

REVIEW ARTICLE

Keywords

Platinum-Group-Elements
PGE in ophiolite complexes of Greece
PGE contents
PGE mineralization
PGE mineralization in porphyry-Cu alkaline intrusions

Table of Contents

Introduction
PGE in ophiolite complexes of Greece
Characteristic features of ophiolite complexes
Ultramafic lavas and high-Mg basalts
Geotectonic setting of ophiolites
Major ophiolite complexes
Ultramafic lavas and high-Mg basalts
Methods of investigation
Characteristics of chromite deposits and occurrences
Compositional variation of chromite
Inclusions in chromite ores
Platinum-group element contents and PGE mineralization
PGE in ultramafic lavas and high-Mg basalts
PGE in chromite deposits and occurrences
Platinum-group minerals in Greek ophiolites
Phase equilibrium constraints on synthetic PGE-minerals
Implications for PGE and chromite mineralization
Evaluation of PGEs as an economic factor in ophiolite complexes
Transport of PGE in hydrothermal systems
Characteristic features of the sulfide ores in the Pindos ophiolite complex
Genetic significance of the platinum and palladium contents
PGE mineralization in porphyry-Cu alkaline intrusions
Introduction
Balkan peninsula
Skouries deposit: case history discovery
Sources of Metals and Sulfur in Porphyry Copper Deposits
Critical factors for the formation of porphyry Cu+Au+Pd ±Pt deposits
Evaluation of Pd and Pt as an economic factor for porphyry Cu–Au systems
Environmental risk
Conclusions
References

Correspondence to:

econom@geol.uoa.gr

Citation

Economou-Eliopoulos, M., Tsoupas, G. and Kioussis, G. 2013. Exploration for Platinum-group elements (PGE) in various geotectonic settings of Greece. In: (Ed.) Emmanuel Skourtsos, The Geology of Greece - Part II, Journal of the Virtual Explorer, Electronic Edition, ISSN 1441-8142, volume 45, paper 2.

Exploration for Platinum-group elements (PGE) in various geotectonic settings of Greece

Maria Economou-Eliopoulos¹, George Tsoupas¹, George Kioussis¹

¹Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15784 Athens, Greece

Abstract The platinum-group elements (Os, Ir, Ru, Rh, Pd and Pt) or PGEs, which are the most valuable elements, are of strategic importance due to their growing use in advanced technologies and automobile catalyst converters. They traditionally are associated with mafic-ultramafic complexes, and have been described in a wide range of geotectonic settings. The majority of the world supply of PGE is produced from magmatic ores derived from basaltic magmas and is associated with primary magmatic. Major Pt and Pd economic mineralization is hosted in well-defined stratiform reefs of large layered intrusions, as is exemplified by the Bushveld Complex (South Africa), the Great Dyke (Zimbabwe) and the Stillwater Complex (USA).

The types of mafic-ultramafic complexes dominant in Greece, which belong to the Balkan-Carpathian system, are ophiolites associated with orogenic zones. Although chromite is major collector of the PGs, their content in chromite deposits, such as the large deposits of Othrys and Vourinos, and chromite occurrences hosted in ophiolites of Pindos, Rhodope and Serbo-Macedonian massifs, Edessa-Veria-Vermio, Euboea and Skyros islands, is generally low (few hundreds of ppb). However, PGE-enrichment: (a) in all PGE, (b) only in Os, Ir and Ru or (c) in Pt and/or Pd, are a common feature of disseminated chromite and/or relatively small chromite occurrences, of both high-Cr and high-Al type, in the uppermost parts of the mantle and/or in the lowest crust sequence. Examples of PGE-enrichment include the ophiolites of Pindos, Skyros Island and Veria (Greece).

The platinum group minerals (PGM) may be precipitated directly from silicate melt (S-poor), immiscible sulfide liquids, and the magmatic volatile phases. PGM can be classified into two subgroups: the more Os-, Ir- and Ru-rich or IPGE (Ir-group) and Pt, Pd-rich or PPGE (Pt-group) assemblages. The more Pt- and Pd-rich assemblages (Pd–Pt, Pd–Pt-alloys, Pt-arsenides, most likely sperrylite) occur interstitial to chromite grains. On the basis of field and experimental data small grains of PGM (average 25 μm) of the IPGE-group, commonly laurite, as inclusion in unaltered chromite have been interpreted as an early magmatic phase formed by direct crystallization of a basaltic magma. The presence of members of the irarsite-hollingworthite solid-solution series and other Os-, Ir, Ru- and Rh-bearing PGM in PGE-enriched altered chromitites from some ophiolite complexes may indicate either in situ alteration or/and remobilization and re-deposition of PGE. A salient feature of the latter case is the presence of extremely large (over 1.3 mm) PGM grains and extremely abundant PGM small grains/fragment (over 100) dispersed along a highly fragment chromitite zone, in a distance over 3 mm. They occur within small chromite occurrences located along a shear zone of strongly brecciated chromite ore of Veria having high PGE (up to 25 ppm) content. Such fluid-driven multistage platinum-mineralization and subsolidus reactions are considered to be widespread, but the system is considered to be a closed one with respect to PGE. The relatively high IPGE-enrichment in chromitites seems to be related to post magmatic processes covering a long period of deformation episodes, starting from the asthenospheric mantle flow (plastic deformation). Thus, most targeting locations general in ophiolite complexes may be (a) for the chromitite-IPGM associations exclusively small chromite occurrences along shearing zones of ophiolite complexes, postdating their initial/magmatic PGE deposition, and (b) for the PPGE the uppermost parts of the mantle and the lowest crust sequence.

Platinum and Pd contents in sea-floor massive sulfides are very limited. However, el-

evated contents, reaching values up to 1 wt % Pt in marcasite and chalcopyrite from massive sulfides on the East Pacific Rise, 1000 ppb Pt in disseminated pyrite and chalcopyrite from brecciated pipeform diabase, underlying the massive ore of the Pindos ophiolite complex (Greece) may indicate that Pt and Pd are quite soluble under a range of hydrothermal conditions. Recently, elevated Pd and Pt contents, reaching values over 5 ppm were determined in certain porphyry Cu-Au deposits (average ≥ 0.4 ppm Au). British Columbia, Colorado and Late Cretaceous to Miocene porphyry Cu deposits, extending from Romania, through Serbia and Bulgaria to Greece are the most important porphyry intrusions of that type, all formed in a supra-subduction zone geotectonic environment.

The Pd-telluride, merenskyite occurs mostly as inclusions or/and at margins of chalcopyrite and bornite or forms intergrowths with Pd-Pt-Bi- and Ag-tellurides. Although the potential for PGE mineralization associated with such large Cu and Au-Cu porphyry deposits is still unknown, the average (Pd+Pt) values (over 5 ppm) are considered to be encouraging for Pd and Pt as by-products, with Au being by- or co-product, and porphyry deposits a good target for Pd & Pt exploration. Porphyry Cu-Au-Pd±Pt deposits show a similarity in terms of their associations with alkaline rocks, in particular those characterized by (a) $\text{SiO}_2 < 65$ wt%, (b) a major contribution by crust material, as is exemplified by the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values, (c) their association with alkaline or K-rich calc-alkaline systems, characterized by relatively high of REE, Th and halogen (F, Cl) contents (d) the close association of the Cu-minerals with the main Pd-bearing mineral, merenskyite, and Au–Ag tellurides, (e) the association of the elevated Pd, Pt and Au contents with magnetite-bornite-chalcopyrite assemblages, and the pervasive potassic alteration type at the central parts of the deposits, and (f) the transportation of Cu and precious metals, as chloride complexes, by relatively hot (400 to 700 °C) and saline to hyper-saline (>70 wt% $\text{NaCl}_{\text{equiv}}$) hydrothermal fluids. Thus, critical factors controlling base/precious metal potential of porphyry Cu+Au+Pd±Pt deposits are considered to be the composition of parent magmas (contribution of mantle, oceanic and continental crust) and the physico-chemical conditions during the formation of porphyry Cu deposits. In addition, experimental work on Cu-concentrates derived from large ore samples, after roasting showed that the leaching process (HCl and H_2O_2 in appropriate proportion) resulted the recovery of $>97\%$ for Pd, Pt and Au. These results are considered to be encouraging for the evaluation of Pd-Pt as an economic factor (as a by-product) for that type of deposits.

INTRODUCTION

Platinum was formally discovered only in 1751, although it was used since the 7th century BC in Egypt. Platinum was originally called “platina” or “little silver” in Spanish, as it was considered a poor-quality by-product of silver mining operations 400 years ago in Colombia. The platinum-group elements (Os, Ir, Ru, Rh, Pd and Pt) or PGEs, which are the most valuable elements, traditionally are associated with mafic-ultramafic complexes, and have been described in a wide range of geotectonic settings. On the basis of their geotectonic environment they can be classified in (a) ophiolites and zoned Alaskan-Ural type (targets of exploration and sources of significant economic platinum placer deposits) emplaced in orogenic zones, (b) layered intrusions, for example the Bushveld Complex (South Africa), the Great Dyke (Zimbabwe) and the Stillwater Complex (USA), characteristic of a cratonic environment, and (c) komatiites which are an important portion of the Archaean greenstone belts. Also, on a variety of criteria, magmatic PGE deposits may be classified into several types. In this review they are classified into two groups, sulphide-poor and sulphide-rich. In the group of the sulphide-poor mineralization belongs the largest known platinum group metal (PGM) deposit in the world, the Bushveld complex in South Africa. The second type contains sulphide deposits, from which Ni, Cu and Co are extracted, the PGE being by products. The majority of the world supply of PGE is produced from magmatic ores derived from basaltic magmas. Major Pt and Pd economic mineralization is hosted in well-defined stratiform reefs of large layered intrusions, as is exemplified by the Bushveld Complex (South Africa), the Great Dyke (Zimbabwe) and the Stillwater Complex (USA) [Lee and Tredoux 1986; Cowden et al. 1986; Barnes and Campbell 1988; Cawthorn 1999; Barnes and Maier 1999, 2002; Cawthorn 1999; Naldrett and

Duke 1980; Campbell et al. 1983].

The type of mafic-ultramafic complexes dominated in Greece, belongs to ophiolites associated with orogenic zones, such as the Balkan-Carpathian system, which is part of the Alpine-Himalayan system, extending from western Europe through Iran and the Himalaya to China and Malaysia. Although chromite is major collector of the PGEs, their content in large chromite deposits, such as the deposits hosted in the Othrys and Vourinos complexes, is relatively (a few hundreds of ppb). However, PGE-enrichment: (a) in all PGE, (b) only in Os, Ir and Ru or (c) in Pt and/or Pd, are a common feature of disseminated chromite and/or relatively small chromite occurrences, of both high-Cr and high-Al type, in the uppermost parts of the mantle and/or in the lowest crust sequence. Examples of PGE-enrichment include the ophiolites of Pindos, Skyros Island and Veria (Greece) [Auge 1985, 1988; Economou et al. 1986; Auge and Legendre 1994; Auge et al. 2005; Konstantopoulou and Economou-Eliopoulos 1991, Economou-Eliopoulos 1996; Economou-Eliopoulos et al. 1999; Ohnenstetter et al. 1999; Economou-Eliopoulos 1996, Kaptiotis et al. 2006, 2009; Prichard et al. 2008; Grammatikopoulos et al. 2009].

Recently, elevated levels of platinum group elements (PGE), particularly Pt, have been reported in sea-floor massive sulfides related to ophiolite complexes indicated that elevated platinum, up to 1000 ppb Pt in an occurrence of brecciated pipeform diabase, underlying the massive ore from the Pindos ophiolite complex [Economou-Eliopoulos et al. 2008]. Elevated levels of Pd and Pt, have been reported in several alkaline porphyry deposits, such as the Skouries porphyry deposit (Greece), Cordillera of British Columbia (Copper Mountain Galore Creek), Allard Stock, La Plana Mountains and Copper King Mine in USA, Elatsite (Bulgaria), Santo Tomas II in the Philippines and elsewhere [Werle et al. 1984, Mutschler et al. 1985, Eliopoulos and Economou-Eliopoulos 1991, Eliopoulos et al. 1995, Tarkian and Koopmann 1995, Tarkian and Stribrny 1999, Economou-Eliopoulos and Eliopoulos 2000, Tarkian et al. 2003; Auge et al. 2005].

This paper focuses on (a) the mineralogical and geochemical characteristics of numerous PGE-sources in Greece, (b) the application of the current state of knowledge on the solubility of PGE in hydrothermal systems, related to ophiolite complexes and porphyry Cu-Mo-Au±Pd±Pt deposits, toward a better understanding of the PGE mineralization in hydrothermal systems (c) the factors controlling precious metal enrichment the PGE mineralization in ophiolite complexes and the unknown Pd and Pt potential in porphyry Cu systems, and (d) the establishment of a probable relationship between the potential in ore deposits and their geotectonic setting at which noble metals become concentrated in Greece.

PGE IN OPHIOLITE COMPLEXES OF GREECE

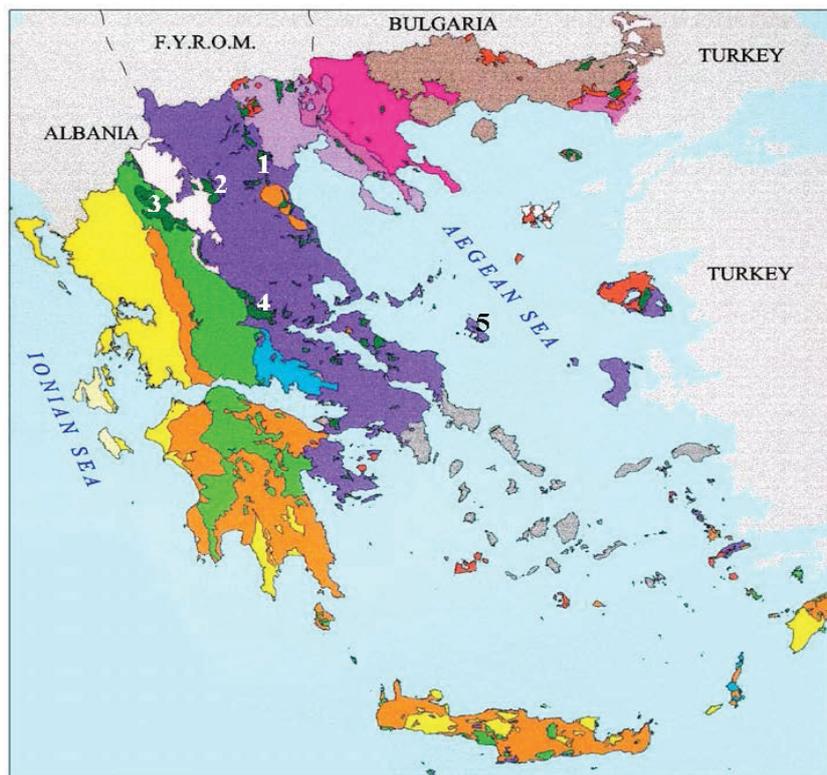
Characteristic features of ophiolite complexes

The ophiolitic complexes in Greece, of Middle to Late Jurassic age of obduction, form two major belts on each side of the Pelagonian zone: an east Pelagonian belt in the Vardarian domain and a Supra-Pelagonian ophiolitic belt to the west (Fig. 1). The emplacement of the ophiolite complexes in Greece from the Pindos–Mirdita Ocean, or from the Vardar Ocean or possibly from both of these oceanic basins is still unclear. The different hypotheses, with respect to the origin of the ophiolites, present geodynamic evolution models accounting for most of the available data: a mid-Triassic episode of rifting; an early Jurassic episode of sea-floor spreading forming the Maliaic Ocean; a Middle to Late Jurassic convergent period with subduction and obduction episodes, and finally, a late episode of Tertiary compressional deformation responsible for the thrusting of the Jurassic ophiolitic nappes over the external zones [Mercier 1966; Ferriere 1982; Smith et al. 1975; Rassios et al. 1994; Rassios and Smith 2000; Rassios and Moores 2006; Saccani et al. 2008 Rassios and Dilek 2009; Sassani et al. 1990, 2003; Saccani et al. 2011; Robertson 2012]. Some authors provide stratigraphic and petrographic arguments supporting a double origin, (western and eastern) [Vergely 1976, 1984; Baumgartner 1985; Mountrakis 1987; Beccaluva et al. 2005]. On the basis of sedimentological data from the margin series and on structural analyses of ophiolitic masses there is strong evidence for the existence of two deep basins on both sides of the Pelagonian continental ridge during Triassic–Jurassic times, corresponding to

the Vardar area to the east and the Pindos domain to the west [Ferriere et al. 2004].

Figure 1

Main geotectonic units of the Hellenides based on Mountrakis [1992]



LEGEND

Metamorphic Massifs	External Geotectonic Zones
 Rhodope Massif	 Parnassus-Ghiona Zone
 Servo-Macedonian Massif	 Olonos-Pindos Zone
Internal Geotectonic Zones	 Gavrovo-Tripolis Zone
 Circum Rhodope Belt	 Ionian or Adriatico-Ionian Zone
 Axios Zone	 Paxos or Pre-Apulian Zone
 Pelagonian & Sub-Pelagonian Zone	 Molasse
 Attico-Cycladic Massif or Complex	 Boetian Zone

Ultramafic lavas and high-Mg basalts

A salient feature of the Greek ophiolites is the spatial association of ultramafic lavas and boninites, which have been described in various localities of Greece, including the Othrys ophiolite complex [Smith et al. 1975; Cameron et al. 1979; Cameron and Nisbet 1982; Paraskevopoulos and Economou 1986; Economou-Eliopoulos and Paraskevopoulos 1989; Kostopoulos 1989; Capedri et al. 1997; Pe-Piper 1998; Pe-Piper et al. 2004; Barth et al. 2008; Barth and Gluhak 2009; Saccani et al. 2011; Koutsovitis et al. 2012]. At the Agrilia formation, highly magnesian lavas of komatiitic affinity occur in outcrops covering an area of at least 2 km². The rocks consist mainly of serpentinized or pseudomorphed olivine and skeletal clinopyroxenes with a random orientation in a matrix of fine-grained clinopyroxenes and devitrified glass (Fig. 2) [Paraskevopoulos and Economou 1986, 1997]. Although the studied lavas from the Agrilia Formation resemble boninites because their high Mg, Cr and Ni contents, they differ as regards their mineralogical composition and mineral chemistry. These lavas are dominated by olivine phenocrysts, are orthopyroxene free, and chromite is preferentially associated with groundmass. These ultramafic lavas are similar to Archean komatiites, in terms of their chemical composition [Arndt and Nisbet 1982]. Such rocks are very rare in the Phanerozoic; they are known at the Gorgona Island, Colombia [Gansser et al. 1979; Echeverria 1980] and the Agrilia formation. The rocks from Gorgona Island are considered to be the nearest Phanerozoic analogues of komatiitic basalts [Cameron and Nisbet, 1982].

Typical pillow lavas [Hynes 1972; Dijkstra et al. 2001] dominate the western part of the Othrys ophiolite complex. Outcrop at the Pournari area occurs with the form of dyke, dominated by clinopyroxenes, which sometimes are skeletal, between large phenocryst of orthopyroxene, clinopyroxene and olivine (Fig. 2c, d). Euhedral to subhedral chromite is an accessory mineral, while clinopyroxenes with an acicular morphology, show a very impressive curved branching comb [Paraskevopoulos and Economou-Eliopoulos 1997].

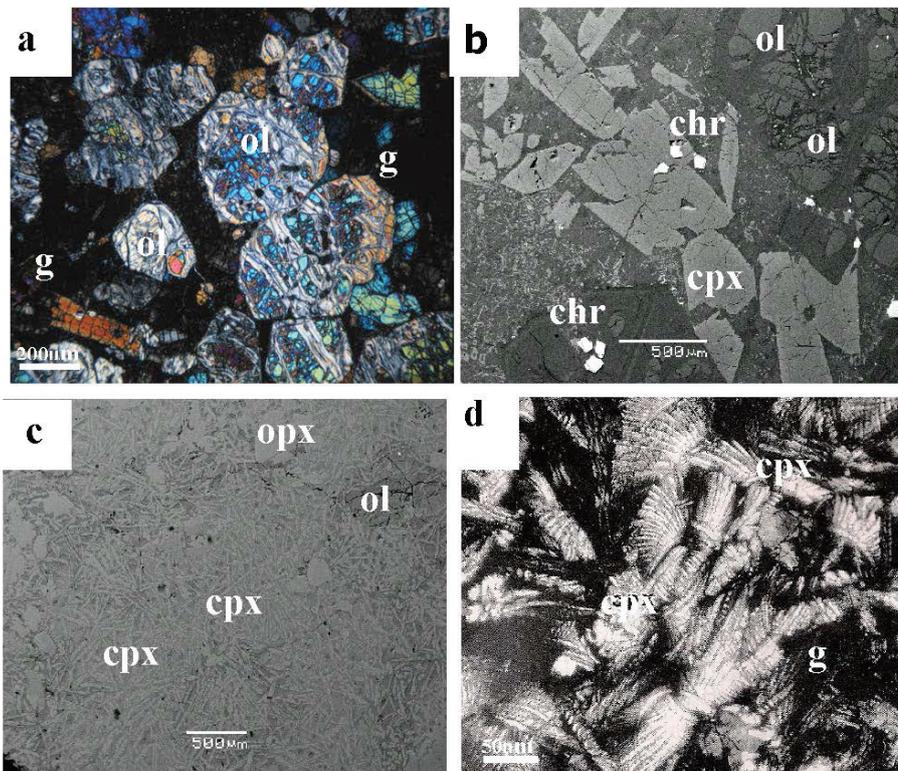


Figure 2

Photomicrographs (2a, d) and back-scattered electron (BSE) images (2b,c) from ultramafic lavas from the Agrilia Formation (2a,b) and high-Mg basalts from the Pournari area (2c,d), Othrys ophiolite complex. Partially serpentinized olivine phenocrysts (ol), clinopyroxene (cpx) and chromite (chr) in a devitrified glass (g) (2a viewed under cross Nichols); most chromite grains occur in the matrix, close to olivine or clinopyroxene phenocrysts (2b). The high-Mg basalts are dominated by acicular clinopyroxenes (2c) which often show the development of curved branching cockscomb forms (2d viewed under parallel nichols).

The liquid composition for the Agrilia lavas has been approached on the basis of the chemical composition of phenocrysts [Economou-Eliopoulos and Paraskevopoulos 1989] combined with experimental data of Fe-Mg partition between olivine and liquid [Bickle 1982]. Thus, using the distribution coefficient $KD = \frac{[(MgO)/(FeO)]_{liquid}}{[(FeO)/(MgO)]_{olivine}}$, where $KD = 0.314$, for olivines (Fo90-91) from the Agrilia ultramafic lavas, they concluded that they would be in equilibrium with liquids containing 17 wt.% MgO, assuming no ferric iron in the liquid, 12.5 wt% MgO [Economou-Eliopoulos and Paraskevopoulos 1989]. As far as the Gorgona Islands, assuming that $Fe^{2+}/\Sigma Fe = 0.90$ for the Gorgona lavas the composition of the parental magma was calculated to contain 19 wt% MgO and suggested that this would crystallize olivine with Fo91.5, maximum observed (Herzberg et al. 2007).

It has been suggested that some lavas differentiate into an upper spinifex and a lower cumulate layer, as is exemplified by changes in their mineralogical and chemical composition, such as an increase in modal olivine and chromite in the cumulate layers, and an increase in MgO, Ni and Cr [Arndt et al. 1977]. In addition, special attention was given to the platinum-group elements, which may provide evidence to assess the fractionation processes in komatiite lavas.

Geotectonic setting of ophiolites

Major ophiolite complexes

Major ophiolites, such as Pindos, Vourinos, Othris, Koziakas, Evia, Skyros, have been interpreted as parts of the same oceanic slab and differences of their geological and petrological data were attributed to intra-slab heterogeneity. MOR- and SSZ-type ophiolites (fore-arc and back-arc ridges) have been obducted, tectonically fragmented and separated by overlapping sediments of the Meso Hellenic trough. The occurrence

of both styles of melting regimes within close spatial and temporal association in the same ophiolite has been explained by intra-oceanic thrusting and forced subduction initiation at (or near) a mid-ocean ridge [Rassios and Moores 2006; Barth et al. 2008].

The Vourinos complex represents an ophiolite, with supra-subduction characteristics and boninitic affinities. The Pindos complex contains a spectrum of lavas from MOR basalts through island arc tholeiites (IAT) to boninite series volcanics (BSV), and the Othrys peridotites range from fertile plagioclase lherzolites (mid-ocean ridge setting) to depleted harzburgites (supra-subduction zone tectonic setting), as residua from variable degrees of partial melting [Smith et al. 1975; Pearce et al. 1984; Rassios and Moores 2006]. The harzburgites from the Othrys and the Vourinos ophiolite are highly depleted, as it is exemplified by the extremely low Al_2O_3 contents in pyroxenes [Economou-Eliopoulos 1996].

Ultramafic lavas and high-Mg basalts

Smith et al. [1975] concluded that in the Othrys complex there were two separate series: an earlier suite formed in a continental margin setting the Agrilia Formation, which was probably related to the opening of the ocean basin, and a later suite (the Mirna group) in which gabbroic cumulates and ultramafics were identified representing spreading in that basin. In general, high SiO_2 , H_2O and unusually high abundances of some incompatible elements have been ascribed to complex mixing preceding boninite genesis [Sun and Nesbitt 1978; Cameron et al. 1979]. The enrichment in main incompatible elements (Sr, Rb, Ba, La), the Ti/V and Ti/Sc ratios, the spinel composition of the Agrilia lavas and the lower MgO content of the parent magma (~ 17 wt.% MgO) compared to that for boninites from Cape Vogel (20 wt.% MgO; Walker and Cameron, 1983), suggest a contribution to the magma composition by a subduction component. The Agrilia lavas have generated by a similar process like that of boninites [Crawford et al. 1981], but probably somewhat further away from the trench (fore-arc setting), where the influence of the subducting slab is smaller and the partial melting degree lower compared to those of boninites [Economou-Eliopoulos and Paraskevopoulos 1989].

Methods of investigation

Polished sections were examined by reflected light microscopy and scanning electron microscope

Quantitative analyses were carried out at the University of Athens, Department of Geology, using a JEOL JSM 5600 scanning electron microscope, equipped with automated OXFORD ISIS 300 energy dispersive analysis system. Analytical conditions were 20 kV accelerating voltage, 0.5 nA beam current, 2 μm beam diameter and 50 second count times. The following X-ray lines were used: OsMa, PtMa, IrM β , AuMa, AgLa, AsLa, FeKa, NiKa, CoKa, CuKa, CrKa, AlKa, TiKa, CaKa, SiKa, MnKa, MgKa, ClKa. 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.

Platinum-group elements (PGE) were determined by ICP/MS analysis after pre-concentration using the nickel fire assay technique from large (30 g) samples, at Activation Laboratories, Ltd, Canada. This method allows for complete dissolution of chromitite. Detection limits are 5 ppb for Ru and Pt, 2 ppb for Os, Ir, Pd and 1 ppb for Rh and Au.

Characteristics of chromite deposits and occurrences

Compositional variation of chromite

The economic deposits in the Vourinos complex are either located in the uppermost part of the tectonized harzburgite within isolated dunite bodies or enclosed in narrow dunite envelopes. The chromite ore has commonly been affected by high-temperature deformation, superimposed on primary magmatic textures. Chromite ores of the South Vourinos area, including Xerolivado, one of the world's largest Alpine-type chromite deposits (about 6 million tons of ore) are remarkably homogeneous in major elements [Fig. 3; Economou et al. 1986]. Although the compositions of rest from North Vourinos differ significantly from those of South Vourinos, in particular the

Kissavos area, at central part of the complex (Fig. 3) the compositional variation in all chromitites throughout the Vourinos complex is consistent with its suprasubduction zone environment [Konstantopoulou and Economou-Eliopoulos 1991; Grivas et al. 1993]. In addition, Dare et al. [2009] provide evidence using the plots of chromitites from the Vourinos ophiolite, on the $\Delta \log fO_2$ versus $Cr/(Cr+Al)$ diagram and $Ti/Fe^{3+}/(Fe^{3+}+Al+Cr)$ vs. $Ga/(Fe^{3+}+Al+Cr)$ diagram, and concluded that they fall within the SSZ field.

The mantle sequence of the Pindos ophiolite complex resembles to that of Vourinos in the presence of extensive and highly depleted harzburgite. However, in contrast to Vourinos there are only a limited number of small chromite occurrences, and thus there is a low potential for exploitation in the Pindos complex [Rassios and Moores 2006]. Due to mantle and emplacement tectonics, a strong plastic and brittle deformation was superimposed on primary magmatic textures and had an important influence on the present form and distribution of chromitites [Rassios 1990]. Chromite composition of massive chromite show a wide variation of the $Cr/(Cr+Al)$ ratio ranging between 0.47 and 0.83, while the $Mg/(Mg + Fe^{2+})$ ratio ranges from 0.42 and 0.73 [Fig. 3; Economou-Eliopoulos and Vacondios 2005]. Recently, Pelletier et al. [2008] suggested that the low light-element contents of primary minerals and whole-rock samples argued against a supra-subduction zone (SSZ) origin of the Dramala mantle section, and against the previous hypothesis of hydrous melting of the Pindos mantle above a subduction zone. They concluded that the Dramala harzburgites represent a mid-ocean ridge (MOR)-type mantle, and not an SSZ-type mantle, juxtaposed with MOR-type and SSZ-type oceanic crust, either in a back-arc or in an intra-oceanic subduction zone setting.

The Othrys complex includes two tectonically separated chromite deposits, namely Eretria and Domokos, hosting about 3 million tons of ore. Massive chromite ores occur as spherical, lenticular or irregular bodies of varying size. The host rock is moderately depleted harzburgite and no systematic relation exists between the distribution or size of the ore bodies to the size of host masses [Economou et al. 1986; Economou-Eliopoulos et al. 1997]. A characteristic feature is a remarkably homogeneous composition type (Fig. 3). The majority of chromite ores are high-Al (of refractory type), although ores with a relatively high-Cr content were also found in a small proportion. They differ from those in the Vourinos complex, which are dominated by high-Cr (metallurgical type) deposits. However, at the central part of the Vourinos complex (Kissavos area) the composition of small chromite occurrences ranges from high-Al to high-Cr, both types being in a comparable proportion (Fig. 3).

Ophiolite masses, mostly serpentinized dunite and harzburgite, in the western margin of the Axios zone, including the areas of Edessa, Vermio, Veria, E. Thessaly (Fig. 1) contain mainly massive chromite bodies of small size. The chromite deposits of W. Chalkidiki peninsula and Serbomacedonian massif occur in altered dunite and serpentinized peridotites [Economou 1986].

The petrological, mineralogical and geochemical characteristics of the Veria ophiolite are typical of ophiolites associated with a SSZ geotectonic environment [Economou et al. 1986]. The main lithologic type making up the Veria ophiolite is a highly melt-depleted mantle harzburgite. Mantle shear zones, several hundreds of meters in width, dominate the mantle sequence of the Veria ophiolite, which are characterized by the presence of fish-shaped serpentinite bodies. Small lens-shaped bodies of massive chromite are common along zones of shearing. More than 100 isolated chromite occurrences, elongated lenses, following the NW-SE trend of the host serpentinized dunite. They are small (5 to 15 m in length, 0.3 to 1 m in thickness), mostly massive and dense disseminated bodies. The majority of the massive chromitites occur as irregular bodies of varying size. Several small chromite bodies are confined to mylonite-shear zones within the Veria ophiolites. They have been affected by intense tectonic activity, which has created faulting, folding, over thrusting, foliation and lineation of minerals [Koukouzas and Kouvelos 1973]. Chromite is dominantly of high-Cr composition.

The compositions of chromitites from the entire Veria area fall within both high-Cr and -Al types according to Koukouzas and Kouvelos [1973]. Detailed investigation of chromitites from the area of Galaktos (Veria) showed a dominance of the high-Cr variety in both PGE-poor and PGE-enriched chromitites [Tsoupas and Economou-Eliopoulos 2008]. The alteration of chromite to ferrian chromite at grain peripheries

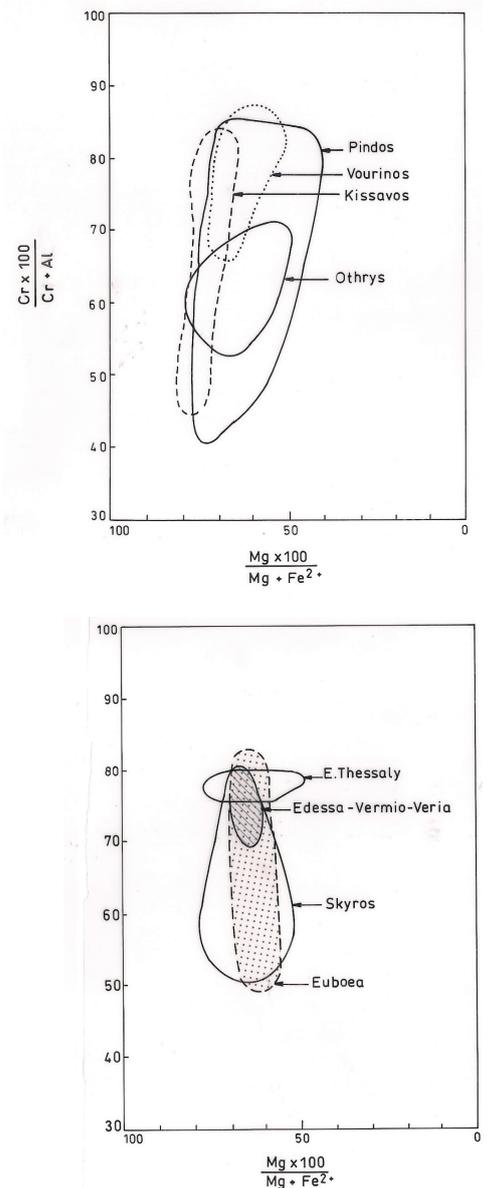


Figure 3

Plot of $Cr/(Cr+Al)$ vs $Mg/(Mg+Fe^{2+})$, showing the compositional variation of chromite from the main ophiolite complexes of Greece. Data from Economou-Eliopoulos [1996].

and along cracks is characterized by a progressive enrichment in the Fetot and Mn contents, and a correspondingly strong depletion in Mg and Al compared to chromite cores (Table 1).

All silicate minerals occurring in interstices between chromite grains have been entirely altered to Fe-poor serpentine (2 to 4 wt.% FeO), and Cr-free chlorite (5 to 11 wt.% FeO). Chromitites from mylonitic shear zones of the Galaktos area (Fig. 1) are characterized by abundant Cr-andradite and uvarovite [$\text{Ca}_3(\text{Fe,Cr})_2(\text{SiO}_4)_3$], and lesser amounts of Fe-poor Cr-chlorite and serpentine flakes as interstitial secondary minerals. The most salient feature of certain garnet-bearing chromitites is the presence of abundant PGM assemblages (see below), whose occurrence seems to be independent of the chemical composition of the host chromite mineralization. Chromite hosting PGM and chromite lacking PGM both fall within the same compositional range, although the former tends to show a strong brittle (cataclastic) and mylonitic deformation [Tsoupas and Economou-Eliopoulos 2008].

Table 1 Representative microprobe analyses of chromite from massive chromitites of the Veria (Galaktos) area

Sample	PGE-poor chromitites								PGE/PGM-rich chromitites					
	G.64 core	G.64 rim	G.64 core	G.64 rim	G.65 core	G.66 core	G.66 core	G.67 core	V.87 core	G.79 core	G.79 rim	G.79 core	G.79 core	G.79 core
Al ₂ O ₃	14.81	1.12	14.11	0.31	11.81	20.48	14.04	11.19	15.75	16.12	15.46	18.78	19.48	23.24
Cr ₂ O ₃	56.65	56.61	58.12	58.33	57.24	50.01	56.32	59.23	54.08	55.72	53.88	51.67	51.11	41.62
Fe ₂ O ₃	0.84	11.27	0.08	11.21	2.42	0.53	2.07	1.51	2.65	0.02	2.13	0.67	0.76	3.96
FeO	14.27	16.39	14.98	18.62	15.86	15.00	13.32	16.95	14.15	15.71	16.83	15.41	13.34	19.71
MgO	13.09	3.72	12.57	3.48	11.56	13.07	13.55	11.04	12.63	12.35	11.51	12.66	13.96	10.94
MnO	n.d.	9.51	n.d.	7.71	n.d.	n.d.	0.54	0.31	0.27	n.d.	n.d.	n.d.	0.37	0.41
Total	99.66	98.62	99.86	99.66	99.00	99.09	99.84	100.23	99.53	99.92	99.81	99.18	99.02	99.88
Cr/(Cr+Al)	71.96	97.12	73.23	99.01	76.49	62.1	72.91	78.09	70.42	69.87	70.04	64.61	63.74	54.56
Mg/(Mg+Fe ₂ +)	62.05	31.42	59.65	31.61	56.50	60.83	64.49	62.28	61.39	58.37	54.91	59.44	65.08	49.76

Sample	PGE/PGM-rich chromitites													
	G.79 core	G.80-1 core	G.80-1 core	G.80 core	G.80 core	G.80 core	G.80A2 core	G80A2 core	G80A3 core	G80A5 core	G.80A6 core	G.80A9 core	G.80B4 core	G.80D1 core
Al ₂ O ₃	16.34	14.64	12.42	11.36	10.79	15.07	13.61	11.18	10.8	17.33	13.05	13.89	14.99	7.24
Cr ₂ O ₃	54.37	56.5	58.67	60.77	60.77	56.01	55.71	58.85	57.01	51.85	57.81	55.77	54.26	64.42
Fe ₂ O ₃	1.58	0.12	0.43	0.11	0.35	0.85	1.5	2.67	4.17	2.22	2.29	3.49	3.93	2.29
FeO	13.45	15.99	15.22	16.48	15.93	15.34	13.61	12.68	12.37	11.27	14.79	9.91	11.01	12.02
MgO	13.45	11.84	12.04	11.28	11.42	12.42	12.9	14.59	13.5	14.84	12.77	15.61	15.13	13.81
MnO	n.d.	0.51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.19	99.6	98.78	100	99.26	99.69	97.33	99.97	97.85	97.51	100.71	98.67	99.32	99.78
Cr/(Cr+Al)	63.12	72.13	76.01	78.19	79.09	71.37	73.31	77.91	77.98	67	74.81	72.91	70.82	85.57
Mg/(Mg+Fe ₂ +)	69.06	56.88	58.51	55.12	56.11	59.07	63	65.62	78	70	60.62	73.8	71	67.25

Inclusions in chromite ores

Primary inclusions in fresh chromite consisting of Ni-Fe-Cu sulfides (pentlandite, pyrrhotite, chalcopyrite, bornite), silicates (olivine, pyroxenes) and the PGM have been documented at the Vourinos chromitites [Garuti and Zaccarini 1997]. Also, a close association of the PGM sulfides with enstatite, Na-rich pargasite, clinopyroxene, phlogopite, and Cu-Ni sulfides have been described at the Othrys chromite ores [Garuti et al. 1999].

The chromite locally shows pull-apart textures and brecciation, and is often transformed into ferrian chromite along the rims and cracks. Secondary opaque-mineral assemblages consisting of milerite, heazlewoodite, Ni-Fe alloys and native copper, occur in the ferrian chromite alteration zones and/or in the silicate matrix, between

chromite grains [Tarkian et al. 1992; Garuti and Zaccarini 1997; Tsoupas and Economou-Eliopoulos 2008]. Inclusions of pentlandite, pyrrhotite, chalcopyrite, less abundant PGE and rarely native iron have been described in chromite ores from the Skyros Island. The silicate matrix is entirely serpentinized and carries numerous grains of heazlewoodite and millerite. Tarkian et al. [1992] indicated that all silicate minerals including inclusions in chromite, magnetite and the matrix of both, have entirely been altered to chlorite and serpentine, and that chlorine, up to 0.34 wt% Cl were detected in the later hydrosilicates. Magnetite ore associated with chromitite has shown a different sulphide assemblage consisting of pentlandite, pyrrhotite, pyrite, Cu-Fe- and Cu sulphides, graphite, tetraauricupride (AuCu) and sperrylite [Tarkian et al. 1992].

Although the majority of the chromite ores is characterized by paucity in fluid inclusions, abundant fluid inclusions were found in chromite hosted by a coarse-grained pyroxenite dike at the Pindos complex. Chromite [average Cr/(Cr+Al) ratio = 0.73] occurs in highly variable proportion in an orthopyroxene matrix or as inclusions in orthopyroxenes, exhibits primary and secondary fluid inclusions. The primary inclusions are of following types: Three-phase solid-liquid-gas, or gas fluid inclusions (4A), which reach up to 50 μm in size. The solid minerals inside the inclusions are idiomorphic in shape and large size. Three-phase liquid-liquid-vapour or gas fluid inclusions (Fig. 4B), with elongated shapes; the size of bubbles is very small and range from 20 to 30 μm . The secondary fluid inclusions are two-phase liquid-gas and mono-phase fluid inclusions. The presence of fluid inclusions in chromite aggregates hosted in orthopyroxenite dikes, in combination with the trace element contents in chromite concentrates and the mineralogical composition of the dikes may indicate that an aqueous phase separated from the magma [Al-Boghdady and Economou-Eliopoulos 2005].

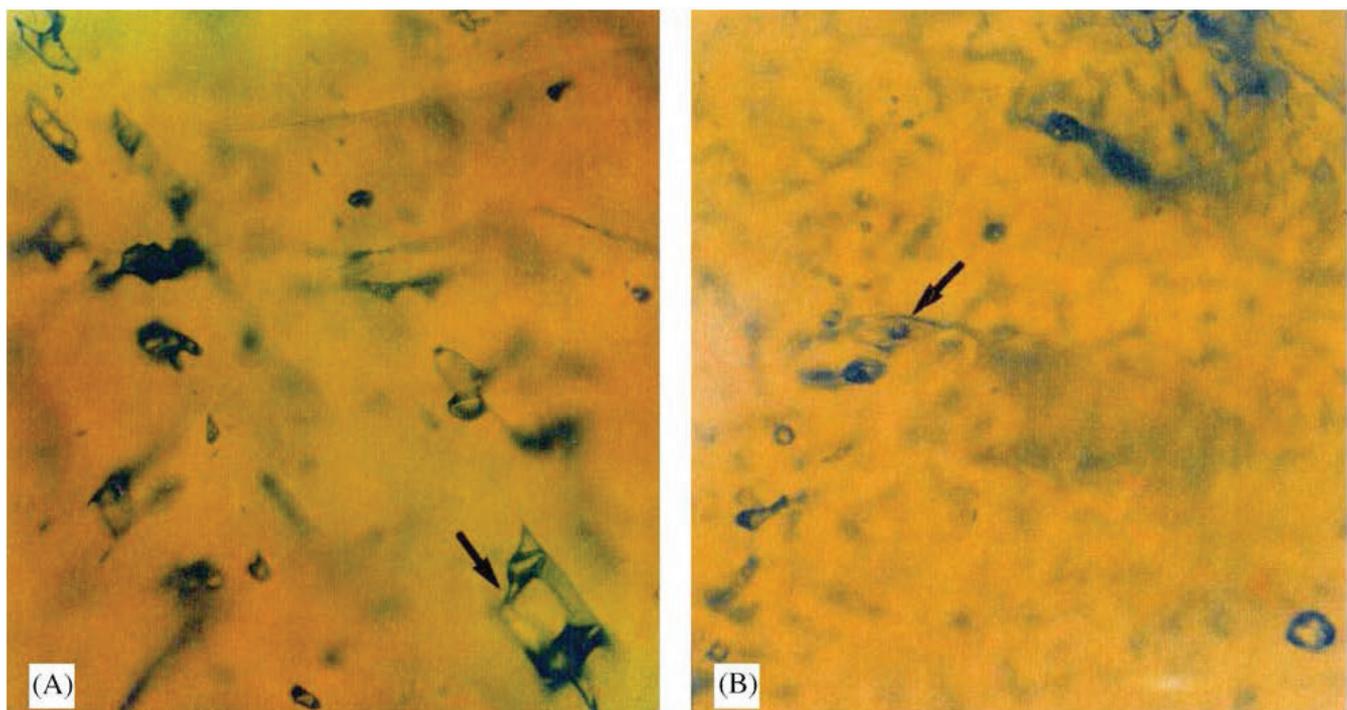


Figure 4

Primary fluid inclusions in chromite. Three-phase solid-liquid-gas fluid inclusions (A), three-phase liquid-liquid-gas fluid inclusions (B) [after Bogdady and Economou-Eliopoulos 2005]

Platinum-group element contents and PGE mineralization

PGE in ultramafic lavas and high-Mg basalts

The PGE contents in the ultramafic lavas from the Agrilia Formation and high-Mg basalts are low. Average platinum-group element (PGE) contents (all in ppb) are: Os 4, Ir 0.7, Ru 7, Pt 5, Pd 18, Rh < 0.5 and Au 15 [Economou-Eliopoulos and Paraskevopoulos 1989]. The low content of PGE, the higher Pd content compared to that of Pt and the lack of detectable Rh appear to be characteristic of the Agrilia ultramafic lavas [Economou-Eliopoulos and Paraskevopoulos 1989]. In a comparison of noble metal contents and PGE patterns made on the studied lavas from Agrilia Formation with

those of highly magnesian rocks, appear similarities to those found in komatiites from Munro Township, Ontario [Crocket and MacRae, 1986].

The crystallization history of Munro Township indicates that the main chemical trends are generated by fractional crystallization of olivine. Pd content in the Agrilia lavas falls within the range of values found in Munro Township komatiites, but Pt is very low. Pd and Pt are preferentially partitioned into the melt, so that these elements are concentrated in spinifex-textured upper flow units in the komatiites [Keays 1982; Crocket and MacRae 1986]. Ir content of the Agrilia lavas is very low (average 0.68 ± 0.08 ppb). Keays [1995] found that olivine in dunitic komatiites at Kambalda, Western Australia, contain the bulk of the Ir and suggest that during differentiation of a mafic melt Ir coprecipitates as Ir-Os alloy with the first silicate (usually olivine) or oxide phases to settle from the magma. The role of oxides (chromite) in the Agrilia ultramafic lavas appears to be minimal; there is not any positive correlation of Ir with Cr. Given the compatible nature of Ir [Crocket and MacRae 1986], the low Ir content in the Agrilia lavas may reflect either Ir removal from the magma, during crystal fractionation in deep crustal magma conduits, prior to lava formation or, if we assume that the Agrilia melts moved rapidly from the source to the surface before significant crystallization, then it may reflect a relatively low degree of partial melting. PGE patterns for primitive rock types (komatiites) are relatively flat, whereas more evolved rock types exhibit fractionated PGE patterns. Further, an increasing Pd/Ir ratio is the characteristic trend to be expected in the normal crystallization of mafic magma [Barnes et al. 1985]. The values (~ 12) of the Pd/Ir ratios for the Agrilia lavas are close to those for typical komatiites (5-10), and their PGE patterns which are almost flat, also resemble komatiites. The slightly higher Pd/Ir ratios of Agrilia lavas compared to komatiites may be related to magma fractionation, and/or a relatively low degree of partial melting, or enrichment in Pd by an alteration process. However, a higher degree of fractionation of the magma would be expected to produce enrichment in Pt and probably Rh as well [Barnes et al. 1985]. In addition, there is abundant evidence to suggest modification of Au and Pd during varying types of metamorphism [Keays 1982; Barnes et al. 1985]. Thus, hydrothermal alteration and/or serpentinization, which have affected those rocks and reactions of hydrating fluids with olivine (and pyroxene) to form alteration products may have inhibited the complexing and transport of elements as Pd and Au. Therefore, although an enrichment of Pd could be due to such an alteration, the relatively low Pd/Ir ratios and PGE patterns being flat, with exception of a negative Pt anomaly, may indicate that the studied rocks from Agrilia represent relatively primitive magmas.

Platinum-group minerals (PGM) in the Agrilia lavas were not identified. In general in komatiites have been described PGM of only small size (18 - 7 μm), which are predominantly sperrylite (PtAs_2), sudburyite (PdSb) and merenskyite (PdTe_2) [Nesbitt et al. 1979; Keays 1995, Herzberg 1995; Barnes and Maier 1999; Maier et al. 2002]. The paucity of PGM in komatiites seem to be consistent with the experimental data by Brenan and Andrews [2001] suggesting that PGM crystallization from basaltic magma may be feasible, but it is possible that the extrusion temperature of komatiites exceeds the maximum thermal stability of the PGM. For example, laurite has been shown to be stable up to the temperature of 1275 °C in mafic magmas [Brenan and Andrews 2001].

PGE in chromite deposits and occurrences

Since chromite is the main PGE collector in ophiolite complexes the PGE distribution in chromitites associated with ophiolite complexes of Greece have become an interest topic for many authors. Platinum-group element (PGE) content in large chromite deposits is generally low (a few hundreds of ppb). However, a PGE-enrichment has been reported in: (a) in all PGE, (b) only in Os, Ir and Ru or (c) in Pt and/or Pd, relatively small chromite occurrences, of both high-Cr and high-Al type, in the uppermost parts of the mantle and/or in the lowest crust sequence of Greek ophiolites. Examples of PGE-enrichment in Greece include the ophiolites of Pindos, (up to 7 ppm total PGE), [Economou-Eliopoulos and Vaconndios 1995, Tarkian et al. 1996, Economou-Eliopoulos et al. 1999; Prichard et al. 2008; Grammatikopoulos et al. 2009], the Skyros island in the Aegean (up to 3 ppm), the Veria (up to 25 ppm) [Table 2; Tsoupas and Economou-Eliopoulos 2005, 2008] and Vourinos (up to 3 ppm) [Konstantopoulou and Economou-Eliopoulos 1991].

More specifically, the PGE total for most of the chromitite samples from the Vourinos complex are less than 200 ppb. However, in a small portion (about 15% of the analysed samples) from the northern and central parts of the complex there unusually high concentrations for one or more PGE (Table 3). The PGE distribution is heterogeneous, the total ranging from 53 to 3,030 ppb. The majority of the analyzed samples from North Vourinos show $Ru \gg (Os+Ir)$ in contrast to the southern part of the complex, where $Ru < (Os + Ir)$. In addition, Pd/Ir and $(Pt + Pd)/(Os + Ir + Ru)$ ratios are much higher in the northern than in the southern part [Konstantopoulou and Economou-Eliopoulos 1991].

The majority of chromite samples show a relatively high Ir, Os and Ru contents, while Pt and Pd are low resulting in chondrite (C2)-normalized PGE patterns with a negative slope (Fig. 5) and a low Pd/Ir ratio. In contrast, some chromitite samples from the Pindos complex, which are Rh, Pt and Pd enriched whilst Ir, Os and Ru contents are low, show smooth sloped to positive slope PGE-patterns (Fig. 5). Moreover, chromitites with a similar major-element composition may exhibit a variation in the PGE-patterns and the values of the Pd/Ir ratios.

The PGE content in chromite ores from the Othrys ophiolite complex is low, while the chondrite normalized PGE-patterns are characterized by a negative slope, which are similar to those for large chromite deposits associated with ophiolite complexes [Economou-Eliopoulos et al. 1997].

Recently, high concentrations of PGE (mostly compatible IPGE), have been determined in chromitites hosted in the Veria ophiolites, northern Greece. Whole ore PGE concentrations in massive chromitites range from < 100 ppb to high PGE concentra-

Table 2. Platinum-group element -enriched chromitite ores from the Vourinos complex

Location	Os	Ir	Ru	Rh	Pt	Pd	Cr/(Cr+Al)
Xerolivado	50	30	60	19	2	3	0.81
Voidolakooos	830	1400	750	35	11	3	0.78
Kerasitsa	160	110	34	14	2	5	0.78
Koursoumia	220	130	240	27	18	8	0.66
Rizo	1000	760	240	6	23	3	0.8
Pefka	10	8	17	5	140	440	0.76
Doumaraki	120	22	560	13	2	2	0.8

tions, reaching 25 ppm Σ PGE (Os = 7,400, Ir = 6,020, Ru = 9,700, Rh = 310, Pt = 760, Pd = 750, all in ppb; Table 4). The high PGE content, and the presence of extremely abundant PGM grains concentrated along a shear zone of strongly brecciated chromite ore associated with garnet was initially described by Tsoupas and Economou-Eliopoulos [2005, 2008].

A negative slope characterizes the chondrite-normalized PGE patterns, for both PGE-depleted and PGE-rich chromitites (Fig. 6). In a comparison of the latter with other PGE-enriched ophiolite-related chromitites, it is clear that the enrichment of refractory PGE in the Veria chromitites is unique.

Platinum-group minerals in Greek ophiolites

Several authors have recorded the presence of platinum-group minerals (PGM) in the chromite deposits of Greece. Laurite, $(Ru,Os,Ir)S_2$, constitutes more than 75% of the platinum group mineral (PGM) population, accounting for the Ru-Os-Ir dominated composition of the chromitite host [Augé 1986; Tarkian et al. 1992, 1996, Garuti and Zaccarini 1997, Garuti et al. 1999, Tsoupas and Economou-Eliopoulos 2005, 2008; Kapsiotis et al. 2006; Prichard et al. 2008; Grammatikopoulos et al. 2009].

The existences of primary PGM (laurite, irarsite, Os-Ir alloys) as inclusions in fresh chromite [Auge 1985, 1988; Auge and Johan 1988], as well as PGM assemblages suggesting origin at low temperature, by desulfurization of pre-existing PGM sulfides [Garuti and Zaccarini 1997; Kaptiotis et al. 2006; Grammatikopoulos et al. 2009] have been well documented.

Platinum-group minerals (PGM) have been identified in chromitite from the Pin-

dos ophiolite complex. The PGM consist of Os-rich laurite, enclosed in chromite, sperrylite, exclusively in the serpentinized matrix of chromitite, and an unidentified phase,

Table 3
Range and average of the PGE contents (in ppb) in chromitites from Greece

Location	$\Sigma(\text{Pt}+\text{Pd})$	$\Sigma(\text{Os}+\text{Ir}+\text{Ru})$	$(\text{Pt}+\text{Pd})/(\text{Os}+\text{Ir}+\text{Ru})$	$\text{Ru}/(\text{Os}+\text{Ir}+\text{Ru})$
VOURINOS				
<i>Northern part (n = 19)</i>				
min	2	36	0.09	1.23
max	46	702	0.01	0.65
average	7.3	140	0.42	3.9
<i>Southern part (n=27)</i>				
min	21	42	0.01	0.13
max	518	2980	0.71	13.6
average	30	292	0.73	2.52
<i>Central part (n = 12)</i>				
min	2	13	0.07	0.93
max	286	68	0.85	5.1
average	37	54	0.27	1.93
PINDOS				
Korydallos	3620	151	24	0.36
	1800	190	9.5	0.42
	5120	82	62	0.7
	2990	297	14	0.37
	6565	207	32	0.16
	3880	164	24	0.49
	2245	292	7.7	0.44
	94	22	4.3	0.5
Koziakas	12	84	0.14	0.57
Dramala	11	81	0.13	0.13
Kampos Despoti	11	98	0.11	0.51
Milia	157	1020	0.15	0.54
SKYROS				
	319	1820	0.18	0.66
	51	400	0.13	0.75
	41	1900	0.21	0.77
VERIA				
	2	1230	0.002	0.5
	1650	7720	0.21	0.3
	1510	23120	0.065	0.42

Pt(Ni,Fe)₃ [Tarkian et al. 1996]. Also, at the Milia area, have been identified Os, Ir, Ru (IPGE) alloys and sulfarsenides, while the Korydallos area is dominated by Pt- and Pd-bearing PGM including Pt–Pd alloys, PGM arsenides and sulfarsenides, sperrylite and members of hollingworthite – irarsite – platarsite solid-solution series [Prichard et al. 2008]. In addition, Ru-rich alloy grains in chromitites from the Milia area, with

relatively high Rh and Pt abundances, have been described by Grammatikopoulos et al. [2009].

PGM identified as inclusions in chromitites of the Othrys ophiolite complex were Os-rich laurite and erlichmanite [Garuti et al. 1999]. They can be classified into two subgroups: the more Os-, Ir- and Ru-rich or IPGE (Ir-group) and Pt, Pd-rich or PPGE (Pt-group) assemblages. The more Pt- and Pd-rich assemblages (Pd-Pt, Pd-Pt-alloys, Pt-arsenides, most likely sperrylite) occur interstitial to chromite grains. The Othrys is similar to that of chromitites located in the mantle unit of other ophiolite complexes of the Balkan peninsula (Vourinos, Skyros Island, Rhodope) in terms of the predominance of Ru-Os-Ir phases, although it is distinguished because of the Os-rich composition of laurite and the presence of erlichmanite. In addition, the significance variation on the Os/Ru ratios, which has been attributed to the fractionation between these two elements [Garuti et al. 1999].

At the area of Veria, laurite inclusions within unaltered chromite grains, and large PGM grains, ranging from 0.8 mm to 1.3 mm in size (Fig. 7) were located in PGE-enriched chromitite. Also, extremely abundant solitary fragmented PGE-minerals (more

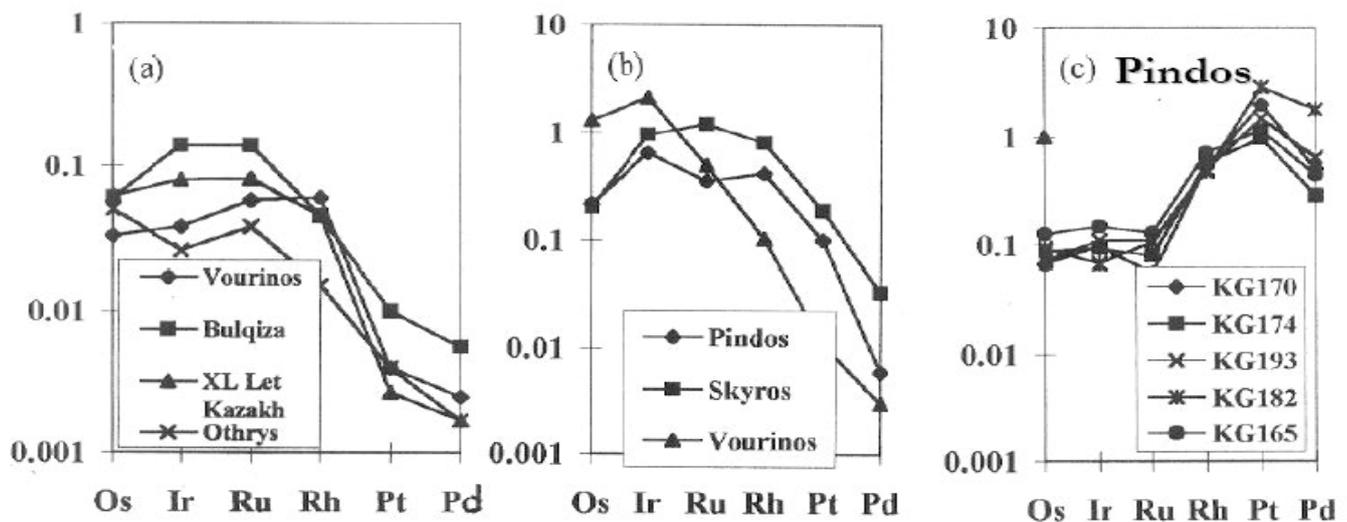


Figure 5
Chondrite-normalized PGE-patterns (sample/C1 chondrite) for chromite ores hosted in ophiolite complexes from the Vourinos and other large chromite deposits (a), IPGE-enriched ores (b) and PPGE-enriched ores. Data from Tables 2 and 4; Tarkian et al. [1996]; Economou-Eliopoulos et al. [1997].

than 100 grains) within sheared massive chromite samples were identified (Fig. 8). At the contact between strongly fragmented chromite and coarse-grained chromite PGM grains are dispersed in a trail up 3 mm in length [Tsoupas and Economou-Eliopoulos 2008]. The PGM fragments may be angular, rarely corroded grains or fine-grained aggregates occurring in a matrix of cataclastic chromite cemented by Cr garnet.

Laurite (RuS_2) was identified as small inclusions within unaltered chromite grains in the Galaktos chromitites, but it mostly occurs as relicts containing very small irregular grains of irarsite within a matrix of Ru-Os-Ir alloy/oxide (Fig. 7), exhibiting a wide compositional variation (Table 5a). Irarsite, displaying varying form and composition, is also a major PGM. It is associated with laurite in the large PGM grain and as intergrowths with platarsite-hollingworthite and garnet [Tsoupas and Economou-Eliopoulos 2008]. Pt-Pd-Rh-minerals occur commonly as relatively fine-grained assemblages (ranging from <2 to $50 \mu\text{m}$) with irarsite and other minerals, and show a wide compositional variation (Table 5b). Pt-alloys show a variation ranging from tetraferroplatinum, with low amounts of other elements, to Pt-Ir-Fe-Ni alloys. Both Pt-alloys and Pt-sulfarsenides are predominant Pt-minerals, whereas Pd-analogues are both very fine-grained and rare. Rhodium-arsenides, close to the composition of hollingworthite, are the commonest Rh-minerals, although sulfarsenides are also present (Table 5b). These compounds form fine grains associated with Pt-Pd-Ni-Fe-arsenides and -alloys (platarsite, vasilite) within a silicate matrix dominated by garnet; they also form intergrowths with garnet. Rh-arsenides are characterized by a strong enrichment in Ni, and can be represented by the general composition RhNiAs (Table 5b). Awaruite (Ni_3Fe), containing small amounts of Co and Cr, heazlewoodite (Ni_3S_2), pentlandite and maucherite commonly occur within fractures and the serpentine-chlorite matrix.

Thus, mineral-chemistry data indicate that the sulfur content decreases gradually outwards the periphery or cracks of IPGM grains in chromite ores, of Greece and

hence the replacement of laurite by Os–Ir–Ru alloys has been well documented [Garuti and Zaccarini 1997; Tsoupas and Economou-Eliopoulos 2005, 2008; Kaptiotis et al. 2006, 2009; Prichard et al. 2008; Grammatikopoulos et al. 2009].

Table 4
Platinum-group element contents (ppb) in chromitites from the Veria area

Samples	G.67	G.64	G.65	G.66	G.80	G.79
Os	10	120	170	550	1520	7400
Ir	26	250	440	440	3900	6020
Ru	15	370	620	830	2300	9700
Rh	11	35	30	19	510	310
Pt	n.d.	n.d.	n.d.	n.d.	1360	760
Pd	n.d.	n.d.	2	n.d.	250	750
ΣPGE	62	775	1262	1839	9840	24940
Au	3	3	3	2	9	4
$\frac{(Rh+Pt+Pd)}{(Os+Ir+Ru)}$	0.22	0.05	0.03	0.01	0.28	0.08
ppm						
Ni	980	1170	960	1100	1150	1100
Co	270	240	190	220	180	240
Zn	1440	640	350	1100	390	1090

ti and Zaccarini 1997; Tsoupas and Economou-Eliopoulos 2005, 2008; Kaptiotis et al. 2006, 2009; Prichard et al. 2008; Grammatikopoulos et al. 2009]. The enrichment in Ir, Pt, Pd, Fe, Ni, Co and Mn, and/or metallic phases, such as metallic Ru, has been interpreted as a replacement association, characterized by in situ desulfurisation products of the PGM sulfides, at relatively low (350–500°C) temperature [Stockman and Hlava 1984; Tarkian and Prichard 1988; McElduff and Stumpfl 1990; Garuti and Zaccarini 1997; Melcher et al. 1997; Ahmed et al. 2003; Tsoupas and Economou-Eliopoulos 2008].

Phase equilibrium constraints on synthetic PGE-minerals

The stability limits and mineral – sulfide melt partitioning behavior of the platinum-group minerals laurite (Ru,Os,Ir)₂S₂ and Ru–Os–Ir alloy, as functions of temperature and sulfur fugacity have been well established. More specifically, experimental data have demonstrated that under appropriate conditions of T, P, fO₂ and fS₂, the precipitation of laurite from basaltic liquids is feasible, laurite can be formed in equilibrium with Os–Ir alloys and it is stable up to the temperature 1275°C (< 1300°C) in mafic magmas [Brenan and Andrews 2001; Andrews and Brenan 2002]. Also, they found that laurite and alloy were Ru–Os–Ir-rich and Pt–Pd-poor, with grains of alloy containing more Os and Ir than laurite, and both phases becoming (Os + Ir)-rich with increasing f(S₂). Bochrath et al. [2004] showed that laurite may be the first sulfide mineral to crystallize directly out of a sulfide-undersaturated silicate melt, under conditions more oxidized than ΔfO₂=FMQ–1.5, which applies to most terrestrial melts. A melt that is more reduced than this value would exsolve a sulfide liquid at the f S₂ in equilibrium with RuS₂, and hence would fractionate all noble metals into sulfide melt, destabilizing discrete PGE sulfides. Initially, laurite is nearly stoichiometric (RuS₂) with very low contents of Os and Ir. As the temperature decreases and fS₂ increases Os is progressively incorporated into the laurite lattice, due to the partition coefficient of Os between laurite and silicate melt, and it significantly increases with decreasing temperature [Andrews and Brenan 2002].

Implications for PGE and chromite mineralization

Despite, the compositional variation of laurite and IPGE-alloys, hosting in chromite ores associated with ophiolites, they are similar in terms of (a) their precipitation di-

rectly out of a sulfide-undersaturated basaltic melt at temperatures higher than 1000°C (lower than 1275°C), (b) their small (< 25 μm) grain size and (c) small whole PGE content in the chromite ore, and their formation is well constrained [Ohnenstetter et al. 1999; Garuti et al. 1999; Matveev and Ballhaus 2002; Cabri 2002; Bockrath et al. 2004]. Liquidus, falling within the two-phase field defined by high- $f(S_2)$ experiments [Andrews and Brenan 2002] suggest high- $f(S_2)$ conditions during their crystallization or that the laurite formed at a lower temperature (1010-1030°C). A close association of the PGM sulfides with enstatite, Na-rich pargasite, clinopyroxene, phlogopite, and Cu-Ni sulfides provide evidence for crystallization at high temperature, under relatively high sulfur fugacity. The Othrys is similar to that of chromitites located in the mantle unit of other ophiolite complexes of the Balkan Peninsula (Vourinos, Skyros Island, Rhodope) in terms of the predominance of Ru-Os-Ir phases, although it is distinguished because of the Os-rich composition of laurite and the presence of erlichmanite. The lower temperature in this case seems to be consistent with the association of hydrous minerals reflecting an increased H₂O content in the crystallized magma [Matveev and Ballhaus 2002].

The members of the irarsite-hollingworthite solid-solution series and other Os-, Ir, Ru- and Rh-bearing PGM in chromitites from some ophiolite complexes, and their association with altered chromitites may indicate either in situ alteration or/and re-mobilization and re-deposition of PGE during at least two stages [Tarkian and Prichard 1987]. The presence of Ru-Os-Ir-Fe-oxides, with significant and variable Fe, Cr, Co, Ni and Mn contents, associated with serpentine, chlorite, Cr-garnet, ferrian-chromite and magnetite in chromite ores, suggest that they may have been derived from in situ alteration of primary PGM, by desulfurization and subsequently oxidation of preexisting sulfides of Os–Ru–Ir [Garuti and Zaccarini 1997]. Apart from the well documented replacement of PGM by desulfurisation products, at relatively low temperature [Stockman and Hlava 1984; Tarkian and Prichard 1987; McElduff and Stumpfl 1990; Garuti and Zaccarini 1997; Melcher et al. 1997; Tsoupas and Economou-Eliopoulos 2005, 2008; Kaptiotis et al. 2006; Prichard et al. 2008; Grammatikopoulos et al. 2009], primary PGE mineralization may provide valuable evidence for the PGE and chromite mineralization.

The geotectonic environments at which noble metals are mobile or become concentrated are considered to be critical for understanding the PGE mineralization and developing strategies for prospecting [Naldrett 1980, Campbell et al. 2010]. The association of laurite with hydrous fluids in immiscible hydrous liquids, the simultaneous precipitation of PGE alloys, laurite, olivine, and chromite consistent with a supra subduction zone (SSZ) geotectonic environment related to chromite deposits hosted in ophiolite complexes [Matveev and Ballhaus 2002]. The experimental data are consistent with the formation of chromite deposits in ophiolite complexes, only in the presence of water-rich magmas saturated in olivine and chromite, in a supra subduction zone (SSZ) environment [Bacuta et al. 1990; Zhou and Robinson 1997; Ohnenstetter et al. 1999; Economou-Eliopoulos et al. 1999; Gervilla et al. 2005]. Although, due to the high solubilities of the PGE in basaltic magma, direct nucleation and crystallization of PGM from silicate melt would be precluded, the majority of the authors agree that laurite and alloys occurring as inclusions within natural chromite crystals may have formed by direct crystallization from a silicate magma under appropriate conditions of T, P, fO_2 and fS_2 [Tredoux et al. 1995; Matveev and Ballhaus 2002; Bockrath et al. 2004]. Matveev and Ballhaus [2002] on the basis of experimental data, found that the liquidus temperature of chromite decreased with increasing H₂O content (4 wt%). With lower water content (1–2 wt% H₂O) higher temperatures (1430–1480°C) at 1.5 GPa have been reported. Also, upon olivine and chromite precipitation, chromite would be collected in the hydrous liquid droplets, accompanied by PGE-rich metallic alloys, while olivine was collected in the basaltic melt [Matveev and Ballhaus 2002]. The PGE distribution in chromite ores, associated with layered intrusion and ophiolites complexes, differs as far as their PGE-type: chromites in the former, such as the UG2 horizon of the Bushveld complex, showing a PPGE-enrichment relative to IPGE, are characterized by a high fractionation of PGE [Naldrett 2004]. In contrast, PPGE contents in chromitites hosted in ophiolite complexes of Greece and elsewhere PPGE are commonly much lower than IPGE, in particular in large chromite deposits [Economou-Eliopoulos 1996]. Although a relationship between sulfur and PGE content is

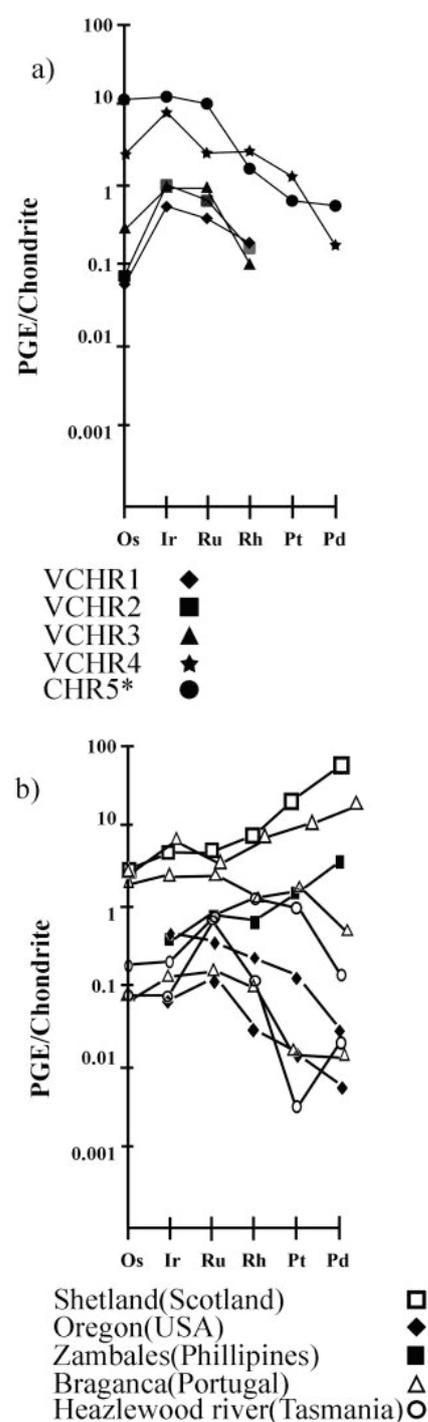
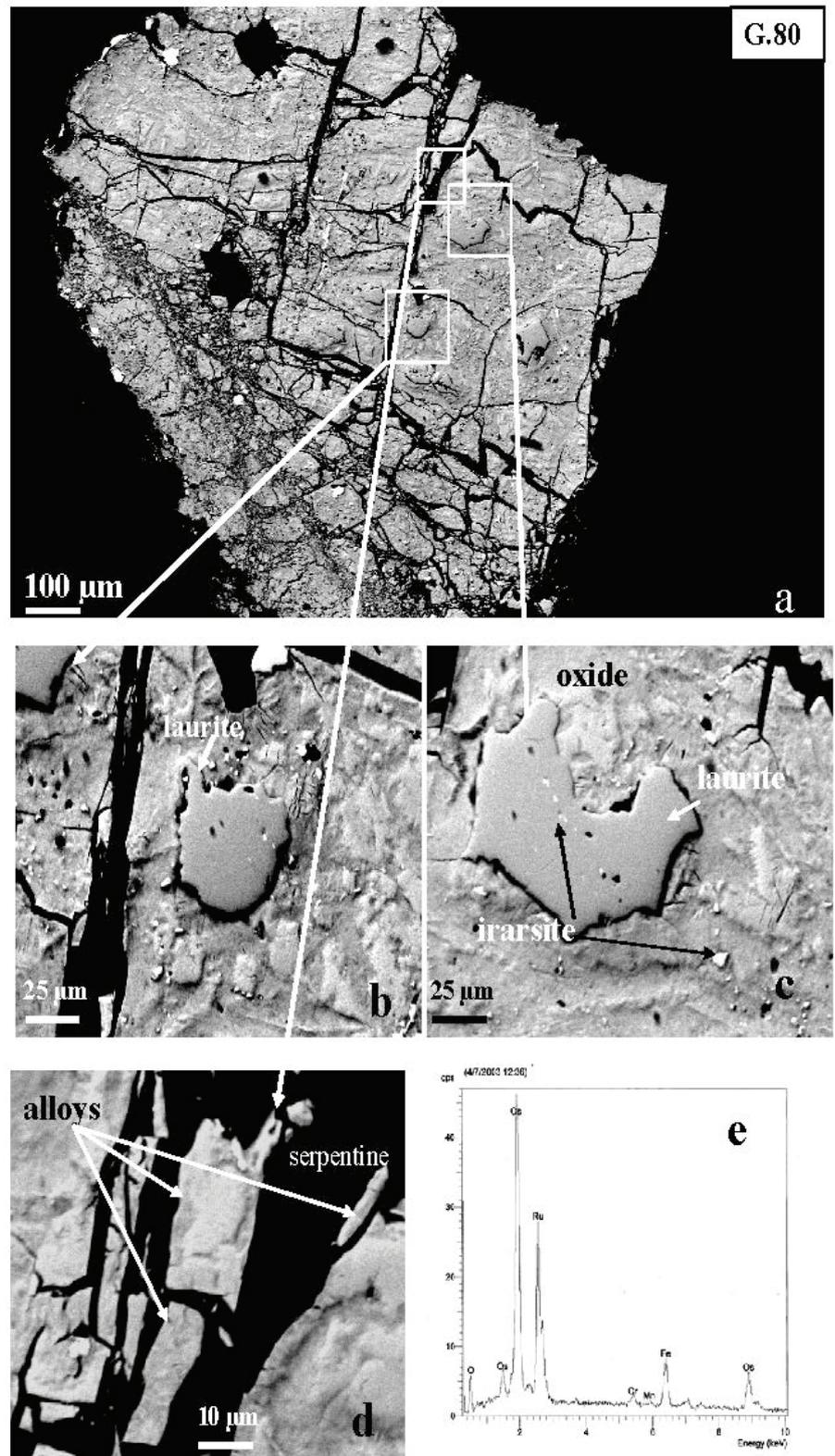


Figure 6 Chondrite-normalized PGE-patterns (sample/C1 chondrite) for the Veria chromite ores and PGE-enriched chromitites related to other ophiolite complexes. Data from Table 4; Stockman et al. [1984] for Heazlewood River, (Tasmania); Bacuta et al. [1990] for Zambales (Phillippines); Peck and Keays [1990] for Oregon (USA); Tarkian and Prichard [1987] for Shetland (Scotland); Bridges et al. [1993] for Braganca (Portugal). Normalization values (C1) after Naldrett and Duke [1980].

unclear, due probably to the desulfurisation of primary PGE-minerals, the presence of sulfur in the parent magma seems to be a major controlling factor for the PGE-con-

Figure 7

Back-scattered electron (BSE) images of extremely large PGM grain, composed by Or-Ir-Ru-oxides and remnants of laurite-irarsite assemblages. It was found at the contact between strongly fragmented chromite in a matrix of garnet (and less amount of serpentine), and coarse-grained chromite. That large PGM grain has probably conserved most of its initial form, and avoided the dislocation along the movement direction, although strongly fragmented. (e) The X-ray spectrum shows the presence of oxygen [from Tsou-pas and Economou-Eliopoulos 2008].



centration and deposition, in particular in PGE-enriched chromitites. Extremely high PPGE-enrichment in certain chromite occurrences of Greece (Tables 2, 3 and 4), and elsewhere, like Shetland, UK [Prichard et al. 1986; Tarkian and Prichard 1987, Prichard et al. 1994], Bulqiza complex, in Albania [Ohnenstetter et al. 1999], Troodos in Cyprus [Prichard and Lord 1990], New Caledonia [Augé et al. 1998], the Zambales ophiolite complex in the Philippines [Bacuta et al. 1990] and in Thetford mines in

Quebec [Corrivaux and Laflamme 1990], are located mostly at the uppermost parts of the mantle and/or the lowest parts of the crust sequence (towards the petrological moho). The occurring enrichment in Pt and Pd may be the result of the sulfur saturation and PPGE deposition in relatively small chromite occurrences, in contrast to large chromite deposits in ophiolite complexes, where parent magmas are PGE diluted [Prichard et al. 2008]. The mineralogical associations of Pt with Ni, and Pd with Cu in

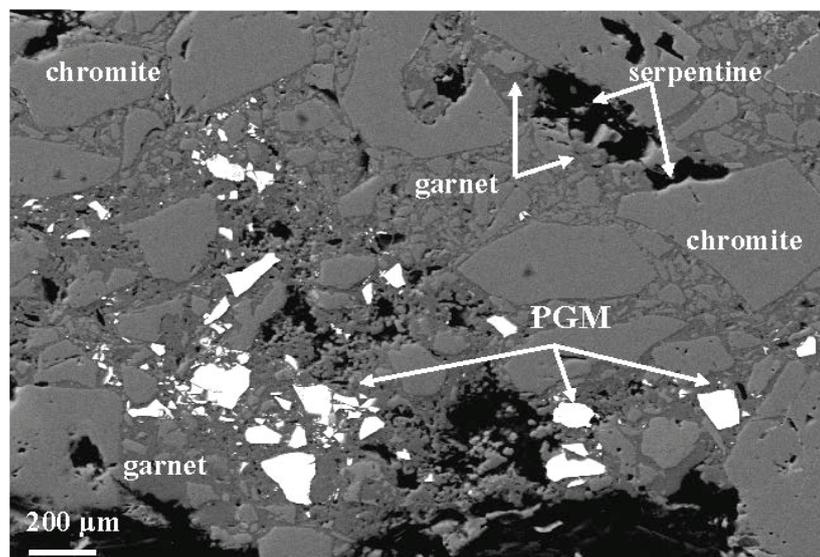


Figure 8

Back-scattered electron (BSE) images of extremely abundant dismembered-fragmented IPGM grains zone. Back-scattered electron (BSE) images of extremely abundant dismembered-fragmented IPGM grains zone, associated with strongly fragmented chromite as well, in a matrix of garnet and lesser amounts of serpentine/chlorite. They are found along a highly shearing zone from the Galaktos area.

the Pindos samples, suggest that the Pt and Pd were collected by the small fraction of base-metal-rich immiscible sulfide liquid and that the Pt collected in the Fe–Ni-rich phase and the Pd with Cu-rich one. The presence of only a small amount of immiscible sulfide liquid led to very high concentrations of Pt and Pd within the sulfide liquid and to the presence of abundant Pt- and Pd-bearing PGM associated with the rare base-metal sulfides [Prichard et al. 2008]. Therefore, the PPGE enrichment can be considered as a sensitive fingerprint for the orientation in the mantle sequence of the ophiolite complexes and hence the exploitation for chromite deposits [Economou-Eliopoulos 1996].

The enrichment in IPGE at Milia is a common feature shown also by the Skyros and Veria chromitite, although the levels of the IPGE exhibit a wide variation [Tsoupas and Economou-Eliopoulos 2005]. Chromitites at Milia, with average $\text{Cr}/(\text{Cr}+\text{Al})$ ratio 0.83 may derived from magma produced by a high degree of mantle melting [Prichard et al. 2008]. However, the $\text{Cr}/(\text{Cr}+\text{Al})$ ratio at the Skyros chromite ores is relatively low (average 0.52) and at Veria it exhibits a wide range (0.5- to 0.85) in a small same, even in the same thin section (Table 1). The wide variation, in both IPGE and PPGE of high-Cr and high-Al ores, through small scale regions (like Pindos, Skyros and Veria) and the highly heterogeneous Os isotopic composition at Cuba [Gervila et al. 2005], may suggest different episodes of partial melting, subduction-related crustal recycling and metasomatism [Ahmed and Arai 2003; Griffin et al. 2003; Walker et al. 2005; Pearson et al. 2007]. Although there is a general acceptance of both the primary magmatic nature of the IPGE-enriched minerals hosted in chromitite and of remobilization of PGE at relatively low temperature during the postmagmatic stage, the relative timing of postmagmatic events and the alteration of the PGM is still uncertain. The IPGE enrichment at Veria, reaching 25 ppm total PGE and resulting in an abundance of PGM grains, may be related to postmagmatic processes covering a long period of deformation, beginning with plastic deformation in the asthenospheric mantle and culminating with brittle deformation in the crust [Tsoupas and Economou-Eliopoulos 2005, 2008]. Among major factors controlling such a wide variability, may be difference as far as: (a) the magmatic sources of the parent magma, (MOR, SSZ or arc regions) during the evolution of the geotectonic environment (b) melt–rock reactions during upwelling basaltic magmas and progressive fractionation of parent magmas [Leblanc 1995; Economou-Eliopoulos 1996; Melcher et al. 1997; Zhou and Robinson 1997; Ahmed and Arai 2003]. The presence of both high-Cr and high-Al chromitites, which

Table 5a
Representative microprobe analyses of IPGM from PGE-rich chromitites of the Veria (Galaktos) area

Mineral	laurite				irarsite					Ir-Os-Ru-alloys/oxides				
	wt%													
Ru	36.05	36.34	39.08	33.13	n.d.	n.d.	3.02	n.d.	4.73	47.45	33.21	7.23	2.79	2.8
Os	24.53	22.24	20.87	29.64	n.d.	n.d.	2.14	n.d.	2.23	29.5	48.09	n.d.	6.19	n.d.
Ir	8.03	6.55	6.02	5.81	62.84	58.32	59.02	58.44	52.11	10.02	8.52	59.71	81.17	64.64
Pt	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3.54	n.d.	n.d.	n.d.	n.d.	6.15	n.d.
Pd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.28	n.d.
Cr	0.81	n.d.	n.d.	n.d.	0.55	1.78	1.27	0.63	n.d.	n.d.	0.77	0.96	n.d.	1.31
Fe	0.29	n.d.	n.d.	n.d.	n.d.	0.99	n.d.	n.d.	0.76	8.11	8.74	22.03	1.39	25.79
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.3	0.76	n.d.	n.d.	1.36
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.54	n.d.	1.71
As	n.d.	n.d.	n.d.	n.d.	23.78	26.88	23.38	26.22	27.64	0.43	n.d.	1.24	n.d.	n.d.
S	30.14	34.77	33.59	29.92	12.47	9.94	11.45	10.72	11.51	0.55	n.d.	n.d.	n.d.	n.d.
Total	99.85	99.9	99.56	98.5	99.64	97.91	100.28	99.55	98.98	97.36	100.09	97.71	99.97	97.61

Table 5b
Representative microprobe analyses of Ph-minerals from PGE-rich chromitites of the Galaktos area

Mineral	sulpharsenide				Rh-arsenides						
	wt%										
Ru	n.d.	2.28	9.02	9.86	25.06	5.81	1.5	n.d.	n.d.	2.03	
Os	n.d.	n.d.	n.d.	n.d.	10.46	n.d.	n.d.	n.d.	n.d.	n.d.	
Ir	9.35	n.d.	n.d.	n.d.	9.16	n.d.	n.d.	n.d.	46.79	25.95	
Rh	41.68	39.51	27.81	25.81	19.27	33.33	39.01	38.03	11.77	10.52	
Pt	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.55	9.06	
Pd	n.d.	n.d.	4.25	6.11	n.d.	2.34	n.d.	5.98	n.d.	n.d.	
Cr	0.45	n.d.	n.d.	n.d.	n.d.	0.68	0.4	n.d.	0.57	n.d.	
Fe	n.d.	0.71	n.d.	n.d.	4.77	0.88	1.15	1.54	15.62	16.45	
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.74	0.73	
Ni	n.d.	23.52	24.72	25.66	11.51	23.64	24.08	20.88	10.08	25.57	
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.99	n.d.	n.d.	
As	35.28	33.63	33.98	31.51	17.31	31.58	30.87	29.58	6.58	8.88	
S	13.43	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Total	100.19	99.65	99.78	98.95	97.54	98.26	97.01	98	97.7	99.19	
Atomic %											
Ru		2.16	7.02	7.72	23.61	4.59	1.22			1.72	
Os					5.23						
Ir	3.61				4.53				25.65	11.59	
Rh	30.03	30.13	21.24	19.85	17.82	25.76	30.98	29.92	12.06	8.76	
Pt									3.01	3.99	
Pd			3.14	4.53		1.76		4.56			
Cr	0.64					1.05	0.63		1.15		
Fe		1.01			8.14	1.26	1.66	2.22	29.47	25.28	
Co									1.33	1.08	
Ni		31.43	33.01	34.58	18.64	32.05	32.69	28.79	18.1	37.39	
Cu								2.54			
As	34.91	35.27	35.64	33.26	22.02	33.46	32.81	31.97	9.23	10.18	
S	31.06										

Symbols: n.d.: below detection limit; F = SEM images of the analysed PGM are shown on the Figure 8

may be PGE-poor and PGE enriched in the Pindos complex [Economou-Eliopoulos and Vacondios 2005] combined with the stable Ga/Fe³⁺+Al+Cr) ratio (~1000) for those ores suggest that magmatic source and fractionation are major factors of their compositional variation rather than melt –rock reactions [Dare et al. 2009].

With respect the origin of coarse-grained platinum-group minerals, reaching values up to a few mm, which have been located in many placer deposits associated with ultramafic-mafic complexes, such as Alaskan and ophiolitic type intrusions is a subject of debate, due to the paucity of coarse-grained PGM in parental mafic-ultramafic complexes. Some authors have suggested that coarse-grained PGM have formed at low-temperature, during the weathering and sedimentation [Augustithis 1965; Bowles et al. 2000]. Others suggested that coarse-grained PGM may have crystallized in late magmatic pegmatitic environments in the mafic/ultramafic complexes [Cabri and Harris 1975; Johan et al. 1990; Johan 2000; Malitch et al. 2003; Hattori et al. 2004; Tolstykh et al. 2005]. In particular, based on the paragenesis of IPGE with silicates it has been suggested that large IPGM-phases, with a grain-size ranging from 400 to 1000 µm, have been formed at temperature from 700 to 850°C [Johan et al. 1991, 2000; Melcher et al. 1997; Tolstykh et al. 2005; Ahmed 2007]. In the case of the extremely large IPGM (1300 µm) at Veria, located exclusively along shear zones of chromitites (Figure 6), it has been suggested that IPGM and accompanying chromite may have re-crystallized during plastic deformation episodes at relatively lower temperatures (800 to 900°C).

Evaluation of PGEs as an economic factor in ophiolite complexes

The geotectonic environments at which noble metals become concentrated are considered to be critical for understanding the PGE mineralization and developing strategies for the chromite and PGEs exploration. The PGE distribution in chromite ores associated with layered intrusion and ophiolites complexes differs as far as the PPGE-enrichment relative to IPGE in the former, suggesting a high fractionation of PGE [Naldrett 2004], in contrast to large chromitites hosted in ophiolite complexes of Greece and elsewhere showing a low ΣPGE content and negligible IPGEs [Economou-Eliopoulos 1996]. The presence of an extremely high PPGE-enrichment in the small chromite occurrences, located towards the petrological moho, such as in Pindos and elsewhere [Prichard et al. 1986; Tarkian and Prichard 1987; Prichard and Lord 1990; Prichard et al. 1994; Tarkian et al. 1996; Ohnenstetter et al. 1999], suggest the presence of only a small amount of immiscible sulfide liquid resulting to very high concentrations of Pt and Pd [Prichard et al. 2008], and can be considered as a sensitive fingerprint for the orientation in the mantle sequence of the ophiolite complexes and hence the exploration for chromite deposits [Economou-Eliopoulos 1996].

The enrichment in IPGE such as the Pindos (Milia), Skyros and Veria in small chromite occurrences has been attributed to different episodes of partial melting, subduction-related crustal recycling and metasomatism [Ahmed and Arai 2003; Griffin et al. 2003; Walker et al. 2005; Pearson et al. 2007]. In particular, the IPGE enrichment at Veria (up to 25 ppm) may be related to postmagmatic processes covering a long period of deformation, at relatively lower temperatures (800 to 900°C), beginning with plastic deformation in the asthenospheric mantle and culminating with brittle deformation in the crust along the permeable shear zones, under appropriate pressure, temperature, redox conditions [Tsoupas and Economou-Eliopoulos 2008]. Thus, the most targeting for PGE locations general in ophiolite complexes may be (a) for the chromitite-IPGM associations exclusively small chromite occurrences along shearing zones of ophiolite complexes, postdating their initial/magmatic PGE deposition, and (b) for PPGE the uppermost parts of the mantle and the lowest crust sequence.

TRANSPORT OF PGE IN HYDROTHERMAL SYSTEMS

The mobilization of PGE by processes involving an aqueous fluid has been well documented. The current state of knowledge of solubility of PGE has been reviewed and applied toward a better understanding of the PGE mineralization in hydrothermal systems [Gammons et al. 1992; Wood 2002; Wilde et al. 2002]. The stable oxidation stages of Pt and Pd in aqueous solution under the most oxidizing conditions are Pt(II) and Pd(II). The Pt and Pd are quite soluble under a range of hydrothermal conditions

(as chloride or hydroxyl species), in hot oxidized brines (as chlorides), and in hot, reduced, sulfur-rich waters (as bisulfide complexes). On the basis of experimental data, it has been concluded that the highest Pt and Pd concentration is attained under both oxidized and acidic conditions and that chloride is the most abundant ligand in hydrothermal solutions, forming strong complexes with Pt and Pd, and it is a potentially important ligand for aqueous transport of these metals [Gammons et al. 1992, Wood 2002]. Also, elements like As, Bi, Sb, Se and Te form very insoluble compounds with PGE.

In hydrothermally altered harzburgite of the Semail ophiolite of Oman, elevated Pt (up to 450 ppb) is associated with silicified and carbonate altered serpentinite (listwaenite), which occurs along Tertiary extensional faults [Wilde et al. 2003]. Also, significant concentrations of PGE (few ppm Pd and Pt) were found in magmatic breccia at the contact between the Bangur intrusion and its ultramafic host, Baula-Nuasahi Complex, India. Based on mineralogical and geochemical data, including oxygen, hydrogen and sulfur isotopes, it has been suggested that the precious metals in the hydrothermal fluids were derived from the magma rather than an external source [Augé and Lerouge 2004]. Platinum and Pd contents in sea-floor massive sulfides and sulfides of Fe-Ni-Cu-Co type in ultramafic parts of ophiolite complexes are very limited [Economou and Naldrett, 1985; Foose et al., 1985]. However, elevated contents (up to 1 wt.% Pt) in marcasite and chalcopyrite from East Pacific Rise, 1000 ppb Pd in sulfide deposits on the mid-Atlantic, and 160 to 1000 ppb Pt in disseminated pyrite and chalcopyrite from brecciated pipeform diabase, underlying the massive ore of the Pindos ophiolite complex (Greece) have been recorded [Economou-Eliopoulos 2005 and references therein].

Characteristics features of the sulfide ores in the Pindos ophiolite complex

A salient feature of the Pindos massive ore from Kondro is the significant contents of Au (up to 3.6 ppm), Ag (up to 56 ppm), high Se contents (up to 1900 ppm), Co (up to 2200 ppm), Mo (up to 310 ppm), Hg (up to 280 ppm) and As up to 150 ppm (Table 6). The ore is mainly comprised of pyrite and chalcopyrite. Bornite, sphalerite, marcasite, covellite and siegenite are found in lesser amounts. Textural relationships indicate that early pyrite, commonly occurring as fractured, large crystals, is extensively replaced by chalcopyrite, and then by bornite in a matrix of quartz. Cu-bearing sphalerite, with up to 3.6 wt.% Fe and 3.2 wt.% Cu, cements minor chalcopyrite and pyrite. Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor sphalerite with an average Cu content of 0.5 wt.%. The latter association, found in cross-cutting veins, hosts selenides (chiefly clausthalite, PbSe), the telluride mineral melonite (NiTe₂), gold, galena and barite. Concentrations of 'invisible Au' in coarse-grained pyrite ranges from 0.7±0.13 to 1.01±0.27 ppm, whereas concentrations in fine-grained pyrite lie between 7.67±1.6 and 5.3±2.7 ppm, accompanied by significant As content [Economou-Eliopoulos et al. 2008]. The Pd content in breccia samples (10 to 27 ppb) is low as compared to that of Pt (160 to 1000 ppb). A significant enrichment in Pt in kaolinite-rich brecciated diabase underlying the Kondro massive ore, and the limited range of δ³⁴S values for pyrite concentrates from the diabase breccia (+1.0 to +1.5‰), are characteristic features [Sideris et al. 1984].

Genetic significance of the platinum and palladium contents

Elevated Pt contents in the mineralized diabase breccia of Pindos compared to massive sulfide ore seems to confirm the higher solubility, and hence further transport, of Au relative to Pt, causing Au enrichment in the massive ore [Pan and Wood 1994]. Thus, assuming that Au and Pt/Pd were derived from the same source area, and that the transporting complexes of these metals are the same [Wood 2002] the concentration of Au in massive sulfide ore and Pt in the underlying diabase breccia may reflect higher solubility of Au that remains more soluble than Pt, and the extent to which these metals are saturated in a given hydrothermal solution. The increasing trend of average Zn, Au, Ag, As, Se, Sb, Mo and Hg contents from the Pindos is similar to that at Mirdita (Albania). They are considered to be [Economou-Eliopoulos et al. 2008] the closest analogues to polymetallic sulfides associated with felsic volcanic rocks at the modern seafloor, and that their formation has taken place during the initial stages of subduction (fore-arc setting).

PGE MINERALIZATION IN PORPHYRY-Cu ALKALINE INTRUSIONS

Introduction

Many giant gold-rich porphyry deposits are generated at convergent margins during or following subduction of lithosphere, in an environment, which may vary from compressional to tensional and shearing [Sillitoe 1997, 2000; Müller and Groves 2000]. The majority of giant gold-rich porphyry deposits are located in the circum-Pacific region and they are commonly emplaced at depths of 1–2 km. Differentiated felsic and volatile-rich intrusions may rise to higher crustal levels, along older fault systems, facilitating the intrusion of porphyry stocks or dikes near surface levels [Sillitoe 2000; Sillitoe and Hedenquist 2003]. 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.% H₂O in the melt. Such hydrous melts may contain metals and ligands of critical significance to the formation of Au-rich porphyry deposits [Sillitoe 2000].

Elevated Pd and Pt contents have been described in the Cordillera of British Columbia (Copper Mountain, Galore Creek), Allard Stock, La Plana Mountains and Copper King Mine in USA, Skouries porphyry deposit, Greece, Elatsite, Bulgaria, and from Santo Tomas II in the Philippines [Werle et al. 1984; Mutschler et al. 1985; El-

Table 6
Geochemical characteristics of sulfide ores hosted in the Pindos ophiolite complex

main minerals	ppb		ppm									wt%		
	Pt	Pd	Ag	Au	Se	As	Mo	Sb	Hg	Ni	Co	Zn	Cu	Fe
<i>Cyprus type</i>														
Kondro: massive ore consisting of pyrite (py), chalcopyrite (cupy), sphalerite (sph), bornite (bn)														
py-cupy	<10	4	56	1.1	170	140	50	9.5	40	180	1400	2.9	6.9	26.9
py-cupy	<10	3	34	1.3	400	150	80	7.1	70	<100	1250	2.6	6.1	21.2
py-cupy-sph	<10	3	38	3.3	1500	90	310	8	170	<100	600	3.2	16.4	26.5
py-cupy-sph	<10	4	32	3.6	1900	64	40	10	280	<100	500	9.8	10.1	22.5
py-bn-cupy	<10	3	39	3.2	850	40	80	2.1	60	<100	2200	1.3	25.4	11.9
py-bn-cupy	<10	5	35	3.4	1100	50	80	1.3	130	<100	870	1.1	19.4	9.5
Aspropotamos (Neropriona): disseminated pyrite (py), chalcopyrite (cupy)														
diabase breccia														
less altered	<10	10		0.011	<5	15	<5	0.3	<1	<100	28	0.007	0.007	6.8
moderately altered	400	20		0.018	<5	25	<5	0.3	<1	<100	27	0.007	0.006	7.1
highly altered	1000	27		0.025	<5	25	<5	0.6	<1	<100	15	0.009	0.007	6.9

iooulos and Economou-Eliopoulos 1991; Piestrzynski et al. 1994; Eliopoulos et al. 1995; Tarkian and Koopmann 1995; Tarkian and Stribny 1999; Economou-Eliopoulos and Eliopoulos 2000; Fig. 9].

Balkan peninsula

Porphyry Cu–(Mo–Au) intrusions located within the metallogenetic belt of the Alpine-Balkan-Carpathian-Dinaride orogenic system (Fig. 9b), of Late Mesozoic to Tertiary age, represent subduction-related magmatism following the change from EW to NS convergence between Africa and Eurasia. Porphyry deposits, extending from Romania to Greece are the most important, and predate the subsequent continental collision and post-collision magmatism. Deposits of Serbia (Majdanpek, Bor and Veliki Krivelj), Bulgaria (ssarel, Elatsite and Medet) and Skouries, Chalkidiki Peninsula in northern Greece belong to the Serbo-Macedonian massif (SMM) [Frei 1995; Heinrich and Neubauer 2002].

Skouries deposit: case history discovery

Geologic framework

The Skouries porphyry Cu–Au deposit, located at the Chalkidiki Peninsula, north-

Figure 9

Distribution of porphyry-Cu±Mo±Au±Pd±Pt deposits, in a global scale.



ern Greece belongs to the SMM. The crystalline basement comprises two lithostratigraphic-tectonic units, the lower Kerdylia Formation and the upper Vertiskos Formation, separated by a NW-striking fault system. The Vertiskos Formation consists of old basement gneiss, amphibolite, schist and marble, Tertiary intrusions, ophiolites (the Therma-Volvi-Gomati). Locations of subvolcanic-porphyrific stocks and volcanic complexes related to porphyry Cu deposits [Kockel et al. 1977; Frei 1995, Tobey et al. 1998; Papanikolaou 1997, 2009] are mainly controlled by deep fracture systems that permitted subvolcanic intrusions to reach higher levels of the crust [Kockel et al. 1977; Frei 1995, Tobey et al. 1998]. Isotope data indicate that subvolcanic-porphyrific stocks such as the Skouries, of Miocene age (18 Ma), are younger than the intrusions of the Serbo-Macedonian massif. The Skouries deposit is related to pipe-like intrusions of subalkaline-alkaline composition, with occasionally inclusions of angular mafic fragments (Fig. 10), extending at surface over an area of approximately 200 m x 200 m. The defined reserves in the porphyry Cu–Au deposit of Skouries are approximately 206 Mt at 0.54 % Cu, and 0.80 ppm Au. Geological data based on recent drilling, provided by TVX Gold Inc Hellas indicated that the Skouries deposit is developed around two related porphyry centers at depths between 650 and 800 m [Tobey et al. 1998]. At least four monzonite porphyries have been described Kroll et al. [2002]. In decreasing age, and increasing degrees of fractionation of the parent magmas, they are: (1) pink monzonite, (2) main monzonite, (3) intra-mineral monzonite, and (4) late-stage porphyry. Highgrade ore is directly associated with the main and intra-mineral monzonite phases. Late-stage monzonite dykes that are barren cut all intrusive phases. The monzonite contains phenocrysts of plagioclase, alkali feldspar and amphibole as well as apatite and titanite microphenocrysts in a fine-grained feldspar-dominated groundmass [Kroll et al. 2002].

Characteristic features of alteration and mineralization

The typical alteration types of the porphyry Cu intrusions described by Lowell and Guilbert [1970] are more or less present in the Skouries intrusion, due to the repeated overprinting and intense silicification, with potassic being the predominant alteration type, whereas the propylitic and surrounding phyllic alteration are limited in extent. Two mineral assemblages of mineralization, occurring as veinlets/disseminations, can be distinguished: (a) magnetite- (reaching up to 10 vol%, average 6 vol%) bornite-chalcocopyrite, linked to pervasive potassic and propylitic alteration type, in the central parts of the deposit, and (b) chalcocopyrite-pyrite, which dominates at the peripheral parts of the deposit.

The Skouries deposit is characterized by relatively high Pd and Pt contents (Table 7). Textural relations between Cu-minerals and the main Pd-bearing mineral, merenskyite, and Au-Ag tellurides, indicate that precious metals are closely associated with

copper vein-type chalcopyrite or bornite, and are deposited during the earliest stages of alteration and mineralization in the central parts of deposits [Figure 11; Tarkian et al. 1991; Kioussis 2005, 2012]. Magnetite is Cr-bearing (0.65 to 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 contains 0.45 to 2.4 wt.% Ni and 0.64 to 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 discovery of palladium and its distribution in the Skouries deposit

In the course of a study of slag from prehistoric or Macedonian gold production in Greece, slag from the Skouries porphyry Cu–Au was found to contain a significant Pd content (40 ppb Pd). The subsequent analysis of representative ore samples showed a



Figure 10

Representative drill core sample of the Skouries Main monzonite porphyry. Representative drill core sample of the Skouries Main monzonite porphyry, showing mineralization (disseminated and vein-type) in angular mafic fragments (stage I), pervasive (stage II), crosscutting relationships between successive quartz veins (stages III and IV) dominated by the magnetite-bornite-chalcopyrite assemblage, and a quartz-biotite vein (stage V), reflecting a range of hydrothermal evolution.

significant Pd-enrichment in mineralised 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 relationships between the Pd–Pt and vein-type Cu mineralization, various alteration types or redistribution by leaching from an early-stage. Relatively high Pd content in the major vein-type mineralization of Skouries ranging between 60 and 200 ppb (average 110 ppb Pd), was documented by analysis of a composite drill hole sample (~15 kg) showing 76 ppb Pd and 5000 ppm Cu [Economou-Eliopoulos and Eliopoulos 2000]. Additional analyses of mineralized material and highly mineralized portions from deeper parts of the deposit (from the potassic, propylitic alteration zone) indicated that there is a relatively high palladium, up to 610 ppb (average 130 ppb) and platinum, up to 150 ppb (average 46 ppb) contents [Table 7, Economou-Eliopoulos and Eliopoulos 2001]. Textural relations between base metal sulfides, PGM and Au–Ag tellurides support the association of precious metals with the Cu-minerals (bornite and chalcopyrite), indicating that the main Pd-bearing mineral merenskyite, was deposited during the major stage of Cu deposition. Assuming that Pd is mainly associated with chalcopyrite in porphyry-copper deposits and calculating the measured Pd contents in chalcopyrite (measured contents are normalized to 100 percent chalcopyrite), then the Pd values in the mineralized samples from deeper parts of the Skouries deposit is 3000 ppb Pd. This content is comparable to that in the chalcopyrite concentrate (2400 ppb Pd to 21 wt.%, and Pt content is 1230 ppb [Economou-Eliopoulos and Eliopoulos 2000].

Native gold and electrum may form intergrowths with Pd–Pt–Bi- and Ag-tellurides, ranging from less than 1 to tens of μm [Tarkian et al. 1991; Tarkian and Koopmann 1995; Tarkian and Stribrny 1999; Kesler et al. 2002; Tarkian et al. 2003]. In addition, gold inclusions in chalcopyrite of the magnetite-bornite-chalcopyrite association tend to be poorer in Ag compared to those (electrum) in the chalcopyrite-pyrite assem-

blages. Subsequent events overprinting early potassic alteration and ore commonly remobilized Cu and Au, resulting in complete destruction of bornite and deposition of new chalcopyrite-pyrite assemblages in which gold is associated with both minerals.

Sources of Metals and Sulfur in Porphyry Copper Deposits

The contribution of mantle, oceanic and continental crust to the parent magmas of porphyry copper intrusions remains still uncertain [Burnham 1979; Burnham and Ohmoto 1980; McInnes and Cameron 1994; Keith et al. 1998; Titley 2001]. Numerous authors have suggested crustal sources for some ore metals in the southern Arizona

Table 7
Precious metal content in flotation concentrate (F.C.) and sulphide concentrate (Sf.C) from porphyry-Cu deposits

Deposit	sample or average	Description	concentration (ppb)			wt%
			Pd	Pt	Au	Cu
Balkan peninsula						
Greece-Skouries						
(a) porphyry	Sk.Po.or (F.C.)	composite	2400	40	22000	21
(b) country rocks	Sk.B.or (F.C.)	composite	75	20	8200	5.6
Bulgaria						
Elatsite	EP1-8	EP(Sf.C) mt-bn-cp	560	160	18700	20.9
Elatsite	n=27	E(Sf.C), cp-py	107	31	3700	10.1
Elatsite	n=3	F.C.	1130	130	16200	23.5
Elatsite	n=18	compact bornite	73	28	12000	
	n=35	chalcocite	n.d.	n.d.	60-1000	
Philippines						
Santo Tomas II	n=3	mt-bn-cp	67	10	3540	0.73
Santo Tomas II	n=2	cp-py	21	20	800	0.2
British Columbia						
Galore Creek	n=2	mt-py-bn-cp	1300	80	64000	17.4
Galore Creek	n=2	cp-py-bn	260	16	4400	12.8
Mt. Milligan	MMSS-1	mt-py-cp	6300	110	18500	6.8
Mt. Polley	88-148	mt-bn-cp-py	320	33	23600	20.6
Ajax	AE-1	cp-py	140	8	990	26.3
Afton	n=60		130		1200	1.5
Allard, La plata	No2	Sf.C (cp)	1920	2880	1230	18
Allard, La plata	No3	F.C.	2320	3935	1740	27
Copper King Mine	n=2	F.C.	2660	900	440	31.5
Copper King Mine	No6	Sf.C (cp), pegmatitic	6430	13600	190	22
Cooper Mountain	n=2	F.C.	2760	190	4800	28.2
Cooper Mountain	No17	Sf.C, bn-cp vein	3250	50	4200	40
Sappho	n=2	Sf (cp), pegmatitic	820	1020	410	5.9

Data from: Mutschler et al.(1985); Tarkian and Stribny (1999); Economou-Eliopoulos & Eliopoulos (2000); Tompson et al.(2001); Dolbear & Company, Ltd (2003);

deposits [Titley 2001]. Evidence from xenoliths, geological, mineralogical, geochemical and isotopic data indicates that the high Pd and Pt mineralization in the porphyry deposits of the British Columbia Cordillera derived probably from an enriched mantle source [McInnes and Cameron 1994]. They may reflect partial melting and incorporation into the melt of destabilized precious metal-bearing Fe-Ni-Cu-sulphides, hosted in the mantle source [Keith et al. 1998; Hattori and Keith 2001]. The occurrence mafic dikes, post-dating the porphyry mineralization at the Elatsite deposit [von Quadt et al. 2002; Strashimirov et al. 2002], and the relatively high Re concentrations (average 1880 ppm) in the molybdenite from main stage stockwork mineralization of the Elatsite Cu-Au deposit, Bulgaria, have been attributed to a direct involvement of mantle in an arc-subduction environment as well [Zimmerman et al. 2003]. Also, the incorporation

of mafic material within the crust, prior to the final emplacement of porphyry, is supported by the presence of mafic fragments within porphyry (Fig. 10) and the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values [Frei 1995; Sillitoe 2000; Müller and Groves 2000; Sotnikov et al. 2000; Tosdal and Richards 2001; von Quadt et al. 2002]. In addition, the enrichment (hundreds ppm) in compatible elements such as Cr, Co±Ni, that occur in the Skouries, Elatsite, Medet, Assarel and Trar Asen porphyry deposits of the Balkan [Eliopoulos et al. 1995; Economou-Eliopoulos 2005], despite their otherwise more evolved geochemical signatures, may indicate a magma mixing with mafic alkaline rocks.

Critical factors for the formation of porphyry Cu+Au+Pd ±Pt deposits

The porphyry Cu±Mo±Au deposits may be developed around single intrusions or within systems that are more complex. Commonly, they are related to multiple and multistage hypabyssal pipe-like intrusions extending at surface over widths ranging from less than 100 m to more than 1 km [Tobey et al. 1998; Müller and Groves 2000; Tosdal and Richards 2001; Kroll et al. 2002]. The wide range of physicochemical conditions and the dynamic interplay between magmatic, hydrothermal and tectonic processes during the formation of porphyry Cu deposits in volcano-plutonic arcs, and the composition of alkaline parent magmas or those of large batholithic bodies underlying at greater depths the porphyry stocks may be major controls of their base/precious metal potential and characteristics. These could include the hydrous and oxidized nature, and their ability to produce hydrothermal systems with ideal chemistry for transporting precious metals. In addition, alkaline magmas are richer in SO_2 and CO_2 than their calcalkaline counterparts are. Also, volatiles that have a significant influence on fluid pressures, brecciation and permeability of host rocks [Mutschler et al. 1985; Corbett and Leach 1998; Eliopoulos and Economou-Eliopoulos 1991; Eliopoulos et al. 1995; Frei 1995; Tarkian and Koopmann 1995; Sillitoe 2000; Müller and Groves 2000; Sotnikov et al. 2000; Strashimirov et al. 2002].

Porphyry Cu-Au-Pd±Pt deposits in the Karpathian-Balkan system show a similarity in terms of their associations with alkaline rocks, in particular those characterized by (a) $\text{SiO}_2 < 65$ wt.%, (b) a major contribution by crust material, as is exemplified by the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values, (c) their association with alkaline or K-rich calc-alkaline systems, characterized by relatively high of REE, Th and halogen (F, Cl) contents (d) the close association of the Cu-minerals with the main Pd-bearing mineral, merenskyite, and Au-Ag tellurides, (e) the association of the elevated Pd, Pt and Au contents with magnetite-bornite-chalcopyrite assemblages, and the pervasive potassic alteration type at the central parts of the deposits, and (f) the transportation of Cu and precious metals, as chloride complexes, by relatively hot (400 to 700°C) and saline to hypersaline (>70 wt.% NaCl equiv) hydrothermal fluids. Thus, critical factors controlling base/precious metal potential of porphyry Cu+Au+Pd±Pt deposits are considered to be the composition of parent magmas (contribution of mantle, oceanic and continental crust) and the physico-chemical conditions during the formation of porphyry Cu deposits. The oxidized nature of parent magmas, as it is exemplified by the abundance of magnetite, may be connected with the ability to produce hydrothermal system with ideal chemistry for transporting precious metal and reflect good exploration target for the precious metals. In contrast, “reduced” porphyry Cu-Au deposits, lacking primary hematite, magnetite, and sulphate minerals (anhydrite), contain abundant pyrrhotite, and are relatively Cu-poor, but Au-rich deposits.

The association, in space and time between porphyry and epithermal deposits may play a major role on the evolution of the whole system and the grade/size of porphyry Cu-Au-Pd-Pt deposits [Werle et al. 1984; Sillitoe 2000; Sillitoe and Hedenquist 2003]. The presence of fluid inclusions hosted by enargite in epithermal deposits, like Chelopech (Bulgaria) and Bor (Serbia), with moderate salinities (4 to 20 wt.% NaCl eq), coupled with the common presence of sericitic roots to lithocaps in general, may suggest that the high-sulfidation ore fluids are affiliated with the sericitic stage of underlying porphyry deposits. Moreover, the Ag/Au ratios may be controlled by the metal endowment of the parent magmas rather than the chloride content of the early sulphide-precipitating fluids [Sillitoe and Hedenquist 2003; Taylor et al. 1994; Müller et al. 2003].

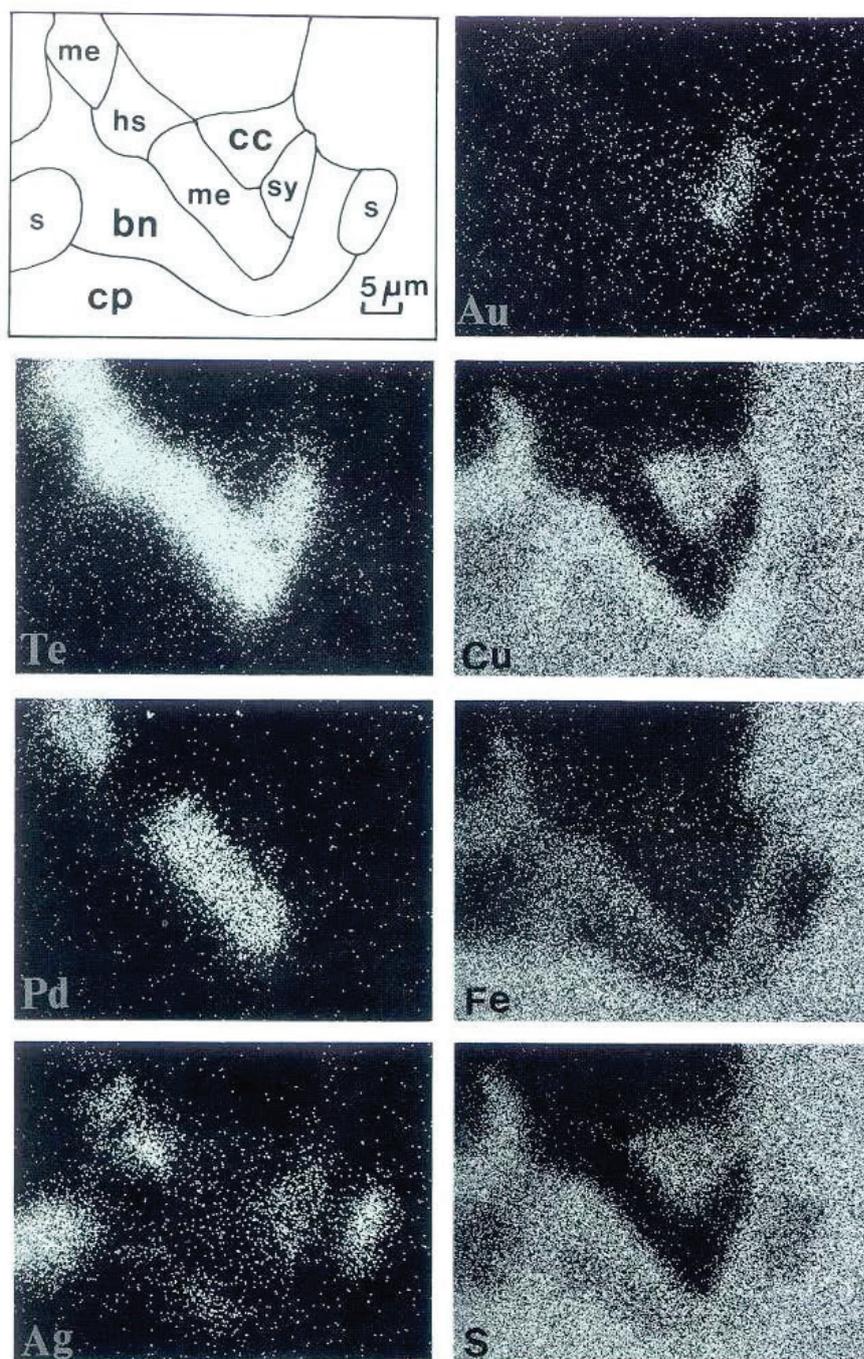
Evaluation of Pd and Pt as an economic factor for porphyry Cu-Au systems

The potential for PGE mineralization associated with such large Cu and Au-Cu por-

phyry deposits is still unknown. The Pd-telluride, merenskyite, which is the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, (Skouries, Elatsite, Medet and Bor/Mad-

Figure 11

Intergrowths of Cu-Fe sulfides and precious metal-tellurides, reflecting the association of the Pd-minerals with Cu-concentrates. Single element scans (Au, Te, Pd, Ag, Cu, Fe and S) for merenskyite, (me), hessite (hs), sylvanite (sy), stromeyerite (s), bornite (bn), chalcopyrite (cp) and chalcocite (cc) [Tarkian et al. 1991].



janpek) occurs mostly as inclusions or at margins of chalcopyrite and bornite (Fig. 11). Relatively high Pd contents in the major vein-type mineralization of Skouries (average 110 ppb Pd) was documented by analysis of a composite drill hole sample (~15 kg), showing 76 ppb Pd to 5000 ppm Cu. Assuming that Pd in porphyry Cu deposits is mainly associated with chalcopyrite (measured contents are normalized to 100 % chalcopyrite), then the average Pd and Pt values (from numerous mineralized samples of the Skouries deposit) are 3000 ppb and 1230 ppb, respectively. Using 206 Mt reserves according to data by TVX [Tobey et al. 1998] and average concentrations (0.5 wt.% Cu, 75 ppb Pd and 17 ppb Pt), then the potential of the Skouries deposit is approximately 15 tons Pd and 3.5 tons Pt. Also, using reserves and average Pd and Pt contents the potential is about 13 tons Pd and 3.7 tons Pt for the Elatsite deposit, 10.5 tons Pd and 1.6 tons Pt for the Santo Tomas II, Philippines deposit, and 10.5 tons [Economou-El-

iopoulos 2005].

A recovery method was applied on chalcopyrite concentrates from the Skouries and other porphyry Cu-Au deposits [Kiouisis et al. 2005; Kiouisis 2012] includes two stages: a) oxidizing roasting of the concentrates at 915°C for 2 h and b) oxidizing leaching of the roasted and grained concentrates at 70°C for 24 h. The leaching was carried out in a spherical reactor, that contains a solution of 500 ml HCl 6 M and H₂-O₂ 0.03

Table 8
Palladium and platinum potential in porphyry-Cu-Au-Pd-Pt deposits

Deposit	Ore tonnage tons x 10 ⁶	Pd	Pt	Pd	Pt
		grade ppm	grade ppm	tonnage tons	tonnage tons
Skouries, Greece	206	0.076	0.017	15	3.5
Elatsite, Bulgaria	185	0.07	0.02	13	3.7
Santo Tommas, Philippines	330	0.032	0.005	10.5	1.6
Afton, B.C.	70	0.13		9	

Data from: Tarkian & Koopmann (1995);Tobey et al., 1998; Economou-Eliopoulos & Eliopoulos; (2000); Strashimirov, et al. (2003); Dolbear and Company (2003)

M, under continuous stirring, and the recovery percentage was more than 85%. Furthermore, based on data from Behre Dolbear and Kvaerner Metals feasibility studies a technico-economical analysis was carried out, and the estimated of the Net Present Value (N.P.V.) was given [Kiouisis and Papavasiliou 2005]. The capacity of a magmatic hydrothermal system in precious metals and the possibility to form economic deposits, combined with the obtained data of the technico-economical approach suggest that the recovery of Pd and Pt, as by-products, the Cu and Au being the main products, may contribute significantly to a N.P.V. increase and improves the economic attractiveness for certain porphyry-Cu deposits.

ENVIRONMENTAL RISK

The mining and smelting operations for PGEs may affect the workers and local population, creating environmental contamination. In addition, traffic emissions and their impact on urban air quality, health, and atmospheric processes has been the subject of increasing interest in recent years [Ely et al. 2001; Dahlheimer et al. 2007]. The increased use of these noble metals in automobile catalyst converters, has led to their release into the environment and biological accumulation on roadsides, since 1974 in USA and 1993 in European countries [Zereini et al.1998; Palacios et al. 2000; Ely et al. 2001; Jarvis et al. 2001; Riga-Karandinos et al. 2006; Croy et al. 2008]. Catalytic converters are used to treat automobile emissions: reduction of nitrogen oxides to nitrogen and oxygen ($2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2$), oxidation of carbon monoxide (toxic) to harmless carbon dioxide ($2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$) and oxidation of unburnt carcinogenic hydrocarbons (HC) to carbon dioxide and water ($2\text{C}_x\text{H}_y + (2x+y/2)\text{O}_2 \rightarrow 2x\text{CO}_2 + y\text{H}_2\text{O}$). However, Pt, Pd and Rh may be released from catalytic converters and their amount and rate is affected by the speed of the automobile, type of engine, type and age of catalyst, and type of fuel additives [Ely et al. 2001; Whiteley and Murray 2003]. The investigation of samples from road dust, soil and grass indicated that greater proportion of PGE emissions is from automobile catalysts, in the form of nanometer-sized catalyst particles. In soil, PGE can be transformed into more mobile species through complexation with organic matter. There are indications that environmentally formed Pd species are more soluble and hence more mobile in the environment than Rh and Pt [Dahlheimer et al. 2007].

Representative dust samples from Katehaki, Messoghion, Iera odos roads and the National high-way road Athens – Thessaloniki of Greece demonstrated that catalytic converter attrition is responsible for elevated abundances and that concentrations of

PGEs increased with traffic density, reaching values up to 2070 ppb Pt and 1980 ppb Pd in dust. Gold, ranging between 14 and 990 ppb (average 310) in dust samples and from 27 and 160 ppb Au (average 95) in soils [Economou-Eliopoulos and Sfondoni 2010]. The PGE level along the highways may be washed by rain and concentrated into local water systems. Also, the determination of the PGE content of different plants grown on contaminated soil close to highways showed a transfer of the PGE from the contaminated soil to the plants. The enrichment of Pd and Pt contents in grasses and tree-leaves (average 5.6 ppb and 3.8 ppb, respectively) along roadsides confirm the aspect that under appropriate pH and redox potential conditions (humic or fulvic acids) they are more mobile [Dahleimer et al. 2007]. The good positive relationship between both Pd and Pt contents in plants with their corresponding contents in soils [Economou-Eliopoulos and Sfondoni 2010] is consistent with their solubility in soils [Wood 1990, 2005; Wood et al. 1994; Rauch and Morrison 2000].

CONCLUSIONS

The platinum-group elements (Os, Ir, Ru, Rh, Pd and Pt) or PGEs, are the most valuable elements in the nature, due to their growing use in advanced technologies and automobile catalyst converters. Also, they provide valuable evidence for the mineralizations associated with ophiolites complexes, such as chromitites and sulfides and the origin of ophiolites themselves, due to differences as far as the geochemical behavior between IPGE (Os, Ir, Ru) and PPGE (Pt, Pd ± Rh), during partial melting in upper mantle and fractionation processes.

The PGE contents in economic chromite deposits such as the Vourinos and Othris ophiolite complexes, which are dominated by high-Cr and high-Al ores, respectively, are low (less than 200 ppb). They are characterized by relatively high IPGE and low PPGE contents, resulting in PGE-patterns with a negative slope, and low Pd/Ir ratio.

Chromite occurrences in the Pindos complex, which are PPGE-enriched, show smooth sloped to positive slope PGE-patterns, comparable and that of the UG2 in the Bushveld complex and high Pd/Ir ratios. The whole ore PGE content is consistent with the dominated Pt- and Pd-bearing PGM, including Pt–Pd alloys, PGM arsenides and sulfarsenides, sperrylite, which were identified exclusively in the serpentinized matrix of chromitite.

The PPGE enrichment in chromitites towards the petrological mocho has been attributed to the presence of only a small amount of immiscible sulfide liquid, and is considered be a sensitive fingerprint for the orientation in the mantle sequence of the ophiolite complexes and hence the exploration for chromite deposits.

The enrichment in IPGE (Os, Ir, Ru), such as the Pindos (Milia), Skyros and Veria in small chromite occurrences, reaching 25 ppm total PGE, may be related to episodes of partial melting and subduction-related crustal recycling, at relatively lower temperatures (800 to 900°C), during a period of deformation, beginning with plastic deformation to brittle deformation in the crust along the permeable shear zones.

The most targeting for PGE locations general in ophiolite complexes may be (a) for the chromitite-IPGM associations exclusively small chromite occurrences along shearing zones of ophiolite complexes, postdating their initial/magmatic PGE deposition, and (b) for PPGE the uppermost parts of the mantle and the lowest crust sequence.

Although the potential for PGE mineralization, associated with such large Cu and Au-Cu porphyry deposits is still unknown, the association of the Pd-telluride, merenskyite, which is the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, with chalcopyrite and bornite, the obtained recovery percentage (~90%) and the estimated value of the Net Present Value suggest that the recovery of Pd and Pt, as by-products (Cu and Au being the main products), may contribute significantly to the economic attractiveness for certain porphyry-Cu deposits.

REFERENCES

- Ahmed, A.H., Arai, S., 2003. Platinum-group minerals in podiform chromitites of the Oman ophiolite. *The Canadian Mineralogist* 41, 597-616.
- Ahmed, A.H. 2007. Diversity of platinum-group minerals in podiform chromitites of the late Proterozoic

- ophiolite, Eastern Desert, Egypt: Genetic implications. *Ore Geology Reviews* 32 (1-2).
- Al-Boghdady and Economou-Eliopoulos, 2005). Fluid inclusions in chromite from a pyroxenite dike of the Pindos ophiolite complex. *Chemie Erde* 65, 191-202.
- Andrews, D.R.A., Brenan, J.M., 2002. Phase-equilibrium constraints on the magmatic origin of laurite + Ru-Os-Ir alloy. *The Canadian Mineralogist* 40, 1705-1716.
- Arndt, N.T., Kerr, A.C., Tarney, J., 1997. Dynamic melting in plume heads: the formation of Gorgona komatiites and basalts. *Earth and Planetary Science Letters* 146, 289– 301.
- Arndt, N.T., Nisbet, E.G., 1982. Komatiites. George Allen and Unwin, London, 1-526.
- Augé, T., 1985. Platinum-group mineral inclusions in ophiolitic chromitite from the Vourinos complex, Greece. *Canadian Mineralogist* 23, 163-171.
- Augé, T., Genna, A., Legendre, O., Ivanov, K.S., Volchenko, Y.A., 2005. Primary platinum mineralization in the Nizhny Tagil and Kachkanar ultramafic complexes, Urals, Russia: a genetic model for PGE concentration in chromite-rich zones. *Economic Geology 100th Anniversary volume*, 707-732.
- Augé, T., Legendre, O., 1994. Platinum-group element oxides from the Pingue ophiolite mineralization, New Caledonia: origin and significance. *Economic Geology* 89, 1451-1468.
- Augé, T., 1988. Platinum-group minerals in the Tiebaghi and Vourinos ophiolitic complexes: genetic implications. *Canadian Mineralogist* 26, 177-192
- Augustithis, S.S., 1965. Mineralogical and geochemical studies of the platinumiferous dunite-birbirite-pyroxenite complex of Yubdo, Birbir, W. Ethiopia. *Chemie der Erde*, 124, 159-196.
- Bacuta G.C., Kay R.W., Gibbs, A.K., Bruce R.L., 1990. Platinum-group element abundance and distribution in chromite deposits of the Acoje Block, Zambales ophiolite complex, Philippines. *Journal of Geochemical Exploration* 37, 113-143.
- Baumgartner P.O., 1985. Jurassic sedimentary evolution and nappe emplacement in the Argolis Peninsula (Peloponnesus, Greece). *Denkschriften der Schweizerischen Naturforschenden Gesellschaft*, 99, 111 pp.
- Barnes, S.-J., Naldrett, A.J., Gorton, M.P., 1985. The origin of the fractionation of the platinum-group elements in terrestrial magmas. *Chemical Geology* 53, 303-323.
- Barnes, S.-J. and Maier, W.D. 2002. Platinum-group element distributions in the Rustenberg Layered Suite of the Bushveld Complex, South Africa. In *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*. Edited by L.J. Cabri, Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume 54, 431-458.
- Barnes, S.-J. and Campell, I.H., 1988. Role of late magmatic fluids in Merensky-type platinum deposits: A discussion. *Geology* 16, 488-491.
- Barnes, S.-J. and Maier, W.D., 1999. The fractionation of Ni, Cu, and the noble metals in silicate and sulphide liquids. In *Dynamic Processes in Magmatic Ore Deposits and Their Application in Mineral Exploration*. Edited by R.R. Keays. Geological Association Canada, Short Course Notes XIII, 69-106.
- Barnes, S.-J. and Maier, W.D., 2002. Platinum-group elements and microstructures of normal Merensky Reef from Impala Platinum Mines, Bushveld Complex. *Journal of Petrology* 43, 103-128.
- Barth, M., Gluhak, T., 2009. Geochemistry and tectonic setting of mafic rocks from the Othris Ophiolite, Greece. *Contributions to Mineralogy and Petrology* 157, 23-40.
- Barth, M.G., Mason, P.R.D., Davies, G.R., Drury, M.R., 2008. The Othris Ophiolite, Greece: a snapshot of subduction initiation at a mid-ocean ridge. *Lithos* 100, 234-254.
- Beccaluva L, Coltorti M, Saccani E, Siena F, 2005. Magma generation and crustal accretion as evidenced by supra-subduction ophiolites of the Albanide-hellenide SubPelagonian zone. *Island Arc* 14, 551-563.
- Bickle, M.J., 1982. The magnesium content of komatiitic liquids. In: N.T. Arndt and E.G. Nisbet (Editors), *Komatiites*. Allen and Unwin, London, 479-494.
- Brenan, J.M., Andrews, D., 2001. High temperature stability of laurite and Ru-Os-Ir alloy and their role in PGE fractionation in mafic magmas. *The Canadian Mineralogist* 39, 341-360.
- Bridges, J.C., Prichard, H.M., Neary C.R., Meireles, C.A., 1994. Platinum-group element mineralization in chromite-rich rocks of Braganca massif, northern Portugal. *Transactions, Institution of Mining and Metallurgy (Section B, Applied Earth Sciences)* 102, 103-113.
- Bockrath, C., Ballhaus, C. and Holzheid, A., 2004. Stabilities of laurite RuS₂ and monosulfide liquid solution at magmatic temperature. *Chemical Geology*, 208, 265-271.
- Bowles, J.F.W., Lyon, I.C., Saxton, J.M. and Vaughan, D.J. 2000. The origin of platinum group minerals from the Freetown intrusion, Sierra Leone, inferred from osmium isotope systematics. *Economic Geology*, 95, 539-548.
- Burnham, C., 1979. Magmas and hydrothermal fluids, in Barnes, H.L. (ed), *Geochemistry of Hydrothermal Ore deposits-second edition*, New York, John Wiley, 71-136.
- Burnham, C. and Ohmoto, H., 1980. Late-stage processes in felsic magmatism, *Mining geology Special Issue*, 8, 1-11.
- Cabri, L.J., 2002. The platinum-group minerals, In: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements*, CIM Special volume 54, 13-129.
- Cabri, L.J. and Harris, D.C. 1976. Zoning in Os-Ir alloys and the relation of the geological and tectonic environment of the source rocks to the bulk Pd:Pt+Ir+Os ratio for placers. *Canadian Mineralogist*, 13, 266-274.
- Cambell, I.H., Naldrett, A.J. and Barnes, S.-J., 1983. A model for the origin of the platinum-rich sulphide horizons in the Bushveld and Stillwater complexes. *Journal of Petrology*, 24, 133-165.
- Cameron, W.E. and Nisbet, E.G., 1982. Phanerozoic analogues of komatiitic basalts. In: E.G. Arndt and

E.G. Nisbet (Editors), Komatiites. Allen and Unwin, London, 29-50.

Cameron, W.E., Nisbet, E.G. and Dietrich, V.J., 1979. Boninites, komatiites and ophiolitic basalts. *Nature* (London), 280, 550-553.

Capedri, S., Toscani, L., Grandi, R., Venturelli, G., Papanikolaou, D., Skarpeles, N.S., 1997. Triassic volcanic rocks of some type-localities from the Hellenides. *Chemie der Erde* 57, 257-276.

Cawthorn, R.G., 1999. The platinum and palladium resources of the Bushveld Complex. *South African Journal of Science*, 95, 481-489.

Cawthorn, R.G., 2001. A stream sediment geochemical re-investigation of the discovery of the platinumiferous Merensky Reef, Bushveld Complex. *J. Geochem. Explor.* 72, 59-69.

Corbert, G.J. and Leach, T.M., 1998. Southwest Pacific rim gold-copper systems: structural, alteration and mineralization. SEG Special publication, 6, p.237.

Cowden, A., Donaldson, M.J., Naldrett, A.J. and Campbell, I.H., 1986. Platinum-group elements and gold in the komatiite-hosted Fe-Ni-Cu sulfide deposits at Kambalda, Western Australia. *Economic Geology* 81, 1226-1235.

Crawford, A.G., Beccaluva, L. and Serri, G., 1981. Tectono-magmatic evolution of the West Philippine-Mariana region and the origin of boninites, *Earth Planet. Sci. Lett.* 54, 346-356.

Crocket, J.H., MacRae, W.E., 1986. Platinum-group element distribution in komatiitic and tholeiitic volcanic rocks from Munro Township, Ontario. *Economic Geology* 81, 1242-1251.

Croy J.A., Mostafa S., Hickman L., Heinrich H., Cuenya R., 2008. Bimetallic Pt-Metal catalysts for the decomposition of methanol: Effect of secondary metal on the oxidation state, activity, and selectivity of Pt. *Applied Catalysis A: General* 350, 207-216.

Dahlheimer, S.R., Neal, C., Fein, A., 2007. Potential Mobilization of Platinum-Group Elements by Siderophores in Surface. *Environmental Science and Technology* 41, 870-875.

Dare, S.A.S, Pearce, J., McDonald, I. and Styles, M. 2009. Tectonic discrimination of peridotites using FO₂-Cr and Ga-Ti-FeIII systematics in chrome-spinel. *Chemical Geology* 261, 199-216.

Dijkstra, A.H., Drury, M.R., Vissers, R.L.M., 2001. Structural Petrology of Plagioclase Peridotites in the West Pthris Mountains (Greece): Melt impregnation in Mantle Lithosphere. *Journal of Petrology* 42, 5-23.

Echeverria, L.M., 1980. Tertiary or Mesozoic komatiites from Gorgona island, Colombia: field relations and geochemistry. *Contributions Mineralogy and Petrology* 73, 253- 266.

Economou, M. 1986. Platinum group elements (PGE) in chromite and sulphide ores within the ultramafic zone of some Greek ophiolite complexes, in: M.J. Gallagher, R.A. Ixer, C.R. Neary, H.M. Prichard (Eds.), *Metallogeny of Basic and Ultrabasic Rocks*, 441- 453.

Economou, M., Dimou, E., Economou, G., Migiros, G., Vacondios, I., Grivas, E., Rassios, A., Dabitzias, S., 1986. Chromite deposits of Greece. Theophrastus Publications, S.A. Athens, Greece, 129-159.

Economou-Eliopoulos, M., 1996. Platinum-group element distribution in chromite ores from ophiolite complexes: implications for their exploration. *Ore Geology Reviews* 11, 363-381.

Eliopoulos, D. G. and Economou-Eliopoulos, M., 1991. Platinum-Group Element and Gold Contents in the Skouries Porphyry-Copper deposit, Chalkidiki Peninsula, N. Greece. *Economic Geology* 86, 740-749.

Eliopoulos, D. G, Economou-Eliopoulos, M., Strashimirov, St., Kovachev, V., Zhelyaskova-Panayotova, M. 1995. Gold, platinum and palladium content in porphyry Cu deposits from Bulgaria: a study in progress. *Geol. Soc. Greece* 5, 712-716.

Economou-Eliopoulos, M. and Eliopoulos, D.G., 2000. Palladium, platinum and gold concentrations in porphyry copper systems of Greece and their genetic significance. *Ore Geology Reviews*, 16, 59-70.

Economou-Eliopoulos, M., Eliopoulos, D.G. and Chyssoulis, S., 2008. A comparison of high-Au massive sulfide ores hosted in ophiolite complexes of the Balkan Peninsula with modern analogues: Genetic significance. *Ore Geology Reviews*, 33, 81-100.

Economou-Eliopoulos, M., 2005. Platinumgroup element potential of porphyry deposits. In: *Exploration for Platinum-group Element Deposits* (J.E. Mungall, ed.). Mineralogical Association of Canada, Short Course 35, 203-246.

Economou-Eliopoulos, M. and Paraskevopoulos G., 1989. Platinum -group elements and gold in komatiitic rocks from the Agrilia Formation, Othrys ophiolite complex, Greece. *Chemical Geology*, 77, 149 - 158.

Economou-Eliopoulos, M., Parry S.J. and Christidis, G., 1997. Platinum-group element (PGE) content of chromite ores from the Othrys ophiolite complex, Greece. In: *Mineral Deposits*, Papunen (ed), Balkema, Rotterdam, 414-441

Economou-Eliopoulos, M. and Sfendoni, Th., 2010. Environmental impact of Pt, Pd, Rh and Au from catalytic converters along roadsides: the case of Attica, Greece . *Proc. of XIX Congress of the Carpathian Balkan Geological Association*, Thessaloniki, Greece, 100, 47-54.

Economou-Eliopoulos M., Tarkian M., Sambanis, G., 1999. On the geochemistry of chromitites from the Pindos ophiolite complex, *Chemie der Erde* 59, 19-31.

Economou, M. and Naldrett, A.J., 1984. Sulfides associated with podiform bodies of chromite at Tsangli, Eretria, Greece. *Mineralium Deposita*, 19, 289-297.

Economou-Eliopoulos, M. and Vacondios I., 1995. Geochemistry of chromitites and host rocks from the Pindos ophiolite complex, northwestern Greece. *Chemical. Geology*, 122, 99-108.

Ely, J.C., Neal, C.R., Kulpa, C.F, Schneegurt, M.A., Seidler, J.A., Jain, J.C., 2001. Implications of platinum-group element accumulation along U.S. roads from catalytic-converter attrition. *Environmental Science and Technology* 35, 3816 -3822.

Ferrière, J., 1982, Paléogéographies et tectoniques superposées dans les Hellénides internes: Les massifs

de l'Othrys et du Pelion: Société Géologique du Nord, 8, 970 p.

Ferrière, J., Reynaud, J.-Y., Pavlopoulos, A., Bonneau, M., Migiros, G., Chanier, F., Proust, J.-., Gardin, S., 2004. Geological evolution and geodynamic controls of the Tertiary intermontane piggy-back Meso-Hellenic Basin, Greece: Bulletin de la Société Géologique de France, 175, 361–381.

Foote, M.P., Economou, M., and Panayotou, A., 1985. Compositional and mineralogic constraints in the Limassol Forest portion of the Troodos ophiolite complex, Cyprus. *Mineralium Deposita*, 20, 234–240.

Frei, R., 1995. Evolution of Mineralizing Fluid in the Porphyry Copper System of the Skouries Deposit, Northern Chalkidiki (Greece): Evidence from combined Pb-Sr and Stable Isotope Data. *Economic Geology*, 90, 746-762.

Gammons, C.H., Bloom, M.S. and Yu, Y., 1992. Experimental investigation of the hydrothermal geochemistry of platinum and palladium: I Solubility of platinum and palladium sulphide minerals in NaCl/H₂SO₄ solutions at 300°C. *Cosmochemica et Cosmochemica Acta*, 56, 3881-3894.

Gansser, A., Dietrich, V.J., Cameron, W.E., 1979. Paleogene komatiites from Gorgona island. *Nature* 278, 545– 546.

Garuti, G., Zaccarini, F., 1997. In situ alteration of platinum-group minerals at low temperature evidence from serpentinized and weathered chromitites of the Vourinos complex (Greece). *The Canadian Mineralogist* 35, 611-626.

Garuti, G., Zaccarini, F., Economou-Eliopoulos, M., 1999. Paragenesis and composition of laurite from the chromitites of Othrys (Greece): implications for Os-Ru fractionation in ophiolitic upper mantle of the Balkan peninsula. *Mineralium Deposita* 34, 312-319.

Gervilla, F., Proenza, J.A., Frei, R., González-Jiménez, J.M., Garrido, C.J., Melgarejo, J.C., Meibom, A., Díaz-Martínez, R., Lavaut, W., 2005. Distribution of platinum-group elements and Os isotopes in chromite ores from Mayarí-Baracoa Ophiolitic Belt (eastern Cuba). *Contributions to Mineralogy and Petrology* 150, 589-607.

Gilg, H., 1993. Geochronology (K-Ar), fluid inclusion, and stable isotope (C,H,O) studies of skarn, porphyry copper and carbonate-hosted Pb-Zn(Ag,Au) replacement deposits in the Kassandra mining district (Eastern Chalkidiki, Greece). Ph.D. Thesis, University of München, p. 153.

Grammatikopoulos, T.A., Kapsiotis, A., Zaccarini, F., Tsikouras, B., Hatzipanagiotou, K., Garuti, G., 2007. Investigation of platinum-group minerals (PGM) from Pindos chromitites (Greece) using hydroseparation concentrates: *Minerals Engineering*, 20, 1170-1178.

Griffin, W.L., O'Reilly, S.Y., Natapov, L.M. and Ryan, C.G., 2003, The evolution of lithospheric mantle beneath the Kalahari Craton and its margins: *Lithos* 71, 215–241.

Grivas, E., Rassios, A., Konstantopoulou, G., Vacondios, I., Vrachatis, G., 1993. Drilling for “blind” podiform chrome orebodies at Voidolakkos in the Vourinos ophiolite complex, Greece. *Economic Geology* 88, 461-468.

Halter, W.E., Pettke, Th. and Heinrich, Ch. A., 2002. The origin of Cu/Au Ratios in Porphyry-Type Ore Deposits. *Science*, 296, 1944-1846.

Hattori, K.H., and Keith, J.D., 2001. Contribution of mafic melt to porphyry copper mineralization: evidence from Mount Pinatubo, Philippines, and Bingham deposit, Utah. *Miner Deposita* 36, 799-806.

Hattori, K.H., Cabri, L.J., Johanson, B. and Zientek, M.L., 2004. Origin of placer laurite from Borneo. Se and As contents, and S isotopic compositions. *Mineralogical Magazine*, 68(2), 353–368

Heinrich, C.A., and Neubauer, F., 2002. Cu-Au-Pb-Zn-Ag metallogeny of the Alpine - Balkan - Carpathian - Dinaride geodynamic province: *Mineralium Deposita*, 37, 533–540.

Herzberg, C.T., 1995. Generation of plume magmas through time: an experimental perspective. *Chemical Geology* 126, 1–18.

Herzberg, C., Asimow, P.D., Arndt, N., Niu, Y., Leshner, C.M., Fitton, J.G., Cheadle, M.J., Saunders, A.D., 2007. Temperatures in ambient mantle and plumes: constraints from basalts, picrites, and komatiites. *Geochemistry, Geophysics, Geosystems* 8. (doi:10.1029/2006GC001390).

Hynes, A.J., 1972. The geology of part of the western Othrys mountains, Greece. Unpublished Ph.D. thesis, University of Cambridge, U.K., 220 pp.

Jarvis K.E., Parry S.J., Piper J.M., 2001. Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. *Environmental Science and Technology* 35, 1031 –1036.

Jensen, E.P. and Barton, M.D., 2000. Gold deposits related to alkaline magmatism. *SEG Reviews*, 13, 279-314.

Johan, Z., 1986. Chromite deposits in the massif du Sud ophiolite, New Caledonia: Genetic considerations. In Petraschek, W., Karamata, S., Kravchenko, G., Johan, Z., Economou, M. and Engin, T. (Eds.), *Metallogeny of Ophiolites, UNESCO IGCP 197 Project: Athens, Theophrastus*, 311-339.

Johan, Z., Slansky, E. and Kelly, D.A., 2000. Platinum nuggets from the Kompian area, Enga, Province. Papua New Guinea: Evidence for an Alaskan-type complex. *Mineralogy Petrology*, 68, 159-176.

Kapsiotis, A., Grammatikopoulos, T.A., Zaccarini, F., Tsikouras, B., Garuti, G., Hatzipanagiotou K., 2006. PGM characterization in concentrates from low grade PGE chromitites from the Vourinos ophiolite complex, northern Greece: *Transactions of the Institution of Mining and Metallurgy, Section B-Applied Earth Science* 115, 49–57.

Kapsiotis, A., Grammatikopoulos, T., Tsikouras, B., Hatzipanagiotou, K., Zaccarini, F., Garuti, G., 2009. Chromian spinel composition and Platinum-group element mineralogy of chromitites from the Milia area, Pindos ophiolite complex, Greece: *The Canadian Mineralogist*, 47, 1037-1056.

Keays, R.R., 1982. Palladium and iridium in komatiites and associated rocks: application to petrogenetic

problems. In: Arndt, N.T., Nisbet, E.G. (Eds.), George Allen and Unwin, London, 435–458.

Keays, R.R., 1995. The role of komatiitic and picritic magmatism and saturation in the formation of ore deposits. *Lithos*, 34, 1-18.

Keith, J.D., Christiansen, E.H., Maughan, D.T. and Waite, K.A., 1998. The role of mafic alkaline magmas in felsic porphyry-Cu and Mo systems. *Mineralogical Association of Canada Short Course Series*, 26, 211-243.

Kesler, S.E., Chryssoulis, S.L. and Simon, G., 2002. Gold in porphyry copper deposits: its abundance and fate. *Ore Geology Reviews*, 21, 103-124.

Kiouis, G., Economou-Eliopoulos, M., Paspaliaris, J. and Mitsis, J., 2005. Gold, palladium and platinum recovery, as by-product, from the Skouries porphyry Cu-Au deposit at Chalkidiki area, N. Greece – preliminary results. In: 8th SGAMeeting, Mao, J. and Bierlein, F.P. (Eds), "Mineral Deposits Research Meeting the Global Challenge" Beijing, August 18-21, 991-994.

Kiouis, G., 2012. Research on the origin of precious and other metals in porphyry Cu-Au-Pd-Pt deposits – sustainable development. PhD Thesis. In greek with English abstract, p. 249.

Kiouis, G. and Papavasiliou, K., 2005. The sustainable development of the Skouries porphyry Cu-Au deposit at Chalkidiki. A new preliminary integrated techno-economical approach and the case of platinoids. *Procceed. 2nd Meeting Society of Economic Geology of Greece, Thessaloniki, October 2005* (in greek with English abstract), 163-171.

Kockel, F., Mollat, H., Walther, H., 1977. Erläuterung zur geologischen Karte der Chalkidiki und angrenzender gebiete . 1:100,000 Nord Griecheland , Hannover, Germany, p. 199.

Konstantopoulou, G. and Economou-Eliopoulos, M., 1991. Distribution of Platinum-group Elements and Gold in the Vourinos Chromitite Ores, Greece. *Economic Geology* 86, 1672 - 1682.

Kostopoulos, D.K. 1989. Geochemistry, Petrogenesis and Tectonic Setting of the Pindos ophiolite, NW Greece. Ph.D. thesis, Univ. of Newcastle, Newcastle, U.K.

Koukouzas, C.N., Kouvelos, C.J., 1973. Mineral wealth investigation of Imathia's district (Macedonia). IGME, Athens Internal Report (in Greek) No 6, p. 207.

Koutsovitis, P., Mugganas, A. and Ntaflou, Th. 2012. Rift and intra-oceanic subduction signatures in the Western Tethys during the Triassic: The case of ultramafic lavas as part of an unusual ultramafic-mafic-felsic suite in Othris, Greece *Lithos* 177–193.

Kroll, T., Müller D, Seifert, T. Herzig, P.M. and Schneider, A., 2002. Petrology and Geochemistry of the shoshonite-hosted Skouries porphyry Cu-Au deposit, Chalkidiki, Greece. *Mineralium Deposita* 37, 137-144.

Leblanc, M., 1995. Chromitite and ultramafic rock compositional zoning through a paleotransform fault, Proust, New Caledonia. *Economic Geology* 90, 2028-2039.

Lee, C.A. and Tredoux, M., 1986. Platinum-group element abundances in the Lower and the Lower Critical Zones of the Eastern Bushveld Complex. *Economic Geology*, 81, 1087-1095.

Lowell, L.D. and Guibert, J.M., 1970. Lateral and vertical alteration mineralization zoning in porphyry ore deposits. *Economic Geology*, 65, 535-550.

McElduff, B., Stumpfl, E.F., 1990. Platinum-Group Minerals from the Troodos Ophiolite, Cyprus. *Mineralogy Petrology* 42, 211-232.

Malitch, K.N, Junk, S.A, Thalhammer, O.A.R., Knauf, V.V., Pernika, E., Stumpfl, E.F., 2003. Laurite and ruarsite from podiform chromitites at Kraubath and Hochgrossen, Austria: New insights from osmium isotopes. *Canadian Mineralogist* 41, 331-352.

Matveev, S. and Ballhaus, C. 2002. Role of water in the origin of podiform chromitite deposits. *Earth and Planetary Science Letters* 203, 235–243.

McInnes, B.I.A. and Cameron, E.M., 1994. Carbonated, alkaline hybridizing melts from a sub-arc environment: Mantle wedge samples from the Tabar-Lihir-Tanga-Feni arc, Papua New Guinea, *Earth and Planetary Science Letters* 122, 125-141.

Melcher, F., Grum, W., Simon, G., Thalhammer, T.V., Stumpfl, E., 1997. Petrogenesis of the ophiolitic giant chromite deposit of Kempirsai, Kazakhstan: a study of solid and fluid inclusions in chromite. *Journal of Petrology* 10, 1419-1458.

Mercier, J., 1966, I -Etudes géologiques des zones internes des Hellénides en Macédoine centrale (Grèce), II –Contribution à l'étude du métamorphisme et de l'évolution magmatique des zones internes des Hellénides [Thèse de doctoratès sciences]: Université de Paris, *Annales Géologiques des Pays Helléniques*, 20, 792 p.

Moudrakis, D., 1992. Introduction to the geology of Macedonia and Trace: aspects of the geotectonic evolution of the Hellenides. *Bull Geol Soc Greece* 30, 31–46.

Mountrakis, D., 1987. The Pelagonian Zone in Greece. A polyphase deformed fragment of the Cimmerian Continent and its role in the geotectonic evolution of the Mediterranean. *J Geol* 94, 335–347.

Müller, D. and Groves, D.I., 2000. Potassic igneous rocks and associated gold-copper mineralization (3rd ed). Springer, Berlin Heidelberg, New York, p. 252.

Müller, D., Pettke, T. and Heinrich, C.A., 2003. Characteristic features of alkaline rocks hosting the Ladolam gold deposit, Lihir Island, Papua New Guinea. 7th Biennial SGA meeting "Mineral Exploration and Sustainable Development" August 24–28, Athens, Greece, *Abs. Vol., Eliopoulos et al. (eds)*, 347-350.

Mutschler, F.E. Griffin, M.E., Scott, S.D. and Shannon, S.S., 1985. Precious metal deposits related to alkaline rocks in the north American Cordillera — an interpretive review. *Geol. Soc. S. Afr. Trans.* 88, 355–377.

Meyer, C. and Hemley, J.J., 1967. Wall rock alteration. In Barnes, H.L. (Ed) *Geochemistry of hydrothermal deposits*, New York, Holt, Rinehart and Winston, 166-235.

- Mutschler, F.E., Griffin, M.E., Scott, S.D., Shannon, S.S., 1984. Precious metal deposits related to alkaline rocks in the north American Cordillera — an interpretive review. *Geol. Soc. S. Afr. Trans.* 88, 355–377.
- Naldrett, A.J., Duke, J.M., 1980. Pt metals in magmatic sulfide ores. *Science* 208, 1417–1424.
- Naldrett, A.J., 2004. *Magmatic sulfide deposits—Geology, geochemistry, and exploration*: Berlin, Springer-Verlag, 727 p.
- Nicolas, A., 1989. *Structural of ophiolites and Dynamics of Oceanic Lithosphere*. Kluwer Academic Publishers, 367 pp.
- Nisbet, E.G., Cheadle, M.J., Arndt, N.T., Bickle, M.J., 1993. Constraining the potential temperature of the Archaean mantle: a review of the evidence from komatiites. *Lithos* 30, 291–307.
- Nesbitt, R.W., Sun, S.-S., Purvis, A.C., 1979. Komatiites: geochemistry and genesis. *Canadian Mineralogist* 17, 165–186.
- Ohnenstetter, M., Johan, Z., Cocherie, A., Fouillac, A.M., Guerrot, C., Ohnenstetter, D., Chaussidon, M., Rouer, O., Makovicky, E., Makovicky, M., Rose-Hansen, J., Karup-Møller, S., Vaughan, D., Turner, G., Patrick, R.A.D., Gize, A.P., Lyon, I., McDonald, I., 1999. New exploration methods for platinum and rhodium deposits poor in base-metal sulphides. NEXTRIM. *Transactions, Institution of Mining and Metallurgy (Section B, Applied Earth Sciences)* 108, B119–B150.
- Pan, P., Wood, S.A., 1994. Solubility of Pt and Pd sulfides and metals in aqueous bisulfide solutions. II Results at 200 °C to 350 °C and saturated vapour pressure. *Mineralium Deposita* 29, 373–390.
- Pearce, J.A., Lippard, S.J., Roberts, S., 1984. Characteristics and tectonic significance of supra-subduction zone ophiolites. *Special Publication — Geological Society of London* 16, 77–94.
- Palacios MA, Moldovan M, Gomez MM., 2000. The automobile catalyst as an important source of PGE in the environment. In: Zereini F, Alt F, editors. *Anthropogenic platinum group element emissions and their impact on man and environment*. Berlin: Springer, 3–14.
- Pearson, D.G., Parman, S.W. and Nowell, G.M. 2007. A link between large mantle melting events and continent growth seen in Osmium isotopes. *Nature*, 449, 202–205.
- Pelletier, L. Vils, F., Kalt, A. and Gméling, K. 2008. Li, B and Be Contents of Harzburgites from the Dramala Complex (Pindos Ophiolite, Greece): Evidence for a MOR-type Mantle in a Supra-subduction Zone Environment *J. Petrology* 49 (11), 2043–2080.
- Papanikolaou, D., 1997. The tectonostratigraphic terranes of the Hellenides. *Annales Géologiques des Pays Helléniques* 27, 495–514.
- Papanikolaou, D., 2009. Timing of tectonic emplacement of the ophiolites and terrane paleogeography in the Hellenides. *Lithos* 108, 262–280.
- Paraskevopoulos, G. and Economou, M., 1986. Komatiite-type ultramafic lavas from the Agrilia Formation, Othrys ophiolite complex, Greece. *Ophioliti* 11 (3), 293–304.
- Paraskevopoulos, G. and Economou-Eliopoulos M., 1997. Geochemistry and geotectonic setting of basaltic rocks from the Othrys ophiolite complex. *Annales Géologiques des Pays Helleniques*, 37, 611–612.
- Peck D.C., Keays R.R., 1990. Geology, geochemistry, and origin of platinum-group elements occurrences in the Heazlewood River complex, Tasmania. *Economic Geology* 85, 765–93.
- Pe-Piper, G., 1998. The nature of Triassic extension-related magmatism in Greece; evidence from Nd and Pb isotope geochemistry. *Geological Magazine* 135, 331–348.
- Pe-Piper, G., Tsikouras, B. and Hatzipanagiotou, K., 2004. Evolution of boninites and island-arc tholeiites in the Pindos ophiolite, Greece. *Geol. Magazine* 141, 455–469.
- Piestrzynski, A., Schmidt, S. and Franco, H., 1994. Pd-minerals in the Santo Tomas II porphyry copper deposit, Tuba Benguet, Philippines. *Mineralogia Polonica*, 25 (2), 12–31.
- Prichard H. M. and Lord, R. A., 1990. Platinum and palladium in the Troodos ophiolite complex, Cyprus: *Canadian Mineralogist*, 28, 607–617.
- Prichard, H.M. and Tarkian, M., 1988. Pt and Pd minerals from two PGE- rich localities in the Shetland ophiolite complexes. *Canadian Mineralogist*. 26, 4, 979–990.
- Prichard, H. M., Ixer, R. A., Lord, R. A., Maynard, J and Williams, N., 1994. Assemblages of platinum-group minerals and sulphides in silicate lithologies and chromite-rich rocks within the Shetland ophiolite. *Canadian Mineralogist* 32 (2), 271–294.
- Prichard H.M., Neary C.R. and Potts P.J., 1986. Platinum-group minerals in the Shetland ophiolite complex. In *Metallogenesis of basic and ultrabasic rocks*. Gallagher M.J., Ixer R.A., Neary C.R. and Prichard H.M. eds. (Inst. Min. Metal. Symposium volume, Edinburgh, 395–414.
- Prichard, H., Economou-Eliopoulos, M. and Fisher, P.C., 2008. Contrasting Platinum-group mineral assemblages from two different podiform chromitite localities in the Pindos ophiolite complex, Greece. *Canadian Mineralogist*. 46/2, 329–341.
- Rassios, A., and Dilek, Y., 2009, Rotational deformation in the Jurassic Mesohellenic ophiolites, Greece, and its tectonic significance: *Lithos*, 108, 192–206.
- Rassios, A., Grivas, E., and Vacondios, I., 1994, The geometry of structures forming around the ductile-brittle transition in the Vourinos-Pindos-Othris oceanic slab: *Bulletin of the Geological Society of Greece*, 30 (2), 109–121.
- Rassios, A., and Moores, E., 2006, Heterogeneous mantle complex, crustal processes, and obduction kinematics in a unified Pindos-Vourinos ophiolite slab (northern Greece), in Robertson, A.H.F., and Mountrakis, D., eds., *Tectonic development of the Eastern Mediterranean region*: Geological Society, London, Special Publications 260, 237–266.
- Rassios, A., and Smith, A.G., 2000, Constraints on the formation and emplacement of western Greek

- ophiolites (Vourinou, Pindos and Othris) inferred from deformation structures in peridotites, in Dilek, Y., Moores, E.M., Ethon, D., and Nicolas, A., eds., *Ophiolites and oceanic Crust: New Insight from Field Results and Ocean Drilling Program: Geological Society of America, Special Paper*, 349, 473–483.
- Rauch S, Morrison GM., 2000. Routes for bioaccumulation and transformation of platinum in the urban environment. In: Alt F, Zereini F, editors. *Anthropogenic Platinum-Group-Element emissions and their Impact on Man and Environment*. Berlin, Springer Verlag.
- Riga-Karandinos, A.N., Saitanis, C. and Arapis, G., 2006. First study of anthropogenic platinum-group elements in Roadside top-soils in Athens, Greece. *Water, Air and Soil Pollution* 172, 3-20.
- Robertson A.H.F., 2012. Late Paleozoic tectonic development of Greece and Albania in the context of alternative reconstructions of Tethys in the eastern Mediterranean region. *Int Geol Rev* 54(4), 373–454
- Sassani, D.C. and Shock, E.L., 1990. Speciation and solubility of palladium in aqueous magmatic-hydrothermal solutions. *Geology* 18, 925-928.
- Saccani E, Photiades A, 2004. Mid-ocean Ridge and supra-subduction affinities in the Pindos ophiolites (Greece): implications for magma genesis in a fore-arc setting. *Lithos* 73, 229–253
- Saccani E, Photiades A, Padoa, E., 2003. Geochemistry, petrogenesis and tectono-magmatic significance of volcanic and subvolcanic rocks from the Koziakas Me'lange (Western Thessaly, Greece). *Ofoliti*, 28, 43–57.
- Saccani E, Beccaluva L, Coltorti M, Siena F, 2004. Petrogenesis and tectono-magmatic significance of the Albanide-Hellenide subpelagonian ophiolites. *Ofoliti*, 29 (1), 75–93.
- Saccani E, Photiades A, Beccalkuva, L., 2008. Petrogenesis and tectonic significance of Jurassic IAT magma types in the Hellenide ophiolites as deduced from the Rhodiani ophiolites (Melagonian zone, Greece). *Lithos* 104, 71–84.
- Saccani E, Beccaluva L, Photiades A, Zeda, O., 2011. Petrogenesis and tectono-magmatic significance of basalts and mantle peridotites from the Albanian-Greek ophiolites and sub-ophiolitic me'langes. New constraints for the Triassic-Jurassic evolution of the Neo-Tethys in the Dinaride sector. *Lithos*, 124, 227–242.
- Sideris, C., Skounakis, S., Laskou, M., Economou, M., 1984. Brecciated pipeform diabase from the Pindos ophiolite complex. *Chemie der Erde* 43, 189–195.
- Sillitoe, R.W., 1979. Some Thoughts on Gold-Rich Porphyry Copper Deposits. *Mineralium Deposita*, 14, 161-173.
- Sillitoe, R.H., 1997. Characteristics and controls of the largest porphyry copper-gold and epithermal gold deposits in the circum-Pacific region. *Aust J Earth Sci* 44, 373–388.
- Sillitoe, R.H., 2002. Gold-rich porphyry deposits: Descriptive and Genetic models and their role in exploration and discovery. *SEG Reviews*, 13, 315-345.
- Sillitoe, R.H. and Hedenquist, J., 2003. Linkages between volcanotectonic setting, ore-fluid compositions and epithermal precious metal deposits. *Society of Economic Geologist, Special Publication*, 10, 315-345.
- Sillitoe, R.H., 2000. Gold-rich porphyry deposits: Descriptive and Genetic models and their role in exploration and discovery. *SEG Reviews*, 13, 315-345.
- Smith, A.G., Hynes, A.J., Menzies, A.J., Nisbet, E.G., Price, I., Welland, M.J.P., and Ferrière, J., 1975. The stratigraphy of the Othris Mountains, eastern central Greece: *Eclogae Geologicae Helveticae*, 68, 463–481.
- Sotnikov, V.I., Berzina, A.N., Economou-Eliopoulos, M. and Eliopoulos, D.G., 2000. Palladium, platinum and gold distribution in porphyry Cu±Mo deposits of Russia and Mongolia. *Ore Geology Reviews* 16, 59-70.
- Stockman H.W., Hlava P.F., 1984. Platinum-group minerals in alpine chromitites from southwestern Oregon. *Economic Geology* 79, 491-508.
- Strashimirov, S., Petrunov, R. and Kanazirski, M., 2002). Mineral associations and evolution of hydrothermal systems in porphyry copper deposits from the Central Srednogorie zone (Bulgaria): *Mineralium Deposita*, 37, 587–598.
- Strashimirov S., Bogdanov, K, Popov, K. and Kehanov, R., 2003. Porphyry Systems of the Panagyurishte Ore Region. In *Cretaceous Porphyry-Epithermal Systems of the Srednogoric Zone, Bulgaria.*, Bogdanov, K. and Strashimirov, S. (Eds) *Guidebook Series*, 36, SEG.
- Strasimirov, S., Kovachev, V., 1982. Temperatures and ore formation in Cu-deposits from Srednogorie zone, based on fluid inclusion studies of minerals. *Rev. Bulg. Geol. Soc.* LIII 2 , 1–12.
- Sun, S. S., and Nesbitt, R. W., 1978. Petrogenesis of Archean ultrabasic and basic volcanics: evidence from rare earth elements.: *Contrib. Mineral. Petrol.*, 65, 301-325.
- Tarkian M. and Stribny B., 1999. Platinum-group elements in porphyry copper deposits: a reconnaissance study. *Mineralogy and Petrology* 65, 161-183.
- Tarkian, M., Economou-Eliopoulos, M. and Eliopulos, D., 1992. Platinum-group minerals and tetraauric-uprite in ophiolitic rocks of the Skyros island, Greece. *Mineralogy and Petrology* 47, 55-66.
- Tarkian, M., Economou-Eliopoulos, M., Sambanis, G., 1996. Platinum-group minerals in chromitites from the Pindos ophiolite complex, Greece. *Neues Jahrbuch für Mineralogie Monatshefte*, 145-160.
- Tarkian, M., Eliopoulos, D.G. and Economou-Eliopoulos, M., 1991. Mineralogy of precious metals in the Skouries porphyry copper deposit, N. Greece. *Neues Jahrbuch für Mineralogie Abhandlungen*, 12., 529-537.
- Tarkian, M., Hunken, U., Tokmakchieva, M. and Bogdanov, K. 2003. Precious-metal distribution and fluid-inclusion petrography of the Elatsite porphyry copper deposit, Bulgaria. *Miner. Deposita*, 38, 261-281.
- Tarkian, M., Koopmann, G., 1995. Platinum-group minerals in the Santo Tomas II Philex porphyry copper-gold deposit, Luzon Island, Philippines. *Mineralium Deposita* 30, 39–47.
- Tarkian, M., Prichard H.M., 1987. Irarsite-hollingworthite solid-solution series and other associated Ru-, Os-, Ir-, and Rh-bearing PGMs from the Shetland ophiolite complex. *Mineralium Deposita* 22, 178-184.

- Taylor, W.R., Rock, N.M.S., Groves, D.I., Perring, C.S. and Golding, S.D., 1994. Geochemistry of Archean shoshonitic lamprophyres from the Yilgarn Block, Western Australia: Au abundance and association with gold mineralization. *Applied Geochemistry*, 9, 197-222.
- Thompson, J.F.H., Lang, J.R. and Stanley, C.R., 2001. Platinum group elements in alkaline porphyry deposits, British Columbia. *Exploration and Mining in British Columbia, Mines Branch, Part B*, 57-64.
- Titley, S.R. 2001. Crustal Affinities of Metallogenesis in the American Southwest. *Economic Geology*, 96, 1323-1342.
- Tobey, E., Schneider, A., Alegria, A., Olcay, L. Perantonis, G. and Quiroga, J. 1998. Skouries porphyry copper-gold deposit, Chalkidiki, Greece. In: Porter TM (ed) *Porphyry hydrothermal Cu-Au deposits. A global perspective* Australian Mineral Foundation Conference Proceedings. Glenside, South Australia, 159-168.
- Tolstikh, N. D., Sidorov, E.G., Krivenko, A.P., 2005. Platinum-group element placers associated with Ural-Alaska type complexes. *Mineralogical Association of Canada Short Course*, 35, 113-143.
- Tompouglou, C., 1981. Les mineralisations Tertiaires, type cuivre porphyrique, du massif Serbo-Macedonien (Macedoine Greece) dans leur contexte magmatique (avec un traitement geostatistique pour les donnees due prospect d' Alexia). Rh.D thesis presented at the L' Ecole Nationale Superieure des Mines de Paris, France, pp. 204.
- Tosdal, R.M. and Richards, J.P., 2001. Magmatic and structural controls on the development of porphyry CuMoAu deposits, *SEG Reviews*, 14, 157-181.
- Tsoupas, G., Economou-Eliopoulos, M., 2005. Extremely abundant platinum-group minerals in chromitites hosted in the Veria ophiolite complex, northern Greece. In: Törmänen, T.O., Alapieti, T.T. (Eds.), *10th International Platinum Symposium*, Oulu, Finland, 592-595.
- Tsoupas, G., Economou-Eliopoulos, M. 2008. High PGE contents and extremely abundant PGE-minerals hosted in chromitites from the Veria ophiolite complex, northern Greece. *Ore Geology Reviews* 33, 3-19.
- Vergely P. 1976. Origine "vardarienne", chevauchement vers l'Ouest et re'trocharriage vers l'Est des ophiolites de Macédoine (Grèce) au cours du Jurassique supérieur-Eocrétacé. *C R Acad Sci Paris* 280, 1063-1066
- Vergely, P. 1984. Tectonique des ophiolites dans les Hellenides internes. Conséquences sur l'évolution des régions téthysiennes occidentales. *These Université Paris sud Orsay* 2, 250-411.
- Von Quadt, A., Peytcheva, I., Kamenov, B., Fanger, L., Heinrich, C.A. and Frank, M. 2002. The Elatsite porphyry copper deposit in the Panagyurishte ore district, Srednogie zone, Bulgaria: U-Pb zircon geochronology and isotope-geochemical investigations of magmatism and ore genesis. in: Blundell, D.J., Neubauer, F. and von Quadt, A. (eds): *The Timing and Location of Major Ore Deposits in an Evolving Orogen*. Geological Society, London, Special Publications 204, 119-135
- Walker, R., Brandon, A.D. Bird, J.M. Piccoli, P.M. McDonough, W.F. Ash, R.D. 2005. 187Os-186Os systematics of Os-Ir-Ru alloy grains from southwestern Oregon, *Earth Planet. Sci. Lett.* 230, 211 - 226.
- Walker, D.A., Cameron, W.E., 1983. Boninite primary magmas: evidence from the Cape Vogel Peninsula, Papua New Guinea. *Contributions to Mineralogy and Petrology* 83, 150-158.
- Werle, J.I., Ikramuddin, M. and Mutschler, F.E. 1984. Allard stock, La Plata Mountains, Colorado — an alkaline rock hosted porphyry copper precious metal deposit. *Can. J. Earth Sciences* 21, 630-641.
- Whiteley, J.D., Murray, F., 2003. Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *The Science of Total Environment* 317, 121-135.
- Wilde, A.R., Edwards, A.C., Yakubchuk, A., 2003. Unconventional deposits of Pt and Pd: a review with implications for exploration: *SEG Newsletter*, 52, pp. 1-18.
- Wood, S.A., Mountain, B.W. and Pujing Pan, 1992. The aqueous geochemistry of platinum, palladium and gold: recent experimental constraints and a re-evaluation of theoretical predictions, *Canadian Mineralogist*, 30, 955-982.
- Wood, S.A., 1990. The interaction of dissolved platinum with fulvic acid and simple organic acid analogues in aqueous solutions: *The Canadian Mineralogist*, 28, 665-673.
- Wood, S. A. 2005. The effect of organic ligands on the mobility of the PGE in soils and natural waters: Implications for exploration and the environment. *Geochimica et Cosmochimica Acta* 69, A329.
- Wood, B.W., 2002. The aqueous geochemistry of the platinum-group elements with applications to ore deposits, in Cabri, L.J., ed., *Geology, Geochemistry, mineralogy, metallurgy and beneficiation of PGE: Canadian Institute of Mining and Metallurgy Special Paper*, 54, 211-249.
- Xiong, Y. and Wood, S.A., 2000. Experimental quantification of hydrothermal solubility of platinum-group elements with special reference to porphyry copper environments. *Mineralogy and Petrology* 68, 1-28.