}Sr/^{86}Sr$ and $^{207}Pb/^{204}Pb$ values (Sillitoe, 2000; Sotnikov et al., 2000; Von Quadt et al., 2002) and the enrichment (hundreds ppm) in compatible elements such as Cr and Co ± Ni, occurring in the Skouries, Elatsite, Medet, Assarel and Trar Asen porphyry deposits of the Balkan (Economou-Eliopoulos, 2005). In addition, elevated initial $^{187}Os/^{188}Os$ ratios (0.5–2.5) that are substantially more radiogenic than mantle indicates a contribution by a crust source (recycled in a metasomatized mantle) (Mathur et al., 2003; Barra et al., 2003). The highest Re (thousands of ppm) and ^{187}Os values have been recorded in the Elatsite Cu–Au–Mo–(PGE) porphyry deposit, reflecting probably higher contribution from mantle of post-collisional mantle-derived magmas (Moritz et al., 2004; Barra et al., 2003; Kehayov et al., 2003; Park et al., 2015; Delibaş et al., 2016)

4.4. The transport of platinum-group elements in magmatic-hydrothermal fluids

The direct partitioning of metals from the silicate melt to the hydrothermal fluid phase as the dominant mechanism for the base and precious metal mineralization in porphyry Cu deposits has been suggested (Audétat et al., 2008; Thompson et al., 2001; Simon and Ripley, 2011; Seo et al., 2009), as well as a contribution by pre-concentration of ore metals in precious metal-bearing Fe–Ni–Cu-sulfides, that subsequently were destabilized and broke down, due to changes in oxidation state and sulfur fugacity (Halter et al., 2002; McInnes and Cameron, 1994). The origin of hypersaline fluids in iron oxide-Cu-Au deposits is a topic of debate. Thermodynamic studies (Sassani and Shock, 1998; Barnes and Liu, 2012; Xiong and Wood, 2000; Wood, 2002; Tagirov et al., 2013) indicated that the solubility of the Pt and Pd in highly saline solution increases with increasing temperature, oxygen fugacity and total chloride content. A series of experimental studies that investigated the compatibility of the PGE in volatile phases at magmatic temperatures (600–1000 °C) showed that they can be dissolved and transported by hypersaline fluid phases (up to 70 wt% $NaCl_{equiv}$) under oxidizing conditions (Ballhaus et al., 2001; Finnigan et al., 2008; Mungall and Brenan, 2014). Transported Cu and precious metals, as chloride complexes, were precipitated during the main stage of mineralization along with early biotite-magnetite and K-feldspar assemblages (Müller and Groves, 2000; Seo et al., 2009). With respect to the importance of vapour phase in the transport of ore elements, on the basis of experimental – metal solubility – studies of porphyry Cu systems, it has been suggested that Cu and Au are concentrated into the saline liquid brine during immiscible phase separation of oxidized high-temperature fluids, and that Au shows a strong partition into the low-density H_2S-rich vapour phase rather than into the coexisting high-density chloride-rich liquid phase (Kehayov et al., 2003). Recently, the application of in situ X-ray absorption near structure spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) to the study of palladium speciation and solubility of PdO(s) and PdS(s) in NaCl–HCl–H_2O solutions (up to 450 °C and 600 bar) indicated that Pd can be significantly mobilized as chloride complexes only in sulfide-free oxidizing geological settings, whereas at typical pH (4–8), chlorinity (<10–15 wt% NaCl) and H_2S contents (0.001–0.1 wt%) of most hydrothermal fluids, the absolute concentration of Pd–Cl complexes is too low to explain Pd enrichment in porphyry Cu–Au–Mo deposits (Bazarkina et al., 2014).

4.5. Criteria for the discrimination between PGE-enriched and PGE-barren porphyry-Cu deposits

In summary, the compilation of a database on barren porphyry deposits and porphyry Cu–Au–Pd ± Pt deposits, may provide some evidence in the exploration of precious metals in porphyry Cu systems, despite their common origin in a supra-subduction geotectonic environment (Xiong and Wood, 2000; Economou-Eliopoulos, 2005; Simon and Ripley, 2011; Barnes and Liu, 2012; Park et al., 2015; Seo et al., 2009).

4.5.1. Characteristics of the favorable tectonic setting

Elevated contents (hundreds of ppm) in Cr, Co, Ni and Re in porphyry Cu–Au–Pd ± Pt may reflect a significant precious/base metal

Table 6
PGE data on sulfide ore from porphyry-Cu deposits.

Location	ppb			Pt/Pt*	Pd/Ir
	Rh	Pt	Pd		
Skouries	1	1	65	0.04	65
	1	2	52	0.09	52
	1	5	260	0.1	260
	1	19	480	0.28	480
Elatsite	0.5	319	3449	1.74	5733
	0.5	64	2070	0.45	5175
	0.5	349	1980	2.51	9900
	0.5	7	292	0.13	1460
	0.5	17	407	0.27	4070
B. Columbia	0.5	54	1040	0.54	10,390
	0.1	15	103	0.47	1030
	0.5	107	1580	0.86	7905
	0.7	28	112	0.85	560
	0.3	17	51	0.76	510
	2.2	23	124	0.47	95
	0.9	62	588	0.82	1960
	2.1	111	6312	0.32	10,520
	0.2	33	320	0.59	3200
	0.7	17	83	0.6	415
	0.3	7	23	0.47	230

Data from Eliopoulos and Economou-Eliopoulos (1991), Thompson et al. (2001), Augé et al. (2005).

endowment of the parent magma, such as in the porphyry deposits of the Balkan Peninsula (bulk analysis) and mineral chemistry (Cr in magnetite and Ni, Co in sulfides), due to a direct input to the magma composition by metasomatized asthenospheric mantle wedge, in contrast to the porphyry Cu–Mo-Au deposits of Russia and Mongolia (Table 4; Economou-Eliopoulos and Eliopoulos, 2000; Sotnikov et al., 2000; Kehayov et al., 2003; Moritz et al., 2004; Augé et al., 2005; Eliopoulos et al., 2014). In addition, elevated (0.5–2.5) initial $^{187}Os/^{188}Os$ ratios (more radiogenic than mantle) indicate a contribution by a crust source (recycled in a metasomatized mantle) (Tagirov et al., 2013; Delibaş et al., 2016).

4.5.2. Mineralogical characteristic of the oxidation stage

Since the oxidized nature of parent magma is connected with the ability to produce a magmatic-hydrothermal system with ideal chemistry that facilitate the capacity for transporting sufficient precious metals (Audétat et al., 2008; Seo et al., 2009; Park et al., 2015), abundant magnetite (reaching up to 10 vol% in the Skouries deposit) linked to pervasive potassic and propylitic alteration type (Economou-Eliopoulos, 2005) is considered to be a characteristic feature of the Pd-bearing porphyry Cu deposits.

4.5.3. Geochemical signature of evolved magmas

In addition to the oxidation stage of the parent magma a significant requirement is the evolved geochemical signature, despite its otherwise recorded Cr- and Ni- enrichment in the mineralized porphyry stocks, as exemplified by the porphyry Cu + Au + Pd ± Pt deposit in the Balkan Peninsula and elsewhere (Table 4; Eliopoulos and Economou-Eliopoulos, 1991; Augé et al., 2005; Eliopoulos et al., 2014). The Pd/Pt ratio in the porphyry Cu–Au deposits, ranging from 0.8 to 65 in the Skouries deposit, and from 0.2 to 41 in the Elatsite deposit (Table 6) as well as in British Columbia (Thompson et al., 2001) are all much higher compared to typical magmatic sulfide deposits, ranging from 0.2 to 0.7 (Naldrett, 2010).

5. Conclusions

The compilation of current knowledge on the PGE distribution in chromitites and sulfides associated with ophiolite complexes and porphyry Cu–Mo-Au ± Pd ± Pt deposits indicate that PGE can be mobile and redistributed, under favorable conditions:

The plots of the Pd/Ir *versus* normalized Pt/Pt^* values suggest that large chromite deposits exhibit (a) low Pd/Ir values, reflecting low degree of fractionation (primitive magmas), (b) negative ($Pt/Pt^* < 1$) Pt/Pt^* values, (partial melting of already depleted mantle), and (c) increasing partial melting trend from high-Al toward to high-Cr deposits.

Relatively small chromite occurrences in ophiolites may exhibit an extreme fractionation for samples with elevated PPGE content.

The similarity between plots of the Pd/Ir *versus* Pd/Pt^* ratios for Fe-Ni-Cu sulfide mineralization in ophiolites and those for PPGE-elevated chromitites, may explain the PPGE-enrichment in chromitites as a result of the sulfide crystallization and reflects a fractionation trend with the proximity towards the petrological Moho of ophiolite complexes, suggesting a sensitive fingerprint for the orientation in the mantle sequence of the ophiolites.

Mineralogical and texture characteristics of IPGE-minerals, coupled with the Pd/Ir and $Pt/Pt*$ values suggest their origin by partial melting of already depleted mantle and increased partial melting degree, during a subsequent crustal/mantle recycling stage and metasomatism.

The oxidized nature of parent magmas that facilitate the capacity for transporting sufficient PGE, and the degree of evolution of the mineralized system, are the most likely critical requirements controlling the Pd and Pt potential of porphyry-Cu deposits.

The estimated Pd, Pt and Au potential for porphyry deposits combined with the association of merenskyite, with the major Cu-minerals (bornite and chalcopyrite) are considered to be encouraging economic factor for Pd and Pt, as by-product, the Au being the main precious metal product.

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