Platinum-group minerals in the Skouries Cu-Au (Pd, Pt, Te) porphyry deposit

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Abstract

The Skouries deposit is a platinum-group element (PGE) enriched Cu-Au porphyry system located in the Chalkidiki peninsula, Greece, with associated Ag, Bi and Te enrichment. The deposit is hosted by multiple porphyritic monzonite and syenite intrusions, which originated from a magma chamber at depth. An initial quartz monzonite porphyry intrusion contains a quartz-magnetite ± chalcopyrite-pyrite vein stockwork with intense potassic alteration. The quartz monzonite intrusion is cross-cut by a set of syenite and mafic porphyry dykes and quartz-chalcopyrite-borite ± magnetite veins which host the majority of the Cu and Au mineralisation. Late stage quartz-pyrite veins, with associated phyllic alteration crosscut all previous vein generations. Electron microprobe and scanning electron microscopy shows that the PGE are hosted by platinum-group minerals (PGM) in the quartz-chalcopyrite-borite ± magnetite veins and within potassic alteration assemblages. The PGE mineralisation in Skouries is therefore part of the main high temperature hypogene mineralisation event. Platinum-group minerals at Skouries include: sopcheite [(Ag,Pd)Te(Sb,Te)], merenskyite [(Pd,Pt)(Te,Bi)] and kotulskite [Pd(Te,Bi)], with rare telargpalite [(Pd,Ag)Te], isomertieite [Pd11Sb2As2], naldrettite [Pd3Sb], testibio palladite [PdTe(Sb,Te)] and sobolevskite [PdBi]. The most common platinum-group mineral is sopcheite. The PGM in Skouries are small, 52 µm on average, and occur as spherical grains on the boundaries between sulphides and silicates, and as inclusions within hydrothermal quartz and sulphides. These observations support a “semi-metal collector model” whereby an immiscible Bi–Te melt acts as a collector for PGE and other precious metals in high temperature hydrothermal fluids. This mechanism would allow the formation of PGM in porphyries without Pt and Pd fluid saturation.

1. Introduction

Porphyry deposits can contain appreciable amounts of platinum-group elements (PGE), in particular Pt and Pd, with the economic extraction of these valuable by-products of increasing interest (Economou-Eliopoulos, 2010, 2005; Tarkian and Stribrny, 1999). Relatively high (~ 1 ppm in whole rock) levels of Pd and Pt are described for several porphyries worldwide (Economou-Eliopoulos, 2010). For example, the Elatatite deposit, Bulgaria has an average whole rock Pt content of 16 ppb and Pd content of 40 ppb. Previous studies on Skouries reported Pd contents between 52 and 610 ppb and Pt contents up to 150 ppb in whole rock samples (Augé al., 2005; Economou-Eliopoulos and Eliopoulos, 2000; Eliopoulos and Economou-Eliopoulos, 1991; Tarkian et al., 2003). Other PGE-enriched porphyries include Santo Tomas II, Philippines; Galore Creek, Lorraine; Mt. Milligan, Mt. Polley & Island Copper, British Columbia; Medet, Bulgaria; Majdanpek, Serbia; Erdenet Bin Obo, Mongolia; Bozhahol, Kazakhstan; Kalmakyr, Uzbekistan; Sora, Aksug, Zhireken and Mikhailovskoe, Russia; Mumut, Malaysia and Fengshan, China (Table 1, Augé et al., 2005; Bath et al., 2014; Berzina et al., 2007; Bogdanov et al., 2005; Eliopoulos et al., 2014; Kehayov and Bogdanov, 1987; Lefort et al., 2011; Micko et al., 2014; Pašava et al., 2010; Pass et al., 2014; Plotinskaya et al., 2018; Prichard et al., 2013; Soninkov et al., 2001; Tarkian et al., 2003; Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Thompson et al., 2001; Wang et al., 2014). Although these PGE-enriched porphyry deposits occur in different geodynamic settings with contrasting ore and...
| Deposit       | Type                        | Area               | Host rock            | Pt (WR) | Pt (conc) | Pd (WR) | Pd (conc) | PGM present          | PGM hosting                                      |
|--------------|-----------------------------|--------------------|----------------------|---------|-----------|---------|-----------|-----------------------|---------------------------------------------------|
| Elatsite     | AlkalineCu-Au               | Bulgaria           | Multiphase monzonite | < 0.0349(74) | 76         | 2–3.44 (3.76) | 347 | Merenskyite, moncheite | Mag-bn-cpy veins, in cpy and bn                   |
| Medet        | Calc-alkalineCu-Au          | Bulgaria           | Granodiorite         | < 0.026  | 8         | 7–50 (29) | 160 | Merenskyite           | In cpy                                           |
| Majdanpek    | Calc-alkalineCu-Au          | Serbia             | Diorite              | < 0.0150 (30) | 16–24     | < 0.010 (33) | 52–490 | Merenskyite           | In cpy                                           |
| Skouries     | Shoshonite(Cu-Au)           | Greece             | Syenite              | < 0.0150 (30) | 16–24     | < 0.010 (33) | 75 – 2400 (1625) | Merenskyite | In cpy                                           |
| Erdenetuin-Oblo | Calc-alkaline(Cu-Mo)     | Mongolia            | Diorite -granite     | < 0.032 (24) | 33        | 7–23 (14) | 20 | Merenskyite, moncheite, kotulskite | Mag-bn-cpy veins, potassic alteration |
| Santo Tomas II (Philes) | Calc-alkaline(Cu-Au) | Philippines          | Quartz diorite       | 0.4      | 22–160    | 2         | Merenskyite, moncheite, kotulskite | Mag-bn-cpy veins, potassic alteration |
| Bozshakol    | Calc-alkaline(Cu-Au-Mo)     | Kazakhstan          | Tonalite             | < 0.011  | 245       |           |           |                       |                                                   |
| Kalmakyr     | K-calc-alkaline(Cu-Au-Mo)   | Uzbekistan          | Monzonite            | < 0.011  | 2–292 (54) |           |           |                       |                                                   |
| Sorra        | K-calc-alkaline(Cu-Au-Mo)   | Russia              | Monzodiorite-diorite-syenite | < 0.011  | 2–292 (54) |           |           |                       |                                                   |
| Aksu         | Calc-alkaline(Cu-Mo)        | Russia              | Diorite- tonalite    | 21–37 (28) | 25–96 (57) | 9–31 (16) | 17–924 (272) | Merenskyite | In cpy                                           |
| Zhireken     | K-calc-alkaline(Cu-Mo)      | Russia              | Diorite-granodiorite | 21–37 (28) | 25–96 (57) | 9–31 (16) | 17–924 (272) | Merenskyite | In cpy                                           |
| Mamut        | Calc-alkaline(Cu-Au-Mo)     | Malaysia            | Adamellite           | 450–490  |           | 1180–1600 |           | Merenskyite, sperrylite | In cpy                                           |
| Galore Creek | Alkaline(Cu-Au)             | BC                  | Trachytes & syenites | 15–107 (48) | 103–1581 (783) |           |           | Merenskyite, naldrettite-stibiopalladinite | In Hg-rich pyrites in late stage veins |
| Lorraine     | Alkaline(Cu-Au)             | BC                  | Monzonites & syenites | 11      | 19        | 51–6312  | 6312      | Merenskyite, naldrettite-stibiopalladinite | In Hg-rich pyrites in late stage veins |
| Mt Milligan  | Alkaline(Cu-Au)             | BC                  | Monzonites & syenites | 17–111 (48) | 111       | 51–6312  | 6312      | Merenskyite, naldrettite-stibiopalladinite | In Hg-rich pyrites in late stage veins |
| Mt Polley    | Alkaline(Cu-Au-Ag)          | BC                  | Monzonite & monzodiorite | 7–33 (19) | 23–320 (142) |           |           |                       |                                                   |
| Island Copper | Alkaline(Cu-Au)             | BC                  | Monzonite            | 31–38    | 63–320    | 8–32 (22) | Merenskyite, sopcheite | In bn-cpy in porphyry-epithermal transition veins |
alteration mineralogy, they share some common features (Table 1). For example, they are almost all Cu-Au porphyries with alkaline to calc-alkaline host rocks and they usually contain primary magnetite indicating an oxidised source magma. However, these features are also shared by the majority of Cu-Au porphyry deposits, including those without a known PGE enrichment (e.g. Richards, 2014; Sillitoe, 2010).

Initial studies of the porphyry related PGE mineralisation at Skouries suggested the PGE enrichment was associated with later, shallower and cooler mineralisation phases (Eliopoulos and Economou-Eliopoulos, 1991). However, PGE have been located within the main potassic ore-forming stage in the Elatsite, Santo Tomas II, Kalmakyr, Mamut and Majdanpek deposits. The Elatsite and Santo Tomas II deposits also contain high salinity (> 50 wt% NaCl equivalent) fluid inclusions with high homogenisation temperatures (> 350 °C) in veins associated with PGE enrichment (Kehayov and Bogdanov, 1987; Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999). These observations suggest that PGE enrichment in porphyries is associated with hypogene ore-forming processes (Economou-Eliopoulos and Eliopoulos, 2000). Fluid inclusions in PGE-bearing veins have high fO2 (shown by the presence of hydrothermal magnetite), temperature and salinity. These fluid conditions favour the hydrothermal transport of Pd as chloride complexes, and this is currently the accepted mechanism of PGE enrichment (Dixon and Dimitriadis, 1984; Frei, 1995). The Serbomacedonian Massif is separated from the Rhodope core, a syn-metamorphic Eocene-Miocene metamorphic core complex, by the Ker- dillon detachment fault (Brun and Sokoutis, 2007). Exhumation of the Rhodope core complex is closely related to post collisional magmatism and mineralisation (Marchev et al., 2005).

Neogene calc-alkaline magmatism in the region was generated during post-collisional extension by partial melting of subduction-modified lithospheric mantle and crust (Richards 2015; Rosu et al. 2005; Harangi et al. 2007; Harris et al. 2013). The Kassandra mining district consists of several magmatic-hydrothermal ore deposits related to Hellenic subduction and subsequent post-collisional extension (Frei, 1995, 1992; Kroll et al., 2002; Siron et al., 2016). These deposits are associated with two distinct magmatic episodes. One in the late Oligocene (27–25 Ma), and one in the early Miocene (20–19 Ma, Siron et al., 2016), which includes the Skouries porphyry deposit (20.56 ± 0.48 Ma from U-Pb of zircon, Hahn, 2015). These early Miocene alkaline magmatic events are interpreted to be the result of extension following exhumation of the Rhodope core complex (Siron et al., 2016), with magma emplacement triggered by a change in the regional extensional stress field (Siron et al., 2018).

The Miocene magmatism consists of porphyritic stocks and dykes with calc-alkaline to shoshonitic compositions (Kroll et al., 2002; Siron et al., 2016). It also includes regional alkaline porphyry dykes, locally described as “black matrix porphyry dykes” because of their dark aphanitic groundmass in hand specimen. These were originally classified as lamprophyles (e.g. Kalogeropoulos et al., 1989), however a recent study has shown them to have a trachy-andesitic composition (Siron et al., 2016). They have been suggested as a potential metal source for the Skouries deposit as they are very close in age, and similar units are present within the deposit (Eliopoulos et al., 2014; Siron et al., 2016).

Skouries has a measured and indicated resource of 289 million tonnes at 0.58 g/t Au and 0.43% Cu for 5.4 Moz Au and 1.2 Mt Cu (Eldorado Gold Corp, 2017). Potassic alteration and copper mineralisation, including veining, extend into the surrounding country rock with approximately two thirds of the measured and indicated ore reserves hosted outside the porphyry (Eldorado Gold Corp, 2017).

2. Deposit geology

The Skouries deposit is hosted in a pipe shaped system 200 m in diameter, exceeding 900 m in depth, which consists of several generations of porphyritic intrusions of monzonitic to syenitic composition (Fig. 2). Intense potassic alteration commonly obscures the original mineralogy. Detailed logging of 3465 m of drill core from five drill holes reveals four porphyry phases: The first phase is an early quartz monzonite containing 40–55% remnant plagioclase feldspar phenocrysts, along with 5–20% primary anhedral biotite phenocrystals 1–2 mm in diameter and 5–10% anhedral quartz phenocrysts 2–5 mm in diameter in an aphanitic matrix. This unit has undergone extensive potassic alteration, with the groundmass and a large proportion of the phenocrysts altered to potassium feldspar. This unit is crosscut by intense early stage veining (Fig. 3a).

The second phase is a syn-mineralisation porphyritic syenite unit which cross-cuts both the initial monzonite, and the early stage veining. The syenite contains 60% anhedral-subhedral feldspar phenocrysts, 5–10% (< 1 mm) anhedral primary biotite and ~2% subhedral

et al., 2016).
(1–2 mm) amphibole (Fig. 3a). These are hosted in a potassium feldspar aphanitic groundmass containing disseminated magnetite. The unit contains rare unaltered plagioclase feldspar phenocrysts, along with potassium feldspar megacrysts 1–4 cm in diameter. At shallow depths this syenite is crosscut by a fine-grained unit with the same mineralogy. However, below depths of > 600 m the two units show mixing textures, with no clear boundaries between the two, suggesting they are the same unit.

The third intrusive phase is represented by a series of porphyritic mela-syenite dykes which cross-cut and are cross-cut by the syn-
mineralisation syenite and brecciate the earlier units (Fig. 3b, c). This intrusive phase consists of 5–20% subhedral to euhedral K-spar phenocrysts (2–3 mm); 5–10% biotite subhedral phenocrysts (1 mm), 3% euhedral amphibole phenocrysts (1 mm) and 1% disseminated magnetite (< 1 mm) in an aphanitic dark grey groundmass. These dykes are similar in appearance and composition to the regional alkaline "black matrix porphyry dykes" described above. The porphyritic syenite and mela-syenite dykes are associated with main stage vein sets which host the majority of the Cu and Au mineralisation. These vein sets and igneous units are crosscut by the fourth igneous phase, a later dark grey porphyritic syenite which does not host any mineralisation (Fig. 3b).

2.1. Alteration and mineralogy

The Skouries deposit is a small (< 400 m in diameter) vertical, pipe-like body of quartz-sulphide vein stockwork mineralisation centred on the host porphyry stock. Based on crosscutting and overprinting relationships 14 stages of veining and associated alteration have been identified (Table 2). These have been classified into three groups: early (E) stage, associated with the initial quartz monzonite porphyritic phase; main (M) stage, associated with the syn-mineralisation porphyritic syenite and the porphyritic mela-syenite dykes; and the late (L) stage which crosscuts all earlier phases and is associated with low temperature alteration assemblages (Fig. 3).
The deposit has pervasive, potassic alteration which has destroyed the original textures and mineralogy (Fig. 4). The large propylitic and phyllic alteration zones commonly found in other porphyries are not present in Skouries. Propylitic alteration is present as an irregular and patchy overprint in a narrow halo around the intrusions, while the later phyllic alteration is only associated with faults and fractures in the deposit. The different alteration phases of the deposit are described in more detail in relation to their associated vein stages below.

2.1.1. Early stage vein sets

Early stage veins (E-1 – E-4; Table 2) are characterised by abundant magnetite and have indistinct, wavy margins suggesting they formed at temperatures consistent with ductile deformation (Fig. 3a). They are associated with pervasive potassic alteration assemblages of orthoclase-biotite-magnetite. These alteration minerals replace primary feldspar, amphibole and biotite phenocrysts, and are also present as disseminated aggregates of biotite–magnetite 1–2 mm across (Fig. 4). The groundmass of the host quartz monzonite is commonly completely altered to orthoclase in areas with a high proportion of early veining (Fig. 3a).

The E-1 vein stage contains orthoclase–biotite–magnetite and consists of wavy to sinuous magnetite-biotite veinlets 1–2 mm across. E-2 veins consist of wavy to sinuous quartz veinlets 2–10 mm across, containing regular anhedral quartz crystals. These veins commonly branch and cross-cut each other and have large secondary orthoclase and biotite phenocrysts overgrowing them.

E-3 veins contain quartz–magnetite ± chalcopyrite. They consist of a wavy, structurally aligned stockwork of quartz veins 8–20 mm across, with magnetite along the margins and disseminated in the centre. Occasionally they also contain minor chalcopyrite disseminated within the vein quartz. They truncate E-1 and E-2 veins and are interpreted to have formed in a semi-ductile regime. The E-3 veins are associated with disseminated magnetite and biotite alteration. The final early stage veins, E-4 veins, contain chalcopyrite-pyrite, and consist of wavy to sinuous sulphide veinlets 1–3 mm across. These crosscut E-1 to E-3 and are often accompanied by a fine-grained magnetite-biotite alteration selvage. These early vein sets, particularly E-3, are also present in the surrounding Vertikos Formation gneisses and schists.

2.1.2. Main stage vein sets

The main stage vein sets (M-1 – M-5) are characterised by a potassic alteration assemblage consisting of orthoclase, biotite and magnetite; as well as the presence of bornite and chalcopyrite. They are associated with the syn-mineralisation porphyritic syenite and the porphyritic mela-syenite dykes, both of which cross-cut the early veins (Fig. 3a, b). Pervasive orthoclase alteration of the groundmass of the syn-mineralisation porphyritic syenite occurs with main stage veining. This is accompanied by secondary biotite and magnetite alteration of the biotite and amphibole phenocrysts in both this unit and the porphyritic mela-syenite dykes. Main stage veining is also associated with disseminated magnetite alteration envelopes, commonly with chalcopyrite and bornite also disseminated with the magnetite (Fig. 4c, f, i, l).

The M-1 vein set contains hydrothermal biotite–magnetite–orthoclase. Two generations of M-1 structures occur: M-1A consists of sinuous biotite–magnetite veinlets 2–5 mm in width, while M-1B consists of irregular hydrothermal orthoclase veinlets 5 mm–10 cm wide which commonly broaden to flood an area, creating large irregular patches of hydrothermal orthoclase. M-1A veins are distinct from E-1 veins as they truncate E-2 veins, and crosscut E-1 and E-3 veins; however they are truncated by M-1B veins. M-2 veins consist of wavy, irregular quartz veinlets 2–4 mm which crosscut the early vein sets (Fig. 3a, b) with a fine-grained orthoclase alteration envelope 1–2 mm wide, which is sometimes altered to sericite.

There are 3 main stage vein sets which are associated with the majority of the Cu-Au mineralisation in the deposit: M-3, M-4 and M-5. The M-3 vein set contains biotite, orthoclase, quartz and
chalcopyrite ± magnetite, with minor bornite. These are wavy, discontinuous and curvilinear quartz veins 8–40 mm wide, with a 5–20 mm wide interlocking potassium feldspar and secondary biotite selvage (Figs. 3b, 4g, h). The crystals of quartz, orthoclase and biotite are euhedral and > 6 mm, with embayments and large crystals of biotite and orthoclase within the vein. M−3 veins have massive chalcopyrite in the centre. This chalcopyrite is 3–30 mm in width, and commonly encloses euhedral quartz crystals towards the edges of the sulphide, rarely with biotite and orthoclase crystal inclusions. Smaller (5–10 mm thick) M−3 veins contain trails of sulphide crystals, including rare bornite, late pyrite and minor galena on the edges of chalcopyrite crystals.

Vein set M−4 contains magnetite, quartz, bornite and chalcopyrite. It consists of veins with sinuous to straight margins 10–50 mm wide, with anhedral quartz crystals, containing trails of chalcopyrite-bornite and magnetite parallel to vein edges. These commonly have an orthoclase selvage 5–10 mm wide, are accompanied by a disseminated magnetite alteration envelope and often form stockworks (Figs. 3c, 4a, b). M−4 veins contain more bornite than chalcopyrite, with chalcopyrite commonly forming a secondary phase in fractures within bornite (Fig. 4i, l). Minor galena is also present on the edge of chalcopyrite crystals.

The M−5 stage veins consist of straight, planar quartz veins 1–3 cm wide, containing sulphides in a linear central suture, with small, regular, subhedral crystals (Fig. 3b, c, d). The sulphides present are pyrite-chalcopyrite-bornite with minor galena rimming sulphide assemblages (Fig. 4f). The earliest phase is pyrite and, unlike the M−4 veins, M−5 veins contain more chalcopyrite than bornite, with the chalcopyrite and bornite co-precipitated. They are associated with biotite-orthoclase-chlorite alteration and commonly have an orthoclase selvage 5 mm

Fig. 4. Photomicrographs of the main alteration and mineralisation stages of Skouries: a.) PPL and b.) XPL photomicrograph of biotite alteration on the edge of an M−4 vein, with a chlorite overprint. c.) Chalcopyrite and magnetite in M−4 vein. d.) PPL and e.) XPL photomicrograph of secondary biotite altering a primary biotite phenocryst, and potassium feldspar replacing primary plagioclase phenocrysts in an altered feldspar groundmass. f.) Chalcopyrite filling cracks in pyrite in M−5 vein. g.) PPL and h.) XPL photomicrograph of euhedral hydrothermal biotite crystals and potassium feldspar phenocrysts at edge of massive chalcopyrite in an M−3 vein. i.) Chalcopyrite infilling cracks in bornite in M−4 vein. j.) PPL and k.) XPL photomicrograph of altered biotite and feldspar phenocrysts in an altered groundmass, crosscut by an E-2 quartz vein. The vein is overgrown by secondary hydrothermal potassium feldspar and biotite crystals. l.) Chalcopyrite, bornite and magnetite in an M−4 vein. Copyright (2016) University of Southampton.
## Table 3

| Sample Position | Drill hole depth (m) | Lithology | Alteration | Sulphides present | Veins present | Pt assay value (ppb) | Pd assay value (ppb) | Au assay value (ppb) | Cu assay value (ppm) |
|-----------------|----------------------|-----------|------------|-------------------|--------------|---------------------|---------------------|---------------------|---------------------|
| 1               | 137                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 3            | 1137                | 9269                | 52                  | 2                   |
| 2               | 139                  | Syn-min   | Potassic M | Pyrite, chalcopyrite, bornite | 3           | 1900                | 4973                | 20                  | 1                   |
| 3               | 134                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 2            | 497                 | 1900                | 497                 | 2                   |
| 4               | 137                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 5            | 145,240             | 165,930             | 145,240             | 5                   |
| 5               | 133.9                | Early monzonite | Potassic & clay | Chalcopyrite, pyrite | 4           | 313                 | 1024                | 1024                | 3                   |
| 6               | 134                  | Syn-min   | Potassic M | Chalcopyrite, pyrite | 5            | 1900                | 5487                | 313                 | 2                   |
| 7               | 133.9                | Early monzonite | Potassic & clay | Chalcopyrite, bornite | 4           | 165,930             | 165,930             | 165,930             | 5                   |
| 8               | 137                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 26           | 11,200              | 145,450             | 15,200              | 3                   |
| 9               | 137                  | Early monzonite | Potassic & clay | Chalcopyrite, pyrite | 3           | 313                 | 1024                | 1024                | 3                   |
| 10              | 137                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 4           | 313                 | 1024                | 1024                | 3                   |
| 11              | 134                  | Early monzonite | Potassic & clay | Chalcopyrite, bornite | 4           | 165,930             | 165,930             | 165,930             | 5                   |
| 12              | 134                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 3           | 1900                | 4973                | 20                  | 1                   |
| 13              | 134                  | Syn-min   | Potassic M | Pyrite, chalcopyrite | 3           | 1900                | 4973                | 20                  | 1                   |

### Note

- Secondary biotite alteration around M–5 veins commonly shows regression to chlorite, and the M–5 veins are commonly associated with minor specular hematite, barite, anhydrite and sericite, and very rare epidote.

### 2.1.3. Late stage vein sets

The late stage (L1 – L4) veins in the Skouries deposit are associated with phyllic alteration assemblages. Alteration minerals present include sericite, quartz, calcite and dolomite, with minor advanced argillic assemblages of kaolinite and pyrophyllite (Fig. 3e). Argillic alteration minerals are also found around cm-scale fractures and metre-scale joints which are present locally in the deposit. L-1 stage veins consist of wavy gypsum veinlets 4–8 mm thick. These are present in areas with phyllic alteration and are associated with disseminated hematite. L-2 stage veins are wavy to sinuous pyrite veinlets 2–10 mm thick with a sericite-phyllicite alteration selvage. These veins develop within fractures and crosscut most lithologies and vein sets. L-3 veins consist of straight sided quartz veins 8–15 mm wide with calcite-sericite in a central suture and a sericite-clay alteration selvage. They are rare and are found in fractures. L-4 veins are irregular quartz-barite veins 5–15 cm thick with large euhedral comb morphology quartz crystals on the outer edges of veins. The centre of L-4 veins consist of white fine-grained quartz interlocked with barite crystals (Fig. 3g). These veins contain irregular masses of pyrite-sphalerite-galena, usually only in the fine grained central section, and occasionally contain apatite. They are surrounded by a calcite-dolomite-sericite-clay alteration envelope and are present in vicinities with intense fracturing, usually aligned with the fractures.

### 2.1.4. Vein densities and mineralisation

Vein densities in Skouries range from 74% (by surface area of bisected core) in the most altered areas to 3.5% in the least altered areas. The vein type with the highest density are the E-3 veins, which commonly show vein densities of > 45%. The mineralising vein sets, M–3, M–4 and M–5 show vein densities of 3.5–11%, with a mean vein density of ~5%. Of these, M–5 veins are the most sparse, rarely occurring in densities > 4%, while M–4 veins form stockworks of up to 11% of total core area and M–3 veins account for up to 10% of the core area in the sections where they occur, although this is mainly due to their variable thickness (up to 4 cm), rather than increased numbers of veins in one section. Vein density is greatest in the core of the deposit, with drill holes logged within the country rock showing significantly lower vein densities of < 5%. M–3 veins are only present within the core of the deposit, whereas M–4 and M–5 veins are both present within the surrounding country rock.

The Cu-Au mineralisation is associated with the main stage veins, particularly M–3, M–4 and M–5, and in disseminated chalcopyrite and bornite in the potassic alteration associated with these vein sets. The Cu in the deposit is primarily hosted in chalcopyrite and bornite, although there is a near-surface oxidation horizon containing malachite and azurite. Other copper secondaries such as covellite and chalcocite are also present down to approximately 60 m below the surface. The Au in the deposit is mainly hosted in electrum, which is an accessory mineral in potassic alteration and in M–3, M–4 and M–5 veins, with native gold also present in M–4 and M–5 veins. The deportment of Au, Ag and PGE is discussed further below.

### 3. Samples and methods

Logging was carried out on 3465 m of drill core across five drill holes in the centre of the deposit (Fig. 2). The visual estimates of vein density made during logging were recorded as a % of the visible surface area in bisected core for each 2 m logging interval. These initial estimates were then validated using the Image-J software package and photographic images of core sections in order to calculate the error of the previously acquired visual estimations. This approach showed that...

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**Note:** The table and figure references are not included in the natural text representation due to the limitations of text-based processing. The table is presented in a markdown format for readability and consistency with the natural text.
the visual estimates were accurate to within 10% in high vein density areas, with a tendency to over-estimate vein density, and to within 3% in low vein density areas.

Drill core samples were then selected for analysis based on palladium and platinum concentrations from company assay data provided by Eldorado Gold Corporation, and on the core logging performed during this study. The company whole rock assay analyses were performed at AcmeLab (Bureau Veritas) with Au analysed by fire assay and all other elements (including Pd and Pt) analysed by ultratracer multi-element ICP-MS after Aqua Regia digest.

Polished thin sections were prepared and examined for visible platinum-group minerals using reflective light microscopy. As the platinum-group minerals are mainly < 20 µm in diameter they were difficult to identify through optical microscopy, so the 12 samples with the highest assay values (Table 3) were selected for further analysis using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS), and electron probe microanalysis (EPMA) using wavelength dispersive X-ray spectrometry (WDS). Samples from the early and late vein sets were also analysed on the SEM in order to provide non PGE-enriched comparators.

Platinum-group minerals (PGM) were characterised at the National Oceanography Centre, University of Southampton using a LEOS1450VP SEM, coupled to an Oxford Instruments X-Act EDS detector. Further characterisation was carried out at Cardiff University using a Zeiss Sigma HD Field Emission Gun Analytical SEM (A-SEM) coupled to two Oxford Instruments EDS detectors and an Oxford Instruments WDS detector. Non-standardised EDS was used for first pass mineral identification and semi-quantitative analysis using spectrum indexes from the AZtec software package (Tables A.1 and A.2), with WDS analysis used to check the stoichiometry of minerals. The area of each PGM was measured from back-scattered electron images using the Image-J™ software package. All relative proportions of mineral phases discussed in this study were determined using semi-quantitative EDS and SEM-WDS are presented in Table 4, along with their host mineral and texture (Fig. 5; Table A.2). The PGM are small, with an average surface area of 52 µm², and a range of 1.7–1088 µm². EPMA-WDS data showing the exact element proportions and confirming the mineral classification of six PGM are presented in Table 5.

There are PGM present in vein sets M−3, M−4 and M−5, with none identified in any of the other vein sets. 20% of the PGM identified were found in M−3, 6% in M−4 and 74% in vein set M−5 (Fig. 6a).

The PGM were classified by their textural association: enclosed in sulphide (Figs. 5c, e, f, 5i, 5j, 5k), enclosed in a hydrothermal alteration silicate mineral (Fig. 5a, h, l) or on a sulphide-silicate boundary (Figs. 5b, d, k, 6c). 18% of the PGM identified are enclosed in sulphides, mostly chalcocytite or bornite in the centre of veins, and this textural association is most common in vein set M−3. 15% of the PGM identified are enclosed in hydrothermal silicate minerals, most commonly within euherdal quartz crystals in the main body of the veins (Fig. 5l). Some are also enclosed in secondary biotite or potassium feldspar in the alteration selvage of the veins (Fig. 5a), and this is most common in vein set M−5. 67% of the PGM are on the boundary between sulphide and hydrothermal quartz in the centre of the vein sets, most commonly in vein set M−5. The PGM fall into two morphological classifications – 79% of the PGM have spherical or oblate rounded morphology (Fig. 5a–c, e, f, i, k, l) and 21% have angular morphology (Fig. 5d, g, h, j). Those enclosed in sulphides and hydrothermal silicate minerals are always rounded, with those on crystal boundaries showing both rounded and angular morphologies, with rare PGM filling fractures in sulphides (Fig. 5g).

All the PGM identified were Pd minerals with only very minor Pt concentrations (up to 3 wt% Pt in three merenskyites), and EPMA-WDS shows only trace amounts (< 1 wt%) of Rh and Os to be present in some PGM. No Ru or Ir was detected in any of the PGM analysed. EPMA-WDS data confirms the presence of sobolevskite, sopcheite, testibio palladite and merenskyite (Table 5). Of all 23 platinum-group minerals analysed using EPMA-WDS, including those with analytical totals outside the 100 ± 3 wt% range, nine are sopcheite, five are sobolevskite, three are merenskyite, two are kotulskite and one is testibio palladite, with three minerals which had too much background interference to determine composition.

The PGM identified using both EPMA-WDS and SEM-EDS are grouped as Pd bismuth-tellurides, Pd bismuthides, Pd tellurides, Pd-Ag tellurides, and Pd antimonides. 77% of the PGM identified are Pd-Ag tellurides, consisting of sopcheite [Ag₃Pd₄Te₄] and rare telargalite [(Pd₄Ag₃)₄Te₆]. Sopcheite is present in vein sets M−3, M−4 and M−5, with the largest area present in vein set M−5 (Fig. 6a). 16% of the PGM identified are Pd bismuth-tellurides, predominately merenskyite [(Pd,Pt)(Te,Bi)₄] and kotulskite [Pd(Te,Bi)]. These are also present in M−3, M−4 and M−5, with M−3 having the largest proportion and M−5 the lowest (Fig. 6a). The merenskyites and kotulskites are Bi-rich rather than Te-rich (Fig. 6b). 5% of the PGM are Pd antimonides, consisting of testibio palladite [Pd₄Te₅(Sb,Te)], isomertite [Pd₁₂Sb₃As₄] and naldrettite [Pd₅Sb], and 2% of the PGM are Pd bismuthides, commonly sobolevskite [PdBi], all of which are only present in vein set M−5.

The samples also contain rounded inclusions of Bi-Te minerals in hydrothermal quartz, chalcocytite and bornite crystals. These are commonly < 10 µm² and so are difficult to analyse with SEM-EDS/EPMA-WDS without interference from surrounding minerals, however they appear to have compositions between those of pliselite [Bi₃Te₅] and tsumoite [BiTe]. This may be due to intergrowths within members of the tetradyptite group at nanoscale (Gobanu et al., 2009; Cook et al., 2007).

4.2. Other precious metal-bearing minerals

A total of 59 grains of other precious metal (Au and Ag with no PGE) bearing minerals were identified (Tables 6, 7, A.3; Figs. 5, 6). EPMA
analysis confirmed the presence of electrum [AgAu], hessite [Ag$_2$Te] and rare stützite [Ag$_{x}$Te$_{y}$, $x = 0.24$–$0.36$] (Table 7). SEM-EDS and SEM-WDS analysis also shows the presence of empressite [Ag$_3$Bi$_2$Te$_3$] and sylvanite [(Ag$_{x}$Bi$_{2-x}$)$_2$Te$_4$], two unnamed Au-Bi-Te minerals [Ag$_{x}$Bi$_2$Te$_y$] and one unnamed Ag-Bi [Ag$_{0.52}$Bi$_{0.48}$] mineral (Table 3.3). The most common of these are electrum, with 15 grains identified in vein sets M – 3, M – 4 and M – 5. 19 crystals of hessite were identified in vein sets M – 3 and M – 5. Nine crystals of volynskite were identified in vein set M – 3, along with rare empressite and muthannite, while rare sylvanite and stützite are found in vein sets M – 3 and M – 5. 87% (by area) of the Au and Ag-bearing minerals identified are encased within hydrothermal alteration minerals, most commonly quartz, with 9% present on the boundary between sulphides and hydrothermal silicate minerals and 4% as inclusions within sulphides (Fig. 6d). 93% of the Au and Ag-bearing minerals have rounded spheric or oblate morphologies, with only 7% having angular morphologies. Hessite is commonly in assemblage with electrum +/- PGM. The electrum in the deposit is gold rich, with an average of 85 wt% Au (from SEM-WDS and EPMA-WDS analysis, Tables 7 and A.2), and six crystals of native Au were identified as inclusions within quartz and pyrite crystals, with an average individual crystal area of 11 $\mu$m$^2$.

### 4.3. Other accessory minerals

Wittichenite [Cu$_6$Bi$_5$S$_{13}$] is present as inclusions within bornite. Rare crystals of claustralith [PbSe] were identified on the edges of sulphide crystals in the main stage vein sets. The late stage galena rimmed sulphides in the main stage vein sets were shown by EPMA-WDS and SEM-EDS analysis to be a galena-claustralith solid solution, containing an average of 4.0 wt% Se (Table 7).

Chromite is commonly present in potassic alteration of the early quartz monzonite, with rare Ni-chromite [(Ni,Cr,Fe)$_{2+}$] (Cr,Fe$_{2+}$,Al)$_2$O$_4$), and managanocromite [(Mn,Fe$_{2+}$)$(Cr,V)$]O$_2$ identified in potassic alteration using SEM-EDS. Thorite crystals 5–10 $\mu$m are present in all samples analysed, and this ties in with the relatively high whole rock XRF Th contents reported for Skouries (Kroll et al. 2002). The thorites are found within potassic alteration, as inclusions in hydrothermal biotite, and associated with disseminated hydrothermal magnetite and orthoclase. This suggests that the thorite is hydrothermal, rather than primary. Rare coffinite [U(SiO$_3$)$_2$]$_2$(OH)$_{4}$]$_n$ is also present in potassic alteration, and Ce and Th rich monazites and zircons were also identified as accessory minerals.

| Sample | Vein set | Mineral         | Host          | Size ($\mu$m$^2$) | Texture     | Host type                  | PGM type |
|--------|----------|-----------------|---------------|------------------|-------------|----------------------------|----------|
| 3      | M - 5    | Sobolevskite    | Bornite       | 32               | Angular     | Edge of sulphide           | PbBi     |
| 3      | M - 5    | Sobolevskite    | Bornite       | 9                | Rounded     | In sulphide                | PbBi     |
| 3      | M - 5    | Sopcheite       | Chalcopyrite  | 6                | Angular     | In sulphide                | PbBi     |
| 3      | M - 5    | Sopcheite       | Chalcopyrite  | 31               | Rounded     | Edge of sulphide           | PbAgTe   |
| 3      | M - 5    | Sopcheite       | Kspar          | 4                | Rounded     | Edge of sulphide           | PbAgTe   |
| 6      | M - 3    | Kotulskite      | Quartz        | 6                | Spherical   | In HT silicate             | PbBiTe   |
| 6      | M - 3    | Merenskyite     | Chalcopyrite  | 10               | Spherical   | In sulphide                | PbBiTe   |
| 6      | M - 3    | Sopcheite       | Chalcopyrite  | 14               | Spherical   | Edge of sulphide           | PbAgTe   |
| 8      | M - 3    | Kotulskite      | Quartz        | 4                | Spherical   | Edge of sulphide           | PbBiTe   |
| 9      | M - 3    | Merenskyite     | Chalcopyrite  | 20               | Spherical   | Edge of sulphide           | PbBiTe   |
| 9      | M - 3    | Sopcheite       | Chalcopyrite  | 50               | Spherical   | In HT silicate             | PbBiTe   |
| 9      | M - 3    | Sopcheite       | Chalcopyrite  | 131              | Spherical   | Edge of sulphide           | PbAgTe   |
| 9      | M - 3    | Sopcheite       | Quartz        | 68               | Spherical   | In HT silicate             | PbAgTe   |
| 11     | M - 5    | Isomerite (?)   | Chalcopyrite  | 65               | Angular     | Edge of sulphide           | PbSb     |
| 11     | M - 5    | Kotulskite      | Quartz        | 8                | Spherical   | In HT silicate             | PbBiTe   |
| 11     | M - 5    | Naldrettite (?) | Chalcopyrite  | 23               | Rounded     | In sulphide                | PbSb     |
| 11     | M - 5    | Sopcheite       | Chalcopyrite  | 14               | Angular     | In sulphide                | PbAgTe   |
| 11     | M - 5    | Sopcheite       | Chalcopyrite  | 1088             | Rounded     | Edge of sulphide           | PbAgTe   |
| 26     | M - 3    | Sopcheite       | Chalcopyrite  | 5                | Angular     | Edge of sulphide           | PbAgTe   |
| 31     | M - 4    | Kotulskite      | Quartz        | 5                | Spherical   | In HT silicate             | PbAgTe   |
| 31     | M - 4    | Merenskyite     | Chalcopyrite  | 50               | Angular     | In sulphide                | PbBiTe   |
| 31     | M - 4    | Sopcheite       | Chalcopyrite  | 32               | Spherical   | In sulphide                | PbAgTe   |
| 31     | M - 4    | Sopcheite       | Quartz        | 50               | Angular     | Edge of sulphide           | PbAgTe   |
| 31     | M - 4    | Sopcheite       | Quartz        | 5                | Spherical   | In HT silicate             | PbAgTe   |
| 34     | M - 5    | Telargpalite    | Chalcopyrite  | 5                | Angular     | In sulphide                | PbAgTe   |
| 34     | M - 5    | Kotulskite      | Quartz        | 5                | Spherical   | In sulphide                | PbBiTe   |
| 34     | M - 5    | Kotulskite      | Clay           | 15.2             | Spherical   | In HT silicate             | PbBiTe   |
| 34     | M - 5    | Merenskyite     | Quartz        | 6                | Spherical   | In HT silicate             | PbBiTe   |
| 34     | M - 5    | Merenskyite     | Chalcopyrite  | 18               | Spherical   | In sulphide                | PbBiTe   |
| 34     | M - 5    | Merenskyite     | Chalcopyrite  | 32               | Spherical   | In sulphide                | PbBiTe   |
| 34     | M - 5    | Merenskyite     | Chalcopyrite  | 32               | Spherical   | In sulphide                | PbBiTe   |
| 34     | M - 5    | Merenskyite     | Quartz        | 42               | Rounded     | Edge of sulphide           | PbBiTe   |
| 34     | M - 5    | Sopcheite       | Biotite        | 28               | Rounded     | Edge of sulphide           | PbAgTe   |
| 34     | M - 5    | Sopcheite       | Chalcopyrite  | 10               | Spherical   | Edge of sulphide           | PbAgTe   |
| 34     | M - 5    | Sopcheite       | Kspar          | 20               | Spherical   | Edge of sulphide           | PbAgTe   |
| 34     | M - 5    | Sopcheite       | Kspar          | 1.7              | Spherical   | In HT silicate             | PbAgTe   |
| 34     | M - 5    | Sopcheite       | Magnetite      | 17               | Angular     | Edge of sulphide           | PbAgTe   |
| 34     | M - 5    | Testibiopalladite| Bornite      | 38               | Spherical   | In sulphide                | PbTe     |
| 36     | M - 3    | Merenskyite     | Chalcopyrite  | 47               | Angular     | In sulphide                | PbBiTe   |
| 36     | M - 3    | Merenskyite     | Chalcopyrite  | 27               | Spherical   | In sulphide                | PbBiTe   |
| 36     | M - 3    | Merenskyite     | Chalcopyrite  | 3                | Spherical   | In sulphide                | PbBiTe   |
| 36     | M - 3    | Merenskyite     | Chalcopyrite  | 56               | Spherical   | In sulphide                | PbBiTe   |
| 36     | M - 3    | Merenskyite     | Chalcopyrite  | 12               | Rounded     | In sulphide                | PbBiTe   |
| 36     | M - 3    | Sopcheite       | Chalcopyrite  | 4                | Angular     | In sulphide                | PbAgTe   |
| 36     | M - 3    | Sopcheite       | Chalcopyrite  | 17               | Spherical   | In sulphide                | PbAgTe   |
5. Discussion

The mineralisation and alteration at Skouries is broadly similar to that in other alkali Cu-Au porphyry deposits such as the Ridgeway deposit, New South Wales (Wilson et al., 2003), and the main stage PGM-bearing veins are similar to those in Elatsite, another PGE-enriched Cu-Au porphyry deposit. The observation of PGE-bearing minerals within the main stage of mineralisation agrees with previous work by Tarkian et al. (1991) and by Economou-Eliopoulos and Eliopoulos (2000) but extends the range of recorded minerals. Importantly it provides clear evidence as to PGE deportment and clues as to the underpinning processes responsible.

5.1. PGM in the Skouries deposit

The Skouries porphyry deposit contains a large diversity of PGE-bearing minerals associated with a range of precious metal-bearing minerals and exotic phases, such as chromite, not commonly observed in porphyry Cu deposits. Skouries contains a more varied suite of platinum-group minerals than Elatsite and Santo Tomas II, the two other porphyries to have undergone thorough in-situ platinum-group mineral surveys (Augé et al., 2005; Tarkian and Koopmann, 1995). Skouries is the only porphyry deposit known to contain sobolevskite, telargpalite, isomertieite and testibiopalladite to date. In contrast to other PGE-enriched porphyry deposits where merenskyite is the most common PGM, sopcheite is the most common PGM present in the Skouries deposit. Elatsite contains merenskyite and merenskyite-moncheite solid solutions (Bogdanov et al., 2005; Tarkian et al., 2003), while Santo Tomas II contains merenskyite, kotulskite and moncheite (Tarkian and Koopmann, 1995). Although these deposits also contain a range of silver tellurides, neither of them are reported to contain sopcheite, suggesting the Ag and PGE in those deposits are either transported by different mechanisms or are temporally or spatially separate. There are a wider variety of PGM reported in the porphyry – epithermal transition
zone of deposits such as Mount Milligan, with naldrettite and stibio-

Table 5

| Sample | PGM # | PGM 1 | PGM 2 | PGM 1 | PGM 2 | Error (2σ) | Detection limit |
|--------|-------|-------|-------|-------|-------|------------|----------------|
| 3      | 3     | 3     | 3     | 3     | 3     | 3          | 3              |
| S*     | 19.5  | 5.3   | 0.4   | 1.3   | 3.0   | 0.9        | 0.6            |
| Pt*    | 0.59  | < dt  | < dt  | < dt  | < dt  | 0.96       | 2.33           |
| Mn     | 2.8   | 0.9   | 0.3   | 1.3   | 4.5   | 1.7        | 0.2            |
| Co     | < dt  | < dt  | < dt  | < dt  | < dt  | 0.05       | 0.03           |
| Ni*    | 14.4  | 2.5   | 1.1   | 1.7   | 3.0   | 2.2        | 0.32           |
| Zn     | < dt  | 0.40  | < dt  | < dt  | < dt  | 0.03       | 0.02           |
| As     | 2.17  | 2.47  | < dt  | < dt  | < dt  | 0.06       | 0.03           |
| Se     | 20.6  | 16.0  | 28.4  | 32.7  | 25.2  | 25.3       | 0.27           |
| Ag*    | < dt  | 25.2  | < dt  | 2.36  | < dt  | 0.52       | 0.33           |
| Sb*    | < dt  | 2.9   | 0.1   | 0.1   | 0.1   | 0.1        | 0.13           |
| Te*    | < dt  | 22.0  | 67.1  | 54.1  | 61.8  | 63.1       | 0.42           |
| Pb*    | < dt  | 20.9  | 1.19  | < dt  | < dt  | < dt       | 0.33           |
| Bi*    | 39.7  | 0.8   | < dt  | 8.7   | 1.7   | 3.2        | 0.50           |
| Cr     | < dt  | < dt  | < dt  | < dt  | < dt  | < dt       | 0.06           |
| Ru     | < dt  | < dt  | < dt  | < dt  | < dt  | < dt       | 0.18           |
| Rh*    | < dt  | 0.3   | 0.8   | 0.5   | 0.7   | 0.8        | 0.23           |
| Os*    | < dt  | < dt  | 0.3   | 0.2   | 0.2   | 0.2        | 0.08           |
| Ir*    | < dt  | < dt  | < dt  | < dt  | < dt  | < dt       | 0.07           |
| Au**   | 0.2   | < dt  | < dt  | 0.1   | 0.1   | 0.14       | 0.19           |
| Si     | 0.2   | 0.7   | < dt  | 0.1   | < dt  | 0.04       | 0.01           |
| Total  | 99.3  | 100.5 | 98.1  | 101.6 | 100.3 | 99.5       |                |
| Mineral| Sobolevskite | Sopcheite | Testibiopalladite | Merenskyite | Merenskyite | Merenskyite | |

This study has confirmed that the PGE in Skouries are associated with the main vein stage of Cu deposition in this deposit. This agrees with work by Eliopoulos and Economou-Eliopoulos (1991), Eliopoulos et al. (2014), who analysed whole rock samples for PGE content and found the potassic alteration zone to have Pd contents of 60–610 ppb and Pt contents of 5–150 ppb. Earlier work suggested that precious metal tellurides were formed in relatively shallow, cool environments, and that the PGE may have been redistributed during a late hydrothermal event (Eliopoulos and Economou-Eliopoulos, 1991; Mutschler et al., 1985). However, this study shows that no PGE mineralization is present within the late stage veins, or associated with argillic alteration. This is similar to the distribution of platinum-group minerals in other porphyry deposits. PGE in Elatsite, Santo Tomas II, Mamut and Maj-danpek deposits are all associated with the main, hypogene mineralisation and with potassic alteration (Tarkian et al., 2003; Tarkian and Kooppmann, 1995; Tarkian and Stirbny, 1999). However, there are documented examples of veins bearing PGE in the porphyry-epithermal transition zone. For example, the late stage ‘sub-epithermal’ veins in the Mount Milligan porphyry deposit, British Columbia contain PGM associated with electrum and Hg-rich pyrite (Lefort et al., 2011), and PGM have also been documented in the epithermal overprint of the Mkhieevskoe porphyry deposit (Plotinskaya et al., 2018).

The platinum-group minerals in Skouries are associated with M–3 and M–4 veins, commonly associated with bornite-chalcopyrite-magnetite assemblages, and in M–5 veins associated with bornite-chalco-

The platinum-group minerals in Elatsite and
Santo Tomas II (Tarkian et al., 2003; Tarkian and Koopmann, 1995) are also found in chalcopyrite-bornite-magnetite assemblages as inclusions in chalcopyrite. In contrast to these deposits the majority of platinum-group minerals in Skouries are present as discrete crystals on the edge of sulphides and magnetite both within the veins, and in potassic alteration selvages surrounding the M−S veins. Only 18% of the PGM in Skouries are present as inclusions in sulphides, with a significant number of PGM (15%) enclosed in hydrothermal quartz, biotite and feldspar with no obvious sulphide association. This suggests they were carried by a hydrothermal fluid (Xiong and Wood, 2000), and that their mechanism of transport and/or precipitation was decoupled from that of Cu. The majority of the Skouries PGM have rounded, droplet-like morphologies. These droplets are present as inclusions within the centre of euhedral hydrothermal quartz crystals, and within other minerals.

Fig. 6. a.) Graph showing PGM type distribution between vein sets b.) Triplot showing the proportion of semi-metals present in merenskyites [(Pd,Pt)(Te,Bi)] (solid circles) and kotulskites [Pd(Te,Bi)] (hollow circles) c.) Graph showing the area and association of platinum group minerals in Skouries (HT = hydrothermal) d.) Graph showing the area and association of precious-metal bearing minerals in Skouries. Copyright (2016) University of Southampton.
precipitated from the hydrothermal fluid (Fig. 5), suggesting that they were trapped as molten droplets and solidified as the liquid cooled (Ciobanu et al., 2005).

5.2. The role of semi-metals in PGE enrichment

One of the problems associated with the formation of PGE-enriched porphyries is that it is very unlikely that hydrothermal fluids will contain enough Pd to reach saturation in order to allow PGM to precipitate directly and be incorporated into quartz rather than within sulphides (Bazarkina et al., 2014). This means an additional mechanism is needed that both sequesters the PGE more strongly than sulphide and allows the metals to remain associated with the hydrothermal fluid in high enough concentrations to precipitate the PGM directly from the fluid when conditions permit.

In principle, co-existing polymetallic melts in hydrothermal systems can partition metals from the fluid and concentrate them as melt components (Douglas, 2000), and sulfosalt melts have been shown to precipitate as the liquid cooled (Biagi and Turi, 1988). In the Skouries deposit (using SEM-EDS and SEM-WDS). HT silicate = hydrothermal alteration silicate mineral.

### Table 6

Other precious metal-bearing minerals identified in the Skouries deposit (using SEM-EDS and SEM-WDS). HT silicate = hydrothermal alteration silicate mineral. Copyright (2016) University of Southampton.

| Sample | Vein set | Mineral | Host | Size (μm²) | Texture | Host type | Type |
|--------|----------|---------|------|------------|---------|-----------|------|
| 1      | M-3      | Muthmannite | Quartz | 5         | Rounded | In HT silicate | Ag-Au-Te |
| 6      | M-3      | Hessite   | Quartz | 4.8       | Rounded | In HT silicate | Ag-Au-Te |
| 6      | M-3      | Hessite   | Quartz | 3.1       | Rounded | In HT silicate | Ag-Au-Te |
| 6      | M-3      | Hessite   | Pyrite | 15        | Angular | Edge of sulphide | Ag-Au-Te |
| 6      | M-3      | Hessite   | Pyrite | 7         | Angular | Edge of sulphide | Ag-Au-Te |
| 6      | M-3      | Unknown   | Chalcopyrite | 27   | Rounded | Edge of sulphide | Ag-Au-Te |
| 8      | M-3      | Electrum  | Quartz | 10        | Rounded | In HT silicate | Ag-Au-Te |
| 8      | M-3      | Empressite| Biotite | 5         | Rounded | In sulphide | Ag-Au-Te |
| 8      | M-3      | Hessite   | Pb-Se-S | 15        | Rounded | In sulphide | Ag-Au-Te |
| 8      | M-3      | Sylvanite | Quartz | 10        | Rounded | In HT silicate | Ag-Au-Te |
| 9      | M-3      | Native Au | Pyrite | 29        | Rounded | In sulphide | Au |
| 11     | M-5      | Electrum  | Quartz | 30        | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Electrum  | Quartz | 2.2       | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Electrum  | Quartz | 1.6       | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Electrum  | Quartz | 7         | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Hessite   | Quartz | 150       | Angular | Edge of sulphide | Ag-Au-Te |
| 11     | M-5      | Hessite   | Quartz | 8.5       | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Hessite   | Quartz | 150       | Angular | Edge of sulphide | Ag-Au-Te |
| 11     | M-5      | Hessite   | Chalcopyrite | 18   | Angular | In sulphide | Ag-Au-Te |
| 11     | M-5      | Native Au | Quartz | 5.4       | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Native Au | Quartz | 5.8       | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Native Au | Kspar  | 5         | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Native Au | Quartz | 18        | Rounded | In HT silicate | Ag-Au-Te |
| 11     | M-5      | Native Au | Quartz | 8         | Angular | In HT silicate | Ag-Au-Te |
| 13     | M-3      | Unknown   | Pyrite | 5         | Rounded | In sulphide | Ag-Au-Te | Bi |
| 13     | M-3      | Unknown   | Pyrite | 3.5       | Rounded | In sulphide | Ag-Au-Te | Bi |
| 31     | M-4      | Electrum  | Quartz | 10        | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Chalcopyrite | 10   | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Quartz | 10        | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Quartz | 10        | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Chalcopyrite | 1.7  | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Chalcopyrite | 1       | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Quartz | 15        | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Electrum  | Quartz | 2         | Rounded | In HT silicate | Ag-Au-Te |
| 34     | M-5      | Hessite   | Chalcopyrite | 4      | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Hessite   | Pb-Se-S | 5.7       | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Stützite  | Magnetite | 15      | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Sylvanite | Quartz | 5         | Rounded | In sulphide | Ag-Au-Te |
| 34     | M-5      | Sylvanite | Quartz | 5         | Rounded | In HT silicate | Ag-Au-Te |
| 36     | M-3      | Electrum  | Quartz | 4360      | Rounded | In HT silicate | Ag-Au-Te |
| 36     | M-3      | Empressite| Chalcopyrite | 25   | Rounded | In sulphide | Ag-Au-Te |
| 36     | M-3      | Hessite   | Chalcopyrite | 10   | Rounded | In sulphide | Ag-Au-Te |
| 36     | M-3      | Hessite   | Chalcopyrite | 15   | Rounded | In sulphide | Ag-Au-Te |
| 36     | M-3      | Hessite   | Chalcopyrite | 11   | Rounded | In sulphide | Ag-Au-Te |
| 36     | M-3      | Hessite   | Chalcopyrite | 13   | Rounded | In sulphide | Ag-Au-Te |
| 36     | M-3      | Hessite   | Quartz | 8         | Rounded | In HT silicate | Ag-Au-Te |
| 36     | M-3      | Hessite   | Quartz | 34        | Rounded | In HT silicate | Ag-Au-Te |
| 36     | M-3      | Hessite   | Quartz | 14        | Rounded | In HT silicate | Ag-Au-Te |
| 36     | M-3      | Volynskite| Chalcopyrite | 1.7   | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 8      | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 14     | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 46     | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 4.5    | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 1.6    | Angular | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 3       | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Chalcopyrite | 7.6    | Rounded | In sulphide | Ag-Au-Te | Bi |
| 36     | M-3      | Volynskite| Quartz   | 3        | Angular | In HT silicate | Ag-Au-Te | Bi |
have condensed from expanding magmatic vapour at temperatures of ~650 °C in the El Indio paleo-fumarole (Henley et al., 2012; Henley and Berger, 2013; Mavrogenes et al., 2010). Semi-metals like Bi and Te at high concentrations can act as powerful fluxes, lowering the melting point of metals such as Au and the PGE - for example the Au-Bi melt has a eutectic at 241 °C (Gather and Blachnik, 1974; Okamoto and Massalaki, 1983). This has led to bismuth being suggested as a ‘collector’ for Au in hydrothermal fluids (e.g. Douglas 2000; Cockerton and Tomkins 2012; Tooth et al. 2008), acting as an independent enrichment mechanism and allowing the formation of hydrothermal ore deposits from fluids that would otherwise be under-saturated in Au. Experimental studies have shown that in Au-Bi-Na-CI-S-H-O systems, Au preferentially partitions into an Au-Bi melt rather than the fluid (Tooth et al., 2011, 2008), and natural examples of liquid bismuth co-existing with hydrothermal fluid have been reported (Cockerton and Tomkins, 2012). Au-Bi melts are only present in a limited range of fO2 conditions, however it is thought that Bi-Te melts may act as Au scavengers in high fO2 conditions, as native tellurium stability is coincident with hematite (Ciobanu et al., 2005; Grundler et al., 2013). Thermodynamic modeling work has shown that at high temperatures (550 °C) an Au-Bi-Te melt will precipitate from an Au-Bi-Te-S-C-Cl-Na-K-Ca-O fluid, even when the fluid is moderately under-saturated with Au, Bi and Te (Wagner, 2007). Bi-Te melts have eutectics of 266 °C (Bi-rich), and 413 °C (Te-rich) (Ciobanu et al., 2005), both within the range of temperatures analysed in porphyry hydrothermal fluids (Wilkinson, 2001). Bi-Te-(+/-Au) droplets have been identified in hydrothermal quartz crystals in deposits such as the Batman Au deposit, Australia; the Bi-Au Stormont skarn deposit, Tasmania and the Larga hydrothermal system, Romania (Cockerton and Tomkins, 2012; Cook and Ciobanu, 2004; Hein et al., 2006) implying they were precipitated in a molten state (Ciobanu et al., 2005; Mavrogenes et al., 2010).

Palladium partitions strongly into semi-metal melts in the magmatic environment even in the presence of a strong sulphide collector mineral such as pentlandite (Helmy et al., 2007; Holwell and McDonald, 2010). Porphyry systems lack significant pentlandite, removing a potential sulphide host for Pd and increasing the tendency for it to combine with semi-metals in porphyry deposits, rather than be hosted in the sulphides (Eliopoulos et al., 2014; Tarkian et al., 2003; Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Thompson et al., 2001). The Pd-Bi-Te system is molten above 489 °C (Cabri, 1981; Cabri and Harris, 1973), which is within the temperature range of porphyry system hydrothermal fluids generally (e.g. Wilkinson, 2001), and within the range of fluid inclusion temperatures for the Skouries deposit (350 °C – > 600 °C; Frei, 1995; McFall et al., 2017). It appears likely that this semi-metal collector mechanism could also scavenge Pd from fluids, concentrating them into a co-existing semi-metal melt.

In order to account for the textural observations at Skouries and other porphyry deposits a model is proposed whereby Pd is scavenged from high temperature (> 490 °C) hydrothermal fluids by a co-existing Bi-Te melt. This creates a Pd-Bi-Te melt which crystallises as palladium bismuthides, tellurides and tellurobismuthides according to the phase diagrams in Cabri (1981). Almost all of the PGM in the Skouries, Elatsite and Santo Tomas II deposits, and indeed in other PGE-enriched porphyries globally, are PGE-Bi-Te minerals, rather than PGE-rich sulphides or minerals containing other semi-metals such as As. The PGM in Skouries are present as rounded inclusions within the centre of euhedral hydrothermal quartz crystals, and within other minerals precipitated from the hydrothermal fluid, and are therefore proposed to represent solidified melt droplets. This model requires both Bi and Te to be present as the Pd-Te binary system is only molten above 720–740 °C (Cabri, 1981; Hoffman and Maclean, 1976), and the Pd-Bi binary system is only molten above 620 °C (Cabri, 1981). Binary systems of palladium with other semi-metals also only produce melts above the temperatures present in porphyry fluids – the Pd-Sb binary system is only molten above 800 °C, the Pd-As system is only molten above 835 °C and the Pd-Se system is only molten above 678 °C (Cabri, 1981), although depending on phase ratios some binary phases may occur at lower temperatures.

The most abundant PGM in Skouries is sropheite, showing Ag to be a major component of any melt phase. The ternary system Pd-Ag-Te has

Table 7

Results from quantitative EPMA-WDS analysis of precious metal minerals in wt.%. *= element has undergone empirical correction to eliminate peak overlap. Cu and Fe concentrations are interpreted to be background interference from the sulphide host minerals due to the small size of the minerals. PMM = precious metal mineral; GAL = galena. Copyright (2016) University of Southampton.

| Sample | MIN # | 34 | 34 | 34 | 34 | 34 | 34 |
|--------|-------|----|----|----|----|----|----|
|        | MIN # | PMM 1 | PMM 2 | PMM 3 | PMM 4 | PMM 2 | GAL 1 |
| S*     | < dt  | < dt  | < dt  | 0.5 | 0.9 | 14.8 | 0.6 |
| Fe*    | < dt  | < dt  | < dt  | 0.24 | 0.14 | 0.05 | 0.03 |
| Mn*    | < dt  | < dt  | < dt  | 2.4 | 7.1 | 0.2 |
| Co*    | < dt  | < dt  | 0.23 | < dt  | 0.06 | 0.03 |
| Ni*    | < dt  | 0.21 | < dt  | 0.06 | 0.03 |
| Cu*    | 0.9   | 0.3  | 2.8  | 7.5  | 0.32 |
| Zn*    | < dt  | < dt  | < dt  | < dt  | 0.03 |
| Se*    | < dt  | 0.11 | 4.0  | 0.06 |
| Pb*    | < dt  | 0.11 | < dt  | 0.06 |
| Sr*    | < dt  | < dt  | 0.11 | < dt  | 0.06 |
| As*    | < dt  | < dt  | < dt  | 0.05 |
| Te*    | 0.63  | < dt  | 37.2 | < dt  | 0.42 |
| Fe*    | < dt  | < dt  | 3.0  | < dt  | 0.33 |
| Mn*    | < dt  | < dt  | < dt  | 0.5 |
| Au*    | < dt  | < dt  | < dt  | < dt  |
| Cu*    | 19.2  | 17.2 | 16.1 | 54.8 | 58.7 | 0.31 |
| Ni*    | < dt  | < dt  | 0.21 | 0.2 |
| Co*    | < dt  | < dt  | < dt  | 0.06 |
| Zn*    | < dt  | < dt  | 0.5  | 0.4 |
| Se*    | < dt  | < dt  | 0.1  | < dt  | 0.05 |
| Pb*    | < dt  | < dt  | < dt  | 0.12 |
| Sr*    | 80.9  | 84.1 | 85.4 | 98.8 | 102.5 | 96.5 |
| Total  | 101.8 | 102.3 | 102.2 | 98.8 | 102.5 |
| Mineral | Electrum | Electrum | Electrum | Stützite | Hessite | Galena |
been modelled, with sphacite shown to be stable up to 383 °C, and to form assemblages with kotulskite and hessite (as in Skouries) at 350 °C (Vymazalová et al., 2015). This provides an upper limit for the temperature of formation of the PGM assemblages containing sphacite, meaning that these must have formed as the co-melt cooled to below 383 °C. Phase diagrams have yet to be defined for the full range of ternary and quaternary PGE-semi-metal systems and so it is possible that there may also be other complexes which have a low enough melting point to act as a PGE collector.

It is also worth noting that the mineralising fluids in porphyry Cu deposits are commonly high-salinity (>{30 wt%), and high temperature (>350 °C) with a relatively high oxygen fugacity. These are conditions which favour the hydrothermal transport of Pd as a Cl complex (Xiong and Wood, 2000). Although it has been shown that Au-Bi-Te melts will precipitate from high temperature and salinity hydrothermal fluids undersaturated in Au (Wagner, 2007). To date no modelling or experimental work has been done on the complex Pd-Bi-Te-S-C-Cl-Na-K-Ca-O-H system. It is therefore unclear what effect the co-existing fluid would have on a Pd-Bi-Te melt and what temperature, salinity and oxygen fugacity conditions would allow the precipitation of a Pd-Bi-Te co-melt.

Nonetheless the ubiquitous association of Pd with Bi-Te assemblages in porphyry deposits may provide an exploration indicator for PGE-enriched porphyry deposits, as high Bi and Te contents in assay may indicate the presence of microscopic platinum-group minerals which may be overlooked during standard ore characterisation if the PGE are not assayed. Although PGE in porphyries globally have been reported to be hosted in semi-metal platinum-group minerals (Tarkian and Stríbrny, 1999), there is a paucity of data on the Te and Bi content of PGE-enriched porphyry systems, or indeed the semi-metal content of porphyry systems generally. Skouries is rich in semi-metals, with Bi concentrations in ore samples of between 0.1 and 390 ppm and Te concentrations of 0 to 16 ppm. Elatsite has Bi concentrations in ore samples of between 0.2 and 291 ppm, and Te concentrations between 0.2 ppm and 3.8 ppm, with a positive correlation reported between Pd, Au, Te and Bi (Tarkian et al., 2003) suggesting that similar semi-metal collector mechanisms may have been operating. However, more data is needed on semi-metal and PGE concentrations in porphyry deposits globally in order to test this hypothesis.

5.3. Other precious metals

The presence of inclusions of droplet-shaped Bi-Te minerals within hydrothermal quartz and sulphides in the Skouries deposit supports the hypothesis that a Bi-Te immiscible melt was present. If this was the case then it would be expected to scavenge Au, and potentially Ag, as well as Pd from the fluid. A range of Au and Ag tellurides and bismuth-tellurides are present in the Skouries deposit, including volynskite (AgBiTe₂) and an unnamed Au-Bi-Te mineral [Au₉Bi₁₀Te₂₂]. These Au-Bi-Te minerals have compositions which are more Bi-rich than the melt compositions calculated for Au-Bi-Te precipitating from a 550 °C multi-cation hydrothermal fluid [Au₉Bi₁₀Te₂₂]. They have similar Au levels, and melts with higher Bi concentrations have been shown to precipitate from fluids with a higher starting Bi concentration (Wagner, 2007). Almost all of the precious metal-bearing minerals in the Skouries deposit have droplet-like spherical morphologies and are present as inclusions in the centre of hydrothermal quartz crystals and other hydrothermal alteration minerals, such as secondary biotite. The most abundant precious metal minerals in the Skouries deposit are hessite and electrum, which are often found together. The Au-Ag-Ternary system has been shown to be molten at temperatures >435 °C (Cabri, 1965), which is within the range of temperatures for main stage ore-forming veins in porphyries. If these minerals were formed from the cooling of a melt then this puts temperature constraints on the system as hessite and electrum co-exist at temperatures >550 °C (Markham, 1960). Sylvinite, however, is only stable up to 360 °C (Markham, 1960) while empressite is stable up to 191 °C (+/-16 °C) (Voronin et al., 2017). The presence of these relatively low temperature minerals is interpreted to represent the changing composition of the co-melt as the system cooled. The range of tellurides present in Skouries suggest the initial co-melt contained Au-Ag-Pd-Te-Bi. This is proposed to have precipitated native Au, electrum-hessite assemblages and Au-Bi-Te minerals as the system cooled below 550 °C, removing the majority of the Au from the melt (Markham, 1960; Voronin et al., 2017; Wagner, 2007). This would leave a Pd-Ag-Te-Cl-Te melt which could precipitate merenskyite-hessite and kotulskite-hessite assemblages as the system cooled below 540 °C, followed by sphacite-kotulskite-hessite assemblages below 383 °C (Vymazalová et al., 2015). This would remove most of the Pd and Bi, leaving a Ag-Te-Pd-Bi-Au melt which could precipitate sylvanite and rare merenskyite-stützite assemblages as it cooled past 350 °C (Markham, 1960; Voronin et al., 2015), leaving an Ag-Te melt phase which could form empressite below 200 °C (Voronin et al., 2017).

The varied suite of precious metal and semi-metal bearing accessory minerals present in Skouries has also been observed in Elatsite and Santo Tomas II, giving further evidence that PGE-enriched porphyry deposits contain an abundance of semi-metals. Stützite, empressite,
hessite and sylvanite are all also present in Elatsite, with only muthmannite and volynskite unique to the Skouries deposit (Augé et al., 2005; Bogdanov et al., 2005; Tarkian et al., 2003; Tarkian and Koopmann, 1995). Skouries also contains witichenite and claushalite, both of which are observed at Elatsite (Bogdanov et al., 2005). Elatsite however also contains native Te and bohdanowiczite (AgBiSe₂), neither of which are observed at Skouries, while Santo Tomas II contains relatively abundant selenides (Tarkian and Koopmann, 1995). This suggests that Skouries is a more Bi-rich and Se-poor system than Elatsite and Santo Tomas II.

6. Conclusions

The Skouries Cu-Au deposit is a multi-stage alkali porphyry system with multiple overprinting intrusions, each associated with hydrothermal vein sets. These can be divided into ‘early stage’ vein sets, which comprise predominantly quartz–magnetite ± pyrite–chalcopyrite veins associated with intense potassic alteration of a host monzonite intrusion. The main Cu and Au mineralisation is associated with the ‘main stage’ vein sets which are associated with syn-mineralisation syenite intrusions. Three vein sets host the majority of the mineralisation – M–3, quartz–massive chalcopyrite ± bornite veins; M–4, quartz–magnetite–chalcopyrite–bornite veins and M–5, quartz–chalcopyrite–bornite veins with the sulphides in a central suite. These are all associated with potassic alteration and are followed by ‘late stage’ vein sets which are associated with phyllic alteration assemblages.

The Skouries deposit is unusually PGE-enriched, with a very high Pd to Pt ratio. This is due to the presence of Pd minerals in the main mineralising vein sets, M–3, M–4 and M–5, associated with potassic alteration minerals. The platinum-group minerals in Skouries have been identified as sopocheite [Ag₃Pd₄Te₃], merenksyite [(Pd,Pt)(Te,Bi)₃] and kotulskite [Pd₄Te₂Bi], with rare telargpalite [(Pd,Au)(Te,Bi)], isomertieite [Pd₃SbAS₂], naldrettite [Pd₃Sb], testibiopalladite [PdTe₃(Sb,Te)], and sobolevskite [PdBi]. The most common platinum-group mineral is sopocheite and the Skouries deposit contains a greater variety of PGM than reported for other PGE-enriched porphyries. The platinum-group minerals in Skouries are small, 52 μm² on average. They are hosted predominantly as sphalerite minerals on the boundary between sulphides and silicates, but also as inclusions within hydrothermal quartz crystals and sulphides. This evidence shows the Pd and Pt in this deposit is part of the same mineralising event as the Cu and Au, and confirms findings that PGE mineralisation in porphyries is a hypogene event associated with potassic alteration.

Skouries contains a variety of other precious-metal and semi-metal minerals, with electrum [Au₃Ag₄Te₅], empressite [Ag₄Te₅], hessite [Ag₄Te₄], stützite [Ag₅xTe₄x (x = 0.24–0.36)], muthmannite [Ag₃Au₄Te₃], sylvanite [(Au,Ag)₂Te₃] and volynskite [AgBiTe₂] having been identified as accessory minerals. These precious-metal and semi-metal minerals are found in all the main stage mineralising vein sets, primarily as spherical inclusions in hydrothermal quartz crystals and in ore minerals, and are often associated with platinum-group minerals.

A semi-metal collector model is proposed for PGE in porphyry deposits, whereby an immiscible Bi-Te melt exsolves and acts as a collector for PGE and other precious metals in high temperature (> 490 °C) hydrothermal fluids and precipitates Pd tellurides and bismuthides upon cooling. This would allow the formation of PGE-enriched porphyries without Pt and Pd fluid saturation, and is supported by the occurrence of droplet-shaped Pd-Bi-Te minerals in the centre of euhedral hydrothermal quartz crystals. High concentrations of Bi and Te could be used to indicate the potential presence of PGE in porphyry Cu deposits.

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A.

See Tables A.1–A.3.

Table A.1

Accuracy and precision for the EPMA data. Analysis performed at the Natural History Museum, London (NHM) with values calculated from NHM in-house pure element standards. STD = published standard values; x = mean value measured; σₓ = standard deviation in standard measurements; %RSD = standard deviation as a percentage of the published value (precision); %RD = difference of measurement with published value as a percentage of published value (accuracy). Copyright (2016) University of Southampton.

| Element | STD (wt.%) | x (wt.%) | σₓ | %RSD | %RD |
|---------|------------|----------|-----|-------|-----|
| Pt      | 100        | 99.41    | 0.11| 0.11  | 0.59|
| Pd      | 100        | 99.76    | 0   | 0     | 0.24|
| Au      | 100        | 99.58    | 0.19| 0.19  | 0.42|
| Ag      | 100        | 99.77    | 0.2 | 0.2   | 0.23|
| Bi      | 53         | 52.82    | 0.11| 0.09  | 0.35|
| Te      | 47         | 47.75    | 0.04| 0.24  | 1.6 |
| Se      | 27         | 27.72    | 0.02| 0.02  | 0.35|
| Pb      | 73         | 72.75    | 0.02| 0.05  | 2.65|
| Cu      | 100        | 100.86   | 0.01| 0       | 0.85|
Table A.2
Analytical SEM-EDS data (in wt.%) for platinum group minerals with mineral identification. Copyright (2016) University of Southampton.

| Sample | PGM # | Mineral     | Pd  | Pt  | Ag  | Bi  | Te  | Sb  | As  | Au  | Se  |
|--------|-------|-------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 3      | PGM1  | Sobolevskite| 36  |     |     |     |     |     |     |     |     |
| 3      | PGM2  | Sobolevskite| 38  |     |     |     |     |     |     |     |     |
| 3      | PGM4  | Sobolevskite| 34  | 1   |     |     |     |     |     |     |     |
| 3      | PGM5  | Sopcheite   | 25  | 39  | 2   |     |     |     |     |     |     |
| 6      | PGM1  | Kotulskite  | 45  |     |     |     |     |     |     |     |     |
| 6      | PGM2  | Merenskyite | 27  | 1   |     |     |     |     |     |     |     |
| 8      | PGM1  | Kotulskite  | 45  |     |     |     |     |     |     |     |     |
| 8      | PGM2  | Sopcheite   | 19  | 27  | 13  |     |     |     |     |     |     |
| 9      | PGM1  | Sopcheite   | 9   | 14  | 7   |     |     |     |     |     |     |
| 9      | PGM2  | Sopcheite   | 9   | 45  | 21  |     |     |     |     |     |     |
| 9      | PGM3  | Kotulskite  | 28  |     |     |     |     |     |     |     |     |
| 9      | PGM4  | Sopcheite   | 22  |     |     |     |     |     |     |     |     |
| 11     | PGM1  | Sopcheite   | 6   | 57  | 8   |     |     |     |     |     |     |
| 11     | PGM2  | Sopcheite   | 9   | 45  | 21  |     |     |     |     |     |     |
| 11     | PGM3  | Isomertieite?| 70  | 4   |     |     |     |     |     |     | 15  |
| 11     | PGM4  | Naldrettite?| 63  | 6   |     |     |     |     |     |     | 15  |
| 11     | PGM5  | Sopcheite   | 34  |     |     |     |     |     |     |     |     |
| 11     | PGM6  | Kotulskite  | 43  |     |     |     |     |     |     |     | 47  |
| 26     | PGM1  | Sopcheite   | 17  |     |     |     |     |     |     |     |     |
| 31     | PGM1  | Sopcheite   | 26  | 2   | 29  |     |     |     |     |     |     |
| 31     | PGM2  | Sopcheite   | 22  | 17  | 11  |     |     |     |     |     | 20  |
| 31     | PGM3  | Sopcheite   | 18  | 15  | 11  |     |     |     |     |     | 21  |
| 31     | PGM4  | Merenskyite | 29  | 2   |     |     |     |     |     |     | 45  |
| 31     | PGM5  | Telargpalite| 32  | 3   |     |     |     |     |     |     | 66  |
| 31     | PGM6  | Kotulskite  | 39  |     |     |     |     |     |     |     | 30  |
| 34     | PGM1  | Testibiopalladite| 28 |     |     |     |     |     |     |     | 67  |
| 34     | PGM10 | Sopcheite   | 23  | 21  | 8   |     |     |     |     |     | 18  |
| 34     | PGM11 | Sopcheite   | 9   | 40  | 22  |     |     |     |     |     | 29  |
| 34     | PGM12 | Sopcheite   | 26  | 6   | 8   |     |     |     |     |     | 60  |
| 34     | PGM13 | Kotulskite  | 30  |     |     |     |     |     |     |     | 29  |
| 34     | PGM14 | Kotulskite  | 29  |     |     |     |     |     |     |     | 71  |
| 34     | PGM15 | Kotulskite  | 43  |     |     |     |     |     |     |     | 47  |
| 34     | PGM16 | Sopcheite   | 19  | 12  | 45  |     |     |     |     |     | 24  |
| 34     | PGM2  | Merenskyite | 13  |     |     |     |     |     |     |     | 25  |
| 34     | PGM3  | Merenskyite | 41  |     |     |     |     |     |     |     | 50  |
| 34     | PGM6  | Sopcheite   | 26  | 12  | 6   |     |     |     |     |     | 55  |
| 34     | PGM9  | Merenskyite | 31  |     |     |     |     |     |     |     | 64  |
| 36     | PGM1  | Merenskyite | 26  | 2   | 5   |     |     |     |     |     | 68  |
| 36     | PGM12 | Sopcheite   | 11  | 2   | 54  |     |     |     |     |     | 29  |
| 36     | PGM18 | Merenskyite | 25  | 3   |     |     |     |     |     |     | 63  |
| 36     | PGM2  | Merenskyite | 25  |     |     |     |     |     |     |     | 63  |
| 36     | PGM3  | Merenskyite | 25  |     |     |     |     |     |     |     | 63  |
| 36     | PGM4  | Merenskyite | 25  |     |     |     |     |     |     |     | 63  |
| 36     | PGM5  | Sopcheite   | 28  | 11  | 11  |     |     |     |     |     | 51  |
Table A.3
Analytical SEM-EDS data (in wt.%) for precious metal minerals with mineral identification. Copyright (2016) University of Southampton.

| Sample | Mineral          | Au  | Ag  | Te  | Bi  |
|--------|------------------|-----|-----|-----|-----|
| 1      | Muthmannite      | 5   | 63  | 31  |     |
| 6      | Hessite          | 62  | 38  |     |     |
| 6      | Hessite          | 62  | 38  |     |     |
| 6      | Hessite          | 62  | 38  |     |     |
| 6      | Hessite          | 60  | 40  |     |     |
| 6      | Hessite          | 60  | 40  |     |     |
| 6      | Unknown          | 51  | 1   | 48  |
| 8      | Electrum         | 74  | 26  |     |     |
| 8      | Empressite       | 66  | 44  |     |     |
| 8      | Empressite       | 46  | 54  |     |     |
| 9      | Native Au        | 100 |     |     |     |
| 10     | Native Au        | 93  | 7   |     |     |
| 11     | Electrum         | 83  | 27  |     |     |
| 11     | Electrum         | 78  | 22  |     |     |
| 11     | Hessite          | 74  | 26  |     |     |
| 11     | Hessite          | 66  | 44  |     |     |
| 11     | Hessite          | 63  | 37  |     |     |
| 11     | Native Au        | 100 |     |     |     |
| 11     | Native Au        | 100 |     |     |     |
| 11     | Native Au        | 100 |     |     |     |
| 11     | Native Au        | 100 |     |     |     |
| 13     | Unknown          | 7   | 21  | 72  |
| 13     | Unknown          | 7   | 21  | 72  |
| 31     | Electrum         | 70  | 30  |     |     |
| 34     | Electrum         | 74  | 26  |     |     |
| 34     | Native Au        | 84  | 16  |     |     |
| 34     | Native Au        | 84  | 16  |     |     |
| 34     | Native Au        | 86  | 14  |     |     |
| 34     | Electrum         | 77  | 23  |     |     |
| 34     | Native Au        | 86  | 14  |     |     |
| 34     | Native Au        | 99  | 1   |     |     |
| 34     | Native Au        | 99  | 1   |     |     |
| 34     | Hessite          | 95  | 5   |     |     |
| 34     | Hessite          | 70  | 30  |     |     |
| 34     | Sützite          | 57  | 43  |     |     |
| 34     | Sylvanite        | 63  | 26  | 11  |     |
| 34     | Sylvanite        | 49  | 15  | 36  |     |
| 36     | Electrum         | 97  | 3   |     |     |
| 36     | Empressite       | 46  | 54  |     |     |
| 36     | Hessite          | 63  | 37  |     |     |
| 36     | Hessite          | 55  | 45  |     |     |
| 36     | Hessite          | 61  | 39  |     |     |
| 36     | Hessite          | 56  | 44  |     |     |
| 36     | Hessite          | 27  | 73  |     |     |
| 36     | Hessite          | 61  | 37  | 1   |     |
| 36     | Hessite          | 62  | 38  |     |     |
| 36     | Volynskite       | 46  | 42  | 12  |     |
| 36     | Volynskite       | 29  | 6   | 65  |     |
| 36     | Volynskite       | 22  | 15  | 63  |     |
| 36     | Volynskite       | 64  | 36  |     |     |
| 36     | Volynskite       | 22  | 29  | 49  |     |
| 36     | Volynskite       | 20  | 27  | 53  |     |
| 36     | Volynskite       | 32  | 30  | 37  |     |
| 36     | Volynskite       | 47  | 37  | 15  |     |
| 36     | Volynskite       | 19  | 9   | 72  |     |

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