

# Platinum-group elements (PGE) in various geotectonic settings: Opportunities and risks

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**ABSTRACT:** The platinum-group elements (Os, Ir, Ru, Rh, Pd and Pt) or PGE, which are the most valuable elements, have been described in a wide range of geotectonic settings, but in most cases they are associated with primary magmatic sulfides. 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). Zoned mafic-ultramafic igneous complexes of the Ural-Alaskan type are targets of Exploration and sources of significant economic platinum placer deposits as well. In ophiolites the major collector of PGE is chromite. The more Pt- and Pd-rich assemblages (Pd-Pt, Pd-Pt-alloys, Pt-arsenides, most likely sperrylite) occur interstitial to chromite grains. Although their content in large chromite deposits is generally low (few hundreds of ppb) there is a PGE-enrichment: (a) in all PGE, (b) only in Os, Ir and Ru or (c) in Pt and/or Pd. It is 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), Bulqiza and Tropoja (Albania), Dobromirci (Bulgaria).

Platinum-group element minerals (PGM), may be precipitated directly from silicate melt (S-poor), from the immiscible sulfide liquids, and the magmatic volatile phases. Small grains of PGM (average 25  $\mu\text{m}$ ) 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 chromites from some ophiolite complexes may indicate either in situ alteration or/and re-mobilization and re-deposition of PGE. Large (over 1.3 mm) PGM grains and extremely abundant PGM small grains/fragments (over 100) are dispersed along a highly fragmented chromite zone, in a distance over 3 mm (Veria, Greece). The origin of the large PGM-grains within small chromite occurrences located along a shear zone having high PGE (up to 25 ppm) content may 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 in ophiolite complexes (a) for the chromite-IPGM associations' exclusively small chromite occurrences along shearing zones of ophiolite complexes, post-dating their initial/magmatic PGE deposition, and (b) for the PPGE the uppermost parts of the mantle and the lowest crust sequence.

Recently, elevated Pd and Pt contents, reaching values over 5 ppm were determined in certain porphyry Cu-Au deposits (average  $\geq 0.4$  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.

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 hypersaline ( $>70$  wt%  $\text{Na-Cl}_{\text{equiv}}$ ) 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.

Environmental pollution is the result of the mining and smelting operations of companies producing PGE and the increasing use of catalytic converters, along with the global pollution growth. Significant Pt and Pd contents (a few ppm) were recorded along roadsides. The enrichment of the Pd and Pt contents in grasses confirm their bioavailability, under appropriate pH and redox potential conditions (humic or fulvic acids).

**Key-words:** *Platinum-group elements, environment, porphyry-Cu deposits, ophiolites, chromite, catalyst converters.*

**ΠΕΡΙΛΗΨΗ :** Τα στοιχεία της ομάδας του λευκοχρύσου (Os, Ir, Ru, Rh, Pd and Pt) ή PGE, τα οποία είναι τα πλέον πολύτιμα μέταλλα, έχουν περιγραφεί σε διάφορα γεωτεκτονικά περιβάλλοντα, αλλά στις περισσότερες περιπτώσεις συνδέονται με μεταλλεύματα πρωτογενών μαγματικών θειούχων. Οι σημαντικότερες από οικονομική άποψη μεταλλοφορίες Pt και Pd φιλοξενούνται σε καθορισμένους στρωματογραφικούς ορίζοντες μεγάλων εστρωμένων διεισδύσεων, όπως είναι το σύμπλεγμα Bushveld (N. Αφρική), το Great Dyke (Zimbabwe) και το σύμπλεγμα Stillwater (USA). Ζωνώδη συμπλέγματα βασικών-υπερβασικών πετρωμάτων τύπου Ουραλίων-Αλάσκας είναι ενδιαφέρουσες περιπτώσεις έρευνας για τον εντοπισμό συγκεντρώσεων PGE και πηγές για σημαντικά προσχωματικά κοιτάσματα επίσης. Στα οφιολιθικά κοιτάσματα ο κύριος συλλέκτης των PGE είναι ο χρωμίτης. Τα ορυκτά που είναι πλούσια σε Pt και Pd-πλούσιες (Pd-Pt, Pd-Pt-κράματα, Pt-αρσενίδια, συνήθως σφαιρίλιθος) εμφανίζονται μεταξύ κόκκων χρωμίτη. Αν και η περιεκτικότητα των PGE σε μεγάλα κοιτάσματα χρωμίτη είναι γενικά μικρή (μερικές εκατοντάδες ppb) υπάρχει εμπλουτισμός σε PGE: (α) σε όλα τα PGE, (β) μόνο σε Os, Ir και Ru ή (γ) σε Pt ή/και Pd. Ο εμπλουτισμός αυτός αποτελεί χαρακτηριστικό διάσπαρτου τύπου

χρωμίτη ή/και σχετικά μικρών εμφανίσεων χρωμίτη, μεταλλουργικού ή πυρίμαχου τύπου, οι οποίες εμφανίζονται στα ανώτερα τμήματα της μανδουακής σειράς ή/και στα κατώτερα τμήματα της μαγματικής ακολουθίας. Παραδείγματα PGE-εμπλουτισμού enrichment αποτελούν οι οφιόλιθοι της Πίνδου, της Σκύρου, της Βέροιας (Ελλάδα), Bulqiza και Trogoja (Αλβανία), Dobromirci (Βουλγαρία).

Τα ορυκτά των στοιχείων της ομάδας του λευκοχρύσου (PGM) είναι δυνατό να αποτεθούν απ' ευθείας από το πυριτικό μάγμα (φτωχό σε S), από θειούχο τήγμα που έχει αποχωριστεί από το πυριτικό μάγμα και από μαγματικές πτητικές φάσεις. Μικροί κόκκοι PGM (25 μm) της ομάδας Os-Ir-Ru συνήθως λωρίτης, που εμφανίζονται ως εγκλείσματα μέσα σε χρωμίτη, θεωρούνται πρώιμες μαγματικές φάσεις που έχουν αποθεθεί απ' ευθείας από βασάλτικο μάγμα. Στα οφιολιθικά συμπλέγματα είναι συχνή και η παρουσία ορυκτών Os-, Ir, Ru- και Rh, Pt, Pd-ούχων PGM σε PGE-πλούσιο χρωμιτικό μετάλλευμα, τα οποία θεωρούνται προϊόντα μετασωμάτωσης ή κινητοποίησης και επαναπόθεσης των PGE. Μεγάλοι (μεγαλύτεροι των 1.3 mm) κρύσταλλοι PGM και πάρα πολλά, μικρά κομμάτια PGM (περισσότερα από 100) εμφανίζονται διεσπαρμένα σε μια απόσταση ~3 mm, κατά μήκος μιας ζώνης σχιστοποιημένου χρωμιτικού μεταλλεύματος. Ο σχηματισμός των μεγάλων κρυστάλλων PGM μέσα σε μικρές χρωμιτικές εμφανίσεις πλούσιες σε PGE (έως 25 ppm) ίσως σχετίζεται με μετα-μαγματικές διεργασίες σε μια μακρά περίοδο παραμόρφωσης που αρχίζει με την ανοδική κίνηση της ασθενόσφαιρας (πλαστική παραμόρφωση). Συνεπώς, οι πλέον ελπιδοφόρες περιοχές σε οφιολιθικά συμπλέγματα είναι (α) για τα στοιχεία Os, Ir και Ru (IPGE) μικρές χρωμιτικές εμφανίσεις κατά μήκος ζωνών σχιστοποίησης των οφιολιθικών συμπλεγμάτων, και (β) για τα στοιχεία Pt, Pd και Rh (PPGE) τα ανώτερα τμήματα της μανδουακής σειράς και τα κατώτερα της μαγματικής ακολουθίας.

Πρόσφατα, προσδιορίστηκαν μεγάλες συγκεντρώσεις Pd και Pt, έως 5 ppm, σε ορισμένα κοιτάσματα πορφυρικού Cu-Au ( $\geq 0.4$  ppm Au). Τα πορφυρικά κοιτάσματα της Βρετανικής Κολομβίας και τα κοιτάσματα, Κρητιδικής έως Μειοκαινικής ηλικίας, που εκτείνονται από την Ρουμανία μέσω Σερβίας και Βουλγαρίας έως την Ελλάδα, είναι οι πλέον σημαντικές πορφυρικές διεισδύσεις. Το Pd-τελλουρίδιο, ο μερενσκήτης, (merenskyite) το οποίο εμφανίζεται κυρίως ως εγκλείσμα ή/και στα περιθώρια του χαλκοπυρίτη και βορνίτη ή σχηματίζει συμφύσεις με Pd-Pt-Bi- και Ag-τελλουρίδια. Αν και το δυναμικό των πορφυρικών συστημάτων σε PGE είναι ακόμη άγνωστο, το άθροισμα (Pd+Pt) που ξεπερνά τα 5 ppm θεωρείται ενθαρρυντικός παράγοντας για την ανάκτηση Pd και Pt ως παραπροϊόντων, με τον Au ως κύριο ή κύριο προϊόν, και τα κοιτάσματα πορφυρικού χαλκού μία ενδιαφέρουσα περίπτωση έρευνας για τον εντοπισμό Pd και Pt. Κοιτάσματα Cu-Au-Pd±Pt εμφανίζουν ομοιότητα ως προς την σύνδεσή τους με αλκαλικά πετρώματα, ιδιαίτερα ως προς (α) SiO<sub>2</sub> <65 wt%, (β) σημαντική συμβολή από τον γήινο φλοιό, όπως προκύπτει από τις τιμές των ισότόπων <sup>87</sup>Sr/<sup>86</sup>Sr και <sup>207</sup>Pb/<sup>204</sup>Pb values, (γ) συνδέονται με αλκαλικά ή Κ-πλούσια ασβεσταλκαλικά συστήματα, τα οποία χαρακτηρίζονται από σχετικά μεγάλη περιεκτικότητα σε REE, Th και αλογόνα (F, Cl), (δ) υπάρχει στενή σύνδεση των Cu-ορυκτών με το κύριο τελλουρίδιο του Pd (μερενσκήτη) και Au-Ag τελλουρίδια, (ε) σύνδεση της σημαντικής περιεκτικότητας σε Pd, Pt και Au με την παραγένεση μαγνητίτη-χαλκοπυρίτη-βορνίτη, και τη καλιούχο φάση εξαλλοίωσης στα κεντρικά τμήματα των κοιτασμάτων, και (ζ) μεταφορά Cu και ευγενών μετάλλων με την μορφή χλωριούχων συμπλόκων, σε σχετικά θερμά (400 to 700 °C) και υδροθερμικά ρευστά μεγάλης αλατότητας (>70 wt% NaCl<sub>equiv</sub>). Συνεπώς, οι κρίσιμοι παράγοντες που ελέγχουν το δυναμικό των κοιτασμάτων πορφυρικού Cu+Au+Pd±Pt σε βασικά και ευγενή μέταλλα θεωρούνται η σύσταση του μητρικού μάγματος και οι φυσικο-χημικές συνθήκες κατά την διάρκεια του σχηματισμού των κοιτασμάτων πορφυρικού-Cu.

Οι περιβαλλοντικές επιπτώσεις είναι αποτέλεσμα κυρίως της λειτουργίας μεταλλείων, της επεξεργασίας των ΟΠΥ για την ανάκτηση των PGE, και της αυξανόμενης χρήσης των καταλυτικών μετατροπέων, παράλληλα με τον αυξανόμενο πληθυσμό της γης. Έχουν προσδιορισθεί σημαντικές περιεκτικότητες Pd και Pt (τάξης μερικών ppm) σε σκόνη κατά μήκος λεωφόρων μεγάλης κυκλοφορίας. Επίσης ο εμπλουτισμός των Pd και Pt σε φυτά επιβεβαιώνουν την βιο-διαθεσιμότητά τους, κάτω από κατάλληλες οξειδο-αναγωγικές συνθήκες και pH (χουμικά οξέα).

**Λέξεις-κλειδιά:** Στοιχεία της ομάδας του λευκοχρύσου, περιβάλλον, κοιτάσματα πορφυρικού χαλκού, οφιόλιθοι, χρωμίτης, καταλυτικοί μετατροπέες.

## INTRODUCTION

The platinum-group elements (Ru, Rh, Pd, Os, Ir, and Pt) or PGE, which are the most valuable elements, are of strategic importance due to their growing use in advanced technologies and the use of Pt, Pd, and/or Rh in automobile catalyst converters. They are a major research topic at the University of Athens for more than two decades and have been described in a wide range of geotectonic settings, but the majority of the world supply of PGE is produced from magmatic ores derived from basaltic magmas. The platinum group elements (PGEs) belong to the transition metals of Group VIII in the Periodic Table, like iron (Fe), nickel (Ni), and cobalt (Co). 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. These metals have similar geochemical behaviour and tend to be concentrated together geologically. 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. Platinum was formally discovered only in 1751, although it was used since the 7th century BC in Egypt. PGE are classified as noble metals (along with gold and silver) because of their high resistance to oxidation and corrosion. The PGMs have

very high melting points, and are chemically inert to a wide variety of substances.

Platinum group elements are generally associated with nickel-copper sulphides in magmatic rocks. Magmatic sulphide deposits can be classified into two major groups, (a) those that are valued primarily for their Ni and Cu and that are mostly sulphide rich (>10% sulphide), and have formed as a result of an interaction of mantle-derived magma with the crust that gave rise to the early sulphide immiscibility, like the komatiite-related deposits and (b) those that are valued primarily for their PGE, concentrated in well-defined stratiform layers (reefs) of large intrusions and are sulphide poor (<5% sulphide), like the Bushveld Complex, South Africa, the largest layered igneous complex in the world.. (NALDRETT, 2010). Also, PGEs are produced in significant quantities from the Great Dyke in Zimbabwe, the Stillwater deposit of the USA, the Norilsk-Talnakh deposit of Russia and the Sudbury deposit of Canada.

The type of mafic-ultramafic complexes dominating in 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, is ophiolites. The platinum-group elements (PGE) content in chromite deposits associated with ophiolite

complexes is generally low (few hundreds of ppb), although a PGE-enrichment occasionally occurs (AUGE, 1985; KONSTANTOPOULOU & ECONOMOU-ELIOPOULOS, 1991; OHNESTETTER *et al.*, 1999; Zhou *et al.*, 1994; ECONOMOU-ELIOPOULOS, 1996; PRICHARD *et al.*, 2008).

Recently, elevated levels of platinum group elements (PGE), particularly Pd and Pt, have been reported from mineralization associated with several of the alkaline porphyry deposits. The association of the palladium telluride, merenskyite, as the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, with Cu-minerals is considered to be an encouraging factor for Pd and Pt as by-products, with Au as a by- or co-product with Cu being the main product.

In this paper the characteristic features of numerous PGE-sources are reviewed and a compilation of published (and some new) mineralogical and geochemical data are given. Factors controlling precious metal enrichment the PGE mineralization in various types of mafic-ultramafic complexes and mostly in porphyry Cu systems (a new source for Pd and Pt), along with the environmental risk are discussed.

## 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: OsMα, PtMα, IrMβ, AuMα, AgLα, AsLα, FeKα, NiKα, CoKα, CuKα, CrKα, AlKα, TiKα, CaKα, SiKα, MnKα, MgKα, ClKα. 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 were used as standards.

Platinum-group elements (PGE) were determined by ICP/MS analysis after preconcentration 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.

## CHARACTERISTIC FEATURES OF THE PGE MINERALIZATION IN VARIOUS GEOTECTONIC SETTINGS

### PGE in mafic-ultramafic complexes

Traditionally PGE are associated with mafic-ultramafic complexes. 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 Stillwa-

ter 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. Important deposits of this type are Noril'sk-Talnakh, Russia; Sudbury, Ontario; and deposits associated with komatiites, like those in Kambalda, Western Australia (NESBITT *et al.*, 1979; COWDEN *et al.*, 1986; KEAYS, 1995; HERZBERG, 1995; CAWTHORN, 1999; BARNES & MAIER, 1999, 2002; MAIER *et al.*, 2002; CAWTHORN & BOERST, 2006; NALDRETT, 2010 and references cited therein).

### Magmatic sulphide deposits

Thin layers (reefs) enriched in platinum-group elements (PGE) and Au are hosted in the Bushveld complex (South Africa) layered intrusion, of 2050 m.y. age. The Merensky Reef is one of the PGE-rich layers of the Bushveld Complex and, after the UG2 chromitite, the second largest PGE resource in the world, both located within the Critical Zone (CAWTHORN, 1999). Three groups of chromitites have been grouped into (i) a Lower Group (LG) of up to seven major layers hosted in pyroxenite, (ii) a Middle Group (MG) with four layers hosted by pyroxenite or norite; and (iii) an Upper Group (UG1 and UG2) hosted in pyroxenite, norite or anorthosite. The Merensky and UG2 reefs are situated in close proximity to each other. The UG2 reef lies anywhere between 20 and 330 metres below the Merensky horizon, and varies in thickness between 0.15 to 2.5 metres. Reserves of PGM plus gold are estimated at 547 million ounces in the Merensky Reef, and more than 1000 million ounces in the UG2 reef (LEE & TREDoux, 1986; BARNES & CAMPBELL, 1988; BARNES & MAIER, 1999, 2002; NALDRETT, 2010). Ore from the Merensky Reef contains up to 3% base-metal sulphide minerals, consisting of pyrrhotite, pentlandite, chalcocopyrite pyrite and chromite (Table 1). The majority of the PGMs in the Merensky ore are associated with pentlandite, occurring either in pentlandite grains or at the pentlandite-gangue grain boundaries. To a lesser extent, the PGE-minerals are associated with other base-metal sulphides or occur in the form of minerals such as braggite, cooperite, laurite, or ferroplatinum. The major gangue minerals are pyroxene, plagioclase feldspar, and biotite (Fig. 1). The principal constituents of UG2 ore are chromitite (~70 %), orthopyroxene, and plagioclase, and in a lesser amounts talc, chlorite, and phlogopite. The base-metal sulphides are predominantly pentlandite, chalcocopyrite, pyrrhotite, pyrite, and millerite. Merensky ore contains much more sulphide than does the UG2 ore, and the minerals are found in a silicate substrate, while UG2 ore has a chromite matrix (Fig. 2).

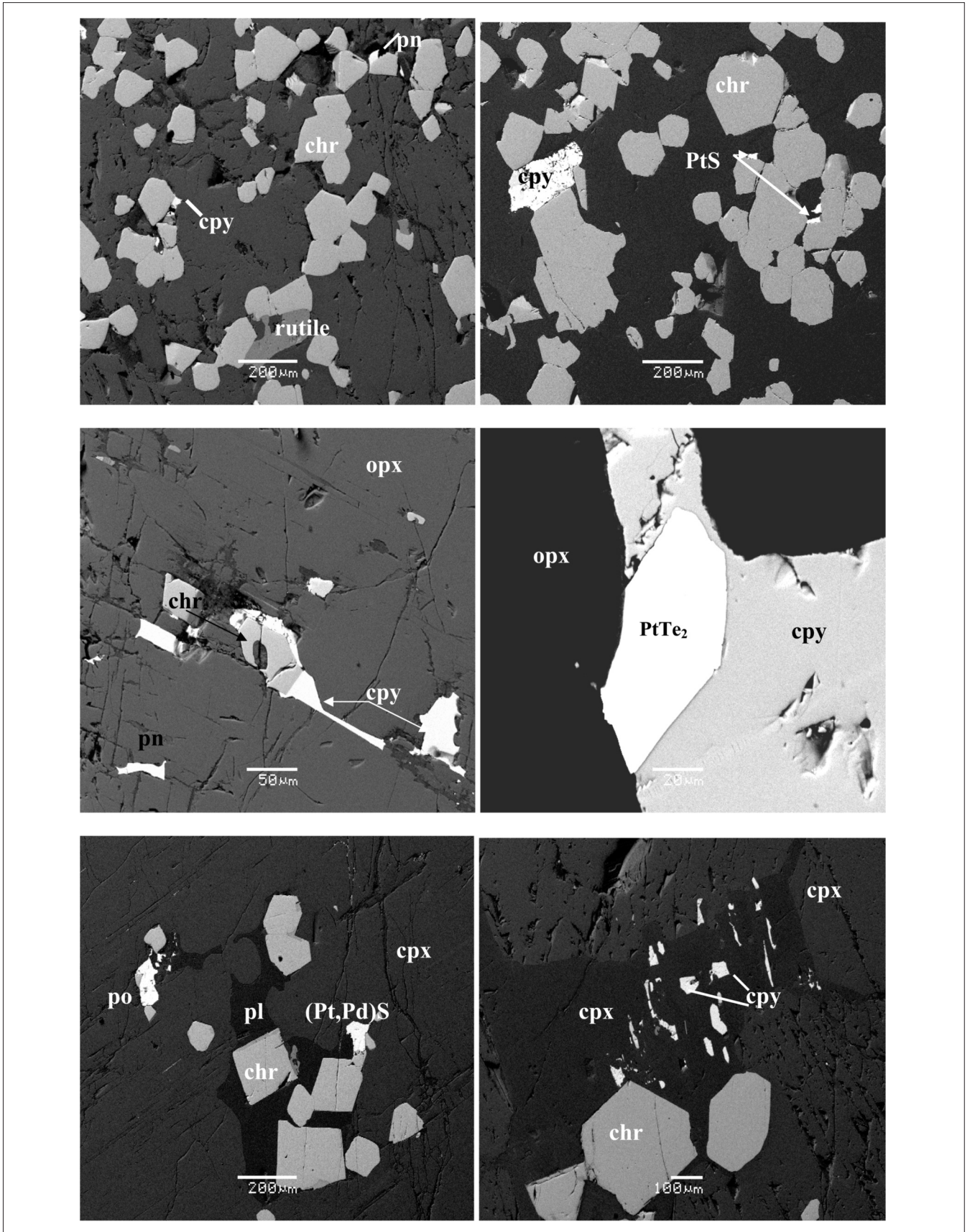


Fig. 1. Back-scattered electron images from Merensky reef of the Bushveld layered complex, showing chromite, sulphides, PGM and silicate minerals. Abbreviations: chr = chromite, cpy = chalcopyrite, pn = pentlandite, opx = orthopyroxene, cpx = clinopyroxene, pl = plagioclase.

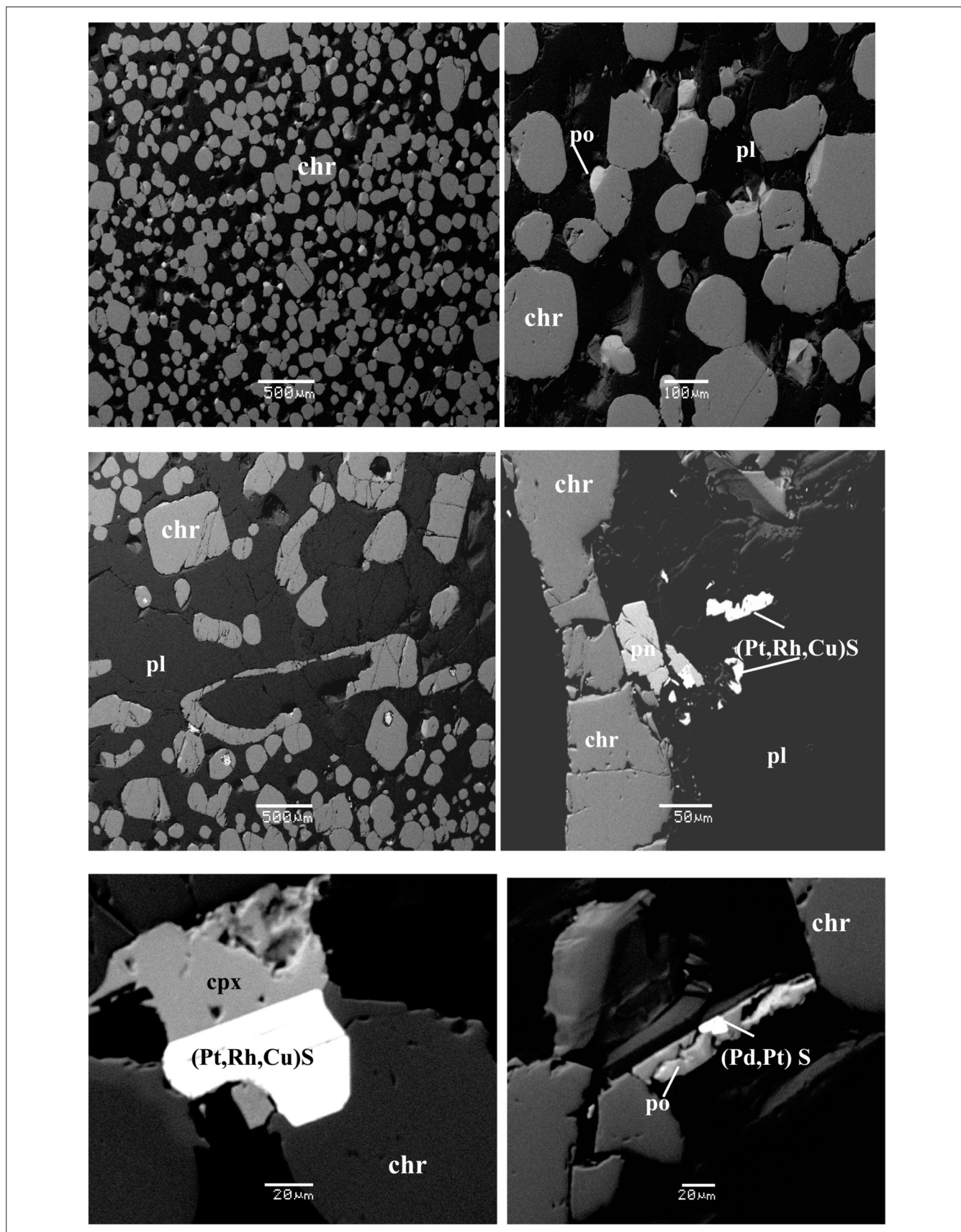


Fig. 2. Back-scattered electron images from the UG2 reef of the Bushveld layered complex, showing the small grain size of chromite, sulphides, PGM and silicate minerals. Abbreviations as on the Fig. 1.

TABLE 1

Representative microprobe analyses of chromite from massive chromitite ore associated with ophiolites and the Bushveld layered intrusion.

	ophiolites complexes				Bushveld complex				
					UG2		Merensky reef		
Al <sub>2</sub> O <sub>3</sub>	10,81	14,82	23,33	30,79	45,66	9,41	9,38	7,24	6,59
Cr <sub>2</sub> O <sub>3</sub>	60,74	56,71	41,58	39,51	21,84	43,22	42,98	40,81	37,41
V <sub>2</sub> O <sub>5</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	0,56	0,66	0,71	1,37
Fe <sub>2</sub> O <sub>3</sub>	0,46	0,91	3,89	0,22	0,55	14,71	14,44	16,56	16,84
FeO	15,89	14,33	19,69	14,31	16,43	26,6	28,02	32,24	33,64
MgO	11,39	12,57	11,04	13,98	14,21	4,81	4,07	0,77	1,93
TiO <sub>2</sub>	0,22	0,21	0,21	n.d.	0,51	0,81	1,02	1,04	1,88
MnO	n.d.	0,31	0,41	0,49	0,42	n.d.	n.d.	n.d.	n.d.
Total	99,51	99,86	100,15	99,3	99,62	100,12	100,57	99,37	99,66
Cr#	78,97	71,95	54,57	0,46	0,24	0,75	0,75	0,79	0,79
Mg#	56,09	62,12	49,81	0,64	0,42	0,24	0,21	0,04	0,09

Symbols: Cr# = Cr/(Cr+Al), Mg# = Mg/(Mg+Fe<sup>2+</sup>), n.d. = lower than the detection limit

### Komatiites

Komatiites are an important portion of the Archaean greenstone belts, because they host or are associated with nickel sulphide deposits. Komatiitic volcanic rocks are generally considered to have a low potential for PGE-rich Fe-Cu sulphide mineralization, as is exemplified in the komatiite flows at Kambalda, W.Australia. Platinum-group elements PGE are produced as a by product from massive to disseminated Fe-Ni-Cu(PGE) sulphide mineralization (NESBITT *et al.*, 1979; KEAYS, 1995; BARNES & MAIER, 1999). The orebodies form lenses composed of massive and disseminated sulphide, created as a result of magmatic segregations. Although there is a paucity, in particular in Os-Ir-Ru minerals, PGM have been reported in komatiitic host rocks of the Kambalda Ni-Cu sulphide deposits (HUDSON, 1986). PGM also have been reported in the komatiite-hosted O'Toole nickel deposit, Brazil (MARCHETTO, 1990; BRENNER, 1990). The primary igneous features have been variably affected by shearing and deformation. The described PGM of a small size (18 - 7 µm) are predominantly sperrylite (PtAs<sub>2</sub>), sudburyite (PdSb) and merenskyite (PdTe<sub>2</sub>). Experimental work by BRENAN & ANDREWS (2001) suggests 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 & ANDREWS, 2001). Nevertheless, the study of platinum-group element (PGE) concentrations in different types of komatiites may constrain the melting processes in the Archaean mantle and magmatic fractionation (NESBITT *et al.*, 1979; KEAYS, 1995; HERZBERG, 1995; BARNES & MAIER, 1999; MAIER *et al.*, 2002).

The Gorgona island, Colombia, is best known for its spinifex-textured Phanerozoic komatiites (GANSSEER *et al.*,

TABLE 2

PGE contents in PGE-enriched chromite ores from Greece.

ppb	Pindos				
	Korydallos	Milia	Skyros	Veria	
Os	60	60	150	140	7400
Ir	50	50	320	480	6000
Ru	70	110	350	1200	9700
Rh	100	100	82	160	310
Pt	1120	2700	150	280	760
Pd	470	1200	7	40	750
ΣPGE	2900	4220	1059	2300	24920
Pd/Ir	9.4	24	0.22	0.1	0.12

TABLE 3

Representative microprobe analyses of Pt-Pd-Rh-minerals from ophiolites (Veria) and the Bushveld complex (Merensky and UG2 reefs).

Mineral	Pt-Fe-Ni-alloys				Pt-sulpharsenides			Pd-mineral	
wt%									
Ru	n.d.	n.d.	n.d.	n.d.	1,06	6,65	6,43	15,4	n.d.
Os	n.d.	n.d.	n.d.	n.d.	1,81	n.d.	n.d.	n.d.	n.d.
Ir	5,11	8,11	n.d.	57,05	38,21	23,55	14,49	7,06	n.d.
Rh	n.d.	n.d.	n.d.	1,16	n.d.	2,61	10,35	2,84	n.d.
Pt	71,26	52,15	35,47	14,79	11,83	26,02	23,92	31,39	n.d.
Pd	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	54,97
Cr	n.d.	n.d.	n.d.	n.d.	n.d.	0,31	2,34	1,27	4,55
Fe	21,02	16,58	21,28	21,22	22,62	n.d.	0,93	0,65	2,88
Co	n.d.	n.d.	n.d.	n.d.	1,15	n.d.	n.d.	n.d.	n.d.
Ni	1,48	22,98	41,28	2,79	21,84	n.d.	n.d.	n.d.	8,91
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12,23
As	n.d.	0,93	n.d.	n.d.	n.d.	30,87	31,29	31,07	n.d.
S	n.d.	n.d.	n.d.	n.d.	n.d.	9,04	9,81	10,79	14,39
Total	98,87	100,75	98,03	97,01	98,52	99,05	99,56	100,47	97,93
cont.									
wt%									
	Merensky				UG2				
Pt	86,11	42,14	80,24		6,08	24,76	45,62	45,92	31,95
Pd	1,43	n.d.	6,21	56,25	63,15	44,31	n.d.	n.d.	n.d.
Rh	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	13,31	13,27	9,45
Fe	n.d.	0,65	n.d.	1,24	0,88	n.d.	1,52	1,07	12,96
Ni	n.d.	0,58	n.d.	n.d.	7,94	9,66	1,98	0,91	4,38
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	12,82	12,08	8,76
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1,15	n.d.
Bi	n.d.	8,37	n.d.	29,13	n.d.	n.d.	n.d.	n.d.	n.d.
Te	n.d.	48,42	n.d.	13,84	n.d.	n.d.	n.d.	n.d.	n.d.
S	13,14	n.d.	13,34	n.d.	21,66	21,64	25,62	25,25	32,12
Total	100,68	100,16	99,79	100,46	99,71	100,37	100,87	99,65	99,62

Symbol: n.d. = below detection limit.

Present study and from TSOUFAS & ECONOMOU-ELIOPOULOS (2008)

1979; ECHEVERRIA, 1980; ARNDT, 1994; ARNDT *et al.*, 1997). Highly magnesian (up to 32 wt.% MgO), high Cr and Ni Triassic lavas of komatiitic affinity, resembling Archean komatiitic suites, have been described in the Othrys ophiolite complex, Greece as well (CAMERON, 1979; CAMERON & NISBET, 1982; PARASKEVOPOULOS & ECONOMOU, 1986; TSIKOURAS *et al.*, 2008). They consist mainly of olivine phenocrysts, clinopyroxenes and chromite, preferentially associated with groundmass. Sometimes, clinopyroxenes with a spectacular skeletal morphology, exhibit the characteristic spinifex texture. Average platinum-group element (PGE) concentrations (all in ppb) are: Os 4, Ir 0.7, Ru 7, Pt 5, Pd 18, Rh < 0.5 and Au 15. Their Ti/V and Ti/Sc ratios, other trace element characteristics, and spinel composition are typical for magmas generated in SSZ geotectonic environment (CAMERON & NISBET, 1982; ECONOMOU-ELIOPOULOS & PARASKEVOPOULOS, 1987). The mineralogical and geochemical characteristics of those Triassic komatiitic lavas, coupled with the tholeiitic lavas with mid-ocean ridge basalt (MORB) affinities of the Othrys complex, have been attributed to changes in the geotectonic setting during the development of the Othrys complex from a fore-arc (formation of the highly magnesian lavas) to back-arc tectonic setting (ECONOMOU-ELIOPOULOS & PARASKEVOPOULOS, 1989).

### **Ophiolite complexes**

The type of mafic-ultramafic complexes dominated in the Tethyan and Balkan-Carpathian system, is ophiolites associated with orogenic zones. Although chromite is a major collector of the platinum-group elements (PGE), their content in large chromite deposits 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 like New Caledonia (AUGÉ *et al.* 1998), the Zambales ophiolite complex in the Philippines (BACUTA *et al.*, 1990), Vourinos in Greece (KONSTANTOPOULOU & ECONOMOU-ELIOPOULOS, 1991), Bulqiza in Albania (OHNSTETTER *et al.*, 1999), Troodos in Cyprus (PRICHARD & LORD, 1990), Shetland in the UK (PRICHARD *et al.*, 1986, TARKIAN & PRICHARD, 1987, PRICHARD *et al.*, 1994), Pindos in Greece (ECONOMOU-ELIOPOULOS & VACONDIOS, 1995, TARKIAN *et al.*, 1996, ECONOMOU-ELIOPOULOS *et al.*, 1999) and Veria in Greece (TSOUPAS & ECONOMOU-ELIOPOULOS, 2005, 2008). The platinum group minerals (PGM), may be precipitated directly from silicate melt (S-poor), from the 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-goup) 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  $\mu\text{m}$ ) of the IPGE-goup, 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 re-mobilization 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 (Fig. 3). 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 (Table 2, Fig. 4, TSOUPAS & ECONOMOU-ELIOPOULOS, 2008). 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 in the Balkan-Carpathian system are (a) for the chromitite-IPGM associations exclusively small chromite occurrences along shearing zones of ophiolite complexes, post-dating their initial/magmatic PGE deposition, and (b) for the PPGE the uppermost parts of the mantle and the lowest crust sequence.

Position of the figures 3 & 4

### **PGE in Alaskan type intrusions and Placer deposits**

Large Alaskan - type complexes exposed along SE Alaska, in the Urals and south-central British Columbia, showing a rough concentric zoning (a dunitic core is surrounded by successive shells of olivine clinopyroxenite, magnetite-rich clinopyroxenite and hornblendite) have been extensively studied. Although Ural-Alaskan intrusions do not contain significant accumulations of Ni-rich sulfides, some of those are targets for Exploration and sources of significant Pt-placer deposits. Placer deposit in Urals related to Alaskan type ultramafic complex was the world's main producer of platinum and platinum-group elements (PGE) before the discovery of the Merensky reef in the Bushveld complex, South Africa. The majority of placer mining was carried out in Russia, particularly in the Urals. Over a period of about 180 years exploitation yielded about 330 tonnes of platinum and are associated with Alaskan-type massifs (NALDRETT & DUKE 1980; MALITCH & THALHAMMER, 2002). Recently, the increasing world-wide demand for platinum, has led to several Pt-bearing placers being reopened (TOLSTYKH *et al.*, 2005 and references therein).

The origin of coarse-grained platinum-group minerals (PGM), reaching size up to a few mm, located in many placers associated with ultramafic-mafic complexes, such as

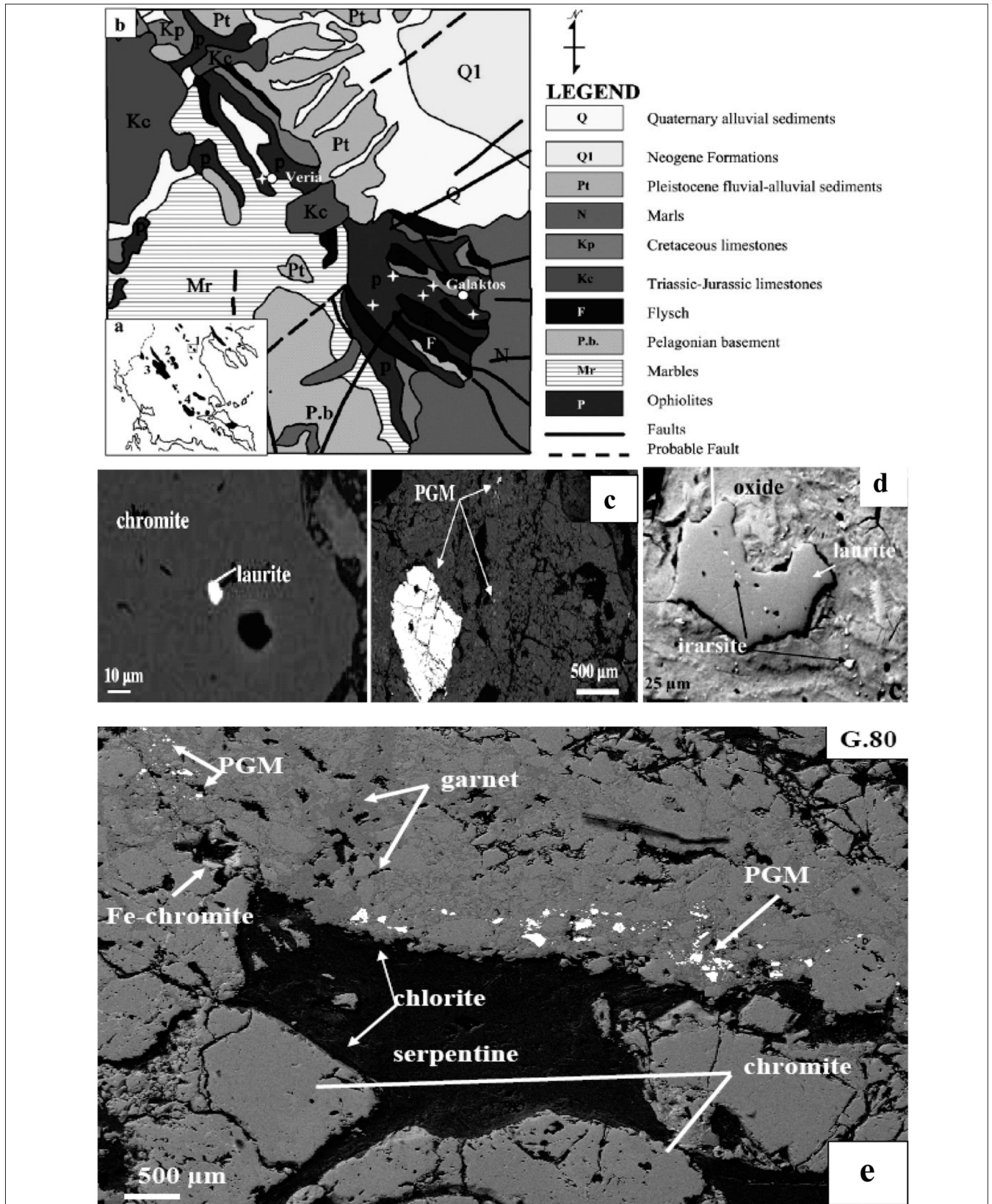


Fig. 3. (a) Location map of the main ophiolites complexes in Greece (1a): Symbols: 1—Veria (Galaktos), 2—Vourinos, 3—Pindos and 4—Othrys. (b): Simplified geological map of the Veria ophiolite, showing the location of the PGE-rich chromitite occurrences (crosses). Scale: 1: 250,000. Back-scattered electron images of a typical fine laurite inclusion within unaltered chromite (c), an extremely large PGM grain (d) and extremely abundant PGM grains zone along a highly shearing zone, containing strongly fragmented chromite from the Veria area (after TSOUPIAS & ECONOMOU-ELIOPOULOS, 2008).



Alaskan and ophiolitic type intrusions is a subject of debate, due to the paucity of coarse-grained PGM in parental rocks (CABRI & HARRIS, 1976; BARKER & LAMAL, 1989; BOWLES *et al.*, 2000; HATTORI, 2004). The estimated value of activation energy (minimum energy that is required for the formation of Ir-group minerals) is about  $425 \text{ kJmol}^{-1}$  (PETROU & ECONOMOU-ELIOPOULOS, 2009). Applying the  $\ln(r)$  (grain-size of IPGM) versus  $1/T$  (temperature) plot to estimate roughly the temperature of Ir-group PGM formation, it has been concluded that the formation of big Ir-group PGE grains can be formed at relatively high temperatures rather than they are of sedimentary origin (ECONOMOU-ELIOPOULOS *et al.*, 2009). Laurite ( $\text{RuS}_2$ ), from placer deposits, like the Pontyn River, Tanah Laut, Borneo, and Tambanio River, southeast Borneo, shows a variety of morphologies, including euhedral grains with conchoidal fractures and pits, and spherical grains. Isoferroplatinum, Os-Ir-Ru alloys, laurite, and sperrylite occur in both PGE placer deposits related to the zoned Ural-Alaskan type and ophiolite complexes.

The investigation of the composition of PGM in placers deposits, the inclusions in PGM and the mineral associations allow us to determine the conditions of their formation and provide evidence for the distinction between Ural-Alaskan intrusions and ophiolite complexes, as parent rocks. An excellent comparative study of the isoferroplatinum, Os-Ir-Ru alloys, laurite, and sperrylite occurring in both PGE placer deposits related to the zoned Ural-Alaskan type versus those related to ophiolite complexes were presented by TOLSTYKH *et al.* (2005). PGM in placer deposits are dominated by Pt-bearing minerals, whilst Os-Ir-Ru-minerals are in a larger proportion in those derived from ophiolite complexes. Furthermore, there is an Os-Ir trend in the former and a Ru trend in the latter, which has been attributed to evolution of the ore-forming system of parent complexes.

### Transport of the PGE in Hydrothermal environments

The mobilization of PGE by processes involving an aqueous fluid has been well documented (WOOD, 2002 and references

therein). 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, sulphur-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 chlorides are the most abundant ligands 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.

The importance of aqueous processes to PGE geochemistry and to the concentration of the PGE to economic levels has been recognized by WAGNER (1929) in the Waterberg deposits (South Africa) and supported by recent investigations (WILDE, 2005). 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, 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 & 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 & ZACCARINI, 1997). 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. On the basis of 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 & LEROUGE, 2004).

Platinum and Pd contents in sea-floor massive sulfides are very limited. However, elevated contents, reaching values up to 1 wt % Pt in marcasite and chalcopyrite from massive sulfides on the 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) may indicate that Pt and Pd are quite soluble under a range of hydrothermal conditions (ECONOMOU-ELIOPOULOS, 2005 and references there in).

### PGE mineralization in Porphyry-Cu alkaline intrusions

Alkaline porphyry deposits represent significant gold resources owing to their large sizes. Recently, elevated levels

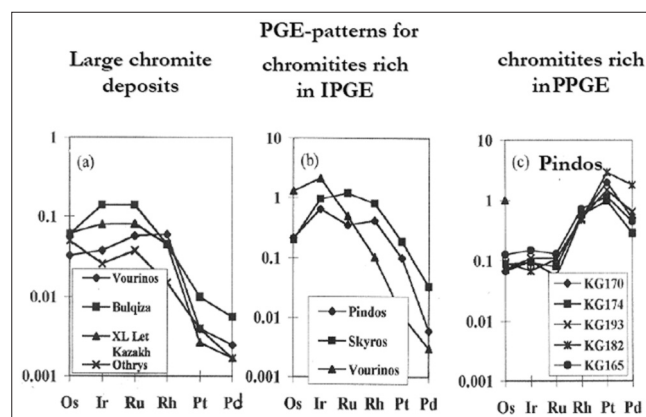


Fig. 4. Chondrite normalized PGE-patterns for chromite ores from large deposits (a), small chromite occurrences of Greece (b and c). Data from ECONOMOU-ELIOPOULOS (1996), TARKIAN *et al.* (1996), ECONOMOU-ELIOPOULOS *et al.* (2001).

of platinum group elements (PGE), particularly Pd and Pt, 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; ELIOPOULOS & ECONOMOU-ELIOPOULOS, 1991; PIETRZYNSKI *et al.*, 1994; ELIOPOULOS *et al.*, 1995; TARKIAN & KOOPMANN, 1995; TARKIAN & STRIBRNY, 1999; ECONOMOU-ELIOPOULOS & ELIOPOULOS, 2000) (Fig. 5). Porphyry Cu deposits are spatially and genetically associated with porphyritic intrusions, emplaced at relatively high levels in the crust (at depths of 1–2 km.) along older fault systems. The majority of giant gold-rich porphyry deposits are located in the circum-Pacific region. (TOSDAL & RICHARDS, 2001).

The Skouries, Elatsite, Medet, Bor/Madjanpek, Santo Tomas II, Grasberg, Bingham, Panguna and other porphyry deposits (Fig. 4), contain ore associated with early potassic alteration, native gold or electrum occurs as small (5–100  $\mu\text{m}$ ) inclusions in chalcopyrite or along bornite margins. Native gold may also form intergrowths with Pd-Pt-Bi- and Ag-tellurides, ranging from less than 1 to tens of  $\mu\text{m}$  (Fig. 6; TARKIAN *et al.*, 1991; TARKIAN & KOOPMANN, 1995; TARKIAN & STRIBRNY, 1999; KESLER *et al.*, 2002; TARKIAN *et al.*, 2003; STRASHIMIROV *et al.*, 2002). 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 assemblages. Subsequent events overprinting early potassic alteration and ore commonly remobilized Cu and Au, resulting in complete destruction of bornite

and deposition of a new chalcopyrite-pyrite assemblages in which gold is associated with both minerals.

### Sources of Metals and Sulphur 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 & OHMOTO, 1980, MCINNES & CAMERON, 1994, KEITH *et al.*, 1998, TITLEY, 2001). Numerous authors have suggested crustal sources for some ore metals in the southern Arizona 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, and the higher Pd and Pt levels in fresh and unaltered samples from the Lihir rocks compared to typical background values for crustal rocks are linked with the genesis of alkaline arc magmas, derived probably from an enriched mantle source (MCINNES & 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 & KEITH, 2001). The occurrence of mafic dikes, post-dating the porphyry mineralization at the Elatsite deposit (Fig. 10-6, VON QUADT *et al.*, 2002; STRASHIMIROV *et al.*, 2002), and relatively high Re concentrations in the molybdenite hydrothermal fluids and were precipitated during the main stage of mineralization, as an association of bornite, chalcopyrite, pyrite and magnetite reaching up to 10 vol.% (average 6 vol.%), as veinlets and disseminations, associated with the

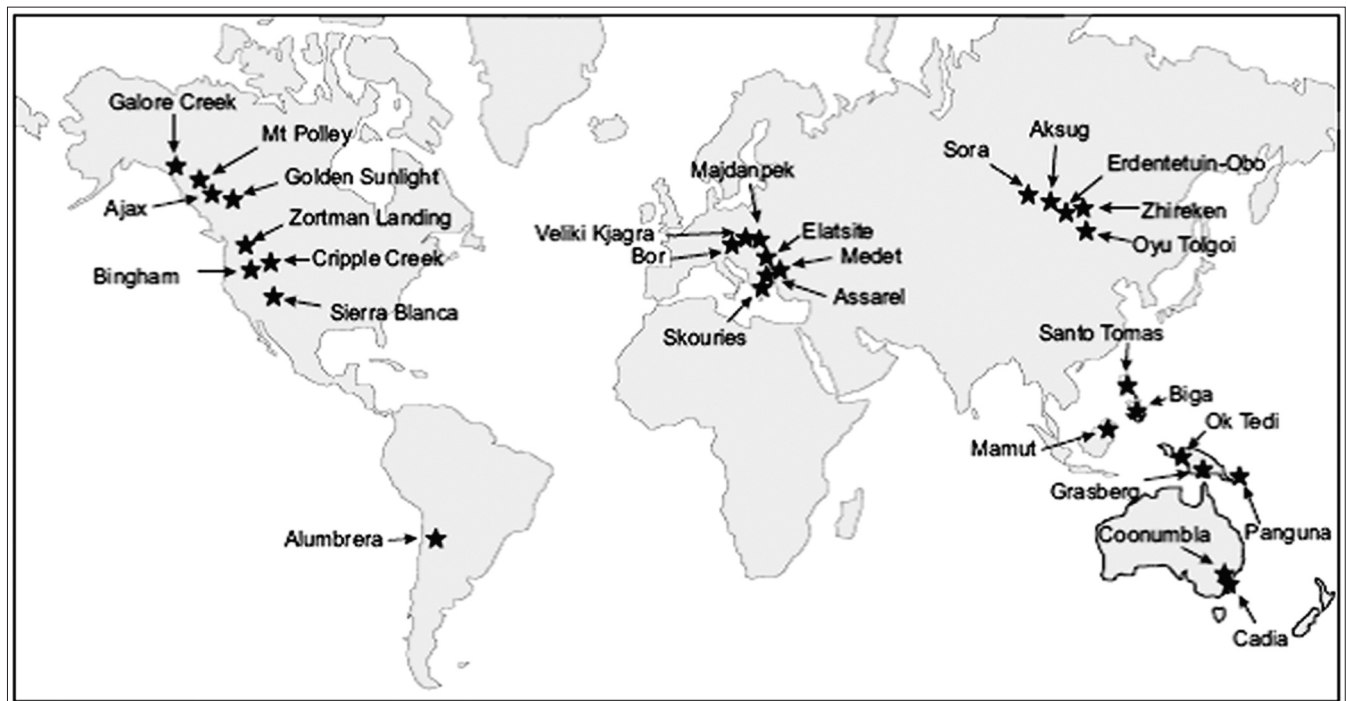


Fig. 5. Location map of porphyry Cu  $\pm$  Mo  $\pm$  Au  $\pm$  Pd  $\pm$  Pt deposits.

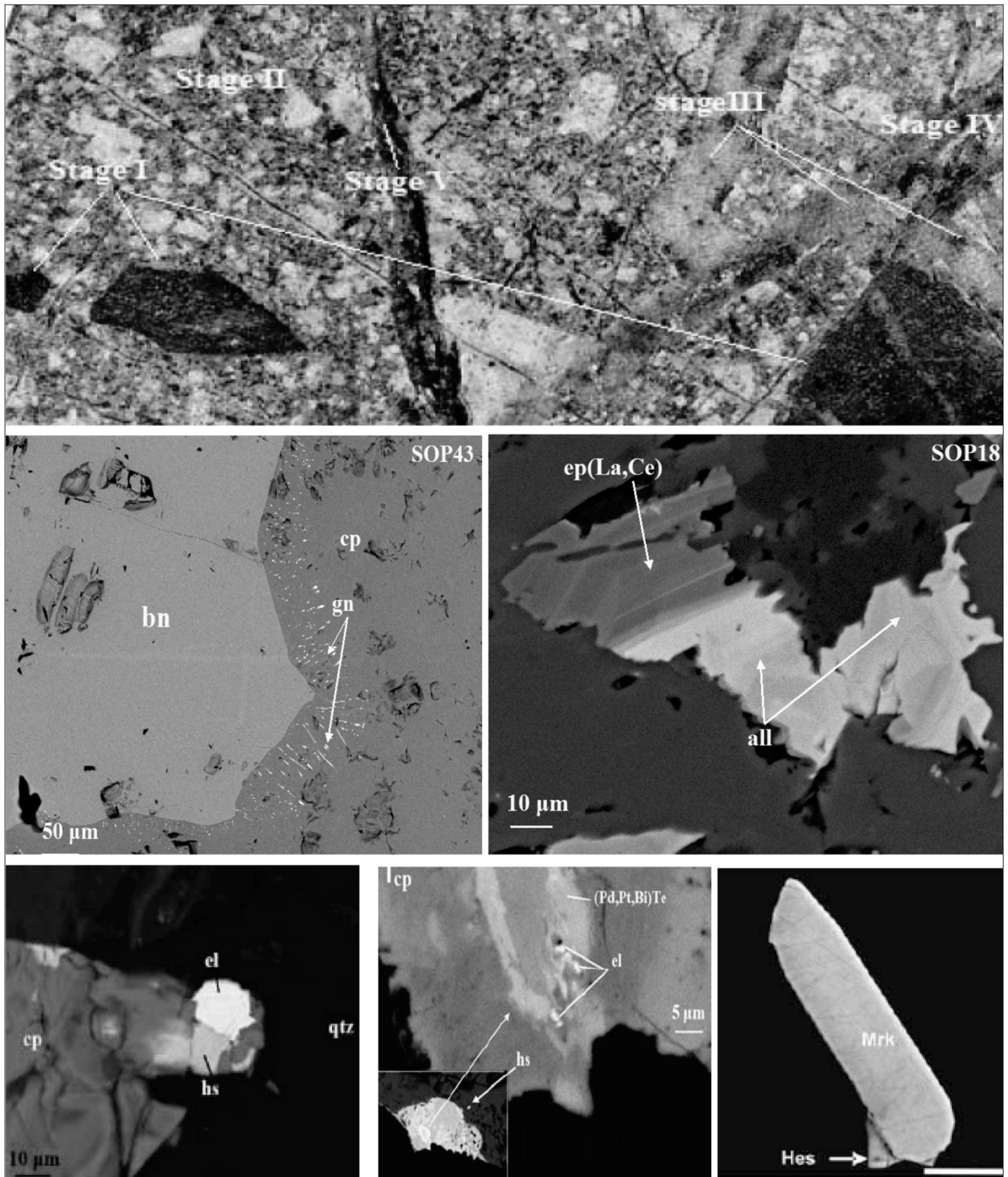


Fig. 6. Representative drill core sample of the Skouries Main monzonite porphyry (core width is about 4 cm), showing mineralization (disseminated and vein-type) in angular mafic fragments (stage I), pervasive (stage II), crosscutting relationships between successive quartz veins (stages III & IV) dominated by the magnetite-bornite-chalcopyrite assemblage, and a quartz-biotite vein (stage V), reflecting a range of hydrothermal evolution. The presence of mineralized mafic xenoliths within main porphyry is consistent with the multiple intrusive phases and mineralising events, and back scattered images from various drill cores of the Skouries porphyry deposit showing textural relationships between base and precious metal minerals/REE minerals. Abbreviations: cp = chalcopyrite, bn = bornite, gn = galena, el = electrum, hs = hessite, ep = epidote, all = allanite and qtz = quartz. Data from ECONOMOU-ELIOPOULOS (2005).

potassic alteration type. 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.

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

The porphyry Cu±Mo±Au deposits may develop around single intrusions or within more complex systems consisting of numerous intrusions and overlapping stages of alteration and ore deposition. Commonly they are related to multiple and multistage hypabyssal pipe-like intrusions extending to surface over widths ranging from less than 100 m to more than 1 km (TOBEY *et al.*, 1998; HERRINGTON *et al.*, 1998, 2003; TOBEY *et al.*, 1998; MÜLLER & GROVES, 2000; TOSDAL & 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 being inherently richer in SO<sub>2</sub> and CO<sub>2</sub> than their calc-alkaline counterparts, have volatiles with a significant influence on fluid pressures, brecciation and permeability of host rocks (MUTSCHLER *et al.*, 1985; CORBETT & LEACH, 1998; ELIOPOULOS & ECONOMOU-ELIOPOULOS, 1991; ELIOPOULOS *et al.*, 1995; FREI, 1995; TARKIAN & KOOPMANN, 1995; SILLITOE, 2000; MÜLLER & GROVES, 2000; SOTNIKOV *et al.*, 2000; STRASHIMIROV *et al.*, 2002).

Porphyry Cu-Au-Pd±Pt deposits of the Karpathian-Balkan system show a similarity in terms of their associations with alkaline rocks, in particular those characterized by (a) SiO<sub>2</sub> <65 wt%, (b) a major contribution by crust material, as is exemplified by the <sup>87</sup>Sr/<sup>86</sup>Sr and <sup>207</sup>Pb/<sup>204</sup>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 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, whilst “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.

#### **Exploration – Key Characteristics of Cu+Au+Pd ±Pt Deposits**

Exploration for alkaline porphyry deposits is encouraged by their large size and high grades and because they are environmentally favourable to mine, due to the low pyrite and high acid-buffering potential (CORBETT & LEACH, 1998). The association of magnetite (>10% by volume) is a common feature of most Au-rich porphyry Cu–Au deposits allowing direct geophysical recognition of the mineralized zones, as exemplified for the Skouries deposit (TOBEY *et al.*, 1998). Geophysical and geochemical signatures of these deposits are variable, but the characteristics of the mineralization and alteration can be recognized in almost all examples, providing an effective exploration tool (SILLITOE, 2000). Copper gold exploration models are based on detailed structural mapping (at surface and in drill holes) and identification of alteration styles and mineralization, with the aim of identifying the optimum sites for maximum fluid permeability and mineralization (CORBETT & LEACH, 1998).

Ore mineral assemblages themselves and the bulk ore chemistry reflect the composition of the parent magma and the nature of the ore fluids, in particular the maximum precious metal endowment of porphyry copper deposits, their chemistry and capacity for transporting sufficient Au and PGE (JENSEN & BARTON, 2000; XIONG & WOOD, 2000; HALTER *et al.*, 2002, 2005; KESLER *et al.*, 2002; SILLITOE & HEDENQUIST, 2003). Apart from the capacity of a magmatic hydrothermal system in precious metals and the possibility to form economic deposits, the association, in space and time (CATHLES, 1997), 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. Many of the porphyry Cu±Mo±Au deposits in Chile, Peru, Philippines and the Balkan Peninsula are located in the same arc region as the high-sulphidation deposits. They are commonly generated in calc-alkaline andesitic to dacitic arcs, characterized by neutral or weakly extensional stress states (WERLE *et al.*, 1984; SILLITOE, 2000; SILLITOE & 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<sub>eq</sub>), coupled with the common presence of sericitic roots to lithocaps in general, may suggest that the high-sulphidation 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 & HEDENQUIST, 2003; TAYLOR *et al.*, 1994; MÜLLER *et al.*, 2003).

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

To assess the PGE budget of a porphyry system, it is important (a) to analyze representative ore samples, and (b) to ensure that the ore samples are not coming from zones dominated by chalcocite and covellite, as they may exhibit high Au contents and negligible Pd–Pt contents, due to preferential mobilization during subsequent epigenetic processes (WOOD, 2002; ECONOMOU-ELIOPOULOS, 2005). Relatively high Pd contents 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 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 (ECONOMOU-ELIOPOULOS & ELIOPOULOS, 2001; KIOUSIS *et al.*, 2005). Using 206 Mt reserves according to recent 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.

Late Cretaceous to Miocene porphyry Cu deposits, extending from Romania, through Serbia and Bulgaria to Greece are the most important porphyry intrusions related to continental collision and post-collision magmatism. The Pd-telluride, merenskyite, has been described as the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, such as Skouries, Elatsite, Medet and Bor/Madjanpek. Merenskyite occurs mostly as inclusions and at margins of chalcopyrite and

bornite or forms intergrowths with Pd–Pt–Bi- and Ag-tellurides. The potential for PGE mineralization associated with such large Cu and Au–Cu porphyry deposits is still unknown. However, the average (Pd+Pt) values (over 5 ppm) are considered to be encouraging for Pd and Pt as by-products, with Au as a by- or co-product, and porphyry deposits a good target for Pd & Pt exploration.

### Environmental risk

Consequences of the environmental pollution created by the mining and smelting operations of companies are known to affect the workers and local population. Besides, 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 (HOFFMAN, 1989; 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 by catalysing the oxidation of carbon monoxide and hydrocarbons, and the reduction of NO<sub>x</sub>. They are constructed by applying a film of 1–3g Pt–Pd–Rh alloy, in proportion typically 0.08% Pt, 0.04% Pd and 0.005–0.007% Rh, on a ceramic “monolith” (HOFFMAN, 1989). The amount and rate of the Pt, Pd and Rh release from catalytic converters 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 & 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, which deposit on roadside surfaces. 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).

Traffic emissions and their impact on urban air quality, health, and atmospheric processes have been the subject of increasing interest in recent years (ELY *et al.*, 2001; DAHLHEIMER *et al.*, 2007). The amount and rate of PGE emissions are affected by the speed of the automobile, and the type and age of the catalyst (ARTELT *et al.*, 1999). Several studies have focused on the comparison between the gasoline engine type (Pt–Pd–Rh and Pd–Rh) and diesel engine catalysts (Pt), and the three-way catalytic converter: Reduction of nitrogen oxides to nitrogen and oxygen ( $2\text{NO}_x \rightarrow \text{xO}_2 + \text{N}_2$ ), oxidation of (toxic) carbon monoxide 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 ( $2\text{C}_x\text{H}_y + (2x+y/2)\text{O}_2 \rightarrow 2x\text{CO}_2 + y\text{H}_2\text{O}$ ). Platinum and rhodium are used as a reduction catalysts, while platinum and palladium are used as an oxidization catalyst (FLY *et al.*, 2001; MOLDOVAN *et al.*, 2002; DAHLHEIMER *et al.*, 2007).

Representative dust samples from Katehaki, Messoghion, Iera odos roads and the National high-way road Athens –

TABLE 4  
Palladium and platinum in porphyry-Cu-Au-Pd-Pt deposits.

Deposit	Ore tonnage tons x10 <sup>6</sup>	Pd grade ppm	Pt grade ppm	Pd tonnage tons	Pt 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 & COMPANY (2003)

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 (Table 5). The PGE level along the highways of Greece (Table 4) that may be washed by rain and concentrated into local water systems, is comparable to that given for many other countries (HODGE & STALLARD, 1986; ELY *et al.*, 2001; DAHLHEIMER *et al.*, 2007).

### Bioavailability of PGE

The determination of the PGE content of different plants grown on contaminated soil close to highways shows a transfer of the PGE from the contaminated soil to the plants (ECONOMOU-ELIOPOULOS & SFENDONI, 2010). The enrichment of the 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 (LUSTIG *et al.*, 1997; LUSTIG & SCHRAMMEL, 2000; DAHLEIMER *et al.*, 2007). The good positive relationship between both Pd and Pt contents in plants with their corresponding contents in soils is consistent with their solubility in soils. It has been demonstrated that the PGEs can be mobilized by natural organic matter and that humic acids and some organic ligands have been shown to enhance the solubility of various forms of Pt and Pd (WOOD, 1990, 2005; ARTELT *et al.*, 1999; RAUCH & MORRISON, 2000). Experimental data on the bioaccumulation of Pt, Pd and Rh by grass grown with nutrient solutions containing these metals showed that most of the metals were accumulated in the roots, and only a small fraction was metabolized and transported to the leaves (LESNIEWSKA *et al.*, 2004).

### Recovery of PGE

Although some authors have suggested that such Pt-Pd concentrations are high enough to recover PGE from roadside soils and/or dust (HILLIARD & HENRY, 1998; HOFFMAN, 1988; HILLIARD, 1998, 2001) available data for Greece are very limited for such an assessment. However the recovery of PGE from scrapped catalysts could contribute to the recycled PGE, in particular Pt, depending on the material composition of the catalyst (HILLIARD & HENRY, 1989) in every country. In addition, GARNICA *et al.* (2007) used an iron electrode process to obtain metallic Pd from various sources or by scrap. Thermodynamic and kinetic results showed that the process is slightly exothermic and can be performed at room temperature and is of low energy consumption cost. The minimum energy required for this process (activation energy) is low (5-10 kcal/mol).

TABLE 5  
Precious metal content in dust and soils along roadside.

Date (year, month) sample location	ppb				
	Pt	Pd	Rh	Au	Pd/Pt
2006-10-KAT1.dust	710	1000	4	14	1.41
2006-10-KAT2.dust	960	1300	5	51	1.35
2007-3-KAT3.dust	440	630	130	60	1.43
2007-04-KAT6.dust	900	670	3	360	0.74
average	750	800	35	121	1.23
2007-04-KAT.S4.dust	1720	1570	6	71	0.91
2007-04-KAT.S5.dust	2420	2400	4	180	0.99
average	2070	1980	5	125	0.95
2007-03-KAT2-3.soil	200	196	bdl	93	0.98
2007-04-KAT-MES1.soil	440	510	bdl	160	1.16
2007-04-KAT-MES2.soil	820	1100	3	120	1.34
average	610	800		140	1.25
2007-04-Pi.soil	60	70	1.5	56	1.17
2006-10-MES1.dust	290	500	3	220	1.72
2007-03-MES2.dust	210	300	26	460	1.43
2007-04-P.MES3.dust	210	300	3	240	1.43
average	255	365	17	307	1.53
2006-10-MES1.soil	44	90	8	150	2.04
2006-10-MES2.soil	36	74	10	6	2.06
average	40	82			2.05
2007-03-MES.soil	230	360	2	143	1.58
2007-03-NAV.soil	150	230	34	26	1.5
2007-04-MIXAL.dust	400	550	bdl	990	1.38
2006-10-Iera Odos1.dust	500	750	22	90	1.5
2006-10-Iera Odos2.dust	230	350	24	25	1.52
average	665	550	23	58	1.51
2006-10-N.h.Ath-Th1.dust	190	220	20	27	1.16
2006-10-N.h.Ath-Th2.dust	120	180	16	70	1.5
average	155	200	18	47	1.33
07-03-N.h.Ath-Th1.soil	92	100	35	27	1.11
2007-05-ACHAR1.dust					
average (n= 15)	227	335	15	530	1.4
STANDARD FA-100S	48.1	48.6		49	

Symbols: KAT=Katehaki; MES=Messoghion; P.MES.=Aghia Paraskevi; NAV=Navarinou; MIXAL.=Michalakopoulou; N.h.Ath-Th=National high-way Athens-Thessaloniki; ACHAR=Acharnon; bdl=below detection limit

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