

Exploration for Platinum-group elements (PGE) in the Carpathian-Balkan system

Economou-Eliopoulos M.

Department of Geology and Geoenvironment, University of Athens, Panepistimiopolis, 15784 Athens GR, econom@geol.uoa.gr

The platinum-group elements (Os, Ir, Ru, Rh, Pd and Pt), which are the most valuable elements, are of strategic importance due to their growing use in advanced technologies and automobile catalyst converters. They 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. In most cases the PGE are associated with primary magmatic sulfides with interstitial textures to the silicate host. 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.

The type of mafic-ultramafic complexes dominated in the Balkan-Carpathian system, is ophiolites associated with orogenic zones. Although chromite is 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 of Pindos, Skyros Island and Veria (Greece), Bulqiza and Tropoja (Albania), Dobromirski (Bulgaria) (Economou-Eliopoulos, 1996; Ohnenstetter et al., 1999). 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 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. 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 (Tsoupas and 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.

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 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). Traditionally PGE are associated with mafic-ultramafic complexes. Although porphyry deposits are major sources of Cu, Au or Mo, recently, in addition to gold the research interest has been focused on the Pd and Pt distribution in porphyry deposits because certain porphyry Cu-Au deposits have shown elevated Pd and Pt contents, reaching values over 5 ppm in high-grade bornite-chalcopyrite and/or flotation concentrates from Au-rich (average ≥ 0.4 ppm Au) porphyry deposits in British Columbia and Colorado (Eliopoulos and Economou-Eliopoulos, 1991; Economou-Eliopoulos, 2005). 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. Porphyry Cu-Au-Pd±Pt deposits of the Carpathian-Balkan system show some 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 (400-700°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 related to the ability of producing hydrothermal system with ideal chemistry for transporting precious metal and represent 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.

References

- 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. & Economou-Eliopoulos, M., 1991. Platinum-Group Element and Gold Contents in the Skouries Porphyry Copper Deposit, Chalkidiki Peninsula, Northern Greece. *Economic Geology*, 86, 740-749.
- Economou-Eliopoulos, M., 2005. Platinum-group 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.
- 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., Pattick, 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 of the Institution of Mining and Metallurgy (Section B, Applied Earth Sciences)* 108, 119-150.
- Tsoupas, G. and 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.