PALLADIUM AND PLATINUM IN HYDROTHERMAL SYSTEMS: THE CASE OF PORPHYRY-CU SYSTEMS AND SULFIDES ASSOCIATED WITH OPHIOLITE COMPLEXES

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Abstract

Data on the Pt and Pd contents in sea-floor massive sulfides related to ophiolite complexes indicated elevated Pt contents, up to 1 wt % Pt in sulfides from East Pacific Rise, up to 1000 ppb Pd or Pt in sulfides from mid-Atlantic Ridge and the Pindos ophiolite complex (Greece). Recently, elevated levels of Pd and Pt, have been reported from mineralization associated with alkaline porphyry deposits, such as the Skouries porphyry deposit (Greece), Cordillera of British Columbia, Elatsite (Bulgaria), Santo Tomas II in the Philippines and elsewhere. Current state of knowledge on the solubility of platinum-group elements was applied on hydrothermal systems related to the mineralization in ophiolite complexes and porphyry Cu-Mo-Au±Pd±Pt deposits toward a better understanding of the PGE mineralization in hydrothermal systems and the unknown Pd and Pt potential in porphyry-Cu systems. Ore reserves, mineralogical and geochemical ore data for porphyry-Cu systems are considered to be an encouraging factor for the presence of precious metals. In particular, the occurrence of merenskyite (palladium telluride) associated with chalcopyrite, coupled with the experimental data indicate that porphyry systems are capable to transport significant amounts of Pd and Pt.

Key words: *Platinum, palladium, sulfides, porphyry, Skouries.*

Περίληψη

Η έρευνα σχετικά με την περιεκτικότητα Pt και Pd σε θειούχα μεταλλεύματα που συνδέονται με οφιολιθικά συμπλέγματα έδειξε σημαντική περιεκτικότητα Pt, μέχρι 1% wt στην μεσο-ωκεάνια ράχη του Ειρηνικού Ωκεανού, μέχρι 1000 ppb Pd ή Pt σε θειούχα της μεσο-ωκεάνιας ράχης του Ατλαντικού Ωκεανού και στο οφιολιθικό σύμπλεγμα της Πίνδου. Επί πλέον σημαντικά επίπεδα Pd και Pt, έχουν προσδιοριστεί σε μεταλλοφορίες που συνδέονται με αλκαλικά κοιτάσματα πορφυρικού τύπου όπως στις Σκουριές Χαλκιδικής, Κορδιλιέρες της Βρετανικής Κολομβίας, ΗΠΑ, Elatsite (Βουλγαρία), Santo Tomas II Φιλιππίνες και αλλού. Πρόσφατα δεδομένα που σχετίζονται με την διαλυτότητα των στοιχείων της ομάδας του λευκοχρύσου εφαρμόσθηκαν σε υδροθερμικά συστήματα που συνδέονται με μεταλλοφορίες που φιλοξενούντα σε οφιολιθικά συμπλέγματα και κοιτάσματα πορφυρικού τύπου Cu-Mo-Au ± Pd±Pt, με σκοπό την ερμηνεία της παρουσίας των στοιχείων αυτών σε υδροθερμικά συστήματα και την δυνατότητα προσδιορισμού του δυναμικού του Pd και

Pt σε συστήματα πορφυρικού-Cu. Το αποθεματικό δυναμικό των κοιτασμάτων πορφυρικού-Cu σε συνδυασμό με τα ορυκτολογικά και γεωχημικά τους δεδομένα αποτελούν ενθαρρυντικούς παράγοντες για την φιλοξενία σε αυτά πολυτίμων μετάλλων. Ειδικότερα, η παρουσία παλλαδίου σε πορφυρικά συστήματα χαλκού με την μορφή μερενσκυίτη (τελλουρίδιο του παλλαδίου) και η σχέση του τελευταίου με τον χαλκοπυρίτη, και σε συνδυασμό με πειραματικά δεδομένα υποδηλώνουν δυνατότητα μεταφοράς και απόθεσης Pd και Pt σε κοιτάσματα πορφυρικού χαλκού και άλλα υδροθερμικά συστήματα.
Λέξεις κλειδιά: λευκόχρυσος, παλλάδιο, θειούχα, πορφυρικός -Cu, Σκουριές.

1. Introduction

Recent data on the platinum and palladium contents in sea-floor massive sulfides related to ophiolite complexes indicated that elevated platinum and palladium contents, up to 1 wt % Pt in massive sulfides from East Pacific Rise (Hekinian et al. 1980), up to 1000 ppb Pd in sulfides from mid-Atlantic Ridge (Crocket 1990), up to 1000 ppb Pt in an occurrence of brecciated pipeform diabase, underlying the massive ore from the Pindos ophiolite complex (Economou-Eliopoulos et al., 2008).

In addition, elevated levels of Pd and Pt, have been reported from mineralization associated with several of the alkaline porphyry deposits in the Cordillera of British Columbia (Copper Mountain Galore Creek), Allard Stock, La Plata 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, Piestrzynski et al. 1994, Eliopoulos et al. 1995, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Economou-Eliopoulos & Eliopoulos 2000, Tarkian et al. 2003). The average Pd and Pt content at the Skouries deposit are about 180 ppb and 26 ppb, respectively (Eliopoulos and Economou-Eliopoulos, 1991). As the ore reserves amount to over 200 million tons, the amounts of Pd and Pt are approximately 15 tons and 3.5 tons, respectively in the Skouries deposit, and 13 tons Pd and 3 tons Pt for the Elatsite deposit (Economou-Eliopoulos, 2005). In addition, the occurrence of these precious metals in porphyry-Cu systems under the form of merenskyite (palladium telluride) and their association with chalcopyrite (Tarkian et al., 1992) were considered to be an encourage factor for the Pd Pt recovery as by products along with gold and copper (Eliopoulos and Economou-Eliopoulos, 1991).

Although the lack of thermodynamic or experimental data preclude a quantitative analysis of Pt and Pd solubility in waters rich in organic material, ammonia, polysulfide, or thiosulfate (Wood 2002, Wilde et al. 2002), experimental data (Gammons et al. 1992) indicated that at about 300ºC, solubilities of Pt and Pd as chloride complexes are restricted to (a) oxidizing conditions over a range of pH < 6, and (b) strongly acidic conditions (pH less than ~3), under reducing conditions (pyrite or pyrrhotite stability fields). Thus, it has been concluded that the highest Pt and Pd concentration will be attained under both oxidized and acidic conditions and that chloride is the most abundant ligand in hydrothermal solutions, forming strong complexes with Pt and Pd, and it is a potentially important ligand for aqueous transport of these metals (Wood 2002).

In the present study the current state of knowledge of solubility of platinum-group elements (Wood, 2002; Hanley, 2005; Simon and Pettke, 2009, and references there in) is applied toward a better understanding of the PGE mineralization in hydrothermal systems and the unknown Pd and Pt potential in porphyry Cu systems.

2. Description of Pt-Pd Enriched Hydrothermal Deposits

2.1. Pt and Pd Contents in Sulfide Mineralization Associated With Ophiolite Complexes

Data compilation of platinum and palladium contents in sea-floor massive sulfides related to ophiolite complexes may indicate that they are quite soluble under a range of hydrothermal conditions. High Pt (up to 1 wt %) contents have been reported in marcasite and chalcopyrite from massive sulfides at 21ºN on the East Pacific Rise (Hekinian et al. 1980). Sulfide deposits at 26ºN on the mid-Atlantic Ridge contain significant palladium, ranging from 3 to 1000 ppb, and gold up to 8 ppb (Crocket 1990). Palladium contents in massive sulphide ores of Cyprus type from the Pindos (Kondro) ophiolite complex, Greece are lower than the detection limit of the method but contain Au up to 3.6 ppm, whilst significant Pt-enrichment, ranging from 160 to 1000 ppb, has been determined in an occurrence of brecciated pipeform diabase, underlying the massive ore of the complex (Economou-Eliopoulos et al., 2008) (Table 1).

Table 1 - Geochemical characteristics of sulfide ores hosted in ophiolite complexes and those from modern seafloor.

Main minerals	ppb						ppm					wt%		
	Pt	Pd	Ag	Au	Se	As	Mo	Sb	Hg	Ni	Co	Zn	Cu	Fe
Pindos														
Kondro: massive ore concisting of pyrite (py), chalcopyrite (cpy), sphalerite (sph), bornite (bn)														
py-cpy	<10	4	45	1.2	750	140	65	8.3	55	90	1300	2.7	8.2	13.2
py-cpy-sph	<10	3.5	35	3.5	1700	80	100	9	425	90	550	6.5	14	24.5
py-bn-cpy	<10	4	37	3.3	970	45	80	1.7	950	90	1500	1.2	22.4	10.8
Aspropotamos (Neropriona): disseminated pyrite (py), chalcopyrite (cpy)														
diabase breccia														
less altered	<10	10		0.011	<5	15	<5	0.3	<1	<100	28	0.007	0.007	6.8
moderatelly altered	400	20		0.018	<5	25	<5	0.3	<1	<100	27	0.007	0.006	7.1
highly altered	1000	27		0.025	<5	25	<5	0.6	<1	<100	15	0.009	0.007	6.9
Abbreviations: py=pyrite; cpy=chalcopyrite; sph=sphalerite; bn=bornite														

2.2. Characteristic Features of the Sulfide Ores in the Pindos Ophiolite Complex

Cyprus-type massive sulfide occurrences in the form of small lenses (maximum 4 by 40 m) are found at Kondro Hill on the SE slopes of Smolicas Mountain. The estimated ore potential is ca. 10,000 tonnes with average 6.6 wt. % Cu and 9.4 wt. % Zn (Skounakis et al., 1980). They occur on the top of diabase (massive or pillow lavas) and are directly overlain by Fe-oxide-bearing sediments. Fragments of limestone, entirely enclosed within massive ore, are occasionally present. A salient feature of the Pindos massive ore from Kondro is the significant contents of Au (up to 3.6 ppm), Ag (up to 56 ppm), as well as high contents of Se (up to 1900 ppm), Co (up to 2200 ppm), Mo (up to 310 ppm), Hg (up to 280 ppm) and As up to 150 ppm (average values are presented in the Table 1). The ore comprises mainly pyrite and chalcopyrite. Bornite sphalerite, marcasite, covellite and siegenite are found in lesser amounts. Textural relationships indicate that early pyrite, commonly occurring as fractured large crystals, is extensively replaced by chalcopyrite, and then by bornite in a matrix of quartz. Cu-bearing sphalerite, with up to 3.6 wt. % Fe and 3.2 wt. % Cu, cements minor chalcopyrite and pyrite. Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor sphalerite with an average Cu content of 0.5 wt. %. The latter association, found in cross-cutting veins, hosts selenides (chiefly clausthalite, PbSe), the telluride mineral melonite ($NiTe_2$), gold, galena and barite. Concentrations of 'invisible Au' in coarse-grained pyrite (associated with chalcopyrite and bornite) range from 0.7±0.13 to 1.01±0.27 ppm, whereas concentrations in fine-grained pyrite lie between 7.67±1.6 and 5.3±2.7 ppm, accompanied by significant As content. Disseminated pyrite within diabase breccia in the

brecciated diabase underlying the Kondro massive ore, disseminated pyrite and minor chalcopyrite occur mostly in vesicles filled by quartz, kaolinite, chlorite and epidote. The Pd content in breccia samples (10 to 27 ppb) is low compared to that of Pt (160 to 1000 ppb). The significant enrichment in Pt in kaolinite-rich samples, and the limited range of $\delta^{34}S$ values for pyrite concentrates from the diabase breccia (+1.0 to +1.5‰), are characteristic features (Economou-Eliopoulos et al (2008).

2.3. Genetic Significance of the Platinum and Palladium Contents

Platinum and palladium contents in seafloor massive sulfides related to ophiolite complexes are generally very low. However, in the hydrothermal breccia underlying the massive ore, Pt reaches values of 1000 ppb; 27 ppb Pd was determined (Table 1). The concentration of Au in massive sulfide ore and Pt in the underlying diabase breccia may reflect differences in the relative solubility of the precious metals, and the extent to which they were saturated in a given hydrothermal solution, as well as the specific deposition mechanisms for each metal (Seward and Barnes, 1997; Wood, 2002). Pan and Wood (1994) pointed out that hydrothermal fluids in equilibrium with pyrite or pyrrhotite and alteration minerals such as chlorite, epidote, albite, calcite, etc., would be incapable of transporting significant amounts of PGE as chloride complexes. These authors instead suggested that a typical seafloor hydrothermal vent fluid could contain a significant amount of Pt and Pd as bisulfide complexes and that gold may also be predominantly transported in the form of bi-sulfide complexes. Moreover, they concluded that, under the conditions of their experiments, the solubility of Au as a bisulfide complex was three orders of magnitude higher than that of Pt and Pd. Thus, the elevated Pt contents in the mineralized diabase breccia of Pindos compared to massive sulfide ore seems to confirm the higher solubility, and thus further transport, of Au relative to Pt, causing Au enrichment in the massive ore. The presence of pyrrhotite remnants within pyrite, surrounded by hydroxides or magnetite within vesicles filled by pyrite, quartz, kaolinite and epidote may indicate that the Pt-precipitation was favoured by weakly acidic and oxidizing conditions (Wood, 2002).

Therefore, assuming that Au and Pt/Pd were derived from the same source area and that the transporting complexes of these metals are the same (Wood 2002) the concentration of Au in massive sulfide ore and Pt in the underlying diabase breccia may reflect a difference of the relative solubility (higher solubility of Au that remains more soluble than Pt) and the extent to which these metals are saturated in a given hydrothermal solution.

3. Pd and Pt Contents in Porphyry Cu ± Mo ± Au ± Pd ± Pt Deposits

Porphyry Cu ± Mo ± Au deposits are major sources of these metals and are associated with alkaline and calc-alkaline rocks. Recently, elevated levels of Pd and Pt, have been reported from mineralization associated with several of the alkaline porphyry deposits in the Cordillera of British Columbia (Copper Mountain Galore Creek), Allard Stock, La Plata 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, Eliopoulos et al. 1995, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Economou-Eliopoulos & Eliopoulos 2000, Tarkian et al. 2003; Table 2).

Late Mesozoic to Tertiaty porphyry Cu-(Mo-Au) porphyry deposits, extending from Romania, through Serbia and Bulgaria to Greece are associated with subduction related magmatism following the change from east-west to north-south converge between Africa and Eurasia, and subsequent continental collision and post-collision magmatism (Kockel et al., 1975; Frei, 1995; Heinrich and Neubauer, 2002).

3.1. Skouries Deposit

The Skouries porphyry Cu-Au deposit, located at the Chalkidiki peninsula, northern Greece belongs to the Serbomacedonian massif consisting of a crystalline basement, which comprise two lithostratigraphic-tectonic units, the lower Kerdylia Formation and the upper Vertiskos Formation. The Vertiskos Formation is consisting of an old basement gneiss, amphibolite, schist and marble (Kockel et al., 1977; Perantonis, 1982; Frei, 1995; Tobey et al., 1998). Isotope data indicated that subvolcanic–porphyritic stocks such as the Skouries are relatively younger, of Miocene age 18 Ma, than the intrusions of the SerboMacedonian massif. The Skouries deposit is related to pipe-like intrusions, of subalkaline-alkaline composition, extending at surface over an area of approximately 200m x 200 m, is developed around two related porphyry centres (Fig. 4a) at depths between 650 and 800 m. The defined reserves in the porphyry Cu-Au deposit of Skouries are approximately 206 Mt at 0, 54 % Cu, and 0.80 ppm Au (Tobey et al., 1998).

Table 2 - Precious metal contents in porphyry Cu-Pd-Pt deposits.

	ppb				wt%
	Au	Pt	Pd	Pd/Pt	Cu
Greece					
Skouries (n=24)	3220	34	140	4.4	1.3
Concentrate (composite)	2400	40	60	0.7	22
Bulgaria					
Elatsite (n=11)	840	13	24	2.3	0.64
Concentrates (n=5)	17000	160	1600	19	31.44
British Columbia					
Galore Creek (n=2, cp-py-bn)	5200	17	410	29	7.63
Galore Creek (n=2, mt-py-bn-cp)	34200	49	780	17	16.01
Mt Milligan (n=4)	9500	56	1780	19	2.4
Mt Polley (n=3)	10500	19	140	5.9	7.9
Allard (n=2)	1485	3408	2120	0.7	22.5
Cooper Mountain (n=2)	4500	120	3005	40	34.1
Philippines					
Santo Tomas II	2230	13	48	5	0.31
Russia					
Aksug (=2)	4100	86	73	0.8	14.9
Sora (n=3)	100	88	50	0.6	5.8
Abbreviations: cp = chalcopytite; py = pyrite; bn = bornite; mt = magnetite					

3.2. Characteristic Features of Alteration and Mineralization

At least five distinct stages of hydrothermal alteration and mineralization are obvious in the main porphyry. The typical alteration types of the porphyry Cu intrusions described by Lowell and Guibert (1970) are more or less presented in the Skouries intrusion, due to the repeated overprinting and intense silicification, with potassic being the predominant alteration type, whereas the propylitic and surrounding phyllitic alteration are limited. Two mineral assemblages of mineralization, occurring as veinlets/disseminations, can be distinguished: (a) magnetite, reaching up to 10 vol % (average 6 vol %)-bornite-chalcopyrite, linked to pervasive potassic and propylitic alteration type, in the central parts of the deposit, and (b) chalcopyrite-pyrite, dominated at the peripheral parts of the deposit. Molybdenite occurs in small amounts, commonly in late pyrite-sericite-carbonate bearing veinlets. Chalcopyrite, and in a lesser extent bornite, contain exsolutions of galena, which commonly has significant concentrations of Se, while clausthalite is

rare. Minor ore minerals are gold-electrum, clausthalite-galena, hessite and merenskyite-moncheite (Tarkian et al., 1991). A salient feature of the Skouries porphyry is the presence of fine-grained magnetite, which is Cr-bearing, ranging from 0.65 to 0.98 wt% Cr_2O_3 in the matrix in contrast to the Cr-free magnetite of the main porphyry. Also, chalcopytite and pyrite, which contains nickel ranging from 0.45 to 2.4 wt% Ni. And Co ranging from 0.64 to 4.18 wt% Co, as well as the high values of the ratios Ce/Lu (>225), relatively high Th and U contents (up to 63 ppm and 9 ppm, respectively), Ba (up to 2260 ppm) and Sr (up to 1230 ppm) contents, reflecting probably a strong fractionation of parental magmas (Eliopoulos and Economou-Eliopoulos 1991).

3.3. Palladium and its Distribution in the Skouries Deposit

The analysis of representative ore samples showed a significant Pd-enrichment in mineralised samples, up to 490 ppb Pd, in oxidized ore samples (Eliopoulos and Economou-Eliopoulos, 1991). Relatively high Pd content in the major vein-type mineralization of Skouries ranging between 60 and 200 ppb (average 110 ppb Pd), was documented by analysis of a composite drill hole sample (~15 kgs) showing 76 ppb Pd to 5000 ppm Cu (Economou-Eliopoulos and Eliopoulos, 2000). The analysis of mineralized material and highly mineralized portions from deeper parts of the deposit indicated relatively high Pd (average 130 ppb) and Pt (average 46 ppb) contents.

Textural relations between base metal sulphides, PGM and Au–Ag tellurides support the association of precious metals with the Cu-minerals (bornite and chalcopyrite), indicating that the main Pd-bearing mineral merenskyite, has deposited during the major stage of Cu deposition. Thus, assuming that Pd is mainly associated with chalcopyrite, when calculating the measured Pd contents in chalcopyrite (which were normalized to 100 percent chalcopyrite), the Pd values in the mineralized samples from deeper parts of the Skouries deposit is 3000 ppb Pd. These values are comparable to that in the chalcopyrite concentrate (2400 ppb Pd to 21 wt%, Economou-Eliopoulos and Eliopoulos, 2000), while the calculated Pt content is 1230 ppb.

4. Comparison with Other Pd, Pt-Bearing Porphyry-Cu Intrusions

4.1. Elatsite Deposit (Bulgaria)

The Elatsite porphyry Cu-Au-PGE deposit, of Upper Cretaceous (92.3 ± 1.4 Ma) age, extends over an area of approximately 1,300 m long and 200 to 700 m wide. At depth the ore-body was traced more than 550 m. The Elatsite porphyry Cu-Au deposit is found in a spatial association (~10 km distance) with the Chelopech Au-Cu high-sulfidation epithermal type deposit, connected by east-northeast – and north-northwest – trending fault system (Popov and Kovachev, 1996; Popov et al., 2000; Bonev et al., 2002). Ore reserves of the deposit are estimated to be 185 million with 0.4 wt % Cu, 0.3 g/t Au, 0.68–1.9 g/t Ag, 0.07 g/t Pd and 0.02 g/t Pt (Strashimirov et al., 2002; Tarkian et al., 2003; Strashimirov et al., 2003).

Precious metal contents are strongly concentrated in the magnetite (ranging from 2 to 10 vol %, reaching locally up to 30 vol %), -bornite-chalcopyrite assemblage, occurring mainly in the southern part of the ore body. Palladium, Pt and Au concentrations in representative mineralized samples from the Srednogorie metallogenetic zone of Bulgaria, including the Elatsite deposit have been published by Eliopoulos et al. (1995) and noticed Pd and Pt contents up to 20 ppb, while Cr and Co reach values up to 100 and 116 ppm, respectively. The average precious metal contents in flotation concentrates (at 23.5 wt% Cu) are 16200 ppb Au, 1130 ppb Pd and 130 ppb Pt (Tarkian and Stribrny, 1999; Tarkian et al., 2003). Gold and Pd correlate with Te, Bi and Se, while Pt shows a strong correlation (r = 0.93) only with Te (Tarkian et al., 2003).

4.2. Santo Tomas II Philex Philippines

The Santo Tomas II Philex porphyry Cu–Au deposit, of Miocene age (3 Ma), is located at the Luzon Island, Philippines, along the margins of a fault system, extending at surface over an area of approximately 600m x 200 m that represents approximately 800 m of vertical section. It consists

of quartz diorite with calk-alkaline affinities, and is spatially associated with volcanic rocks of dacite composition (Tarkian and Koopmann, 1995).

The predominant wall rock alteration associated with the mineralised zone is potassic and propylitic, with a common overlapping between of these alteration types. Phyllic alteration is of limited extent, overprints earlier potassic and inner propylitic assemblages. Two types of mineral assemblages have been distinguishes: (a) bornite-chalcopyrite-magnetite, which is concentrated in the inner part of the potassic zone (biotite and quartz), and (b) chalcopyrite-pyrite, occurring in the outer part of the potassic zone and in the propylitic zone. The merenskyite occurs exclusively as inclusions in chalcopyrite and bornite (Tarkian and Koopmann, 1995).

4.3. British Columbia Cordillera

Porphyry Cu-Au deposits located in the British Columbia Cordillera are associated with alkaline, subalkaline to calc-alkaline rocks stocks, dikes and sills, which have emplaced into two allochthonous terranes, Quesnellia and Stikinia, North America (McMillan et al., 1995). The majority of these intrusions are Early Jurassic in age (205-195 Ma) although some intrusions in Quesnellia are distinctly younger (~185 Ma; Mortensen et al., 1995). Given that many of those Cu-Au porphyry deposits have formed in areas of long-lived magmatism and subsequent thermal overprinting, age data may reflect cooling rather than actual ages on intrusions.

Apart from Au, elevated levels of platinum group elements (PGE), particularly Pd and Pt, have been reported in high-grade bornite-chalcopyrite and/or flotation concentrates from porphyry Cu-mineralization associated with the alkaline porphyry intrusions at Copper Mountain-Ingerbelle (up to 3.2 ppm Pd and 0.15 ppm Pt), Allard stock, La Plata Mountains (up to 2.3 ppm Pd and 3.9 ppm Pt), Galore Creek, Copper King Mine, Comstock Mine and Sappho in the British Columbia Cordillera (Werle et al., 1984; Mutschler et al., 1985). It has been suggested that the Pd and Pt mineralization in the above porphyry deposits is linked with the genesis of alkaline arc magmas, derived probably from an enriched mantle source. They may reflect partial melting and incorporation into the melt of destabilized precious metal-bearing sulfides, hosted in the mantle source.

5. Critical Factors for the Formation of Porphyry Cu+Au+ Pd ±Pt Deposits

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 may be major controls of their base/precious metal potential and characteristics. Experimental, thermodynamic, and fluid inclusion studies strongly suggest that Cu and precious metals in potassic alteration zones are transported as an aqueous chloride complex in high temperature (350 to >700°C) and relatively oxidized hydrothermal brines (Burnham & Ohmoto 1980). Given that significant quantities of Au can be transported by hot, saline, magmatic fluids under either reducing or oxidizing conditions, whereas Cu transport is much more favoured in the oxidizing environment. In contrast, "reduced" porphyry Cu–Au deposits that lack primary hematite, magnetite, and sulfate minerals (anhydrite) and contain abundant hypogene pyrrhotite, are relatively Cu-poor, but Au-rich deposits (Hemley et al. 1992, Williams et al. 1995, Rowins 2000).

Experimental studies have constrained the solubilities of As, Au, Cu, Ag and Mo (ore metals in magmatic volatile phases in equilibrium with silicate melts (Candela and Holland, 1984; Williams et al., 1995; Simon et al., 2005) and these data have been used to model quantitatively the behaviour of metals at conditions relevant to shallow-level magma degassing. One important group of ore metals for which there are only very limited solubility data at magmatic conditions is the platinum group elements (PGE). Several experimental studies have been performed to characterize the behaviour of the PGE in low-temperature fluids; however, the mobility of the PGE in fluid-saturated silicate melt assemblages remains almost completely unconstrained.

Recently, experimental data on the solubility and partitioning of Pt in an S-free vapour – brine – rhyolite melt – Pt metal assemblage indicated that the vapour and brine were in equilibrium with the melt at the time of trapping (Simon and Pettke, (2009). Platinum solubilities in vapour, brine and glass (quenched melt) were quantified by using laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS). Based on the major and trace element concentrations of glass-hosted fluid inclusions as well as the silicate melt, they estimated platinum solubility values. Furthermore, they used these data to calculate Nernst-type partition coefficients for Pt between vapour/melt, brine/melt and vapour/brine. The partitioning data were used to model the Pt-scavenging capacity of vapour and brine during the crystallization-driven degassing (i.e., second boiling) of a felsic silicate melt over a depth range of 3–6 km (magmatic-hydrothermal ore deposits). Model calculations suggest that aqueous vapour and brine can scavenge sufficient quantities of Pt, and by analogy Pd to produce economically important PGE-rich magmatic-hydrothermal ore deposits in Earth's upper continental crust.

6. Evaluation of Pd and Pt as an Economic Factor for Porphyry Cu Systems

The palladium telluride, merenskyite, as inclusions in chalcopyrite and bornite, has been described as the main PGE mineral in porphyry Cu–Au–Pd–Pt deposits, such as Skouries, Santo Tomas II, Biga, Elatsite, Mamut (Tarkian et al. 1991; Tarkian et al. 2003; Tarkian & Koopmann 1995, Tarkian & Stribrny 1999). Assuming that Pd in porphyry Cu deposits is mainly associated with chalcopyrite (measured contents are normalized to 100 % chalcopyrite), and using reserves for each deposit, then the Pd and Pt potential in porphyry systems can be estimated (Table 3).

The potential for PGE mineralization associated with such large Au-Cu porphyry deposits is still unknown. Although the analytical data required for the evaluation of the precious metal potential of porphyry deposit are limited, the existence of (Pd+Pt) values (>5 ppm) are considered to be encouraging for Pd and Pt as by-products and porphyry deposits a good target for Pd & Pt exploration.

Table 3 - Palladium and platinum potential in porphyry-Cu-Au-Pd-Pt deposits.

Deposit	Ore tonnage tons x 10^6	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	

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