

CHAPTER 10: PLATINUM-GROUP ELEMENT POTENTIAL OF PORPHYRY DEPOSITS

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INTRODUCTION

Porphyry Cu ± Mo ± Au deposits are major sources of these metals and are associated with alkaline and calc-alkaline rocks. Porphyry-type deposits range from porphyry Cu–Au, like Grasberg (Indonesia), Mamut (Malaysia), Santo Tomas II (Philippines), Skouries (Greece), Cadia (Australia), British Columbia (Copper Mountain, Ajax/Afton, Mount Polley, Galore Creek, Mt Milligan), Cu–Au–Mo deposits, like the giant deposit at Bingham Canyon, Utah, to porphyry Mo such as the Boss Mountain (central British Columbia). A variety of porphyry Cu, Mo, Cu–Mo and Au-rich deposits define the metallogeny of the Andean belt, extending from Ecuador, Peru, and Bolivia to Argentina and Chile, covering the early Cretaceous to Pleistocene age span (Sillitoe 1979 1997, 2000, 2004, Titley 1993, Kirkham & Sinclair 1996, Corbett & Leach 1998, Bookstrom *et al.* 1998, Brooks *et al.* 2004, Seedorff & Einaudi 2004). The Alpine-Balkan-Carpathian Dinaride belt belongs to the Alpine-Himalayan system, extending from

western Europe through Iran and the Himalaya to China and Malaysia, and is the result of convergence of the African, Arabian and Indian plates and their collision with Eurasia. Major calc-alkaline magmatism, extending over at least 25 million years (from about 90 to 65 Ma) in each segment of the metallogenic belt, is associated with certain segments only, due probably to the complex geometry of the collision interface (Heinrich & Neubauer 2002, Strashimirov *et al.* 2002). Although the Andes and Alpine-Balkan-Carpathian belts differ in terms of the subduction age span, they host some of the world's largest porphyry-type deposits and oldest mining areas (Kirkham & Sinclair 1996, Heinrich & Neubauer 2002).

Alkaline porphyry deposits represent significant gold resources owing to their large sizes. Recently, elevated levels of platinum group elements (PGE), particularly Pd and Pt, have been reported from mineralization associated with several of the alkaline porphyry deposits (Fig. 10-1) in the Cordillera of British Columbia (Copper Mountain,



FIG. 10-1. Location map of porphyry Cu ± Mo ± Au ± Pd ± Pt deposits

Galore Creek), Allard Stock, La Plana Mountains and Copper King Mine in USA, Skouries porphyry deposit, Greece, Elatsite, Bulgaria, and from Santo Tomas II in the Philippines (Werle *et al.* 1984, Mutschler *et al.* 1985, Eliopoulos & Economou-Eliopoulos 1991, Piestrzynski *et al.* 1994, Eliopoulos *et al.* 1995, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Economou-Eliopoulos & Eliopoulos 2000, Tarkian *et al.* 2003). The role of magma mixing, saturation of a sulfide melt or of a magmatic volatile phase to the base and precious metal potential of porphyry systems, and the investigation of the contribution of mantle, oceanic and continental crust to the parent magmas of porphyry Cu subvolcanic intrusions remains still uncertain (Burnham 1979, Burnham & Ohmoto 1980, McInnes & Cameron 1994, Keith *et al.* 1998, Titley 2001, Hattori & Keith 2001, Halter *et al.* 2002, Ivascanu *et al.* 2003, Halter *et al.* 2002–2005).

In this paper the characteristics of numerous porphyry Cu–Au–Pd±Pt-enriched systems are reviewed. Porphyry Mo deposits, although similar to porphyry Cu, are different in terms of their Pd and Pt contents and are not discussed in this review. Here we compile published (and some new) mineralogical and geochemical data and discuss factors controlling precious metal enrichment in the porphyry Cu systems, key characteristics of Pd–Pt-enriched porphyry deposits, which may be used in exploration, and the evaluation of Pd–Pt as an economic factor (as a by-product) for that type of deposit. Most references cited in this review are recent summary papers, which can be used as sources for more extensive research.

DISTRIBUTION OF PORPHYRY Cu DEPOSITS ALONG CONVERGENT PLATE MARGINS

Porphyry Cu deposits are spatially and genetically associated with porphyritic intrusions, emplaced at relatively high levels in the crust, which are characterized by phenocryst assemblages consisting of one or more minerals (K-feldspar, plagioclase, hornblende, quartz or biotite) in a fine-grained matrix. The majority of giant gold-rich porphyry deposits are located in the circum-Pacific region. A linear zone of volcanism at the boundary between the Pacific and adjacent Australia-India, Philippines, and Eurasian plates define the “ring of fire” (Corbett & Leach 1998, Tosdal & Richards 2001).

Many giant gold-rich porphyry deposits are generated at convergent margins during or

immediately following subduction of lithosphere, although there is a variation in the style of the tectonism in time and space. The genetic significance of the tectono-magmatic controls on large Cu±Mo±Au deposits, and the differing stress conditions in the overriding plate in arcs, which influence the style of major structures, have been emphasized by many authors. They may vary from compressional to tensional and shearing, in three dimensions: vertically (through the lithosphere), laterally (along the arc), and transversely (from forearc to back-arc) (Sillitoe 1997 2000, Müller & Groves 2000, Tosdal & Richards 2001, Richards 2003). Also, differences in oxidation state of parent magmas are reflected in the magmatic oxidation state of the ore assemblages (Mungall 2002, Sillitoe & Hedenquist 2003, Einaudi *et al.* 2003).

Fundamental changes in subduction geometry and convergence rates may result in the development of dike-like forms of many porphyry Cu deposits during periods of low differential or near isotropic horizontal stress in the arc environment. Porphyry intrusions are commonly emplaced at depths of 1–2 km. Differentiated felsic and volatile-rich intrusions may rise to higher crustal levels, whereas large batholithic bodies occur at greater depths (Corbett & Leach 1998, Tosdal & Richards 2001). The majority of these deposits are located along older fault systems. Fractures connected with tectonic and magmatic processes facilitate the intrusion of porphyry stocks or dikes near surface levels and facilitate volume expansion of the hydrothermal fluids (Lang & Titley 1998, Sillitoe 2000, Tosdal & Richards 2001, Sillitoe & Hedenquist 2003).

Dehydration of the subducting oceanic crust resulting in hydration of the overlying mantle seems to be the most favorable aspect of the arc magmatogenesis. Hydrous basaltic melts, derived by partial melting in the asthenospheric mantle wedge, intrude the overlying lithosphere, rising at the base of the crust, where they may fractionate and interact with crustal material. Furthermore, more evolved magmas (less dense) rise into the high levels of the crust, where they may undergo volatile exsolution and crystallization as porphyritic stocks. Parental magmas are considered to be moderately water-rich as indicated by the presence of hydrous minerals (amphibole, biotite), whose stability requires at least 3 wt.% H₂O in the melt. Such hydrous melts may contain metals and ligands of critical significance to the formation of Au-rich porphyry deposits (Sillitoe 2000, Tosdal & Richards

2001, Sillitoe & Hedenquist 2003). Some investigators have emphasized that uplift and crustal thickening of the continental crust has played a major role in the breakdown of hydrous minerals, as is exemplified by the central Andean Miocene porphyry deposits, formed in the shallow dip ($<30^\circ$) of the subducting plate compared to other circum-Pacific subduction zones (Isacks 1988, Allmendinger *et al.* 1990, Cahill & Isacks 1992, Kay *et al.* 1999). Mungall (2002) has suggested instead that the optimum conditions for generation of chalcophile-element-rich arc magmas involve the relatively rare process of partial melting of the subducting oceanic crust to produce adakitic or alkaline magmas.

CHARACTERISTICS OF ALKALINE INTRUSIONS

Following the definition based on total (K_2O+Na_2O) versus SiO_2 (Irvine & Baragar 1971, Jensen & Barton 2000), alkaline rock types associated with gold mineralization, range from ultramafic lamprophyres (<40 wt.% SiO_2) to fractionated, high-K rhyolite (up to 75 wt.% SiO_2), including subduction-related potassic calc-alkaline rocks and shoshonite. A subdivision of alkaline rocks, depending on the proportion of K and Na, is the shoshonitic rocks, which are potassic varieties and are considered to be particularly favorable for hosting porphyry Cu–Au deposits (Müller & Groves 2000). Less-evolved alkaline diorite, mafic syenite, and monzonite, ranging from silica-undersaturated

(quartz is absent) to silica-saturated tend to be associated with Cu (Au) base metal-rich hydrothermal systems as well (Jensen & Barton 2000). Also, alkaline-related hydrothermal systems, show distinct characteristics, including quartz-poor (or quartz-absent) style of alteration and mineralization. Quartz is variably present. It is absent from strongly silica-undersaturated deposits (Galore Creek, B.C.) but can be abundant in silica-saturated systems (Goonumbla, Australia). The degree of K enrichment in the potassic zone of alteration is variable, reaching values >10 wt.% K_2O , such as in the Galore Creek, the Allard stock and Goonumbla (Jensen & Barton 2000).

ALTERATION TYPES OF PORPHYRY INTRUSIONS

The porphyry Cu±Mo±Au deposits may develop around single intrusions or within more complex systems consisting of numerous intrusions and overlapping stages of alteration and ore deposition. Commonly they are related to multiple and multistage hypabyssal pipe-like intrusions extending at surface over widths ranging from less than 100 m to more than 1 km; their vertical extents may exceed 2 km (Tobey *et al.* 1998, Herrington *et al.* 1998, 2003, Tobey *et al.* 1998, Kroll *et al.* 2002).

Cooling of porphyry intrusions in the upper crust may be accompanied by the development of the initial alteration zone (Fig. 10-2). The subsequent alteration exhibits a zonation from K



FIG. 10-2. Representative drill core sample of the Skouries Main monzonite porphyry (core width is about 4 cm), showing mineralization (disseminated and vein-type) in angular mafic fragments (stage I), pervasive (stage II), crosscutting relationships between successive quartz veins (stages III & IV) dominated by the magnetite-bornite-chalcopyrite assemblage, and a quartz-biotite vein (stage V), reflecting a range of hydrothermal evolution. The presence of mineralized mafic xenoliths within main porphyry is consistent with the multiple intrusive phases and mineralising events.

silicate (potassic) to propylitic, intermediate argillic, sericitic (phyllitic) and advanced argillic as described by Meyer & Hemley (1967), Lowell & Guilbert (1970), Sillitoe (1997, 2000), Corbett & Leach (1998). Advanced argillic alteration and silification are strongly structurally controlled by faults, including those which initially facilitated the emplacement of the multiple porphyry intrusions.

Fluid-inclusions provide evidence of genetic importance. They suggest that relatively hot (400° to 700°C) and saline to hypersaline (up to 70 wt.% NaCl_{equiv}) magmatic-hydrothermal fluids transported Cu and precious metals as chloride complexes that were precipitated during the main stage of mineralization with the K-assemblages. The cooler, more dilute and more oxidized character of meteoric water-dominated fluids may permit the outward transport of Au as bisulfide complexes (Sillitoe 1993, Lang *et al.* 1995, Jensen & Barton 2000) in hybrid fluids produced by mixing of these with the orthomagmatic fluids. Although alteration type is an important indicator of fluid composition, the ore mineral assemblages themselves reflect the nature of the ore fluids (Sillitoe & Hedenquist 2003).

MINERALIZATION OF PORPHYRY Cu SYSTEMS

Porphyry deposits constitute major sources of Cu, Cu+Mo, or Cu+Au, although many shallow-level porphyritic intrusions are devoid of, or are accompanied by, weak mineralization. The Au-rich porphyry deposits comprise a continuum of systems from Cu plus by-product Au, through Au plus by-product Cu to Au-only end members. Porphyry deposits with average gold contents \geq 0.4 ppm Au may be defined as gold-rich, commonly deficient in Mo (Sillitoe 1979, 2000, Kesler *et al.* 2002). Gold-rich deposits are mostly linked to alkaline magmatic systems including a number of Cu(Au) and Mo(Au) in Colorado and the British Columbia Cordillera (Table 10-1) deposits, which may grade upward and/or outward into telluride-rich epithermal deposits, both characterized by high halogen (chlorine, fluorine) concentrations and by high oxygen fugacities. Epithermal parts are base-metal poor and have Au>Ag, whereas porphyry parts have significant Au and Ag>Au in a base metal-rich core.

Recently, elevated levels (over 5 ppm) of platinum group elements (PGE), particularly Pd and Pt, have been reported in high-grade bornite-chalcopyrite and/or flotation concentrates from porphyry deposits, associated mostly with several of the alkaline type including the Copper Mountain-

Ingerbelle, Afton-Ajax, Mount Polley, Galore Creek and Mount Milligan deposits in British Columbia, Allard stock, La Plata Mountains (Colorado) (Werle *et al.* 1984, Mutschler *et al.* 1985, Mutschler & Mooney 1993, Thompson *et al.* 2001), Skouries in Greece (Eliopoulos & Economou-Eliopoulos 1991), Santo Tomas II in the Philippines (Piestrzynski *et al.* 1994, Tarkian & Koopmann 1995), Elatsite, Bulgaria and elsewhere (Eliopoulos *et al.* 1995, Tarkian *et al.* 2003, Tarkian & Stribrny 1999). A review of characteristics features of some porphyry Cu–Mo–Au–Pd±Pt-enriched systems associated with alkaline magmas follows (Table 10-1, App. 10-A).

TRANSPORT OF PGE IN HYDROTHERMAL SYSTEMS

Experimental Data

The current state of knowledge of solubility of PGE has been reviewed and applied toward a better understanding of the PGE mineralization in hydrothermal systems by Wood (2002) and by Hanley (2005). The stable oxidation stages of Pt and Pd in aqueous solution under the most oxidizing conditions are Pt(II) and Pd(II). In that oxidation state strong complexes with soft (HS⁻, Cl⁻) ligands are the most common. The oxidation states of Os, Ir, Ru and Rh are more variable. Recently, Sassani & Shock (1990) have predicted that the divalent states Ru(II) and Rh(II) are likely to be their predominant oxidation state in hydrothermal solutions, which has been supported by experimental solubility measurements by Xiong & Wood (2000).

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), and measurements of the stability of Pd-chloride complexes at temperatures above 300°C, the Pt and Pd are quite soluble under a range of hydrothermal conditions (as chloride or hydroxyl species), in hot oxidized brines (as chlorides), and in hot, reduced, sulfur-rich waters (as bisulfide complexes). More specifically, experimental data (Gammons *et al.* 1992) indicated that at about 300°C, solubilities of Pt and Pd as chloride complexes are restricted to (a) oxidizing conditions (in the hematite stability field) 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

TABLE 10-1. SELECTED CHARACTERISTICS AND PRECIOUS METAL CONTENT IN FLOTATION CONCENTRATE (F.C.) AND SULFIDE CONCENTRATE (Sf.C) SAMPLES FROM PORPHYRY-CU DEPOSITS.

Deposit	Setting	Age (Ma)	Host porphyry type	Affinity	Alteration type	sample or average	Description	Ore tons (t x 10 ⁶)	concentration (ppb)			Pd / Pt	Pd/ Cu	Cu wt. %	Ref.		
Balkan peninsula																	
Greece-Skouries																	
(a) porphyry	C(col)	18	Monz	A	K, Prop, Q	Sk.Po.or	composite	206	76	<10	910		152	0.5	1,2,3		
						Sk.Po.or (F.C.)	composite		2400	40	22000	60	114	21	3		
(b) country rocks						Sk.Po.or (F.C.)	composite		75	20	8200	3.8	13	5.6	3		
Bulgaria																	
Elatsite	C(col)-IA	92	Monzdi	A	K, Prop, ser	n=8	EP(Sf.C) mt-bn-cp	260	540	160	18700	3.5	26	21	4,5		
Elatsite						n=27	E(Sf.C), cp-py		107	31	3700	3.5	11	10	4,5		
Elatsite						n=3	F.C.		1130	130	16200	8.7	48	24	4,5		
Medet	C(col)	92	Qmonz	A	K, Prop, ser	n=1	F.C.	244	160	8	5600	20	11	15	4,5		
Assarel	C(col)	92	Qmonz	A	Prop, ser	n=1	F.C.	360	54	14	4800	3.9	2	28	4,5		
Serbia																	
Bor	C	78-90	Qdi	CA	K, Prop, Q	n=1	F.C.	450	40	19	1700	2.1		n.d.	4,6,7		
Majdanpek	C	78-90	Monzdi	CA	Q	n=2	F.C.	570	180	20	4600	9	7	26	4,6,7		
Veliki/Krivelj	C	Late Cret.	Qdi	CA	K, Prop, Q	n=1	F.C.	1000	70	16	2250	4.4		n.d.	4,6,7		
Philippines																	
Santo Tomas II	IA	1.4	Di	CA	K, Prop, Q	n=3	mt-bn-cp	330	67	10	3540	6.7	92	0.7	7,8		
Santo Tomas II						n=2	cp-py		21	20	800	1.05	105	0.2	7,8		

Abbreviations: Sf.C = sulfide concentrate; F.C = flotation concentrate; mt = magnetite; bn = bornite; cp = chalcopyrite; py = pyrite; C= continental margin, Col = during or following collision, IA = island arc; Monz = monzonite, Monzdi = monzodiorite, Qmonz = quartz monzonite; Di = diorite, Qdi = quartz diorite, Granod = granodiorite; Gran = granite; Syen = syenite; A = alkaline, CA = calc-alkaline, KCA = high K calc-alkaline (shoshonite), K = K silicate, Na = Na silicate, Prop = propylitic, Q = silicification, Ser = sericitic, Ca,-K = calc-potassic, Na-Ca = sodic-calcic; (1) = Tobey *et al.* (1998); (2) = Kroll *et al.* (2002); (3) = Economou-Eliopoulos & Eliopoulos (2000); (4) = Tarkian & Stribny (1999); (5) = Tarkian *et al.* (2003); (6) = Herrington *et al.* (1998); (7) = Tarkian & Koopmann (1995); (8) = Sillitoe (2000); (9) = Berzina *et al.* (2005); (10) = Lebedev & Kuzhuget (1998); (11) = Kovalenker *et al.* (1996); (12) = Blevin (2002); (13) = Lickfold *et al.* (2003); (14) = Thompson *et al.* (2001); (15) = Mortensen *et al.* (1995); (16 = Dolbear & Company (2003); (17) = Mutschler *et al.* (1985).

TABLE 10-1 (CONTINUED). SELECTED CHARACTERISTICS AND PRECIOUS METAL CONTENT IN FLOTATION CONCENTRATE (F.C.) AND SULFIDE CONCENTRATE (SF.C) SAMPLES FROM PORPHYRY-CU DEPOSITS.

Deposit	Setting	Host porphyry			Alteration type	sample or average	Description	Ore tons (t x 10 ⁶)	concentration (ppb)			Pd / Pt	Pd/Cu	Cu wt. %	Ref.
		Age (Ma)	type	Affinity					Pd	Pt	Au				
Papua New Guinea															
Ok Tedi	C(col)	1.2	Monz	KCA	K	n=1	F.C.	768	980	24	28000	40.8	26	37	4, 8
Panguna	IA	3.4	Di,Qdi	CA	K, Prop, ser	n=1	F.C.	328	40	8	520	5	0.1	35	4, 8
Indonesia															
Grasberg	C(col)	2.8	Monzdi	KCA	K, Prop	n=1	F.C.	1952	58	15	18000	3.9	2.4	24	4
Malaysia															
Mamut	IA(Col)	5.9	Qmonz	KCA	K, Prop, ser	n=2	F.C.	1950	1400	470	15200	3	69	20	4
Russia (Siberia)															
Aksug	IA(Col)	401-404	Granod	CA	Prop, Q, ser	S-2392	Sf.C F.C., Cu/Mo=7-200	337	920	25	1200	36.8	170	5.4	9, 10
Aksug						n=2	F.C., Cu/Mo=0.4-185		73	86	4900	0.8	4.9	15	9, 10
Sora	IA(Col)	388-405	Gran	KCA	K, Na	n=3	F.C., Cu/Mo=0.4-185	325	50	88	100	0.6	8.6	5.8	9, 10
Zhireken	IA(Col)	155-160	Gran	KCA	K	S-0508	F.C., Cu/Mo=0.5	100	680	300	140	2.3	252	2.7	9, 10
Ryabinovoye	IA(Col)	137-146	Syen	CA	K, Na, Ser	n=4	Sf.C		85	150		0.6			11
Mongolia															
Erdenetuin-Obo	C(col)	220-240	Granod	CA	K, Na, Ser	S-0572	Sf.C, Cu/Mo=2.5	1200	20	33	74	0.6	333	0.06	9, 10
Australia															
Cadia (Hill & East)	IA	440	Qmonz	KCA	K, Na			480			600			0.3	7, 12
Goonumbla	IA	439	Qmonz	KCA	K, Q			64			500			0.5	7, 13

See page 207 for abbreviations.

TABLE 10-1 (CONTINUED). SELECTED CHARACTERISTICS AND PRECIOUS METAL CONTENT IN FLOTATION CONCENTRATE (F.C.) AND SULFIDE CONCENTRATE (Sf.C) SAMPLES FROM PORPHYRY-CU DEPOSITS.

Deposit	Setting	Age (Ma)	Host porphyry type	Affinity	Alteration type	sample or average	Description	Ore tons (t x 10 ⁶)	concentration (ppb)			Pd / Pt	Pd/ Cu	Cu wt. %	Ref.
British Columbia Cordillera															
Galore Creek	IA(Col)	210	Syen	A	K, Ca-K	n=2	mt-py-bn-cp	159	1300	80	64000	16.2	76	17	7, 14, 15
Galore Creek						n=2	cp-py-bn		260	16	4400	10	20	13	7, 14, 15
Mt. Milligan	IA	183	Monz	A	K, Prop	MMSS-1	mt-py-cp		6300	110	18500	57	926	6.8	7, 14, 15
Mt. Polley	IA	205	Monz	A	K, K-Na, Ca-K	88-148	mt-bn-cp-py	49	320	33	23600	9.7	16	21	7, 14, 15
						88-143	cp-py-mt		83	17	6200	4.9	72	1.1	14
						88-150	cp-py		23	7	1600	3.3	12	1.1	14
Ajax	IA	195-205	Monz	A	K, K-Na, Ca-K	AE-1	cp-py	284	140	8	990	17.5	5.3	26	7, 14, 15
Afton	IA	204	Di	A	K, K-Na, Ca-K	n=60		69	130		1200		87	1.5	7, 14, 15
Cooper Mountain	IA			A		n=2	F.C.		2760	190	4800	14.5	98	28	16
Cooper Mountain						No17	Sf.C, bn-cp vein		3250	50	4200	65	81	40	16
Colorado															
Allard, La Plata	IA	70-85	Syen	A		No2	Sf.C (cp)		1920	2880	1230	0.7	107	18	16
Allard, La Plata	IA					No3	F.C.		2320	3935	1740	0.6	86	27	16
Wyoming															
Copper King Mine		Triassic		A		n=2	F.C.		2660	900	440	3	84	32	16
Copper King Mine						No6	Sf.C (cp), pegmatitic		6430	13600	190	0.5	292	22	16

See page 207 for abbreviations.

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). Furthermore, it is emphasized that in the presence of significant concentrations of other metal ions, like Ca^{2+} , Mg^{2+} , Fe^{2+} , and Cu^+ , complexation of chloride by these metals would reduce the activity of free the chloride ion, resulting in reduced solubilities of Pt and Pd minerals. On the other hand, elements like As, Bi, Sb, Se and Te form very insoluble compounds with PGE.

Hanley *et al.* (2005) have shown that hot, moderately oxidized hypersaline fluids can dissolve Pt and Au at concentrations on the order of parts per million, confirming that orthomagmatic fluids derived from arc magmas are capable of transporting and depositing significant amounts of these metals.

Field Observations

The importance of aqueous processes to PGE geochemistry and to the concentration of the PGE to economic levels has been recognized by Wagner (1929) in the Waterberg deposits (South Africa) and supported by recent investigations (see also reviews by Hanley 2005 and Wilde 2005). Based on the presence of abundant hematite, Cr (VI)-bearing minerals and Pt-oxides in those deposits, the replacement of K-feldspar by muscovite, and fluid inclusion data, McDonald *et al.* (1999) concluded that Pt and Pd were mobilized under strongly oxidizing conditions, in moderately acidic fluids (pH 4 to 5) as chloride complexes, at temperatures of 200 to 300°C.

In hydrothermally altered harzburgite of the Semail ophiolite of Oman, elevated Pt (up to 450 ppb) is associated with silicified and carbonate-altered serpentinite ("listwaenite"), which occurs along Tertiary extensional faults (Wilde *et al.* 2003). Also, the members of the irarsite-hollingworthite solid-solution series and other Os-, Ir, Ru- and Rh-bearing PGM in chromitites from some ophiolite complexes, and their association with altered chromitites may indicate either *in situ* alteration or/and re-mobilization and re-deposition of PGE during at least two stages (Tarkian & Prichard 1987). The presence of Ru-Os-Ir-Fe-oxides, with significant and variable Fe, Cr, Co, Ni and Mn contents, associated with serpentine, chlorite, Cr-garnet, ferrian-chromite and magnetite in chromite ores, suggest that they may have been

derived from *in situ* alteration of primary PGM, by desulfurization and subsequently oxidation of pre-existing sulfides of Os-Ru-Ir (Garuti & Zaccarini 1997). Also, significant concentrations of PGE (few ppm Pd and Pt) were found in magmatic breccia at the contact between the Bangur intrusion and its ultramafic host, Baula-Nuasahi Complex, India. On the basis of mineralogical and geochemical data, including oxygen, hydrogen and sulfur isotopes, it has been suggested that the precious metals in the hydrothermal fluids were derived from the magma rather than an external source (Augé & Lerouge 2004).

Platinum and palladium contents in sea-floor massive sulfides related to ophiolite complexes are very limited, but may indicate that PGE 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 21°N on the East Pacific Rise (Hekinian *et al.* 1980). Sulfide deposits at 26°N on the mid-Atlantic Ridge contain significant palladium, ranging from 3 to 1000 ppb, and gold up to 8 ppb (Crockett 1990). Palladium and platinum contents in massive sulfide 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. In contrast, 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. The mineral assemblage found in the brecciated diabase includes plagioclase (altered), clinopyroxene (altered) + chlorite + kaolinite + quartz + epidote + calcite and disseminated pyrite mineralization. Remnants of pyrrhotite within pyrite surrounded by hydroxides or magnetite are common (Economou-Eliopoulos & Eliopoulos 1998). Assuming that Au and Pt/Pd were derived from the same source area and that the transporting complexes of these metals are the same, the concentration of Au in massive sulfide ore and Pt in the underlying diabase breccia may reflect a difference of the relative solubility and the extent to which these metals are saturated in a given hydrothermal solution and the mechanism of deposition of each metal (Wood 2002). Pan & 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. They suggested that a typical seafloor hydrothermal vent fluid could contain a significant amount of Pt

and Pd as bisulfide complexes and that gold is transported predominantly as a bisulfide complex too. In addition, 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 of Au that remains more soluble than Pt, and therefore massive ore is accompanied by Au.

Applications to Porphyry Systems

The presence of significant Pd–Pt concentrations (over 5 ppm) in certain porphyry Cu–Au, and to a lesser extent in Cu–Mo, deposits (Mutschler *et al.* 1985, Werle *et al.* 1984, Eliopoulos & Economou-Eliopoulos 1991, Eliopoulos *et al.* 1995, Piestrzynski, *et al.* 1994, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Stribrny *et al.* 2000, Tarkian *et al.* 2003, Strashimirov *et al.* 2003) is an important support to the view of the hydrothermal mass transfer. The occurrence of the main Pd-tellurides in porphyry Cu ± Mo deposits at grain boundaries of, or exclusively as inclusions in, chalcopyrite and bornite from various porphyry deposits, indicates that Pd and Pt were deposited during the major vein stage of Cu deposition and suggest that chloride was the principal ligand for aqueous transport significant amounts of both base and precious metals in these ore-forming systems (Tompouloglou 1981, Eliopoulos & Economou-Eliopoulos 1991, Tarkian *et al.* 1991, Tarkian & Koopmann 1995, Frei 1995).

Under acid and oxidizing conditions and temperatures up to 300°C, both Pd and Pt may be transported as chloride complexes (Gammons *et al.* 1992, Wood *et al.* 1992) with these complexes becoming increasingly important for Pd at higher temperatures (Sassani & Shock 1990). Chloride transport is generally invoked for Cu and Au in the porphyry environment (*e.g.*, Sillitoe 1993) and therefore the association of Cu, Au, Pd and Pt may be explained in part by a similar transport and deposition mechanism. Pd and Pt may also be transported as bisulfide complexes, but at levels one to three orders of magnitude lower than Au under the same conditions (Wood 2002). This difference in the efficiency of transport is similar to the relative difference in concentration between Au and Pd in the samples analysed in this study. Hanley *et al.* (2005) have suggested a dominant role for

hydroxide complexes in the transport of Pt at high temperatures. Sharp reductions in Pt solubility with diminishing temperature and oxygen fugacity might cause precipitation of Pt minerals during hydrothermal fluid evolution.

PGE MINERALIZATION IN PORPHYRY SYSTEMS

Summary geological descriptions of PGE-bearing porphyry deposits worldwide is presented in Appendix 10-A. The following discussion synthesizes these observations to describe a generalized ore deposit model.

Distribution of Au in Cu-minerals, Gold and Electrum

The Skouries, Elatsite, Medet, Bor/Madjanpek, Santo Tomas II, Grasberg, Bingham, Panguna and other porphyry deposits (Fig. 10-1), contain ore associated with early potassic alteration, native gold or electrum occurs as small (5–100 µm) inclusions in chalcopyrite or along bornite margins. Native gold and electrum may also form intergrowths with Pd-Pt-Bi- and Ag-tellurides, ranging from less than 1 to tens of µm (Figs. 10-2, 10-3 & 10-4, Table 10-2, Tarkian *et al.* 1991, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Kesler *et al.* 2002, Tarkian *et al.* 2003, Strashimirov *et al.* 2003). In addition, gold inclusions in chalcopyrite of the magnetite-bornite-chalcopyrite association tend to be poorer in Ag compared to those (electrum) in the chalcopyrite-pyrite assemblages (Tarkian *et al.* 2003).

In deposits that contain abundant bornite, it is the preferred host for, or is associated with gold. For example, at the Grasberg deposit more than 60% of gold grains are associated with bornite (Rubin & Kyle 1997). In contrast, gold is associated with chalcopyrite in deposits where bornite is rare or absent, such as at the Island Copper deposit, or where bornite is found in a lesser proportion compared to chalcopyrite (Ballantyne *et al.* 1997, Kesler *et al.* 2002). Subsequent events overprinting early potassic alteration and ore commonly remobilized Cu and Au, resulting in complete destruction of bornite and deposition of a new chalcopyrite-pyrite assemblages in which gold is associated with both minerals. In several deposits, these later gold-bearing overprints show a greater structural control than the initial mineralization (Cuddy & Kesler 1982). SIMS (ion probe) analyses of ore minerals from the gold-rich Batu Hijau, King King and Skouries porphyry copper deposits

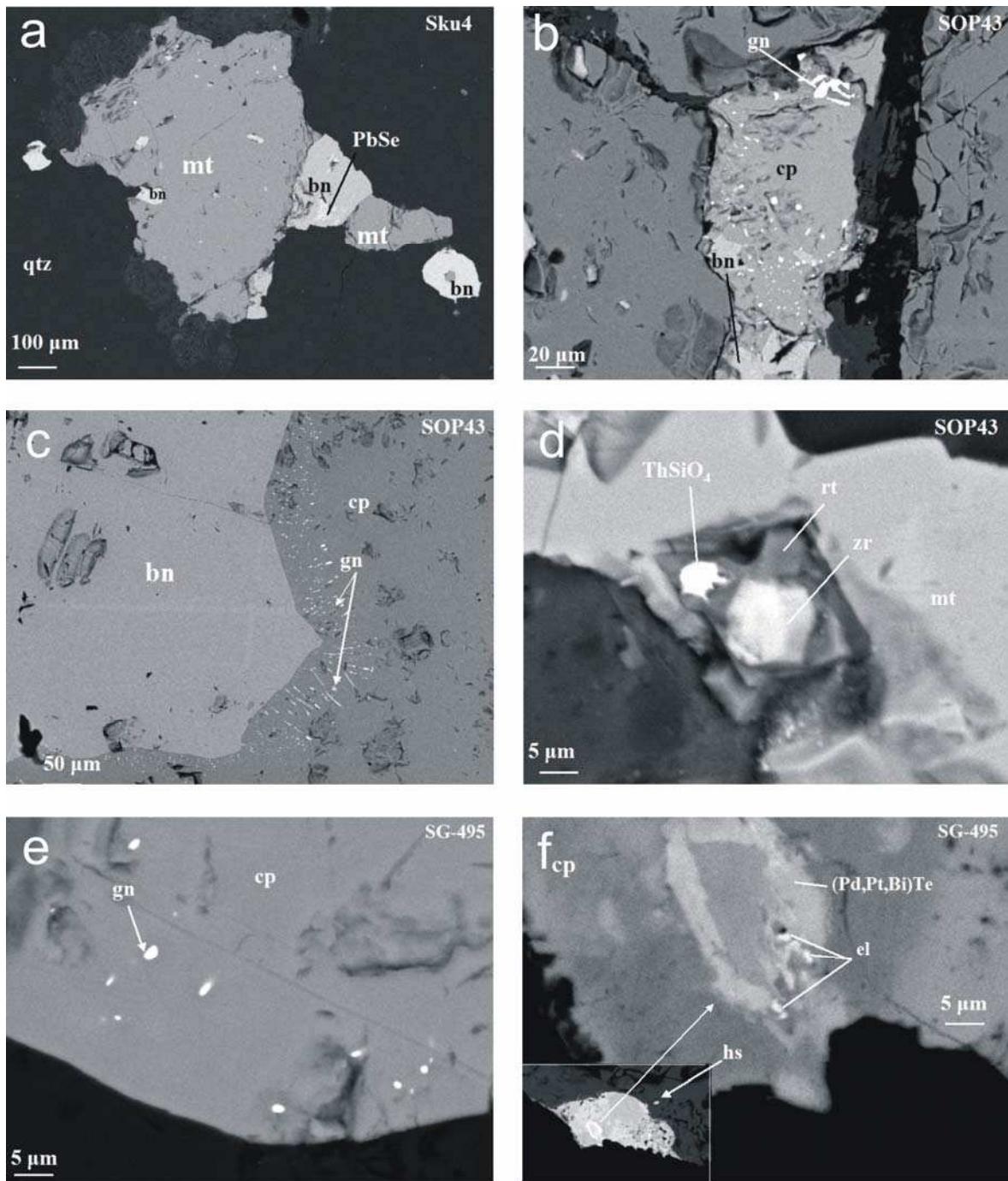


FIG. 10-3. Back-scattered electron images from various drill core samples of the Skouries porphyry deposit, showing textural relationships between base and precious metal minerals, and rare accessory minerals. **a**) clauthalite and bornite forming compound grains with magnetite; **b**) isolated grains of galena within chalcopyrite, with minor bornite; **c**) vermicular intergrowth of galena with chalcopyrite adjacent to bornite grain; **d**) association of rare accessory minerals with Ti-magnetite; **e**) rare bornite blebs hosted by chalcopyrite; **f**) intergrowth of electrum, $(\text{Pd},\text{Pt},\text{Bi})\text{Te}$ and hessite with chalcopyrite.

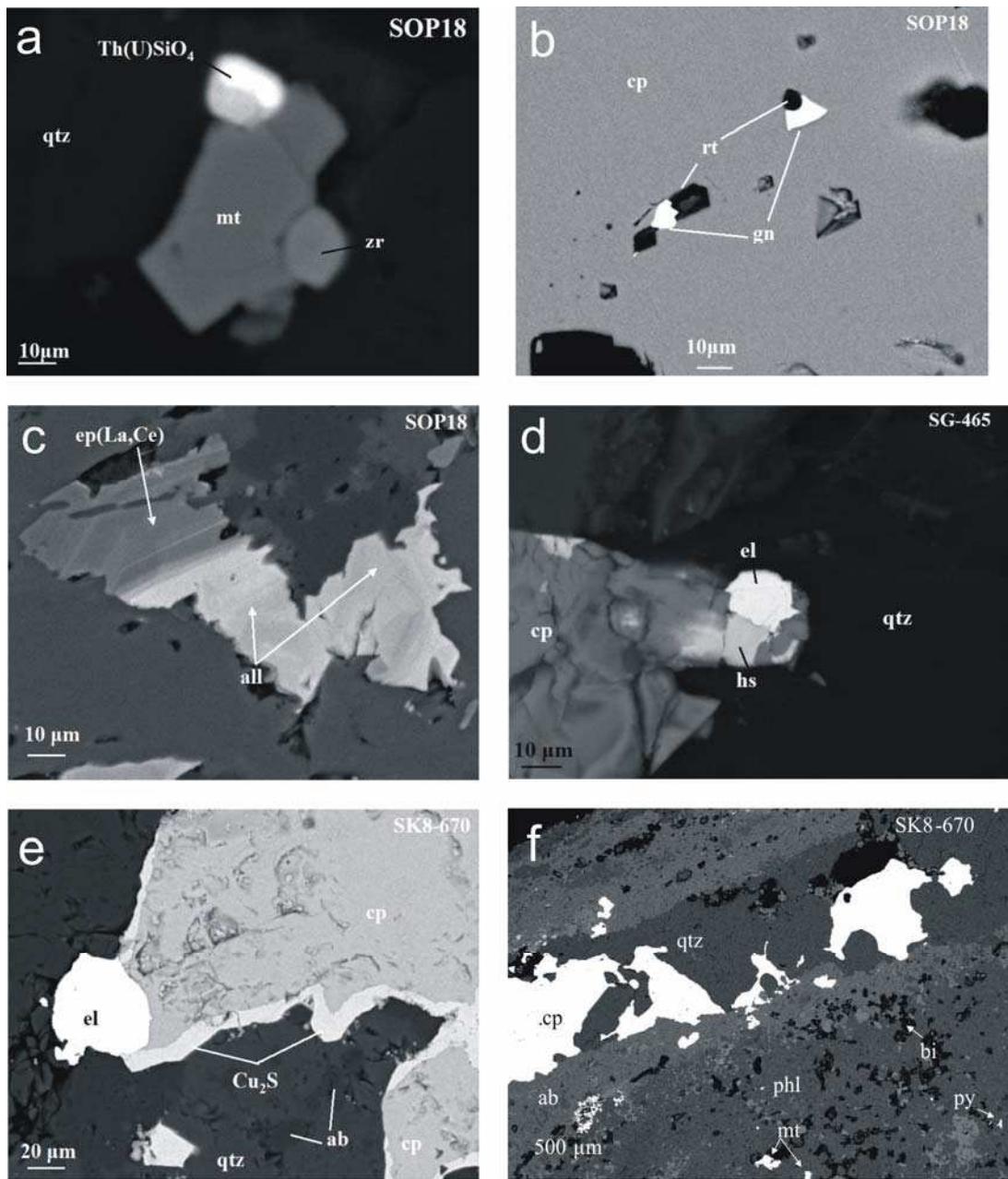


FIG.10-4. Backscattered electron images from drill core samples from Skouries porphyry deposit. **a)** Uranium-rich thorite and zircon associated with Ti-magnetite hosted by quartz; **b)** galena and rutile association hosted by chalcopyrite; **c)** REE-enriched epidote overgrown by allanite; **d)** association of hessite and electrum with chalcopyrite and quartz; **e)** electrum and chalcocite overgrowing chalcopyrite; **f)** quartz-chalcopyrite vein crosscutting biotite- and magnetite-rich potassically altered porphyry.

showed that bornite commonly contains about 1 ppm Au, whereas chalcopyrite contains about an order of magnitude less. Although both supergene and hypogene chalcocite and covellite contain up to 10–24 ppm Au, typically they are not sufficiently abundant to account for a significant part of the

average gold grades of bulk ore in many porphyry copper deposits. In the Skouries deposit, gold in covellite has been attributed to deposition as gold colloid particles, during the supergene enrichment (Kesler *et al.* 2002).

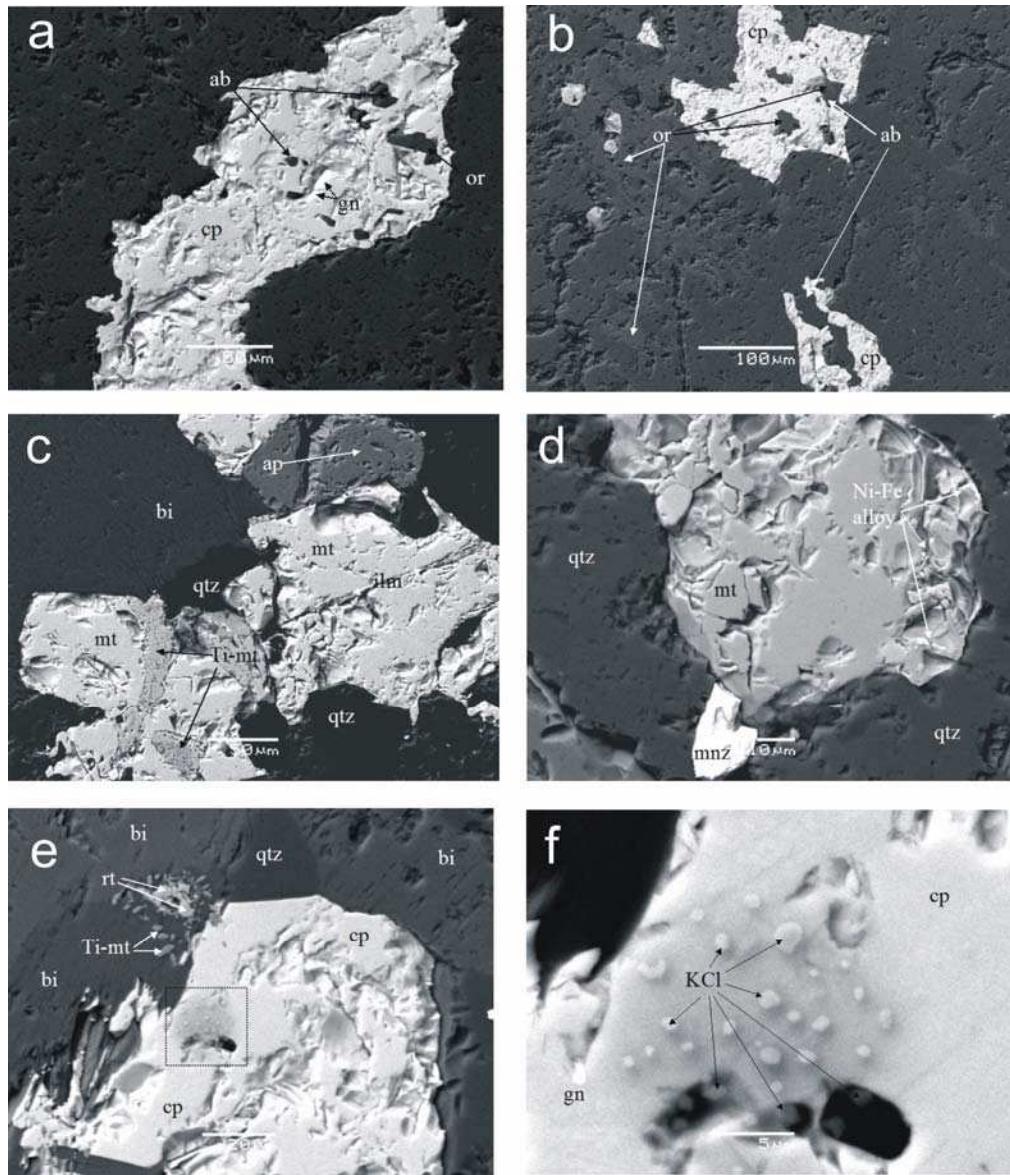


FIG. 10-5. Backscattered electron images from drill core samples at Skouries porphyry deposit. **a,b)** chalcopyrite-galena intergrown with alkali feldspars; **c**) Ti-bearing magnetite-ilmenite intergrowths with apatite; **d**) association of Ni-Fe alloy with magnetite and monazite; **e,f)** sylvite crystals deposited around a decrepitated fluid inclusion hosted by chalcopyrite, associated with rutile-Ti magnetite intergrowths.

Pd-Pt-minerals

The palladium telluride, merenskyite, has been described as the main PGE mineral in porphyry Cu-Au-Pd-Pt deposits, such as Skouries, Santo Tomas II, Biga, Elatsite, Madjadanpek, Mamut (Fig. 10-1, 10-2, Tarkian *et al.* 2003). It occurs mostly as inclusions in chalcopyrite and bornite, as euhedral crystals at the margins of chalcopyrite or enclosed by electrum and hessite in chalcopyrite. Merenskyite may have only traces of

platinum or may occur as a member of the merenskyite-moncheite solid solution series, with small contents of Ni, Bi, and Ag. Intergrowths of merenskyite (PdTe_2) with kotulskite (PdTe), unnamed phases such as $(\text{Pd},\text{Ag})_3\text{Te}_4$ and the silver telluride, hessite (Ag_2Te), are also common (Fig. 10-3, Tarkian *et al.* 1991, Piestrzynski *et al.* 1994, Tarkian & Koopmann 1995, Tarkian & Stribrny 1999, Tarkian *et al.* 2003, Strashimirov *et al.* 2003).

TABLE 10-2. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF SOME ORE MINERALS FROM THE SKOURIES AND ELATSITE DEPOSITS

Deposit	Sk	Sk	Sk	Sk	St	EL	EL	EL	EL	MAJ	MAJ	Sk	Sk	EL	Sk	Sk
Mineral	me	me	Pd, Bi-Tel.	me	el	el	el	he	sy							
Pd	27.51	26.8	16.35	14.87	29.41	28.4	26.01	15.15	17.38	27.6	28.44	n.d.	n.d.	n.d.	n.d.	
Pt	0.6	1.21	14.69	8.86	3.33	0.82	3.28	16.14	13.47	1.1	0.03	n.d.	n.d.	n.d.	n.d.	
Te	71.22	70.33	53.05	26.82	63.23	67.92	66.31	64.5	60.47	68.29	69.63	n.d.	n.d.	n.d.	37.35	59.19
Bi	n.d.	n.d.	15.15	46.27	3.35	0.11	1.29	0.66	3.23	2.86	0.27	n.d.	n.d.	n.d.	n.d.	n.d.
Au	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	96.98	86.65	81.39	n.d.	24.15	
Ag	n.d.	n.d.	n.d.	1.21	n.d.	n.d.	0.55	1.03	1.57	0.02	0.01	1.96	10.42	16.34	60.21	14.81
Cu	n.d.	n.d.	n.d.	n.d.	n.d.	0.97	0.5	0.57	1.89	n.d.	n.d.	0.54	0.72	3.97	0.51	0.82
Ni	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35	1.41	n.d.							
Total	99.33	98.34	98.22	98.29	99.32	99.24	98.03	99.46	98.01	99.87	98.38	99.48	97.79	101.7	98.07	98.97
Cont.																
Deposit	EL	EL	EL	EL	EL	EL	EL	EL	MED	MED	MED	Sk	Sk	Sk	Sk	Sk
Mineral	lin	lin	lin	lin	sieg	sieg	sieg	sieg	py	Co-py	car	py	py	py	py	py
Fe	0.29	4	0.67	0.5	6.47	2.42	3.1	1.76	38.2	33.85	1.85	46.69	42.32	45.63	45.76	46.69
Cu	18.99	19.95	13.19	14.17	11.08	1.51	0.19	0.38	0.1	0.1	15.9	n.d.	n.d.	n.d.	n.d.	n.d.
Ni	1.39	7.84	8.63	11.91	24.82	33.2	39.52	41.14	5.3	0.4	3.2	1.01	2.41	0.45	1.16	1.03
Co	37.95	31	35.99	33.05	18.33	21.21	14.48	15.13	2.2	12.45	37.55	n.d.	4.18	0.64	0.72	n.d.
S	41.2	41.16	41.99	41.53	40.82	41.24	42.21	41.82	53.9	53.15	41.6	53.6	52.17	52.56	52.91	52.61
Total	99.82	101	100.5	101.2	101.5	99.58	99.5	100.2	99.7	99.95	1001	101.3	101.1	99.28	100.6	100.3

Abbreviations: me = merenskyite; el = electrum; he = hessite; sy = sylvanite; lin = linnaeite; Sieg = siegenite; py = pyrite; car = carrolite; Tel = tellurides; Sk = Skouties; St = Santo Tomas II; EL = Elatsite; MAJ = Majdanpek; MED = Medet; Data from: Tarkian *et al.* (1991); Piestrzynski *et al.* (1994); Tarkian & Stribny (1999); Tarkian *et al.* (2003); Present data (Pd-Bi-tellurides and pyrite from the Skouries deposit).

Tetrahedrite-tennantite

Tetrahedrite and tennantite are frequently associated with the magnetite-bornite-chalcopyrite assemblage of an early stage of mineralization (Tarkian *et al.* 2003). They are commonly located in those porphyry deposits which are in a spatial association with epithermal deposits, such as the Elatsite deposit associated with the Chelopech Au-Cu high-sulfidation epithermal deposit, the Assarel deposits in Bulgaria, and the Bor/Majdanpek porphyry deposits in Serbia, whereas in the Skouries deposit are rare.

Galena-clausthalite

In the Skouries porphyry deposit galena exsolution with significant selenium contents are very common in chalcopyrite, whereas in bornite they are very rare (Figs. 10-2 to 10-4). Solid solutions between galena and clausthalite are the dominant compositions, whereas end-member galena and clausthalite are rare (Tarkian *et al.* 2003). The presence of the independent selenium mineral clausthalite, in association with galena in porphyry Cu deposits, such as the Elatsite deposit, may be related with the evolution of the ore forming system (Xiong 2003).

Linnaeite-siegenite-carrollite

Carrolite with average Ni and Co contents of 2.73 and 26.22 wt.%, respectively, and Ni-Co-pyrite with Ni ranging from 0.05 to 5.3 wt.% Ni and 2.2 to 17.85 wt.% Co have been reported in the Medet porphyry deposit (Strashimirov 1982). Also, in addition to high Ni (0.5–6.7 wt.%) and Co (1.6–14.9 wt.%) in pyrite from the Elatsite deposits, members of the linnaeite-siegenite-carrollite solid-solution series have been described being replaced by chalcopyrite in the assemblages of magnetite-bornite-chalcopyrite and chalcopyrite-pyrite. Their Ni contents Ni (1.39–41.14 wt.%), and Co contents (14.48–37.95 wt.%) show a wide variation, with a preference of the Ni-poor, Co(Cu)-rich members in former assemblage (Tarkian *et al.* 2003).

SIGNIFICANT Pd AND Pt CONTENTS IN ONLY CERTAIN PORPHYRY COPPER DEPOSITS WORLDWIDE

As described in the Appendix to this article, certain porphyry Cu-Au deposits have elevated Pd-Pt contents, including Copper Mountain, Allard stock, Copper King Mt Milligan, Galore Creek, Ajax/Afton, Skouries, Elatsite, Santo Tomas II and Mamut (Table 10-1, Werle *et al.* 1984, Mutschler *et*

al. 1985, Eliopoulos & Economou-Eliopoulos 1991, Eliopoulos *et al.* 1995, Tarkian & Koopmann 1995, Tarkian & Stribny 1999), Economou-Eliopoulos & Eliopoulos 2000, Tarkian *et al.* 2003). Lower, but elevated Pd±Pt concentrations compared to those in typical porphyry deposits, have been reported in porphyry deposits such as Bor/Majdanpek, Serbia, Ok Tedi, Papua New Guinea, Grasberg, in Indonesia, Panguna, Papua New Guinea, Goonumbla/North Parkes, and Cadia-Ridgeway, in New South Wales (Table 10-1, Jankovic 1980, Muller *et al.* 1994, Piestrzynski *et al.* 1994, Tarkian & Stribny 1999, Holliday *et al.* 2002).

Mineralization, consisting mainly of disseminated and vein-type magnetite and Cu-minerals (chalcopyrite and/or bornite), associated with central parts of the deposits exhibits the highest Pd and Pt enrichment. Although there is a variation throughout each mineralized zone the Pd/Pt and Pd/Cu ratios seem to be a characteristic feature of each porphyry Cu–Au±Mo deposit (Table 10-1) reflecting possibly the essential role of the composition of parent magmas, and in turn the genesis of alkaline arc magmas. Halter *et al.* (2002) demonstrated, by integrated microanalysis of major and trace elements in sulfide and silicate melt inclusions by laser ablation–ICP–MS, that parent magmas define the Cu/Au ratio of a related deposit, such as the Alumbra porphyry Cu–Au deposit, Andes.

TYPICAL CHARACTERISTICS OF PORPHYRY Cu–Au–Pd±Pt DEPOSITS

The geological descriptions in Appendix A show that, in general, porphyry Cu–Au–Pd±Pt deposits are associated with alkaline rocks, in particular with alkaline porphyry systems characterized by $\text{SiO}_2 < 65$ wt.%. Enriched mantle sources or major contributions by crustal material, are evidenced by strongly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values. Parental magmas were volatile-rich, and moderately fractionated, characterized by relatively high concentrations of halogens (F, Cl), REE and Th, but commonly also showing elevated (several hundreds ppm) Cr and Ni contents (Eliopoulos *et al.* 1995, Economou-Eliopoulos & Eliopoulos 2001). Albitic (sodic) and calc-silicate (actinolite, epidote, diopside, garnet) minerals are common members of alteration assemblages in addition to biotite and K-feldspar. Copper and precious metals appear to have been transported as chloride complexes, by relatively hot (400° to 700°C) and saline to hypersaline (>70 wt.%

$\text{NaCl}_{\text{equiv}}$) hydrothermal fluids and were precipitated during the main stage of mineralization, as an association of bornite, chalcopyrite, pyrite and magnetite reaching up to 10 vol.% (average 6 vol.%), as veinlets and disseminations, associated with the potassic alteration type. Textural relations between Cu-minerals and the main Pd-bearing mineral, merenskyite, and Au-Ag tellurides, indicate that precious metals are closely associated with copper vein-type chalcopyrite or bornite, and are deposited during the earliest stages of alteration and mineralization in the central parts of deposits. Hydrothermal breccias are particularly abundant in large alkaline Au-Cu deposits (Jankovic 1980, Mutschler *et al.* 1985, Corbett & Leach 1998, Eliopoulos & Economou-Eliopoulos 1991, Eliopoulos *et al.* 1995, Frei 1995, Tarkian & Koopmann 1995, Sillitoe 2000, Müller & Groves 2000, Sotnikov *et al.* 2000, Tarkian *et al.* 2003, Strashimirov *et al.* 2003).

CRITICAL FACTORS FOR THE FORMATION OF PORPHYRY Cu+Au+Pd \pm 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 volcanoplutonic arcs, and the composition of alkaline parent magmas or those of large batholithic bodies underlying at greater depths the porphyry stocks may be major controls of their base/precious metal potential and characteristics. These could include such things as the hydrous and oxidized nature, and their ability to produce hydrothermal systems with ideal chemistry for transporting precious metals. In addition, alkaline magmas are inherently richer in SO_2 and CO_2 than their calc-alkaline counterparts, volatiles that have a significant influence on fluid pressures, brecciation and permeability of host rocks (Sillitoe 2000, Müller & Groves 2000, Tosdal & Richards 2001, Richards 2003).

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 $>700^\circ\text{C}$) and relatively oxidized hydrothermal brines that are produced mainly (but not always) by aqueous fluid immiscibility (Burnham & Ohmoto 1980). In contrast, 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 favored in the oxidizing environment, “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). Halter *et al.* (2002) have focussed their investigation on sulfide melt and silicate melt inclusions on the Farallon Negro volcanic complex, hosting the Alumbra porphyry Cu-Au deposit. Most major and trace elements in silicate melt inclusions follow the differentiation trend defined by bulk rock composition, except for Cu, varying at all stages of magmatic evolution. They concluded that magmatic sulfide melts can act as intermediate metal hosts, which preconcentrate Cu and precious metals during the evolution of the magmatic system before volatile saturation, and probably participate in an important step in the genesis of porphyry-type deposits. The ore-forming hydrothermal fluid acquired its high metal content and characteristic Au/Cu ratio by bulk destabilization of magmatic sulfides with similar metal ratios.

Sources of Metals and Sulfur in Porphyry Copper Deposits

The contribution of mantle, oceanic and continental crust to the parent magmas of porphyry copper intrusions remains still uncertain (Burnham 1979, Burnham & Ohmoto 1980, McInnes & Cameron 1994, Keith *et al.* 1998, Titley 2001, Hattori & Keith 2001). Numerous authors have suggested crustal sources for some ore metals in the southern Arizona deposits (Titley 2001). Evidence from xenoliths, geological, mineralogical, geochemical and isotopic data indicates that the high Pd and Pt mineralization in the porphyry deposits of the British Columbia Cordillera, and the higher Pd and Pt levels in fresh and unaltered samples from the Lihir rocks compared to typical background values for crustal rocks (Taylor & McLennan 1985) are linked with the genesis of alkaline arc magmas, derived probably from an enriched mantle source (McInnes & Cameron 1994). They may reflect partial melting and incorporation into the melt of destabilized precious metal-bearing Fe-Ni-Cu-sulfides, hosted in the mantle source (Keith *et al.* 1998, Hattori & Keith 2001). The occurrence of mafic dikes, post-dating the porphyry mineralization at the Elatsite deposit (Fig. 10-6, von Quadt *et al.* 2002, Strashimirov *et al.* 2003), and relatively high Re concentrations in the molybdenite

from main stage stockwork mineralization of the Elatsite Cu–Au deposit, Bulgaria (average 1880 ppm), has been attributed to a direct involvement of mantle in an arc-subduction environment as well (Zimmerman *et al.* 2003). In addition, Xiong & Wood (2002), based on experimental data, suggested that reducing fluids containing sulfur have much less capacity for transporting Re, and environments dominated by reducing fluids are not favorable to Re deposition. However, mixing processes involving an oxidized Re-containing solution and a solution with reduced sulfur should be effective depositional mechanisms for rhenium.

Although intense hydrothermal alteration has commonly destroyed any record of possible magmatic sulfide blebs, they have been reported in submarine alkaline volcanic rocks in the Tabar-Lihir-Tanga-Feni chain and latite dikes related to the Bingham porphyry deposit (Keith *et al.* 1998, Hattori & Keith 2001, Thompson *et al.* 2001). These blebs, due probably to degassing during crystallization of high level intrusions or lavas, contain elevated Au and Pd, which may be subsequently oxidized or altered, resulting in release of the metals to the volatile phase during magmatic-hydrothermal activity. On the other hand, the oxidized nature of the alkaline arc magmas inhibits fractionation of sulfides, allowing the precious metals to remain in the magmas, and thus they were transported by magmatic-hydrothermal fluids and precipitated in the porphyry environment (McInnes & Cameron 1994, Thompson *et al.* 2001).



FIG.10-6. Mafic dike crosscutting granodiorite from the central part of the Elatsite porphyry deposit (after Strashimirov *et al.* 2003).

The incorporation of PGE-enriched material in the mantle source and/or within the crust at depth, prior to the final emplacement, may be evidenced by the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ values (Fig. 10-7, Jankovic 1980, Frei 1995, Sillitoe 2000, Müller & Groves 2000, Sotnikov *et al.* 2000, Tosdal & Richards 2001, von Quadt *et al.* 2002) and would supply PGE to the porphyry stocks or hydrothermal systems. The contribution of crustal material and the presence of mafic/ultramafic rocks among country rocks has been suggested in the porphyry Cu systems of the Serbo-Macedonian massif (Balkan Peninsula) (Jankovic 1980, Frei 1992, Gilg 1993, Ciobanu *et al.* 2002, Heinrich & Neubauer 2002), Russia and Mongolia (Sotnikov *et al.* 2000), and the Ajax/Afton deposits, British Columbia (Ross *et al.* 1995). Also, Perugini *et al.* (2004) emphasized the spatial and temporal association of the subvolcanic stocks with lamprophyres, mafic microgranular and alkaline dikes in the Serbo-Macedonian massif, and proposed the interaction processes between mantle-derived and crustal melts. Moreover, the enrichment (hundreds ppm) in compatible elements such as Cr, Co±Ni, that occur in the Skouries, Elatsite, Medet, Assarel and Trar Asen porphyry deposits of the Balkan Peninsula (Table 10-2, 10-3, Eliopoulos *et al.* 1995), despite their otherwise more evolved geochemical signatures, may have been inherited due to magma mixing with mafic alkaline rocks. Moreover, mafic fragments with disseminated and vein-type mineralization (Fig. 10-2), Cr-bearing magnetite, Ni, Co-bearing pyrite and chalcopyrite (Tables 10-2 & 10-4), are common in particular at the peripheral parts of the Skouries main porphyry stock. Although the assimilation of amphibolites (meta-mafic rocks) and the supply of metals is not precluded, the possibility that the country rocks (amphibolites) could be a significant Cu, Pd and Pt source is inconsistent with the presence of only a narrow (< 50 m wide) halo of alteration (Frei 1995). Additional evidence for incorporation of PGE, Cr, Co, Ni-enriched material in the mantle source and/or during the upward ascent of magma within the crust, prior to the final emplacement, is the presence of linnaeite-siegenite-carrollite solid solution series and Ni-Co-pyrite in the assemblages of magnetite-bornite-chalcopyrite and chalcopyrite-pyrite of the Medet and Elatsite porphyry deposits (Tables 10-2 & 10-3, Strashimirov 1982, Tarkian *et al.* 2003).

TABLE 10-3. PRECIOUS METAL AND ASSOCIATED TRACE ELEMENT DATA FROM THE SKOURIES PORPHYRY CU DEPOSIT.

sample	depth	ppb Pd	ppb Pt	ppb Au	Cu/A u	Pd/Pt	Pd/Cu	Au/Ag	ppm Ag	Wt.% Cu	ppm Zn	ppm Pb	ppm Cr	ppm Ni	ppm Co	ppm Mo
sku400	surface	30	<10	2210	5.9	>0.3	23	540	4.1	1.31	50	30	30	40	20	2
SOP 01	219	27	28	1170	10.8	0.96	21	509	2.3	1.29	80	64	160	140	24	2
SOP 01	326	54	43	4790	4.15	0.8	20	1842	2.6	1.99	100	80	130	300	30	2
SOP 01	328	53	42	4930	3	0.8	36	704	7	1.47	97	40	110	250	25	1
SOP 01	635	5	<10	190	3.2	>0.5	83	>95	<0.2	0.06	38	21	50	42	26	2
SOP 01	636	3	<10	50	12	>0.3	50	>950	<0.2	0.06	32	15	60	71	21	8
SOP 06	363	85	20	683	7.5	4.2	167	190	3.6	0.51	39	52	3	8	31	1
SOP 06	365	49	49	3880	3.3	1	39	<388	>10	1.27	80	60	10	210	24	2
SOP 06	525	29	22	549	12.4	0.76	42	422	1.3	0.68	110	34	260	310	62	1
SOP 06	527	6	<10	120	11.7	>0.6	43	>600	<0.2	0.14	77	32	80	224	38	4
SOP 09	252	31	33	1410	7.8	1.06	28	>7050	<0.2	1.1	73	30	8	50	35	3
SOP 18	142	42	64	3850	3.9	1.52	28	1604	2.4	1.52	75	84	4	50	22	2
SOP 18	178	16	26	532	15	1.62	20	760	0.7	0.8	67	110	6	30	30	11
SOP39	446	606	73	9600	2.6	8.3	29	806	11.9	2.53	60	29	10	8	74	3
SOP 43	200	15	<10	1520	10.3	>1.5	10	894	1.7	1.56	130	13	484	560	56	1
SOP46	50	1	<10	70	223	>0.1	7	>350	<0.2	0.14	94	50	125	127	29	240
SOP76	170	2	<10	590	12.03	>0.2	3	983	0.6	0.71	180	12	690	504	41	100
SG-6	30	360	31	3050	10.2	11.6	118	924	3.3	3.1	50	23	17	13	27	7
SG-6	110	28	10	850	4.6	2.8	72	1700	0.5	0.39	66	71	6	17	62	2
SG-6	465	410	26	5280	3.6	15.8	216	1650	3.2	1.89	46	31	7	7	41	1
SG-6	494	420	150	12900	2.2	2.8	53	2795	3.4	2.84	60	21	17	10	43	<1
SK8	130	20	<10	1700	7.1	>2	17	1210	1.4	1.21	53	43	8	21	48	<1
SK8	620	17	<10	1520	34.9	>1.7	3.2	585	2.6	5.3	100	26	59	70	24	<1
SK8	671	140	<10	1580	7.3	>14	120	1215	1.3	1.16	63	19	61	48	38	25

TABLE 10-4. REPRESENTATIVE ELECTRON MICROPROBE ANALYSES OF REE-MINERALS FROM THE SKOURIES DEPOSIT

Sample Minera l	SOP46	SOP43	SOP18	SK8	SK8	SOP18	SOP18	SOP18
	Monazite	Thorite	U-Thorite	U-Thorite	U-Thorite	Epidote	Allanite	Allanite
SiO ₂	1.15	18.82	15.63	15.17	15.41	38.34	32.13	35.37
Al ₂ O ₃	n.d	n.d	n.d	n.d	n.d	27.18	16.18	14.11
FeO	n.d	n.d	0.57	4.26	2.64	8.32	13.91	17.41
CaO	0.76	n.d	n.d	n.d	n.d	n.d	12.38	13.59
P ₂ O ₅	30.26	n.d	n.d	n.d	n.d	22.17	n.d	n.d
La ₂ O ₃	17.21	n.d	n.d	n.d	n.d	n.d	5.11	3.89
Ce ₂ O ₃	31.57	n.d	n.d	n.d	n.d	0.85	14.53	12.54
Nd ₂ O ₃	10.45	n.d	n.d	n.d	n.d	2.16	4.74	2.18
Pr ₂ O ₃	2.76	n.d	n.d	n.d	n.d	n.d	n.d	n.d
ThO ₂	5.06	79.44	70.68	50.84	66.03	n.d	n.d	n.d
UO ₃	n.d	n.d	11.68	29.12	15.21	n.d	n.d	n.d
Total	99.22	98.26	98.56	99.39	99.29	99.02	98.98	99.09

Porphyry Cu–Mo±Pd±Pt deposits of Russia and Mongolia are more or less characterized by relatively large crustal contributions (Sotnikov *et al.* (2000). Although giant porphyry Cu–Mo deposits in the central Andes are characterized by a lesser degree of crustal contribution, a porphyry-skarn Cu–Au–Mo deposit at Bingham Canyon, Utah, has a strong crustal signature (Keith *et al.* 1998). The enrichment (hundreds ppm) in compatible elements, such as Cr and Ni, that occur in the relatively more siliceous rock units of the Bingham system, may

have been inherited from magma mixing with mafic alkaline magmas capable of carrying more than 3000 ppm dissolved S. Such a mixing of the silica-undersaturated component into already existing calc-alkaline, subvolcanic magma chambers could have added significantly to the overall budget of water, sulfur, and ore metals in evolving felsic magmas that eventually gave rise to the Bingham ore deposit (Waite *et al.* 1997, Hattori & Keith 2001, Maughan *et al.* 2002).

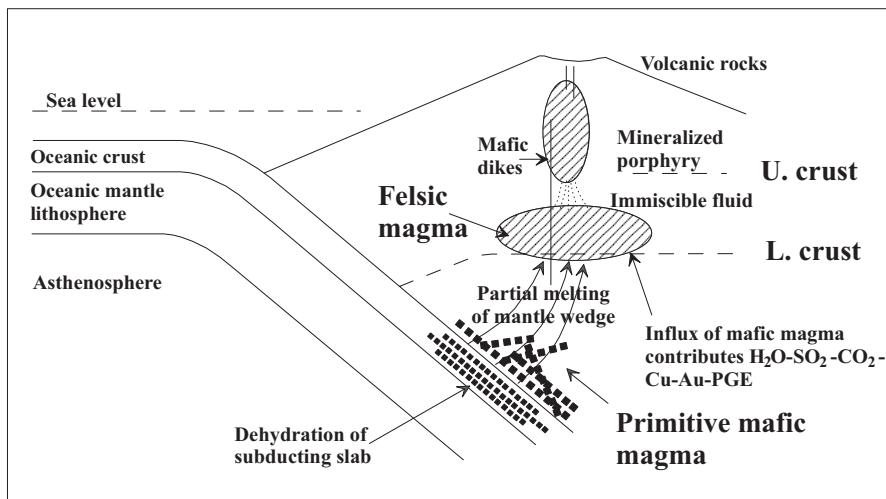


FIG.10-7. Schematic section of a subduction zone and continental arc (at convergent plate boundaries), showing the geotectonic setting for porphyry Cu mineralization. Hydrous, metal-bearing-melt extracted from the subducting slab, rising into the mantle wedge causes metasomatism. Partial melting of metasomatized mantle generates mafic melts, which at depth may contribute metal, including PGE, and sulphur, which are incorporated into the overlying felsic magma chamber (compilation from Sillitoe 2000, Richards 2003, Hattori & Keith 2001).

Evolution of Mineralized Systems

Evidence for the evolution of mineralizing fluids in porphyry systems is provided by isotope and/or fluid inclusion data. The oxygen and hydrogen isotope investigation in the Skouries deposit revealed high $\delta^{18}\text{O}$ (8 to 10 per mil) and low δD values (-95 to -70 per mil) for fluids in equilibrium with vein quartz/main stage of mineralization, and $\delta^{34}\text{S}$ values from vein and disseminated sulfides (-2.1 to +0.3 per mil) falling within the typical range of early ore-forming fluids, whereas low $\delta^{18}\text{O}$ and high δD values for fluids are linked with the pyrite-chalcopyrite mineralization (Gilg 1993, Frei 1995). Fluid inclusion studies provide evidence for two different fluid types, an early CO_2 -rich fluid of an early intermediate salinity, which locally boiled on ascent to shallower parts of the deposit and thereby formed brine and vapor-rich inclusions synchronous with the main stage of mineralization, and late low salinity fluids (Gilg 1993, Frei 1995, Kehayov *et al.* 2003).

Available analytical data (Tables 10-1 & 10-2) indicate that Pd, Pt and Au contents are relatively higher in the magnetite-bornite-chalcopyrite assemblages associated with pervasive potassic alteration found at the central parts of the deposits, than in the chalcopyrite-pyrite ores linked to the phyllitic-argillic alteration type, characteristic of the upper and marginal parts of the deposits (Tarkian *et al.* 1991, 2003, Frei 1995, Economou-Eliopoulos & Eliopoulos 2000, Kouzmanov *et al.* 2001, 2003, Strashimirov *et al.* 2003). Thus, isotopic and fluid inclusion trends in porphyry Cu deposits seem to be systematic, beginning with high $\delta^{18}\text{O}$ and low δD values, and CO_2 -rich fluid/ intermediate salinity for fluids in equilibrium with vein quartz/main stage of Cu, Au, Pd, Pt mineralization to low $\delta^{18}\text{O}$ and high δD values/low salinity fluids for fluids linked with the pyrite-chalcopyrite mineralization.

Given that both Pd and Pt may be transported as chloride complexes in the porphyry environment under acid and oxidizing conditions, the association of Cu, Au, Pd and Pt in porphyry Cu deposits may be explained in part by a similar transport and deposition, with decreasing temperature to approximately 400°C (to allow the precipitation of chalcopyrite \pm bornite), an increase in pH, and a decrease in $f(\text{O}_2)$ and $a(\text{Cl}^-)$ (Gammons *et al.* 1992, Wood *et al.* 1992, Sillitoe 1993, Xiong & Wood 2000). Kesler *et al.* (2002), based on SIM (ion probe) analyses of ore minerals from numerous porphyry Cu deposits, concluded that primary gold mineralization is overprinted by secondary enriched

zones containing covellite and chalcocite with inclusions of gold and that the maximum gold endowment of porphyry copper deposits is probably fixed by the amount of gold that will go into solid solution in Cu-Fe sulfides when the deposit forms at high temperature. Gold is not commonly added later from other sources, although it can be redistributed during cooling or later events. Furthermore, the evolution of the magmatic-hydrothermal systems has been investigated on the basis of EMP, microthermometric and laser ablation-ICP-MS analyses of silicate and sulfide melt inclusions (Halter *et al.* 2002, 2005, Ivascanu *et al.* 2003).

Importance of Vapor Phase in the Transport of Ore Elements

Quartz predating the bulk of bornite precipitation in the porphyry Cu deposit of Apuseni Mountains (Romania) hosts sulfide melt inclusions and silicate melt, together with highly saline brine inclusions, providing evidence for immiscibility between magmatic liquid and hydrous salt melt as the primary source of ore metals in porphyry Cu systems (Pintea 1995). On the basis of experimental metal-solubility studies of porphyry Cu systems it has been demonstrated that Cu and Au partition into the saline aqueous brine during immiscible phase separation of oxidized high-temperature fluids (Williams *et al.* 1995). Furthermore, new micro-analytical methods, using proton-induced X-ray emission (PIXE) and laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) studies of fluid inclusions from reduced porphyry Sn-W-Ag deposits and porphyry-related Au-Mo breccias indicate that Cu, and very likely Au, strongly partition into the low-density H_2S -rich vapor phase rather than the coexisting high-density chloride-rich liquid phase (Heinrich *et al.* 1999). Halter *et al.* (2002) have suggested that ore-forming hydrothermal fluids can acquire high metal content and characteristic Au/Cu ratio by bulk destabilization of magmatic sulfides with similar metal ratios. Textural relationships between successive quartz generations, microthermometry and laser ablation-ICP-MS analysis of fluid inclusions from the Elatsite, Bulgaria, deposit revealed a trend of decreasing Na, K, Cu, Ag, Bi, Sn, and Ce with decreasing temperature, while the Mo, Pb, Zn, Sr, Mn concentrations increased (Fig. 10-8), and copper in the fluids decreases from 40000 ppm in magnetite-bornite-chalcopyrite stage (with the precipitation of the Cu-minerals) to about

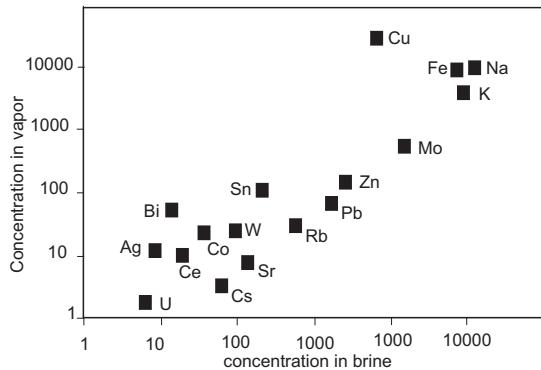


FIG.10-8: Correlation between metal contents in vapor and coexisting brine inclusions from boiling assemblages of the qtz-mt-cp-pn stage of mineralization (after Kehayov *et al.* 2003).

4000 ppm in the chalcopyrite-pyrite stage, and about 1000 ppm in the quartz-pyrite stage (Kehayov *et al.* 2003).

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

Elevated PGE (Pt and Pd) contents, reaching hundreds of ppb, have been recorded in both Cu(Au) and Cu–Mo–Au porphyry deposits, but the Pd and Pt contents are much higher in the former (characterized by $\text{SiO}_2 < 65$ wt.-%), than in the latter (Table 10-1, Mutschler *et al.* 1985, Tarkian & Stirbrny 1999, Economou-Eliopoulos & Eliopoulos 2000, Sotnikov *et al.* 2000, Thompson *et al.* 2001). Moreover, many alkaline systems contain much less hydrothermal quartz compared to most subalkaline systems and quartz is even absent in some high-temperature alkaline deposits, like porphyry Cu–Au–Pd–Pt deposits of British Columbia (Jensen & Barton 2000, Thompson *et al.* 2001).

Exploration for alkaline porphyry deposits is encouraged by their large size and high grades and because they are environmentally favorable to mine, due to the low pyrite and high acid-buffering potential (Corbett & Leach 1998). The association of magnetite (>10% by volume) is a common feature of most Au-rich porphyry Cu–Au deposits; this coupled with the predominant association of PGE mineralization with the magnetite-rich potassic phase of alteration allows direct geophysical recognition of the mineralized zones (*e.g.*, the Skouries deposit, Tobey *et al.* 1998). Geophysical and geochemical signatures of these deposits are variable, but the characteristics of the mineralization and alteration can be recognized in

almost all examples, providing an effective exploration tool (Sillitoe 2000). The most productive deposits show evidence for voluminous metasomatism and multiple magmatism. Copper-gold exploration models are based on detailed structural mapping (at surface and in drill holes) and identification of alteration styles and mineralization, with the aim of identifying the optimum sites for maximum fluid permeability and mineralization (Corbett & Leach 1998). Although the alteration type is an important indicator of the fluid composition, ore mineral assemblages themselves and the bulk ore chemistry reflect the composition of the parent magma and the nature of the ore fluids, in particular the maximum precious metal endowment of porphyry copper deposits, their chemistry and capacity for transporting sufficient Au and PGE (Jensen & Barton 2000, Xiong & Wood 2000, Halter *et al.* 2002, 2005, Kesler *et al.* 2002, Sillitoe & Hedenquist 2003).

The presence of elevated concentrations of Co, Ni and Cr either in the whole ore analysis or in minerals (linnaeite-siegenite-carrollite solid solution series and Ni-Co-pyrite) in the assemblages of magnetite-bornite-chalcopyrite and chalcopyrite-pyrite, and the presence of Cr-bearing magnetite (Table 10-2, 10-3, Strashimirov 1982, Tarkian *et al.* 2003), may provide evidence for incorporation of PGE, Cr, Co, Ni-enriched material in the mantle source and/or during upward-rising of magma within crust prior to the final emplacement (Waite *et al.* 1997, Hattori & Keith. 2001, Maughan *et al.* 2002).

However, only certain porphyry-Cu-Au deposits are Pd-Pt-enriched, that seems to be a characteristic feature of each deposit, despite their variation throughout a deposit (Table 10-1, Halter *et al.* 2002). Apart from the capacity of a magmatic-hydrothermal system in precious metals and the possibility to form economic deposits, the association, in space and time (Cathles 1997), between porphyry and epithermal deposits may play a major role on the evolution of the whole system and the grade/size of porphyry Cu–Au–Pd–Pt deposits. Einaudi *et al.* (2003) suggested deep porphyry Cu environments as transitional into shallower porphyry-related base metal vein and replacement deposits, and near surface into epithermal Au–Ag deposits. They concluded that the majority of porphyry Cu deposits containing magnetite in association with Cu-minerals (bornite, chalcopyrite)±pyrite are of intermediate sulfidation state.

Many of the porphyry Cu±Mo±Au deposits in Chile, Peru, Philippines and the Balkan Peninsula are located in the same arc region as the high-sulfidation deposits. They are commonly generated in calc-alkaline andesitic to dacitic arcs, characterized by neutral or weakly extensional stress states (Werle *et al.* 1984, Sillitoe 1997, 2000, Sillitoe & Hedenquist 2003). Extension, deduced from graben control of volcanism, during intermediate to high-K calc-alkaline volcanism and formation of major high-sulfidation deposits, such as the Bor (Serbia) and Chelopech (Bulgaria) have been described too (Hedenquist *et al.* 1998, Popov *et al.* 2000, Ciobanu *et al.* 2002, Strashimirov *et al.* 2003, Sillitoe & Hedenquist 2003). The presence of fluid inclusions hosted by enargite in epithermal deposits, like Chelopech (Bulgaria) and Bor (Serbia), with moderate salinities (4 to 20 wt.% NaCl_{eq}), coupled with the common presence of sericitic roots to lithocaps in general, may suggest that the high-sulfidation ore fluids are affiliated with the sericitic stage of underlying porphyry deposits. Moreover, the Ag/Au ratios may be controlled by the metal endowment of the parent magmas rather than the chloride content of the early sulfide-precipitating fluids (Sillitoe & Hedenquist 2003).

Low-sulfidation deposits are associated with bimodal (basalt-rhyolite) volcanism and may accompany extension-related alkaline magmatism, which is capable of generating porphyry Cu deposits. For example the Porgera and Ladolam deposits, Papua New Guinea, both associated with alkaline rocks, have been interpreted as a transition stage between an early stage, low-grade porphyry gold system and that evolved into low-sulfidation epithermal conditions (Ronacher *et al.* 2000, Moyle *et al.* 1990, Carman 1994, 2003, Müller *et al.* 2002). Elevated precious metal (Au–Pt–Pd) concentrations have been interpreted as primary magmatic features suggesting a precious metal pre-enrichment of the mantle source beneath the Ladolam deposit (Taylor *et al.* 1994, Müller *et al.* 2003).

A salient feature of the Assarel and Bor porphyry deposits, which are found in close proximity (transitional) to epithermal gold deposits (Strashimirov *et al.* 2003) is their much lower Pd and Pt contents compared to those of the Elatsite porphyry Cu–Au deposit, which is found at a ~10 km distance from the Chelopech Au–Cu high-sulfidation epithermal type deposit, and the Skouries deposit, where there is no association with epithermal deposits (Table 10-1). This seems to be

consistent with the lower solubilities of Pd and Pt than Au (Wood 2002). Therefore, Pd and Pt seem to be precipitated during an earlier stage in the Elatsite deposit and hence the Chelopech area epithermal systems in general and porphyry systems with transitional features are not good targets for Pd, Pt exploration.

EVALUATION OF Pd AND Pt AS AN ECONOMIC FACTOR FOR PORPHYRY Cu–Au SYSTEMS

To assess the PGE budget of a porphyry system, it is important (a) to analyze representative ore samples, and (b) to ensure that the ore samples are not coming from zones dominated by chalcocite and covellite, as they may exhibit high Au contents and negligible Pd–Pt contents, due to preferential mobilization during subsequent epigenetic processes (Wood 2002). For example, ore samples from the Assarel deposit, Bulgaria, have gold content up to 20 ppm Au, 3 ppb Pd and < 10 ppb Pt (Eliopoulos *et al.* 1995). Therefore, although the analytical data required for the evaluation of the precious metal potential of the majority of porphyry deposit are limited, the available data are considered to be encouraging for Pd and Pt as by-products, with Au as a by- or co-product with Cu.

Relatively high Pd contents in the major vein-type mineralization of Skouries ranging between 60 and 200 ppb (average 110 ppb Pd) was documented by analysis of a composite drill hole sample (~15 kg) showing 76 ppb Pd to 5000 ppm Cu. Assuming that Pd in porphyry Cu deposits is mainly associated with chalcopyrite (measured contents are normalized to 100 % chalcopyrite), then the average Pd and Pt values (from numerous mineralized samples of the Skouries deposit) are 3000 ppb and 1230 ppb, respectively (Table 10-5, Economou-Eliopoulos & Eliopoulos, 2001).

Using 206 Mt reserves according to recent data by TVX (Tobey *et al.* 1998), and average concentrations (0.5 wt.% Cu, 75 ppb Pd and 17 ppb Pt, then the potential of the Skouries deposit is approximately 15 tons Pd and 3.5 tons Pt. Also, using reserves and average Pd and Pt contents the potential is about 13 tons Pd and 3.7 tons Pt for the Elatsite deposit, 10.5 tons Pd and 1.6 tons Pt for the Santo Tomas II, Philippines deposit, and 10.5 tons Pd for the Afton deposit, B.C.

PALLADIUM AND PLATINUM RECOVERY

Significant quantities of Pd and Pt have been recovered at the final stages of copper refining in

TABLE 10-5. 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	

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

the U.S.A., although their concentration in the ores are very low (Jolly 1978). Approximately one ounce is the estimated amount of PGE that is recovered from each 35 tons of copper produced in the U.S.A. (Ageton & Ryan 1970). However, only limited data are available for roasted concentrates (Parker 1978).

Samples of milled flotation concentrates derived from large (~15 kg) composite drill-hole porphyry samples from the Skouries porphyry Cu–Au deposit were used for the extraction of Pd, Pt and Au (Kiousis 2004, Kiousis *et al.* 2005). The applied process method in this study was based on one of the methods used by the U.S. Bureau of Mines for the treatment of sulfide concentrates coming from the Stillwater deposit (Baglin 1988). This method was finally selected as it best meets the technical and environmental processing requirement of the present concentrates and its ability to minimize the environmental impacts. The recovery method includes two stages: roasting of the concentrates at 900°C for 2 h (transformation of metal sulfide to native metals), and a leaching procedure. At temperatures above 800°C the sulfides and the tellurides of palladium and platinum (merenskyite) can be oxidized and subsequently, as the roasting temperature increases, these oxides are split into native metals. Only this form of precious metals is leachable in dense aqueous solutions of hydrochloric acid plus H₂O₂ 0.03M, for 24h at 70°C. (Baglin 1988). The leaching process resulted in the recovery of 96.6% Au, 97.7% Pd and 100% Pt. Although more research is required, these results are considered to be highly encouraging and this leaching method can be environmentally friendly under certain conditions.

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Appendix 10-A: A Review of Porphyry Cu±Mo±Au ±Pd±Pt Deposits

BALKAN PENINSULA

Late Mesozoic to Tertiary porphyry Cu–(Mo–Au) intrusions located within the metallogenic belt of the Alpine-Balkan-Carpathian-Dinaride orogenic system represent subduction-related magmatism following the change from east–west to north–south convergence between Africa and Eurasia. Late Cretaceous porphyry deposits, extending from Romania, through Serbia and Bulgaria to Greece are the most important, and immediately predate the subsequent continental collision and post-collision magmatism. Deposits of Majdanpek, Bor and Veliki Krivelj in Serbia; Assarel, Elatsite and Medet in Bulgaria; and Skouries, Chalkidiki Peninsula in northern Greece (Fig. 10-1), belong to the Serbo-Macedonian massif (SMM) (Kockel *et al.* 1977, Frei 1995, Ciobanu *et al.* 2002, Heinrich & Neubauer 2002, Kouzmanov *et al.* 2003).

Skouries deposit: case history discovery

Geologic framework

The Skouries porphyry Cu–Au deposit, located at the Chalkidiki Peninsula, northern Greece belongs to the SMM. The crystalline basement comprises two lithostratigraphic-tectonic units, the lower Kerdylia Formation and the upper Vertiskos Formation, separated by a NW-striking fault system. The Vertiskos Formation consists of old basement gneiss, amphibolite, schist and marble, Tertiary intrusions, ophiolites (the Therma-Volvi-Gomati). Locations of subvolcanic-porphyritic stocks and volcanic complexes related to porphyry Cu deposits (Kockel *et al.* 1977, Perantonis 1982, Frei 1992, 1995, Tobey *et al.* 1998) are mainly controlled by deep fracture systems that permitted subvolcanic intrusions to reach higher levels of the crust (Zachos 1963, Kockel *et al.* 1977, Perantonis 1982, Frei 1995). Isotope data indicate that subvolcanic-porphyritic stocks such as the Skouries, of Miocene age (18 Ma), are younger than the intrusions of the Serbo-Macedonian massif.

The Skouries deposit is related to pipe-like intrusions of subalkaline-alkaline composition, extending at surface over an area of approximately 200 m x 200 m. The defined reserves in the porphyry Cu–Au deposit of Skouries are approximately 206 Mt at 0.54 % Cu, and 0.80 ppm Au. Geological data based on recent drilling, provided by TVX Gold Inc Hellas indicated that the Skouries deposit is developed around two related porphyry centers at depths between 650 and 800 m (Tobey *et al.* 1998). At least four monzonite porphyries have been described Kroll *et al.* (2002). In decreasing age, and increasing degrees of fractionation of the parent magmas, they are: (1) pink monzonite, (2) main monzonite, (3) intra-mineral monzonite, and (4) late-stage porphyry. High-grade ore is directly associated with the main and intra-mineral monzonite phases. Late-stage monzonite dykes that are barren cut all intrusive phases. The monzonite contains phenocrysts of plagioclase, alkali feldspar and amphibole as well as apatite and titanite microphenocrysts in a fine-grained feldspar-dominated groundmass (Kroll *et al.* 2002).

Analytical methods

Platinum, palladium and gold were determined at X-ray Assay Laboratories (XRAL), Ontario, and Canada using the ICP–MS method, after preconcentration (lead fire assay technique) from large (30 g) samples. The detection limit is 10 ppb for Pt, 1 ppb for Pd and 5 ppb for Au. Copper, Ag, Pb, Zn, Cr, Ni, Co and Mo were determined at XRAL, using the ICP/MS method.

Mineral compositions were determined by electron microprobe analysis at the National University of Athens, using a Cambridge Microscan–5 instrument and a JEOL JSM–5600 scanning electron microscope, both equipped with automated energy dispersive analysis system, Link 2000 and ISIS 300 OXFORD, respectively. Accelerating voltage and beam current were kept at 20.0 kV and 0.5 nA, respectively.

Characteristic features of alteration and mineralization

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

bearing veinlets (Kockel *et al.* 1977, Perantonis 1982, Frei 1995, Tobey *et al.* 1998). The Skouries deposit is characterized by relatively high Pd and Pt contents (Table 10-5). Chalcopyrite, and to a lesser extent bornite, contain exsolution of galena, which commonly has significant concentrations of Se, whereas clauthalite is rare. Minor ore minerals are gold-electrum, clauthalite-galena, hessite and merenskyite-moncheite (Tarkian *et al.* 1991, Figs 10-2 to 10-4, Table 10-2). Inclusions of silicates (commonly albite and orthoclase) and crystals of sylvite (KCl) are occasionally trapped in chalcopyrite (Fig. 10-4). Sphalerite with a low iron (~3 wt.% Fe) content is rare. At the periphery of the porphyry stock pyrite occurs as thin replacive overgrowths on chalcopyrite. Also, chalcopyrite in places is surrounded by digenite suggesting relatively oxidized fluids with a high ratio of metal to reduced sulfur during the evolution of the mineralized ore forming system.

Dark green fine-grained xenoliths within mineralized porphyry are mainly composed of orthoclase, phlogopite, and lesser amounts of relict biotite, fine-grained magnetite, pyrite and chalcopyrite (Fig. 10-2 & 10-3). They may be derived from the fragmentation of mafic rocks that lie beneath the porphyries. The pervasive and vein-type mineralization in xenoliths (stage I) may be related with the hydrothermal system of an earlier porphyry stock of Skouries (Kroll *et al.* 2002). It is remarkable that magnetite is Cr-bearing, the Cr content ranging from 0.65 to 2.26 wt.% Cr₂O₃ in the matrix, to 0.29 wt.% Cr₂O₃ in magnetite of vein type, in contrast to the Cr-free magnetite of the main porphyry. Chalcopyrite and pyrite contains 0.45 to 2.4 wt.% Ni and 0.64 to 4.18 wt.% Co. Ti-magnetite, with titanium content ranging from 17.5 to 23.5 wt %, is commonly associated with rutile, both postdating the main stage of the magnetite deposition (Fig. 10-4).

A salient feature of the Skouries porphyry is 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 & Economou-Eliopoulos 1991). Furthermore, the investigation using SEM/probe reveals the frequent association of magnetite and Cu-minerals (bornite and chalcopyrite) with inclusions of thorite, U-bearing thorite, hydroxyl-apatite and rare earth element (REE)-enriched silicates of the epidote-group (allanite), zircon and rutile, (Fig. 10-2 to 10-4). More specifically, Al and Ca decrease as iron and REE (La, Ce, Nd) increase outward, attaining values up to 24.4 wt.% total REE content, due probably to the substitution of Al by Fe³⁺ and Ca by La, Ce and Nd. Also, the average F content (whole rock) is 900 ppm F (Eliopoulos & Economou-Eliopoulos 1991), while mica phases contain up to 0.19 wt.% Cl and 2.48 wt.% F (Kroll *et al.* 2002). However, despite such an evolved geochemical signature of the Skouries deposit there is a Cr-and Ni-enrichment, reaching values up to 690 ppm Cr and 560 ppm Ni, and a negative relationship with the Pd, Pt contents (Table 10-5, Economou-Eliopoulos *et al.* 2001).

The discovery of palladium and its distribution in the Skouries deposit

In the course of a study of slag from prehistoric or Macedonian gold production in Greece, slag from the Skouries porphyry Cu–Au was found to contain a significant Pd content (40 ppb Pd). The subsequent analysis of representative ore samples showed a significant Pd-enrichment in mineralised samples, up to 490 ppb Pd in oxidized ore samples (Eliopoulos & Economou-Eliopoulos 1991). Subsequently, a more detailed study in the Skouries and other deposits of the Balkan Peninsula was carried out to define relationships between the Pd–Pt and vein-type Cu mineralization, various alteration types or redistribution by leaching from an early-stage. Relatively high Pd content in the major vein-type mineralization of Skouries ranging between 60 and 200 ppb (average 110 ppb Pd), was documented by analysis of a composite drill hole sample (~15 kg) showing 76 ppb Pd and 5000 ppm Cu (Economou-Eliopoulos & Eliopoulos 2000). Furthermore the analysis of mineralized material and highly mineralized portions (up to 3.4 wt.% Cu) from deeper parts of the deposit (from the potassic, propylitic alteration zone) indicated that there is a relatively high palladium, up to 610 ppb (average 130 ppb) and platinum, up to 150 ppb (average 46 ppb) contents (Table 10-5, Economou-Eliopoulos & Eliopoulos 2001).

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

With respect to Au, native gold or electrum occur as small (5–100 µm) inclusions in chalcopyrite or along bornite margins; it may also form intergrowths with Pd–Pt–Bi- and Ag-tellurides, ranging from less than 1 to tens

μm (Tarkian *et al.* 1991). Where primary mineralization is overprinted by secondary covellite and chalcocite, these minerals contain inclusions of gold (Kesler *et al.* 2002). Moreover, SIMS (ion probe) analyses of ore minerals from the Skouries deposit showed that bornite contains about 1 ppm Au, whereas chalcopyrite contains about an order of magnitude less. Although both supergene and hypogene chalcocite and covellite contain 10–24 ppm Au, commonly they are not abundant enough to account for a significant part of the average gold grades of bulk ore in many porphyry copper deposits. In the Skouries deposits, gold in covellite has been attributed to deposition as gold colloid particles, during the supergene enrichment rather than from exsolution from sulfides (Kesler *et al.* 2002).

Elatsite, Medet and Assarel deposits (Bulgaria)

The Elatsite, Medet and Assarel porphyry–Cu deposits, in the central Srednogorie metallogenetic zone are related to multiphase monzonitic-monzdioritic stocks and dikes of Upper Cretaceous (92.3 ± 1.4 Ma) age. Mafic dikes post-date mineralization, and may be porphyritic, but are generally aphanitic, are present both outside of the Elatsite deposit and in the pit (von Quadt *et al.* 2002). Ages based on the $^{40}\text{Ar}/^{39}\text{Ar}$ laser probe radiometric data for hornblende and biotite from igneous rocks indicated age of emplacement around 90.8 ± 0.5 Ma for both Elatsite and Medet areas, whereas all analyses of alteration minerals (white mica) indicated younger alteration at 79.5 to 80 Ma, suggesting a time gap between the dominant intrusions and hydrothermal alteration (Lips *et al.* 2004). The porphyry rocks may have been derived from an enriched mantle source, with a contribution by crust material, as is exemplified by the $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.702356 to 0.706728 and moderately radiogenic Pb (von Quadt *et al.* 2002).

Elatsite

The Elatsite porphyry Cu–Au–PGE deposit extends over an area approximately 1,300 m long and 200 to 700 m wide. The ore body has been traced to a depth of more than 550 m. Mafic dykes crosscutting granodiorite and associated with intense potassic alteration (K-feldspar, biotite and quartz), are characteristic at the central part of the deposit. 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 systems (Popov & Kovachev 1996, Popov *et al.* 2000). Pre-mining ore reserves of the deposit were estimated to be 185 million tonnes 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).

The various alteration types cannot be clearly distinguished, due to the repeated overprinting and intense silicification. Four mineral assemblages can be distinguished: (a) magnetite–bornite–chalcopyrite, which is linked to pervasive potassic and propylitic alteration types, in the central parts of the deposit, crystallized from high-salinity aqueous fluids with 60–42 wt.% NaCl_{equiv}, (b) quartz–chalcopyrite–pyrite, (c) quartz–pyrite and (d) quartz–galena–sphalerite. The three latter assemblages are linked to phyllitic–argillitic alteration and characterize the upper and marginal parts of the deposit, and may have precipitated from progressively cooler and less saline fluids with 44–20 wt.% NaCl_{equiv}. The oxidized zone of the deposit does not exceed 50 m depth, whereas the zone of secondary sulfide enrichment is limited (less than 30 m) (Kehayov & Bogdanov 2002, Kehayov *et al.* 2003, Tarkian *et al.* 2003). The Re–Os ages (92.43 ± 0.04 to 92.03 ± 0.05 MA) of molybdenite samples, representing the main stage stockwork mineralization, suggest a minimum absolute life span of $400,000 \pm 90,000$ years in a magmatic-hydrothermal system (Zimmerman *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. Pd, 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) who documented Pd and Pt contents up to 20 ppb, while Cr and Co reach values up to 100 and 116 ppm, respectively. Furthermore, precious metal contents in 35 ore samples (normalised to 1% Cu, in order to obtain comparable data) are given by Tarkian *et al.* (2003): the average contents 890 ppb Au, 40 ppb Pd and 16 ppb Pt are higher in ore samples dominated by magnetite, bornite and chalcopyrite, compared to 460 ppb Au, 14 ppb Pd and 4 ppb Pt in samples consisting mainly of chalcopyrite and pyrite. 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 & 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).

The mineralogical data indicate that Pd, Pt and the associated Co, Ni, Te, Se, Bi, Au, and Ag occur under the form of the following minerals: merenskyite-moncheite, carrolite, nickeliferous linnaeite, pyrrhotite, hessite, clauthalite-galena, kawazulite, naumannite, eucairite, bohdanowiczite, weissite, gold-electrum, tetrahedrite-tennantite, and unnamed phases such as $(\text{Pd}, \text{Ag})_3\text{Te}_4$ (Tables 10-2 & 10-4). Coarse-grained native gold (up to several millimetres) occurs within thin veinlets cutting the above association or under the form of individual crystals in small cavities within bornite. Minor molybdenite and sphalerite are also present (Petrunov *et al.* 1992, Petrunov & Dragov 1993, Dragov and Petrunov 1996, Tarkian *et al.* 2003, Strashimirov *et al.* 2003). The distribution of these minerals is irregular throughout the deposit, forming lenses dominated by magnetite and hematite.

Medet

The Medet porphyry deposit, discovered in 1955, the first known porphyry deposit in Bulgaria, is linked to the Assarel volcanic complex, and it is among the largest ones in Bulgaria, with defined reserves of approximately 244 Mt, grading 0.37 % Cu (Herrington *et al.* 1998). The Cu-mineralization of stockwork type is hosted by a quartz monzonite intrusion, and is associated with quartz-magnetite and K-silicates. Rutile, ilmenite, Mn-ilmenite, pseudobrookite, Co-Ni assemblages (carrollite, vaesite), Co- and Ni-bearing pyrites, reaching values up to 17.8 wt.%, and 5.3 wt.%, respectively. Cu-Sn-V-minerals (colusite and sultanite) and micron-sized inclusions of Bi-Ag tellurides (hessite and tetradyomite) within chalcopyrite have been described (Strashimirov *et al.* 2003). Molybdenite occurs mostly as polymorphic 2H and it is characterized by a high Re content (average 905 ppm) (Todorov & Staikov 1985). The quartz-pyrite association forms veins and veinlets in the middle part of the deposit, whereas the quartz-galena-sphalerite association only occurs locally at the uppermost and marginal parts of the deposit. Late hydrothermal activity was marked by precipitation of anhydrite-gypsum and calcite-zeolite (laumontite, heulandite, stilbite) in veinlets up to 2–3 cm wide that replace and crosscut the opaque minerals common in the upper marginal parts of the deposit.

Palladium, Pt and Au concentrations in representative mineralized samples from the Medet deposit indicated up to 50 ppb Pd, 26 ppb Pt and 360 ppb Au. It is remarkable that samples with the highest Cr (130 ppm) and Co (170 ppm) contents exhibit the lowest (<10 ppb) Pd and Pt contents (Eliopoulos *et al.* 1995). In addition, the reported precious metal contents in flotation concentrate (at 14.9 wt.% Cu) are 160 ppb Pd, 8 ppb Pt and 5600 ppb Au (Tarkian & Stribny 1999).

Assarel

The Assarel granodiorite porphyry deposit, with defined reserves of approximately 360 Mt, grading 0.44 % Cu (Herrington *et al.* 1998), is located in the central part of the Assarel volcano, composed predominantly of lavas of andesitic composition, and latite-andesite pyroclastic rocks. The Assarel deposit is related to two pipe-like intrusions that join at depth. The northern one crops out in an open pit. The ore mineralogy and alteration at Assarel is particularly complex compared to the other deposits. An early quartz-magnetite-hematite association, which is typical of the porphyry copper deposits in the region, occurs only in a limited part of the Assarel deposit. The dominant alteration types are: K-silicate, propylitic and advanced argillic-acid-chlorine and acid-sulfate sub-types. Porphyritic textures in many places are overprinted by a sequence of acid-chlorine and acid-sulfate alteration-types. Transition zones between propylitic-argillic and propylitic-sericitic alteration types are well exposed. Also, a transitional sericitic-advanced argillic type of alteration defined by the assemblage illite + quartz + pyrite + pyrophyllite (kaolinite) has been described (Kanazirski 2000).

A quartz-pyrite-chalcopyrite association is widespread in the middle and marginal parts of the deposit, whereas a quartz-galena-sphalerite association is rare and is found mainly in the uppermost part of the deposit.

Several high-sulfidation-style assemblages are also established in the uppermost levels of the deposit. These assemblages include enargite and goldfieldite (Cu-As ± Te assemblage), colusite, As-sultanite and sultanite (Cu-Sn-V assemblage), aikinite and wittichenite (Cu-Bi assemblage), and hessite and tetradyomite (Bi-Ag-Te assemblage) found as fine mineral inclusions in chalcopyrite. This latter assemblage is related spatially to sericitic and advanced argillic alteration-type of the volcanic rocks in the uppermost parts of the deposit. It is noteworthy that this alteration type, which is developed at depth in the porphyry Cu deposit, has been overprinted by high sulfidation-style mineralisation in the upper parts of the deposit (Strashimirov *et al.* 2002, Strashimirov *et al.* 2003). Assarel is the only major deposit in the district showing much secondary chalcocite and covellite, which is of major economic importance. The zone of supergene enrichment is a band 60–70 m thick that lies

above the primary quartz-pyrite-chalcopyrite but below the oxidation zone (10–15 m). In contrast to the other deposits in the region, native gold is rare here, although near the contact between the zone of oxidation and that of the secondary enrichment exceptionally high Au contents have been reported (Strashimirov *et al.* 2003).

It is remarkable that ore samples dominated by chalcocite and covellite, with gold content up to 19.5 ppm Au contain only 3 ppb Pd and < 10 ppb Pt, and relatively high Cr, Ni and Co contents reaching values up to 110, 280 and 150 (all in ppm), respectively. In general, precious metal levels in mineralised samples from the main part of the porphyry deposit are 140 ppb Au, 10 ppb Pd and 33 ppb Pt, while Cr, Ni and Co contents are lower than 35 ppm (Eliopoulos *et al.* 1995), which may point to an epigenetic Cr, Ni and Co-enrichment, along with Au. The precious metal contents in flotation concentrates (at 27.9 wt.% Cu) are 4800 ppb Au, 54 ppb Pd and 14 ppb Pt, which are lower than those in the Medet and Elatsite porphyry deposits (Tarkian & Stribrny 1999).

Bor-Majdanpek (Serbia)

The Bor porphyry Cu and high-sulfidation epithermal deposits, the gold-poor Veliki Krivelj porphyry and Majdanpek porphyry Cu and high-sulfidation epithermal deposits in Serbia, which are hosted in a volcanic-intrusive complex with calc-alkaline affinity (Jankovic 1997), are the largest deposits in Europe. The volcanic activity at the Bor region, over 80 km long and 20 km wide, is confined to the emplacement of 90–78 Ma hornblende (-biotite) andesite and dacite (Karamata *et al.* 1997, Lips *et al.* 2004). Furthermore, Lips *et al.* (2004) indicated a close link between host-rock emplacement, mineralization and alteration in the Bor area, suggesting that formation of the porphyry mineralization during an early stage of hydrothermal alteration.

Approximately 450 Mt of ore grading 0.6% Cu, 570 Mt grading 0.44 % Cu, and 1000 Mt grading 0.6 % Cu have estimated resources for Bor, Veliki Krivelj and Majdanpek deposits, respectively (Herrington *et al.* 1998). Approximately 1500 m of vertical section has been exploited for more than 80 years.

At Bor the mineralization is continuous from massive high-sulfidation ore near surface, to porphyry-type mineralization below. The predominant rock type in the Bor area is hornblende-biotite andesite. At Veliki Krivelj the mineralization is hosted by porphyry dike swarms and by skarns, while the Majdanpek deposit is hosted by andesite dykes (Jankovic 1997, Lips *et al.* 2004). Chalcopyrite and pyrite are major components, with lesser bornite, molybdenite, magnetite pyrrhotite and enargite.

The Majdanpek deposit is dominated by porphyry mineralization in a mineralised zone approximately 4 km long and 300 m wide, with an increase in copper grade in zones of potassium silicate alteration. Propylitic alteration is less well developed with a grade 0.3 % Cu. The uppermost part of the ore body is Au-enriched (average 1 ppm Au), whereas below 300 m grade dropped to average 0.25 ppm Au. Chalcopyrite and lesser amounts of pyrite and magnetite mainly compose mineralization. Molybdenite, pyrrhotite, bornite, galena, sphalerite, marcasite, tetrahedrite, enargite, arsenopyrite, tellurides ($PdAgTe_2$), selenides and native gold are also present (Jankovic 1997, Herrington *et al.* 2003). The Mo content deposit is low ranging between 30 and 80 ppm, but the Re content in molybdenite reaches values up to 2700 ppm (Herrington *et al.* 1998). The Pd and Pt contents in the Majdanpek deposit are more elevated (130–240 ppb Pd and 16–19 ppb Pt in flotation concentrates, at 22–30 wt.% Cu) compared to those in Bor (40 ppb Pd and 19 ppb Pt) and Veliki Krivelj (70 ppb Pd and 16 ppb Pt) deposits (Tarkian & Stribrny 1999). Although the Pd and Pt levels in those deposits are much lower than in the Skouries deposit, Greece, in the copper production of Serbia (1988) 50 kg Pd and 3 kg as by-products along with Au and Ag have been reported (Herrington *et al.* 2003).

Santo Tomas II, Philex Philippines

The Santo Tomas II Philex porphyry Cu–Au deposit, of Miocene age (3 Ma), is located on Luzon Island in the Philippines, along the margins of a fault system. It extends at surface over an area of approximately 600m x 200 m representing approximately 800 m of vertical section. This quartz diorite porphyry with calk-alkaline affinities is spatially associated with volcanic rocks of dacite composition (Tarkian & 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. Phyllitic alteration, of limited extent, overprints earlier potassic and propylitic assemblages. Two types of mineral assemblages have been distinguished: (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 central high grade copper zone (>0.3 wt.% Cu) of the deposit is surrounded by lower grade

zone (0.2–0.3 wt.% Cu). There is a positive correlation between Cu and precious metals, in particular with gold (average 1.8 ppm Au), Pd (up to 290 ppb), Pt (up to 45 Pt) and Ag (up to 100 ppb). Merenskyite occurs exclusively as inclusions in chalcopyrite and bornite. Polyphase fluid inclusions in quartz veins associated with a PGM-bearing bornite–chalcopyrite–magnetite assemblage, are characterized by high salinity 35–60 wt.% NaCl_{equiv}, and high-trapping temperature 380–520°C (Piestrzynski *et al.* 1994, Tarkian & Koopmann 1995).

Grasberg deposit, Indonesia

The Grasberg intrusive and volcanic rocks are situated in the highlands of Irian Jaya, Indonesia, and lie on the still-active collisional boundary between the north-moving Australian plate and the SW-migrating Indo-Pacific plate. This plate interaction has resulted in extensive uplift in the area to form the central ranges of Indonesia and Papua New Guinea. Numerous mineralised intrusions, dominantly calc-alkaline to alkaline, are of age ranging from Tertiary to recent, but the largest deposits are the youngest (<9 Ma), and active volcanism and mineralization continue today at several places, such as Ladolam (Meinert *et al.* 1997).

Among the world's major Cu–Au mines is the Grasberg Cu–Au deposit, of Pliocene age, discovered in 1988. The multistage Grasberg and Kali intrusions are overprinted by extensive hydrothermal alteration. The intrusions have strontium (⁸⁷Sr/⁸⁶Sr values varying from 0.70626 to 0.70707), neodymium ($\epsilon_{\text{Nd}} = -13.7$ to -15.3) and lead isotopic characteristics suggesting that the parental magmas have been affected by a substantial crustal component (Housh & McMahon 2000).

The Grasberg deposit is hosted within intrusive rocks, has a pipe-like form, approximately 950 m in diameter, and 2.4 by 1.7 km at surface. Extensive skarn deposits surround the porphyry deposit. Probable mineral reserves in the Grasberg deposit/ Ertsberg district are approximately 2,515 million tons with average 1.1 wt.% Cu, 1 ppm Au and 3.4 ppm Ag. Palladium and platinum in flotation concentrate (at 23.8 wt.% Cu) were 58 ppb and 15 ppb, respectively, while the gold content was 18 ppm (Tarkian & Stribny 1999). Thus, although Pd and Pt data in concentrates is limited the comparison of the Au content between the average value (1 ppm at 1.1 wt.% Cu) and that in a flotation concentrate (18 ppm Au, at 23.8 wt.% Cu) point to much lower Pd and Pt (average) contents compared to those in the Skouries, Greece, and Elatsite, Bulgaria porphyry deposits.

The sulfide mineralization can be grouped into three main stages: (1) heavy sulfide zone, (2) Grasberg copper-gold stage, and (3) late copper mineralization (mixed copper sulfides, covellite-enargite-pyrite and pyrite-covellite-marcasite). The Grasberg copper-gold stage is a major chalcopyrite-bornite-pyrite-gold-hematite event, related to high-K calc-alkaline to shoshonitic intrusive rocks, extending to depth > 2500 m, while at the peripheral zones overprints the heavy sulfide zone (McDowell *et al.* 1996). Late copper mineralization comprises several stages and is dominantly disseminated in character. The early stages are dominated by chalcopyrite, bornite, digenite-chalcocite, covellite-nukundamite, and colusite, with the later stages containing pyrite, marcasite, covellite, and enargite and minor chalcopyrite. Late copper mineralization is essentially a high-sulfidation system, and is associated with zones of andalusite alteration, and abundant intermediate argillic alteration (McDowell *et al.* 1996).

Ok Tedi, Papua New Guinea

Ok Tedi porphyry Cu–Au deposit is associated with a younger (1.2 Ma) latite porphyry stock, of calc-alkaline affinity (Page & McDougall 1972), compared to that of the Grasberg deposit (Meinert *et al.* 1997). Mineralization, associated with the potassic alteration zone, consists mainly of chalcopyrite with subordinate bornite, chalcopyrite, covellite, pyrite, and marcasite. Molybdenite is present in lesser amounts, whereas magnetite occurs in skarns in the peripheral parts of the deposit (Bamford 1972). Pre-mining mineral reserves at Ok Tedi were approximately 275 million tons with average 0.75 wt.% Cu and 0.5 ppm Au (Gilmour 1982, Rush & Seegers 1990). Gold in the supergene zones reaches values of 3 ppm, and in the skarn mineralization 1.8 ppm. Pd and Pt in a flotation concentrate (at 37.3 wt.% Cu) were 980 ppb and 24 ppb, respectively (Tarkian & Stribny 1999).

Ladolam deposit, Papua New Guinea

The Ladolam deposit on Lihir Island is among the world's largest, containing more than 1300 tons of Au. It has been interpreted as a transition stage between an of early-stage, low-grade porphyry gold system and that evolved into a low-sulfidation epithermal deposit (Moyle *et al.* 1990, Carman 1994, Müller *et al.* 2002). Alkaline rocks that range from trachybasalt through trachyandesite to latite, which are cut by late-stage monzodiorite

intrusions, host the Ladolam gold deposit. Their geochemical signature is typical of high-K igneous rocks transitional to shoshonite. Unaltered samples, from the Lihir rocks contain elevated noble metal abundances of up to 4 ppb Au, 13 ppb Pd, and 12 ppb Pt. These elevated precious-metal (Au–Pt–Pd) concentrations have been interpreted as primary magmatic features suggesting a precious metal pre-enrichment of the mantle source beneath the island Ladolam (McInnes & Cameron 1994, Taylor *et al.* 1994, Mungall 2002, Müller *et al.* 2003). Also, the proximity of the Ladolam epithermal gold deposit to the Conical seamount on nearby Lihir island, coupled with the similarity of the mineralogy, alteration, geochemistry and vein textures to those of some subaerial epithermal gold deposits, indicate that some features long considered to define a subaerial setting can be also formed in a submarine environment (Petersen *et al.* 2002).

Porgera deposit, Papua New Guinea

The Porgera gold deposit, located in the Pliocene fold and thrust belt that forms the highlands of Papua New Guinea, is associated with sodic-alkalic, hypabyssal intrusions of alkali basaltic composition. Reserves and resources were estimated to 113 Mt of ore at a grade of 3.5 ppm (Ronacher *et al.* 2004). The intrusions were emplaced into Cretaceous mudstone and siltstone in the latest Miocene (6 Ma). Both igneous and sedimentary rocks are mineralized. Three types of veins occur: (1) magnetite-sulfide ± Au-carbonate veins (prestage I); (2) base-metal sulfide ± Au-carbonate veins (stage I); and, (3) quartz-roscoelite-pyrite-gold veins and breccias (stage II), which is economically the most important. Laser $^{40}\text{Ar}/^{39}\text{Ar}$ dating of magmatic biotite (5.99 ± 0.11 Ma) dates the intrusive event and hydrothermal biotite (5.98 ± 0.13 Ma) and roscoelite (5.92 ± 0.08 Ma), date the mineralising event, indicating that the magmatic and ore-forming system at Porgera was short-lived (Ronacher *et al.* 2000).

Compilation of petrological, fluid inclusion and oxygen and hydrogen isotope data, coupled with the presence of organic-derived volatiles suggest that an ascending fluid interacted with sedimentary rocks, probably at depth prior the site of ore deposition. Furthermore, modelling the analytical data suggest that more than one process was involved in stage II mineralization, including boiling, mixing and fluid-rock reaction (Ronacher *et al.* 2004).

Mamut deposit, Malaysia

The Mamut Cu–Au deposit, east Malaysia, of upper Miocene age, belongs to the mineralised belt along a NW–SE striking tectonic zone of Sabah. It is associated with a monzonitic-granodioritic porphyry stock with calc-alkaline affinity, although approximately 40% of the mined ores were hosted in a serpentized body. Reserves in the Mamut deposit were approximately 179 million tons with average 0.48 wt.% Cu and 0.6 ppm Au (Tarkian & Stribrny 1999). Mineralization is associated with potassio-propylitic alteration zones. Chalcopyrite and lesser amounts of pyrrhotite are principal ore minerals. Biotite is common in the outer potassio alteration zone. Strong silicification is characteristic. Overlapping Pb and Zn and subsequent Sb mineralization is associated with NNE-trending fractures accompanying the phyllitic and advanced argillic alteration envelope (Imai 2000). Although magnetite is locally abundant in the propylitic zones, an abundance of pyrrhotite may suggest less reducing and locally lower pH environment (Kosaka & Wakita 1978, Corbett & Leach 1998). Palladium, platinum, and gold in flotation concentrates (at 20.3 wt.% Cu) were 1400 ppb, 470 ppb and 15200 ppb, respectively (Tarkian & Stribrny 1999).

Bajo de la Alumbrera, Andes

The Bajo de la Alumbrera deposit, one of the world's largest Cu–Au deposits, is associated with Miocene magmatism in the central Andes. Production plus remaining resources attain 780 Mt ore at 0.52% Cu and 0.67 g/t Au (Sasso & Clark 1998). Detailed studies of the Alumbrera deposit documented eight distinctive porphyritic intrusions, which form stocks and dike-like bodies, showing a general evolution from early silica-rich dacite toward intermediate andesite (Ulrich, 1999, Proffett 2003). Following a barren intrusion that pre-dates the porphyry stock, primary (unweathered) ore mainly consists of chalcopyrite (+/ bornite), native gold and pyrite. The highest copper-gold grades are associated with intense potassio (quartz-magnetite) alteration of two of the earliest mineralised porphyritic intrusions. Younger porphyries are less mineralized or in some cases barren (Proffett 2003). Halter *et al.* (2002, 2004, 2005) have focussed their investigation on sulfide melt inclusions on the best-exposed part of Farallon Negro volcanic complex, hosting the Alumbrera porphyry Cu–Au deposit, and provide evidence for magma mixing and evolution of the magma chamber. They demonstrate an intense magma mixing (hybridization) process of a rhyodacitic magma with a crustal component, and a very mafic mantle-

derived magma resembling the composition of lamprophyre dikes. In addition, they concluded that ore metals and most of the sulfur in the ore fluid are derived from the magmatic sulfide liquid, and that Cu/Au ratios in the ore bodies are equal to that of the precursor sulfide.

Cripple Creek, Rocky Mountains, U.S.A.

The Cripple Creek deposit is one of the largest in the world (having produced nearly 700 metric tons of Au) and belongs to an important group of alkaline-related porphyry, epithermal and skarn gold deposits, occurring in a north-south belt that extends from Canada to eastern Mexico along the eastern edge of the North American Cordillera (Mutschler *et al.* 1985). Deposits in the North American Cordilleran belt, including deposits in the Black Hills, South Dakota and Galore Creek (Strike Copper), British Columbia, and Cripple Creek, to the south have produced nearly 13% of the total production in the United States and Canada (Mutschler & Mooney 1993).

Geochronological, geochemical, and isotopic data from some of these deposits suggest a genetic relationship between alkaline magmatism and gold mineralization. Gold deposits at Cripple Creek formed between 32 and 27 Ma, corresponding to the final stages of Laramide subduction-related magmatism in this region, like the giant Bingham Cu–Au deposit, Utah (Mutschler & Mooney 1993, Sillitoe 2000, Kelley & Ludington 2002). The most salient feature of these porphyry-Au deposits is the near-surface emplacement of the related porphyry intrusions, the relatively oxidized volatile-rich alkaline nature, the contribution of crustal material, and the anomalously hot, low density and thick crust (about 50 km) beneath Colorado (Kelley & Ludington 2002).

Bingham porphyry Cu–Au deposit, Utah

The Bingham Cu–Au–Mo porphyry (Fig. 10-1) is one of the largest porphyry copper deposits in the world, with combined reserves and production of more than 18 Mt of Cu (Babcock *et al.* 1995). It is spatially associated with several small monzonite and quartz monzonite stocks of Eocene age (39.8 to 37.5 Ma) emplaced in Paleozoic quartzite and limestone (Warmaars *et al.* 1978, Babcock *et al.* 1995, Ballantyne *et al.* 1997, Maughan *et al.* 2002). Some intrusions vented to the surface forming volcanic rocks, the older unit being comagmatic with the intrusive complex. Their composition has been attributed to a combination of fractional crystallization, magma mixing and assimilation (Keith *et al.* 1998). The largest porphyry-skarn Cu–Au–Mo deposit in North America, at Bingham Canyon, Utah, has a strong crustal contamination signature, although primitive alkaline lava flows are spatially and temporally associated with it. Such an association of mafic alkaline dikes with giant porphyry Cu–Mo deposits in Andes has been emphasised (Keith *et al.* 1998). Mineralization consists mainly of chalcopyrite, bornite, molybdenite and pyrite. The porphyry ore occurs mainly in monzonite, quartz monzonite porphyry, quartz latite porphyry, latite porphyry, and quartz latite porphyry breccia with large adjacent Cu skarns, vein and Manto Ag–Pb–Zn deposits, and distal disseminated Au deposits (Phillips *et al.* 1997). There is an enrichment of Pd, Pt (up to tens of ppb) and Au, which is similar to that seen in other young shoshonitic alkalic systems like those of Fiji and Lihir, Papua New Guinea. (Müller *et al.* 2003).

The relatively Pd- and Pt-rich character of the Bingham ore, and the trend of the younger Bingham intrusions to be more Cr- and Ni-rich despite their otherwise more evolved geochemical signatures is a salient feature (Atkinson & Einaudi 1978, Waite *et al.* 1997). Also, a volcanic section that is co-magmatic with ore-related porphyries is very heterogeneous containing clasts of latite and minette, flows of melanephelinite, shoshonite, and olivine latite, in addition to volumetrically dominant dacite to trachyte (Keith *et al.* 1998).

British Columbia, Cordillera

Porphyry Cu–Au deposits located in the British Columbia Cordillera are associated with alkaline, subalkaline to calc-alkaline stocks, dikes and sills, which have been emplaced into two allochthonous terranes, Quesnellia and Stikinia, North America (McMillan & Panteleyev 1995). The majority of these intrusions are late Triassic to early Jurassic in age (205–195 Ma) although some intrusions in Quesnellia are distinctly younger (~185 Ma; Mortensen *et al.* 1995). Recent U-Pb geochronology of some intrusive rocks associated with porphyry Cu–Au deposits in Cordillera, indicated that the crystallization ages obtained for porphyry-related intrusions in both alkaline and calc-alkaline composition and both Quesnellia and Stikinia units (Copper Mountain, Ajax/Afton, Mount Polley, Galore Creek, Cat Mountain and Kemess intrusions) are in the range of 210 Ma to 200 Ma, (Mortensen *et al.* 1995). Evidence from xenoliths, geological, mineralogical, geochemical, and isotopic data

indicate that this suite of intrusions belong mostly to a distinctive variety of alkaline arc magmas that were largely derived from an enriched mantle source region and that these intrusions were emplaced during collisional events (McInnes & Cameron 1994, Lang *et al.* 1995, Cassidy *et al.* 1996).

Alteration assemblages including potassic, calc-potassic and sodic/sodic-calcic characterize deposits associated with alkaline intrusions in Quesnellia and Stikinia, all show a distinct lack of associated quartz veining. Mineralization occurs in sulfide/oxide vein systems, breccias and disseminated zones, consisting mainly of Cu-minerals (chalcopyrite and/or bornite) and Au, with varying Cu/Au ratios among districts, and among and within zones in individual districts, while significant Mo is rare. The Copper Mountain and the Iron Mask Batholith have been mined extensively and significant resources exist at Galore Creek, Mt. Polley, and Mt. Milligan (Lang *et al.* 1995).

Mount Polley

The Mount Polley deposit is characterized by multiple intrusions that vary from diorite to nepheline syenite. Mineralization, consisting of chalcopyrite, bornite and magnetite, is associated with hydrothermal breccia at two main areas: The West zone, extending to a drilled depth of at least 275 m, and the central zone, approximately 200 m to 300 m width by 1100 m north-south, that is contained within an eastward dipping breccia body. Mineralization in the core of the deposit is associated with a chalcopyrite-bornite-chalcopyrite assemblage, passing out into magnetite-pyrite-chalcopyrite (Fraser *et al.* 1995). Palladium and Pt contents in sulfide concentrates from Main zone are higher (up to 320 ppb Pd and 33 ppb Pt) compared to the West zone (Thompson *et al.* 2001).

Galore Creek

Galore Creek is well known for its high Au content and close spatial relationship with high level syenitic and monzonitic intrusions. A complex succession of intrusive and hydrothermal events characterizes the Galore Creek deposits, with an intense alteration and mineralization (Lang *et al.* 1995, Bottomer & Leary 1995). The highest gold grades, exceeding 1 ppm, are associated with bornite-rich mineralization situated in the northern and southern parts of the central zone, dominated by Ca-K-silicate alteration, with a combined resource of 284 million tones at 0.67 wt.% Cu (Enns *et al.* 1995). Palladium and platinum contents vary among and within zones of the Galore deposit, the Pd/Cu ratio ranging between 5.7 and 53.3 in the central zone, to 120 at the Southwest zone (Thompson *et al.* 2001, Table 10-1).

Mt. Milligan

The Mt Milligan deposits are large, low grade, porphyry Cu–Au deposits hosted by monzonite stocks and adjacent volcanic rocks within the Early Mesozoic Quesnel Terrane. The measured and indicated resource for the combined deposits is 299 million tons of 0.22 wt.% Cu and 0.45 ppm Au. A biotite-rich subzone forms the core of an extensive potassic alteration zone and hosts most of the copper and gold, although numerous polymetallic veins lie within the propylitic alteration zone (Sketchley *et al.* 1995). The Au, Pd and Pt reach values up to 18500 ppb, 6310 ppb and 110 ppb, respectively, while the Pd/Cu ratio ranges from 78 to 5100 (Thompson *et al.* 2001, Table 10-1).

Ajax/Afton

The Ajax/Afton deposits, extending for over 20 km from NW to SE, and approximately 5 km width, are located at the contact between two stages of the Iron Mask intrusion, the hybrid diorite and the younger Sugarloaf diorite, which is the probable source of the Cu–Au mineralization. Along the faults system, controlling that mineralization-bearing diorite, serpentinized picrite bodies, with chromium content >2000 ppm and >900 ppm Ni, have been also distributed (Ross *et al.* 1995).

Reconnaissance data given by Thompson *et al.* (2001) indicate that, in most cases, Pd concentrations are two to three orders of magnitude lower than Au, and Pt approximately one order of magnitude lower than Pd. With the exception of occasional elevated Ru and modest Rh, most of the other PGE have low concentrations. In addition, DRC Resources Corporation estimated the mineral resources of the two deposits that comprise the Afton copper/gold project in B.C. (Dolbear & Company 2003). The assumption that the deposit delineated at Afton (1978) was a supergene-enriched porphyry Cu was the reason for the termination of mining in 1987, when at a depth of 275 m, supergene native copper, chalcocite and chalcopyrite ores were not of economic

interest. However, further drilling below the pit bottom revealed higher copper and precious metal grades at depths, and outlined a measured and indicated resource of 69 million tons characterized by the increase of Cu, Au, Ag and Pd from top 0.79 (wt.%), 0.62 (ppm), 1.96 (ppm) and 0.09 (ppm), respectively, downward to 2.76 wt.% Cu, 2.04 ppm Au, 8.02 ppm Ag, and 0.19 ppm Pd (Dolbear & Company 2003).

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. The oxidized nature of the alkaline arc magmas inhibits fractionation of sulfides, while the precious metals remaining in the magmas were transported by magmatic-hydrothermal fluids and were precipitated in the porphyry environment (Thompson *et al.* 2001).

Russia (Siberia)

Siberian (Russia) and Mongolian fragments of the Central Asian Fold belt comprise numerous porphyry Cu–Mo deposits (Fig. 10-1). The mineralization in the Sora (Kuznetsk Alatau), Aksug (Tuva) and Zhireken (Eastern Transbaikalia) is associated in time and space, with porphyry stocks and dikes formed during periods of a decreasing magmatic activity. There is a time gap of 20–30 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$ dating) between the porphyries and older granite intrusions (Berzina & Sotnikov 2000).

Stocks and dikes of the Cu–Mo-porphyry of quartz-diorite-granodiorite intrude a pluton of similar composition with subordinate diorite, tonalite and gabbro. $^{40}\text{Ar}/^{39}\text{Ar}$ dating indicated that porphyries are younger, of 404–401 Ma age than other intrusions of 497–462 Ma age (Sotnikov *et al.* 2003). The chemical compositions of the porphyries are similar to that of the host granitoid plutons. The Aksug porphyries belong to the calc-alkaline series and of an andesitic parental magma. They are characterized by low Rb, Cs, Th, Ta, and REE contents, high K/Rb ratios, and low F/Cl in magmatic fluids. In addition, the deposit is dominated by a mantle source component, with initial $(^{87}\text{Sr}/^{86}\text{Sr})$ varying from 0.70458 to 0.70496 (Sotnikov *et al.* 2000). The stockwork mineralization, consisting mainly of pyrite, chalcopyrite, molybdenite, and minor enargite, galena, and sphalerite, occurs in quartz-sericite altered rocks. At a lower level, the rocks are rich in anhydrite, and, to a lesser extent, in barite and celestite (Berzina & Sotnikov 2000).

Sora Mo–Cu porphyry deposit

The porphyry stock is characterized by potassic alteration (biotite, K-feldspar) and strong albition with limited sericitization and silicification. The Sora deposit is characterized by Mo mineralization, consisting of molybdenite accompanied by pyrite and chalcopyrite. Small amounts of sphalerite, galena, and tetrahedrite are also present. The Mo ranges between 0.04 and 0.10 wt.% and Cu from 0.02 to 0.20 wt.%. Early stage of mineralization, including chalcopyrite and molybdenite disseminations, is related with quartz-biotite-K-feldspar altered rocks. The breccia ore consists of intensely K-feldspathized and albited angular fragments of hosting rocks, cemented by quartz-fluorite matrix, containing molybdenite, pyrite, and chalcopyrite. Quartz-fluorite-galena-sphalerite veinlets, hosted in sericitized and pyritized rocks are the final products of the ore-bearing process.

Zhireken Mo–Cu porphyry deposit

The Late Jurassic age Zhireken porphyry molybdenum–copper deposit is located in Eastern Transbaikalia. Host rocks comprise a calc-alkaline suite of normal to elevated alkalinity dominated by granodiorite, syenite and granite. The Zhireken subvolcanic stocks are of K-calc-alkaline affinity, mainly diorite, syenite, and subalkaline granite porphyries. Geologic and isotopic data suggest that these high REE porphyries were related to the beginning of rifting during late Jurassic–Cretaceous time. Among the other deposits discussed, the Zhireken subvolcanic stocks exhibit high Rb, Cs, Li, and Th contents and low K/Rb ratios. Halogen-containing minerals are characterized by elevated F contents, although F/Cl ratios are generally lower than those of the Sora deposit (Sotnikov *et al.* 2000, Berzina *et al.* 2005). The most salient feature of the Zhireken deposits is elevated initial $(^{87}\text{Sr}/^{86}\text{Sr})$ values of 0.70510–0.70642, indicating a significant crustal contribution to the parent magma of these porphyries. Hydrothermal alteration consists of well-developed potassic (K-feldspar) and argillic assemblages, with ore mineral associations including molybdenite accompanied by pyrite, chalcopyrite and traces sphalerite, rutile, tetrahedrite.

The Pd and Pt contents of both chalcopyrite and molybdenite in flotation concentrates in the above porphyry Cu ± Mo of Russia are relatively low, varying from 9 to 83 ppb Pd and from <10 to 110 ppb Pt. The

highest values recorded are 920 ppb Pd in sulfide concentrates from the Aksug deposit, and 680 ppb Pd and 300 ppb Pt in sulfide concentrate from breccia of the Zhireken deposit (Table 10-1). The available analytical data indicated a positive trend between Pd and Pt in both sulfide and molybdenite concentrates (Sotnikov *et al.* 2000).

Mongolia

Several porphyry copper systems are known in Mongolia, among which the Erdenetuin and Oyu Tolgoi deposits attain the status of significant deposits (Perelló *et al.* 2001 and references therein).

Erdenetuin-Obo, northern Mongolia

The Triassic Erdenetuin-Obo Cu–Mo deposit (approximately 1,700 million Mt at 0.54% Cu, 0.016% Mo, 0.01 ppm Au) (Sotnikov *et al.* 2000, Perelló *et al.* 2001) is located in the Selenga-Vitim belt of northern Mongolia. Granite and andesite are the most volumetrically important rock types, with minor quartz diorite and granodiorite. Isotope data suggest that the host granitoid rocks formed synchronously with early volcanism at a continental margin, whereas the ore-bearing porphyries are coeval with bimodal rift-related volcanism (Sotnikov *et al.* 1995). The porphyry-generating magmas at Erdenetuin-Obo deposit had initial strontium isotope signatures ($^{87}\text{Sr}/^{86}\text{Sr}$) of 0.70406–0.70424, which suggest a mantle source. High Sr and Ba and moderate HFSE and REE contents characterize these porphyries (Berzina & Sotnikov 2000). Ore minerals occur as disseminations and veinlets in a NW-trending zone of sericitized and silicified rocks.

Mineralization is most closely related to diorite and granodiorite porphyries with minor copper associated with the granite porphyries. The ore zone is 2.8 km long and 0.3 to 1.3 km wide, hosted by the porphyry stock and extends into the neighboring granite up to 300–500 m, and a depth of 900–1000 m. Mineralization consists of chalcopyrite with pyrite, molybdenite and traces sphalerite, tetrahedrite, and hydrothermal rutile. Dominant hydrothermal alteration consists of silicification and sericitization of host rock silicates. Potassic and chloritic alteration is minor (Sotnikov *et al.* 2000). The Pd and Pt contents are relatively low (a few tens of ppb) are comparable to those in the above porphyry Cu±Mo deposits of Russia (Table 10-1, Sotnikov *et al.* 2000).

Oyu Tolgoi, southern Mongolia

The Oyu Tolgoi porphyry Cu–Au–(Mo) deposit of Silurian–Devonian age was discovered in 1996 in the Gobi Desert of southern Mongolia, and is associated with bimodal basalt–peralkaline magmatism (Kovalenko & Yarmolyuk 1995). The deposit consists of three main mineralized zones (North, Central, and South Oyu), with an areal extension of approximately 2.5 x 1.5 km, and is interpreted to constitute at least two separate porphyry copper centers (Perelló *et al.* 2001). Central Oyu consists of a multiple-phase hydrothermal breccia crosscutting an altered fine-grained feldspar porphyry containing porphyry-type alteration and mineralization. At South Oyu, a feldspar-hornblende porphyry of monzonitic composition intrudes a sequence of fine-grained andesite and basaltic andesite. The bulk of the Cu–Au–Mo mineralization occurs in an early magnetite-rich, pyrite-poor zone dominated by quartz, chalcopyrite, bornite and trace molybdenite. Magnetite averages 7 to 10 vol %, and copper and gold grades vary sympathetically. At central Oyu, copper mineralization is present in a supergene chalcocite blanket that formed at the expense of a pyrite-rich, hypogene chalcocite-covellite-tennantite sulfide suite that accompanied the advanced argillic alteration event (Perelló *et al.* 2001).

In general, although the information on the PGE content in Cu–Mo ores is limited, it seems likely that both chalcopyrite and molybdenite concentrates exhibit an enrichment in Pd and Pt, and sometimes lower values of the Pd/Pt ratios compared to those of Porphyry Cu–Au deposits (Table 10-1). In addition, the average ($n = 4$) Pd and Pt contents in sulfide concentrates from the Ryabinovoye alkaline Cu–Mo porphyry, Central Aldan, Russia, were 85 ppb and 150 ppb, respectively (Kovalenker *et al.* 1996). The Cu–Mo deposits in Armenia are considered to be similar in age and genesis to those in the Andes and western Cordillera of North America (Pokalov 1977). Highly mineralised samples contain 10–80 ppb Pd, and up to 18 ppb Pt. Molybdenum concentrates contain 5–220 ppb Pd and 12–390 ppb Pt, and copper concentrates contain from 9 to 160 ppb Pd and up to 20 ppb Pt (Faramazyan *et al.* 1970).

Cadia–Goonumba–Copper Hill, Australia

Mineralised igneous complexes of Ordovician age from New South Wales range in composition from quartz-rich medium-K dacite (Copper Hill), to quartz-poor, high-K to ‘shoshonitic’ monzodioritic to monzonitic

complexes (Goonumbla & Cadia) (Blevin 2002, Holliday *et al.* 2002). The Cadia district lies within shoshonitic volcanic rocks of a Late Ordovician Volcanic Belt in the eastern Lachlan Fold Belt of New South Wales. Mineralization occurs in four principal porphyry deposits (Cadia Hill, Cadia Ridgeway, Cadia East/Cadia Far East and Cadia Quarry) showing a close spatial association with shoshonitic monzodiorite to quartz monzonite dykes and stocks of the Cadia Intrusive Complex. Gold-copper mineralization is hosted by these intrusions and also by the enclosing volcanic wall rocks. Hydrothermal alteration associated with mineralization is potassic, which is overprinted by selectively pervasive propylitic and silica-albite assemblages. Petrological studies and major and trace element analysis of unaltered samples from the Cadia porphyry complex are characterized by high K₂O contents (up to 6.5 wt.%) and molecular K/Na ratios consistently >1, confirming the alkalic and shoshonitic nature of the complex. A similar association occurs at the economic Goonumbla (North Parkes) porphyry gold-copper deposits in the eastern LFB, whereas sub-economic gold-copper mineralization at Copper Hill is associated with calc-alkaline quartz diorite and dacitic intrusions (Heithersay *et al.* 1990, Holliday *et al.* 2002, Blevin 2002). At Copper Hill, a porphyritic quartz-diorite, diorite-tonalite complex intrudes an andesite protolith and locally limestone. Geological, geochemical and recent geophysical data for Copper Hill suggest that the main mineralization zone occurs at the western part, over an area approximately 200 m wide and 1000 m long. Due to intense faulting of the area, it has been suggested that the mineralised block is an uplifted deeper portion of the porphyry system (GCO 2004).

The Cadia porphyry gold-copper district is the largest hydrothermal, intrusion-related gold deposit in eastern Australia. The measured resources at Cadia Hill are 260 Mt at 0.17 wt.% Cu and 0.73 ppm Au; inferred resources at East Cadia are 220 Mt at 0.37 wt.% Cu and 0.43 ppm Au. The dominance of magnetite (quartz-magnetite veins or stockwork, adjacent to monzodiorite-monzonite intrusions, at Cadia Hill and East Cadia, is distinctly different from the Ridgeway deposits which contain abundant chalcopyrite, bornite and visible gold (Blevin 2002, GCO 2004). Cadia Hill, Cadia East, and Cadia Far East are relatively large, low-grade porphyry deposits dominated by spaced, sheeted quartz vein systems. Ridgeway (78 Mt 2.0 g/t Au and 0.67 % Cu) and a deep zone in Cadia Far East are smaller but higher grade porphyry deposits characterized by Au and Cu-rich cores with intense sheeted, layered quartz-magnetite-bornite-(chalcopyrite) veins grading outward into chalcopyrite dominated assemblages. Big Cadia and Little Cadia are peripheral Au–Cu–Fe skarns. Cadia Quarry between Cadia Hill and Ridgeway contains transitional features between magmatic and hydrothermal conditions (Wilson 2003, Wilson *et al.* 2004).

Four economic porphyry Cu–Au deposits occur within the Goonumbla volcanic complex. Together these deposits have a combined ore reserve of approximately 64 million metric tons (Mt) at 1.1 wt.% Cu and 0.5 g/t Au (Lickfold *et al.* 2003). There are many similarities to the Skouries deposit, Greece, in terms of (a) both systems are characterized by small finger-like and dike systems monzonite intrusions on which individual deposits are centred. These intrusions have been interpreted to have formed as late-stage differentiates of andesitic parental magmas with shoshonitic compositions, (b) these porphyry intrusions host bornite-chalcopyrite dominated stockwork mineralization, and (c) the hypogene mineralization in both systems includes high-grade zones containing > 0.7 wt.% Cu and > 0.7 ppm Au (Kroll *et al.* 2002).

The Copper Hill deposit is much smaller and subject to on going exploration efforts. To date exploration revealed a zone of mineralization, 300 m long, 50 m wide and up to 200 m deep, consisting of magnetite, chalcopyrite, pyrite, gold, and merenskyite. Grades are similar to that at the Cadia Gold Mine: 0.5 to 1.0 wt.% Cu, 0.5 to 1.5 ppm Au, while Pd reaches values up to 900 ppb (Blevin *et al.* 2002, Holliday *et al.* 2002, GCO 2004).

