Platinum-group elements in porphyry copper deposits: a reconnaissance study

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With 8 Figures

Summary

Sulphide and flotation concentrates from 33 porphyry copper deposits have been investigated for platinum-group elements (PGE), Au, Cu and platinum-group minerals (PGM). The major sulphides in the samples studied are chalcopyrite and pyrite. Bornite is less frequent and molybdenite occurs in traces only. PGM (merenskyite, sperrylite and an unidentified Pd-Sb telluride) have been found as inclusions in chalcopyrite.

Pd and Pt are present in concentrations above the analytical detection limit (> 8 ppb) in 70% respectively 30% of the deposits studied. The contents of Os, Ir, Ru and Rh are below detection limits in all samples. The analytical results show that 7 deposits (six of island arc and one of continental margin setting) reveal relatively high Pd contents (130–1900 ppb) which are associated with high Au contents (1–28 ppm). In five of them discrete PGM can be identified in accordance with elevated levels of Pd. Correlations of Au, Pd and Pt point towards a common origin.

Even though the data base is relatively small, a trend is obvious, suggesting that Au-rich island arc porphyry copper deposits might host more Pd and Pt than the continental margin type ones. Other aspects of intrusive rocks, such as geological age, chemical composition and magma type do not seem to influence PGE contents.

Zusammenfassung

Platingruppen-Elemente in porphyrischen Kupfer Lagerstätten: eine Überblicksstudie

Es wurden Sulfid- und Flotationskonzentrate aus 33 Porphyry Kupfer Lagerstätten auf Platingruppenelemente (PGE), Au, Cu und Platingruppenminerale (PGM) untersucht. Die Hauptsulfide im untersuchten Probenmaterial sind Chalkopyrit und Pyrit. Bornit ist

weniger häufig und Molybdänit tritt nur in Spuren auf. An PGM wurden Merenskyit (in den Lagerstätten Elacite, Majdanpek und Skouries), Sperrylith und ein nicht näher identifizierbares Pd-Sb- Tellurid (in der Lagerstätte Mamut) als Einschlüsse in Chalkopyrit festgestellt.

Pd ist in 70% und Pt in 30% der untersuchten Lagerstätten nachweisbar (> 8 ppb), während die Gehalte von Os, Ir, Ru und Rh in allen Proben unterhalb der Nachweisgrenze liegen. In 7 Lagerstätten (davon sechs vom Inselbogen- und eine vom Kontinentalrandtyp) wurden relativ hohe Pd-Konzentrationen (130–1900 ppb) festgestellt, die auch durch hohe Au-Gehalte (1–28 ppm) gekennzeichnet sind. In 5 Lagerstätten sind entsprechend den hohen Pd-Gehalten PGM nachweisbar.

Geochemische Korrelationen zwischen Au, Pd und Pt weisen auf eine gemeinsame Herkunft dieser Metalle hin. Obwohl der Datenbestand noch relativ klein ist, ist ein Trend bereits sichtbar, daß Au-reiche Inselbogenporphyries höhere Pd- und Pt- Gehalte erwarten lassen als der Kontinentalrand-Typ. Andere Aspekte wie geologisches Alter, Magmentyp und Chemismus der betreffenden Intrusivgesteine spielen bei der PGE-Führung offensichtlich keine Rolle.

Introduction

The significance of porphyry copper deposits as potential PGE source has not been investigated so far. PGE contents in porphyry ores and in sulphide concentrates have been reported from a few occurrences only. Pd contents reach up to 500 ppb in ores and up to six ppm in sulphide concentrates (*Mutschler* et al., 1985; *Eliopoulos* and *Economou-Eliopoulos*, 1991; *Tarkian* and *Koopmann*, 1995; *Eliopoulos* et al., 1995; *Thompson* et al., 1999). There are sparse data on background contents of Pd and Pt in intermediate magmatic rocks. Granodiorite-Standard GSP-1 displays 0.5–0.6 ppb Pd and less than 0.5 ppb Pt (*Crocket*, 1981). PGM are reported from three porphyry copper deposits (*Tarkian* et al., 1991; *Petrunov* et al., 1992; *Piestrzynski* et al., 1994; *Tarkian* and *Koopmann*, 1995).

In the present study a large number of porphyry copper deposits have for the first time been investigated for PGE and PGM, with the aim of determining indications for commercial grades of PGE. Possible connections between PGE contents and geological-petrological characteristics of the respective intrusive rocks, such as geotectonic setting, geological age, magma type and chemical composition have been considered.

Samples

The contents of PGE, Au, Cu and PGM have been investigated in 42 samples (19 flotation concentrates and 23 sulphide concentrates separated from ore samples of hypogene mineralisation zones) from 33 porphyry copper deposits in Chile, Peru, Argentina, USA, Canada, Serbia, Greece, Bulgaria, Iran, Russia, Armenia, Uzbekistan, Kazakhstan, Indonesia, Malaysia, Papua New Guinea and the Philippines. Location and names of the deposits are given in Fig. 1. With the exception of the skarn type Sayak ores all others are typical porphyry copper deposits. Determination of modal mineralogy of all samples and of the alteration type of ores is based on microscopic and microprobe investigations (Table 1). Most samples carry high contents of chalcopyrite and pyrite. In larger or smaller
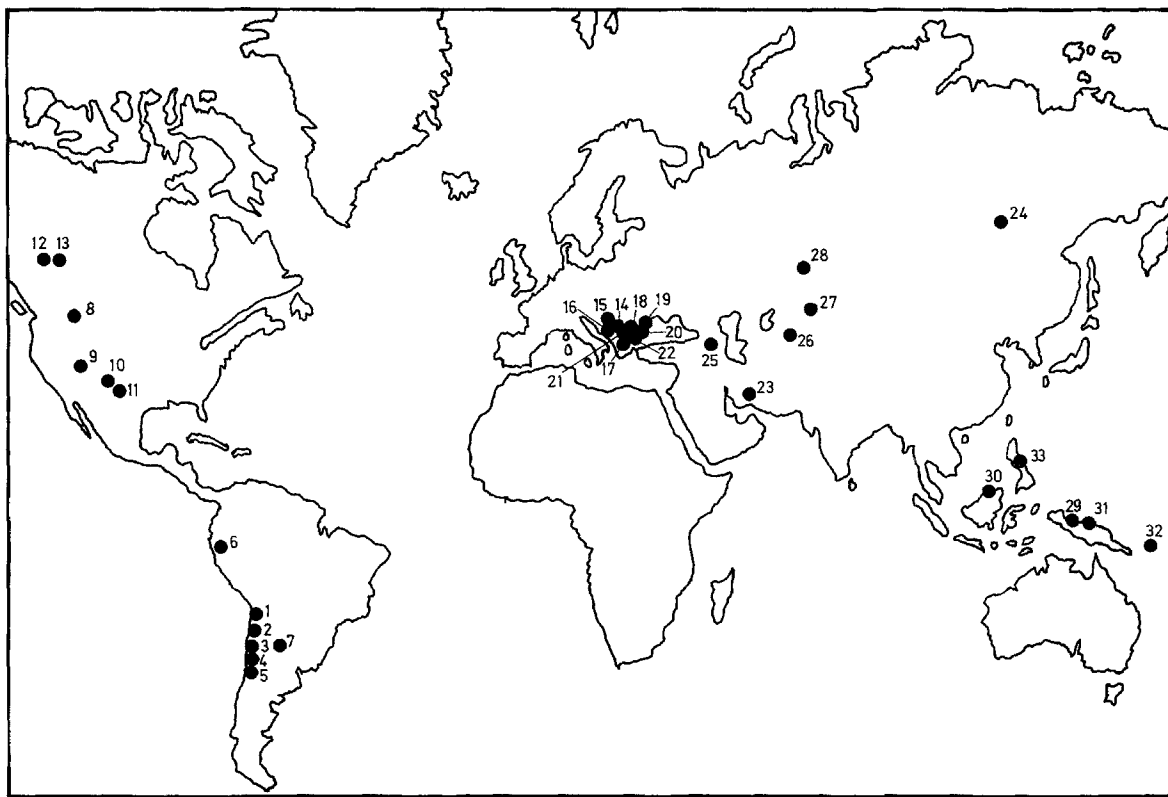
Fig. 1. Localities of the porphyry copper deposits investigated for platinum-group elements. *1* Chuquicamata; *2* La Escondida; *3* El Salvador; *4* Andina; *5* El Teniente (Chile); *6* La Granja (Peru); *7* Alumbrera (Argentina); *8* Butte; *9* Bingham; *10* Morenci; *11* Magma (USA); *12* Bethlehem; *13* Gibraltar (Canada); *14* Bor; *15* Majdanpek *16* Veliki Krivelj (Serbia); *17* Skouries (Greece); *18* Elacite; *19* Medet; *20* Prohorovo; *21* Tzar Assen; *22* Assarel (Bulgaria); *23* Sar Cheshmeh (Iran); *24* Ryabinovoje (Russia); *25* Kadzharan (Armenia); *26* Almalyk (Uzbekistan); *27* Sayak; *28* Bozshakol (Kasakhstan); *29* Grasberg (Indonesia); *30* Mamut (Malaysia); *31* Ok Tedi; *32* Panguna (Papua New Guinea); *33* Biga (Philippines)

amounts, bornite, magnetite, hematite and occasionally supergene chalcocite and covellite also occur. Molybdenite and other minerals occur in traces only.

Methods

Analytical work was performed on flotation concentrates supplied by mining companies and on sulphide concentrates separated from ore samples. Fine intergrowths precluded the preparation of pure sulphide concentrates in some disseminated ores. In these cases, the volume percentage of silicates was estimated microscopically and is summarized in Table 2.

The concentrates were analysed for PGE and Au by Genalysis Laboratories, Maddington, W. Australia, using inductively coupled plasma mass spectrometry (ICP-MS) after preconcentration by Nickel Fire Assay. The amount analysed was 12.5 g for all samples. Detection limits are 8 ppb for Os, Ir, Ru, Pt and Pd, 4 ppb for

Table 1. *Description of samples analysed for Cu, PGE and Au*

	Deposit/sample	Ore type	Ore minerals	Alteration type/silicates
CHILE:	Chuquicamata	F.C.	cp, py (M), bo(Mi), mt, hm, Cu (Tr)	—
	La Escondida	F.C.	cp. py (M), cc, cv (Mi)	—
	El Salvador	F.C.	cp, py (M), bo, cc, cv (Mi), mt(Tr)	—
	Andina	F.C.	cp(M), py(Mi), bo, mt, hm, cc, cv (Tr)	—
	El Teniente	F.C.	cp, py (M), bo, cc, cv (Mi), mb(Tr)	—
PERU:	La Granja	F.C.	py, cv, cc(M), cp, bo, en(Mi), mb, mt(Tr)	—
ARGENTINA:	Alumbrera	F.C.	cp(M), py, cv, cc(Mi), bo, po, mb, mt, hm, Au(Tr)	Silicification-argillic/qz-kaol-chl
	Butte/1	veinlet	bo(M), cp, py, mt (Mi)	Silicification-argillic/qz-kaol-chl
	Butte/2	veinlet	py(M), cp, bo, mt, cc (Mi)	Propylitic-sericitic/chl-ep-ser-qz
	Bingham	Disseminated	cp, bo, py (M), mb, mt, hm (Mi)	Silicification-argillic/qz-kaol
	Morenci	Diss./veinlet	py(M), hm(Mi), mt(Tr)	Silicification-argillic/qz-kaol
	Magma	veinlet	bo(M), cp, py (Mi), gn, mt (Tr)	Silicification-argillic/qz-kaol
CANADA:	Bethlehem	veinlet	bo(M), cp, mt (Mi), hm(Tr)	Silicification/qz-ser
	Gibraltar	veinlet	py(M), cp, mt (Mi), bo(Tr)	Silicification/qz-ser
SERBIA:	Bor	Diss.	py, cv, cc(M), cp, en(Mi), bo, mt, hm(Tr)	
	Majdanpek/1	F.C.	cp(M), py(Mi), po, mb, sl, mt, el, Au, hs, me (Tr)	Silicification-argillic/qz-chl-kaol
	Majdanpek/2	Diss/veinlet	cp(M), py, mt, hm (Mi), bo, mb, po, el, Au, hs, me (Tr)	
	Veliki Krivelj	F.C.	cp. py(M), bo, po, mt, cv(Tr)	—
GREECE:	Skouries	Diss.	cp(M), bo, py, mt (Mi), Au, me (Tr)	K-silicate-propylitic/bi-ser-chl-ep-qz
BULGARIA:	Elacite/1	F.C.	cp(M), py(Mi), bo, mb, mt, clt, In, hs, Au, me (Tr)	
	Elacite/2	Diss.	cp(M), py, mt (Mi), bo, fa, clt, Au, me (Tr)	K-silicate/K-feldspar-bi-chl-qz
	Medet	Diss.	cp, py(M), mt, hm(Mi), mb, sl, rt(Tr)	Sericitic/ser-qz-chl
	Prohorovo	veinlet	cp(M), py, mt, rt (Mi), mb, sl, po, cb, In, el (Tr)	Sericitic-propylitic/chl-ser-qz
	Tzar Assen	Diss.	cp(M), py(Mi), mb, po, mt, rt, cb (Tr)	Sericitic-argillitic/ser-kaol–montm-qz
	Assarel	Diss.	cp. py(M), cv, cc(Mi), bo, po, mb, mt, hm(Tr)	Sericitic-propylitic/ser-chl-qz
IRAN:	Sar Cheshmeh/1	F.C.	cp, py (M), fa, cv (Tr)	—
	Sar Cheshmeh/2	F.C.	cp, py (M), cc, cv (Mi), bo, mt, po (Tr)	—
RUSSIA:	Ryabinovoje	U	bo(M), cc, cv (Mi), cp, py, gn, car, hs (Tr)	U
ARMENIA:	Kadzharan	U	cp, bo, py (M), mb, sl, fa (Mi), wi, gd, car, stue, cbi, tet, Au (Tr)	U
UZBEKISTAN:	Almalyk/1	veinlet	py(M), cp, rt (Mi), mt, hm, po (Tr)	Propylitic-sericitic/chl-ser-qz-cal
	Almalyk/2	veinlet	cp(M), py, mt, hm, sl (Mi), mb, el (Tr)	Propylitic-sericitic/chl-ser-qz-cal
KASAKHSTAN:	Sayak/1	veinlet	asp, mt (M), cp, py, mc, po (Mi), fa, can, bism, Bi, gbsm, ing, Au (Tr)	U
	Sayak/2	veinlet	cp(M), py, po, mc, asp (Mi), mt, fa, Au (Tr)	U
	Bozshakol	veinlet	cp(M), mb, py (Mi), gn, sl (Tr)	Propylitic-sericitic/cal-chl-ser-qz
INDONESIA:	Grasberg	F.C.	cp(M), py, bo, cv, cc(Mi), mb, mt, hm (Tr)	—
MALAYSIA:	Mamut/1	F.C.	cp(M), py, po (Mi), mb, sl, fa, mt, cb, cv, el, Au, sp (Tr)	—
	Mamut/2	F.C.	cp(M), py(Mi), po, mb, mt, cv, el Au, sp (Tr)	—
PNG:	Ok Tedi/1	F.C.	cp(M), py, bo, cc, cv (Mi), mb, po, mc, Cu, Au (Tr)	—
	Ok Tedi/2	F.C.	cp(M), py, cc (Mi), bo, mb, Cu, Au (Tr)	—
	Panguna/1	veinlet	cp(M), mb, sl, mt, tet, py, hs (Tr)	Propylitic-sericitic/chl-ser-ep-qz
	Panguna/2	veinlet	cp, py (M), mb(Mi), bo, cc (Tr)	Propylitic-sericitic/chl-ser-ep-qz
PHILIPPINES:	Biga	Diss.	py(M), cp, bo, mt (Mi), mb, fa, Au, me (Tr)	Propylitic/chl-ep-ser-cal

F.C. Flotation concentrate; *M* major; *Mi* minor; *Tr* trace; *U* unknown. *asp* arsenopyrite; *Au* native gold; *Bi* native bismuth; *bi* biotite; *bism* bismuthinite; *bo* bornite; *cal* calcite; *can* cannizzarite; *car* carrolite; *cb* cubanite; *cbi* cupro-bismutite; *cc* chalcocite; *chl* chlorite; *cp* chalcopyrite; *clt* clausthalite; *Cu* native copper; *cv* covellite; *el* electrum; *en* enargite; *ep* epidote; *fa* tetrahedrite-tennantite; *gbsm* galenobismutite; *gd* gladite; *gn* galena; *hm* hematite; *hs* hessite; *ing* ingodite; *kaol* kaolinite; *ln* linneite; *mb* molybdenite; *mc* marcasite; *me* merenskyite; *montm* montmorillonite; *mt* magnetite; *po* pyrrhotite; *py* pyrite; *qz* quartz; *rt* rutile; *ser* sericite; *sl* sphalerite; *sp* sperrylite; *stue* stuetzite; *tet* tetradymite; *wi* wittichenite

Table 2. *Au, Pd, Pt and Cu contents in concentrates of porphyry copper deposits*

Deposit/sample	Geotectonic setting	Au (ppb)	Pd (ppb)	Pt (ppb)	Cu (%)	Au/Pd	Pd/Pt	Silicate content (vol %)
CHILE								
Chuquicamata*	C	470	36	n.d.	28.3	13		–
La Escondida*	C	2050	44	8	33.0	46	5.5	–
El Salvador*	C	1250	16	8	28.3	78	2.0	–
Andina*	C	220	n.d.	n.d.	32.9			–
El Teniente*	C	300	32	8	32.1	9	4.0	–
PERU								
La Granja*	C	760	10	n.d.	n.a.	76		–
ARGENTINA								
Alumbrera*	C	31000	35	8	29.5	885	4.4	–
USA								
Butte/1[+]	C	180	n.d.	n.d.	56.1			–
Butte/2[+]		310	n.d.	n.d.	20.4			–
Bingham[+]	C	1350	8	n.d.	0.7	168		40
Morenci[+]	C	360	n.d.	n.d.	4.1			–
Magma[+]	C	1350	n.d.	n.d.	46.9			–
CANADA								
Bethlehem[+]	C	210	n.d.	n.d.	49.6			–
Gibraltar[+]	C	280	n.d.	n.d.	7.1			–
SERBIA								
Bor*	IA	1700	40	19	n.a.	42	4.4	–
Majdanpek/1*	IA	2250	130	16	30.1	17	8.1	–
Majdanpek/2[+]		7000	240	24	22.4	29	10.0	25
Veliki Krivelj*	IA	2250	70	16	n.a.	32	4.4	–
GREECE								
Skouries[+]	C	7300	160	8	2.4	45	20.0	80
BULGARIA								
Elacite/1*	IA	7600	760	170	19.0	10	4.5	–
Elacite/2[+]		27000	1900	72	25.9	14	26.4	20
Medet[+]	IA	5600	160	8	14.9	35	20.0	40
Prohorovo[+]	IA	200	n.d.	n.d.	4.3			25
Tzar Assen[+]	IA	130	8	n.d.	15.9	16		20
Assarel*	IA	4800	54	14	27.9	88	3.8	–
IRAN								
Sar Cheshmeh/1*		360	8	n.d.	21.8	45		–
Sar Cheshmeh/2*	C	840	24	n.d.	32.9	35		–
RUSSIA								
Ryabinovoje[+]	U	720	32	88	58.8	22	0.4	–
ARMENIA								
Kadzharan[+]	C	3400	24	84	31.7	141	0.3	–
UZBEKISTAN								
Almalyk/1[+]		505	n.d.	n.d.	19.1			–
Almalyk/2[+]	U	9800	20	n.d.	31.3	490		–
KASAKHSTAN								
Sayak/1 (sk)[+]		20500	n.d.	n.d.	1.4			–
Sayak/2 (sk)[+]	C	25000	n.d.	n.d.	28.4			–

(continued)

Table 2 *(continued)*

Deposit/sample	Geotectonic setting	Au (ppb)	Pd (ppb)	Pt (ppb)	Cu (%)	Au/Pd (%)	Pd/Pt	Silicate content (vol %)
Bozshakol[+]	IA	1080	245	n.d.	13.9	4		–
INDONESIA								
Grasberg*	IA	18000	58	15	23.8	310	3.9	–
MALAYSIA								
Mamut/1*		17000	1600	490	20.7	10	3.3	–
Mamut/2*	IA	13500	1180	450	20.0	11	2.6	–
PAPUA NEW GUINEA								
Ok Tedi/1*		28000	980	24	37.3	28	40.8	–
Ok Tedi/2*	IA	16200	650	n.d.	26.5	25		–
Panguna/1[+]		520	40	8	35.2	13	5.0	–
Panguna/2[+]	IA	1550	52	n.d.	7.7	30		10
PHILIPPINES								
Biga[+]	IA	2350	56	8	n.a.	42	7.0	40

C continental margin; *IA* island arc; *U* unknown. *: Flotation concentrates; [+] Sulphide concentrates. *nd* not detected; *n.a.* not analysed; *(sk)* skarn type deposit

Rh, and 10 ppb for Au. Analytical precision is ±15, ±10 and $\pm5\%$ relative for Au, Pd and Pt, respectively. Copper contents were determined using XRF at the Federal Institute for Geosciences and Natural Resources, Hannover.

Analyses of PGM were carried out by a Cameca Camebax Microbeam wavelength-dispersive electron microprobe at the Department of Mineralogy and Petrology, University of Hamburg. Operating conditions were 20 kV and 22 nA. The following X-ray lines were used: $PdL\alpha$, $PtL\alpha$, $NiK\alpha$, $FeK\alpha$, $CuK\alpha$, $AgL\beta$, $TeL\alpha$, $SbL\alpha$, $BiM\alpha$. Pure elements (for Pd, Pt, Ni, Ag, Bi), covellite (for Cu), stibnite for Sb, pyrite (for Fe), and synthetic PdBiTe (for Te) were used as standards. Corrections were applied using the "PAP" on-line program (*Pouchou* and *Pichoir*, 1991).

PGE contents

PGE and Au contents of the samples investigated are summarized in Table 2. All samples assayed Au above the detection limit. Pd concentration is above the detection limit (8 ppb) in 23 and Pt in 10 deposits. The contents of Os, Ir, Ru and Rh are below detection limits in all samples. Pd- and Pt-contents of up to 15 ppb in concentrate can be considered as normal. Particularly high Pd contents have been analysed in samples from Elacite, Mamut and Ok Tedi with 760–1900, 1180–1600 and 650–980 ppb Pd, which also carry high Au with 27, 17 and 28 ppm Au, respectively. Pd values for Majdanpek (130–240 ppb), Skouries (160 ppb), Medet (160 ppb) and Bozshakol (245 ppb) can be considered exceptionally high. Silicate contents in samples from Skouries (80 Vol.%) and Medet (40 Vol.%) are high, and pure sulphide concentrates have thus not been obtained due to the fine- grained intergrowth with silicates. PGE contents are linked exclusively to sulphides;
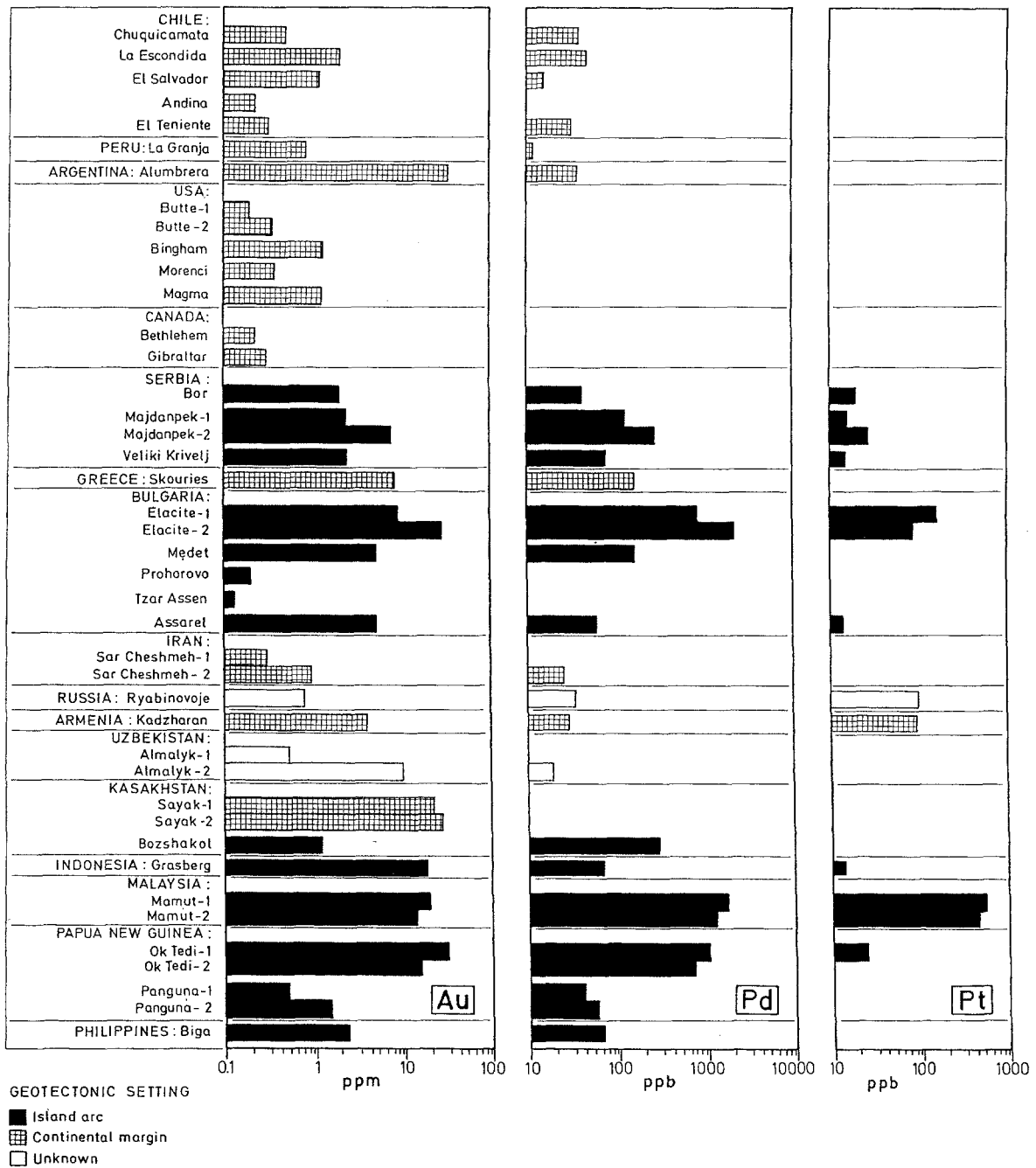
Fig. 2. Graphic illustration of gold, palladium and platinum contents in concentrates and geotectonic setting of the porphyry copper deposits

accordingly Pd contents is pure sulphide fractions of these occurrences may be higher by a factor of 2–5.

All Au, Pd and Pt-contents which are over 10 ppb are graphically presented in Fig. 2. 17 of the investigated deposits are continental margin type porphyries, 14 are island arc type. The geotectonic position of two deposits is not known. It is
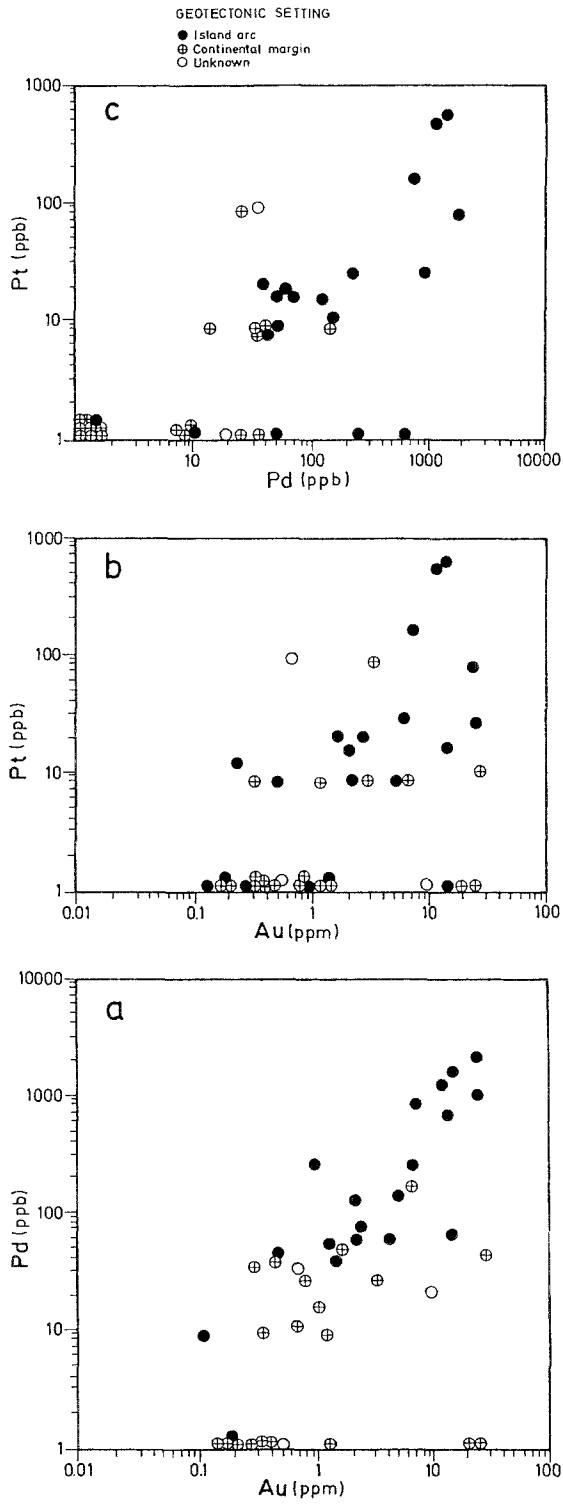
Fig. 3. Plots of Pd versus Au, Pt versus Au (**a, b**) and Pd versus Pt (**c**)
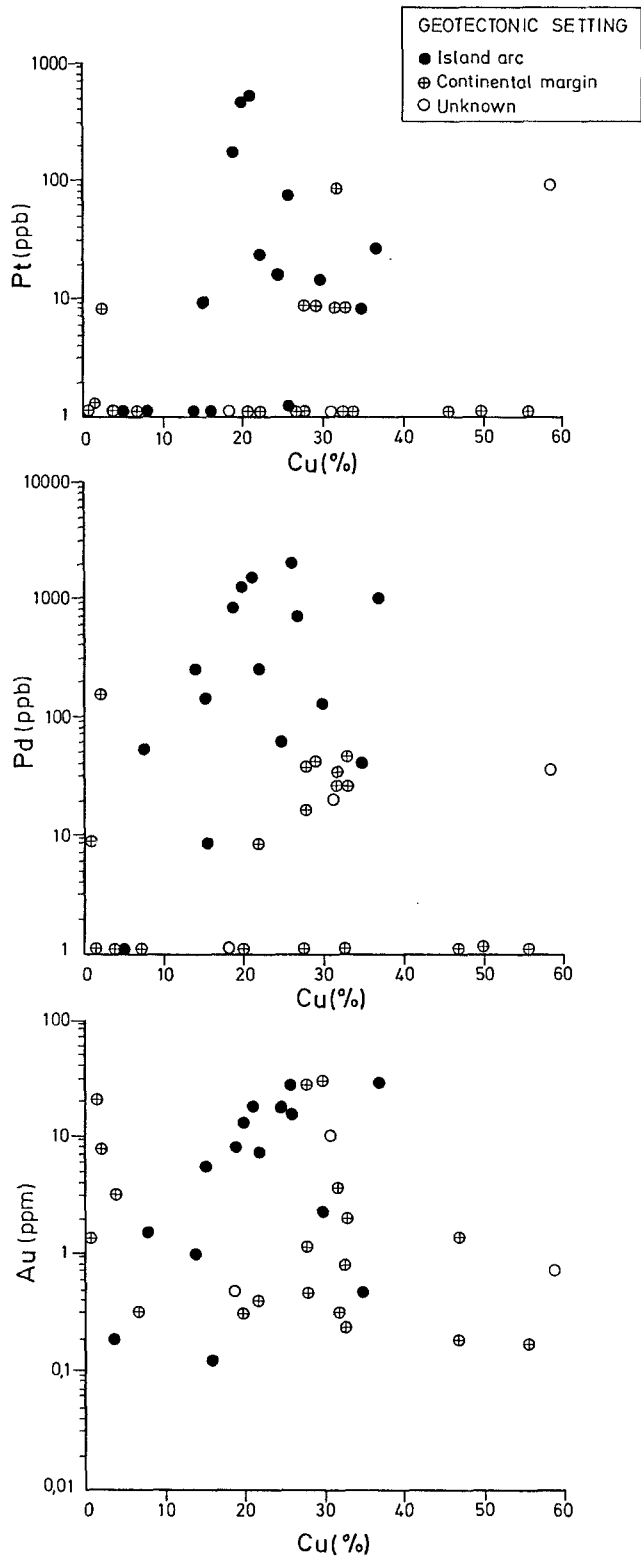
Fig. 4. Plots of Au, Pd and Pt versus Cu

remarkable that out of seven occurrences with high Pd contents, six are island are type, (Mamut, Ok Tedi, Majdanpek, Elacite, Medet, Bozshakol) and only one (Skouries) is of continental margin type. Taking a value of 45 ppb Pd as the cut-off between the groups, the Pd contents are relatively high in 11 out of 14 island arc, but only in one out 17 continental margin type deposits. In comparison the Pt values are mostly low (Table 2).

There is a positive correlation between Pd and Au and this is particularly pronounced in island arc porphyries (Fig. 3a). The Au/Pd ratios tend to be high (Table 2); the variation of ratios in island arc porphyries is smaller than in the continental margin porphyries (Table 2). Pt and Au, as well as Pt and Pd reveal tentative correlation (Fig. 3b, 3c). On the whole neither the Pt and Pd nor Au correlate with Cu (Fig. 4). Weak correlations of Cu with Au and Pd are obvious in island arc type deposits only. However, the geochemical relationship between Pd, Pt, Au and Cu should be investigated in different mineralisation zones within one porphyry copper deposit.

Table 3. *Microprobe analyses of merenskyite (1–9) and sperrylite (10)*

No.	1	2	3	4	5	6	7	8	9	10*
Pd	27.60	28.44	28.28	17.66	17.54	17.38	15.15	22.67	22.19	–
Pt	1.10	0.03	0.04	13.73	13.81	13.47	16.14	3.83	4.49	55.19
Rh	–	–	–	–	–	–	–	–	–	1.26
Ni	–	–	–	–	–	–	1.41	2.20	2.23	–
Fe	–	–	–	–	–	–	0.28	0.67	0.71	–
Cu	–	–	–	1.82	1.59	1.89	0.57	1.07	1.15	–
Ag	0.02	0.01	–	1.40	1.43	1.57	1.03	1.44	1.41	–
Te	68.29	69.63	68.92	60.77	60.86	60.47	64.50	68.88	67.49	–
Sb	–	–	–	0.37	0.33	0.37	0.36	0.42	0.42	–
Bi	2.86	0.27	0.19	3.33	3.16	3.23	0.66	0.30	1.26	–
As	–	–	–	–	–	–	–	–	–	43.55
Total	99.87	98.38	97.43	99.08	98.72	99.38	100.10	101.48	101.35	100.00

Atomic proportions ($\sum$ atoms = 3)

	1	2	3	4	5	6	7	8	9	10
Pd	0.96	0.98	0.99	0.64	0.64	0.64	0.55	0.74	0.74	–
Pt	0.02	–	–	0.27	0.28	0.27	0.32	0.07	0.08	0.97
Rh	–	–	–	–	–	–	–	–	–	0.04
Ni	–	–	–	–	–	–	0.09	0.13	0.13	–
Fe	–	–	–	–	–	–	0.02	0.04	0.05	–
Cu	–	–	–	0.11	0.10	0.11	0.04	0.05	0.06	–
Ag	–	–	–	0.05	0.05	0.06	0.03	0.05	0.04	–
$\sum$ Me	0.98	0.98	0.99	1.07	1.07	1.08	1.05	1.08	1.10	1.01
Te	1.97	2.01	2.01	1.86	1.86	1.85	1.93	1.89	1.87	–
Sb	–	–	–	0.01	0.01	0.01	0.01	0.02	0.01	–
Bi	0.05	0.01	–	0.06	0.06	0.06	0.01	0.01	0.02	–
As	–	–	–	–	–	–	–	–	–	1.99
$\sum$	2.02	2.02	2.01	1.93	1.93	1.92	1.95	1.92	1.90	1.99

1–3 Majdanpek; *4–9* Elacite; *10* Mamut. *:EDS analysis; –: not detected

Platinum group minerals

PGM have been identified as inclusions in chalcopyrite in the Elacite (16 grains), Majdanpek (3 grains), Mamut (2 grains), Biga and Skouries (1 grain each). The size of these inclusions varies from 2 to 50 μm. These PGM are mostly merenskyite or solid solutions of merenskyite-moncheite. The Pt-contents of merenskyite from Elacite are significantly higher than those from Majdanpek and Skouries (Table 3 and Fig. 5). In samples from Elacite merenskyite frequently shows columnar to acicular crystals of 50–100 micrometer in lengths; the shape and distribution suggest exsolution from Cu-Fe sulphides (Fig. 6a–c). In one sample from the Mamut deposit sperrylite and an unidentified Pd-Sb telluride occur as inclusions in chalcopyrite (Fig. 7). Because of the extremely small grain size this telluride has been analysed semiquantitatively only. The composition probably corresponds to Pd(Sb,Te)$_2$. Sperrylite carries 1.3 wt.% Rh (Table 3).

O   Skouries, Greece (Tarkian et al. 1991)

□   Santo Tomas, Philippines (Tarkian & Koopmann, 1995)

●   Elacite, Bulgaria ⎤
                        ⎬ this study
▲   Majdanpek, Serbia ⎦
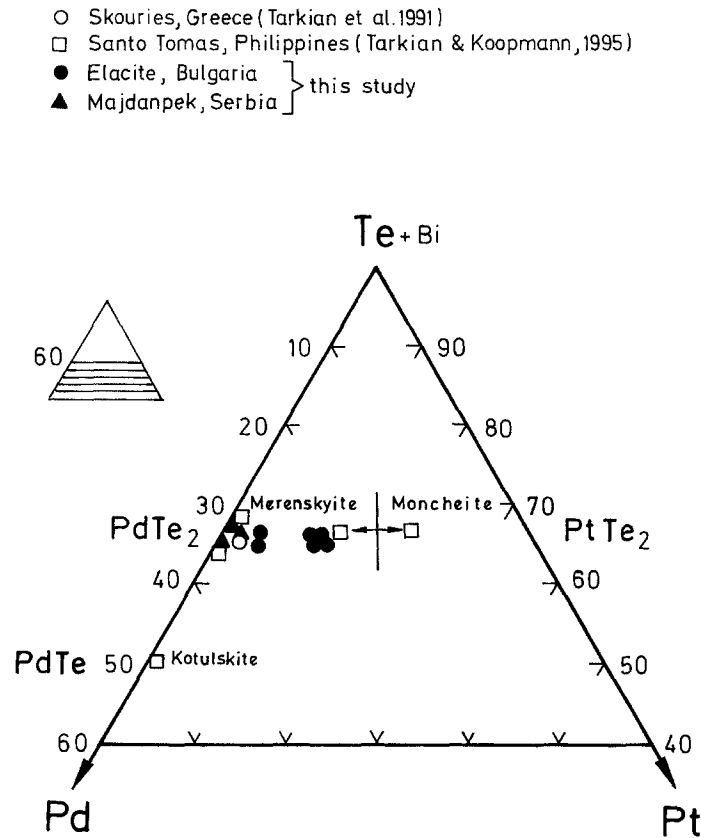
Fig. 5. Compositional variations of merenskyite from Elacite and Majdanpek in a Pd-Pt-(Te+Bi) ternary diagram
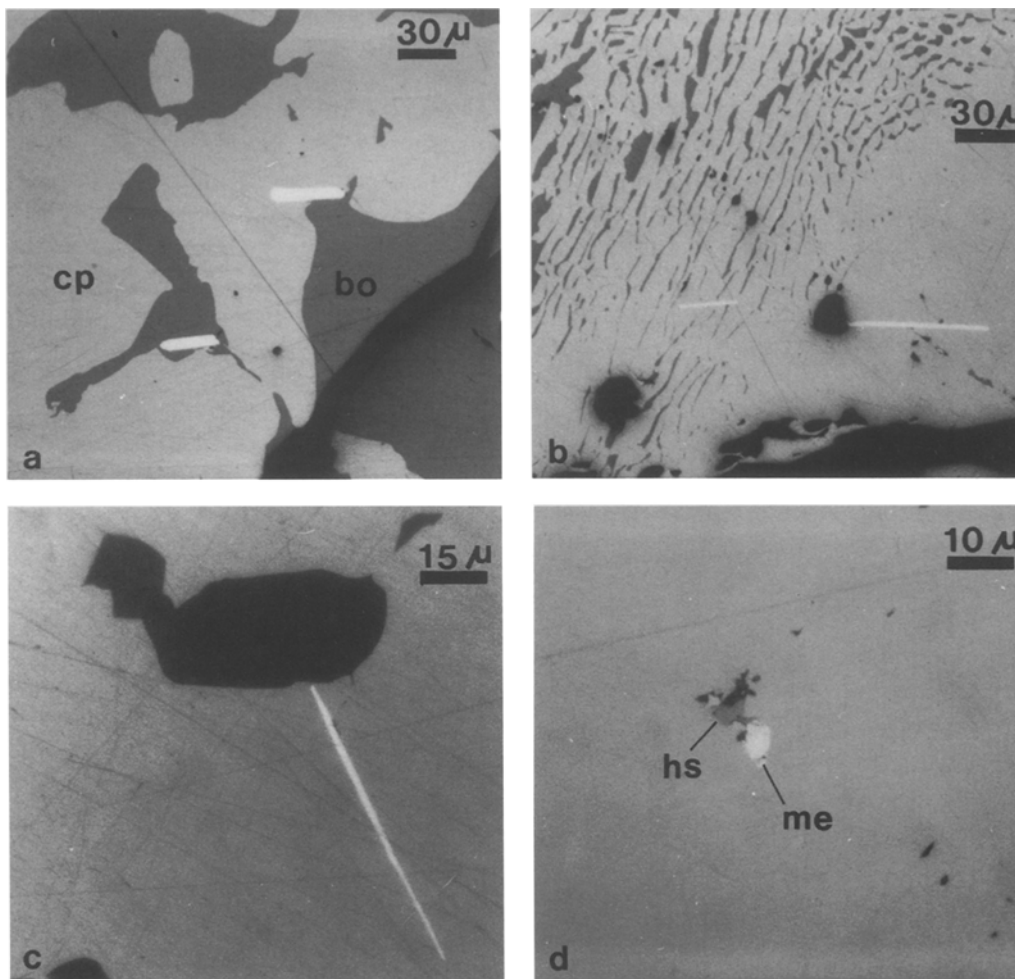
Fig. 6. **a–c** Elongate inclusions of merenskyite in chalcopyrite (cp) and bornite (bo), Elacite. **d** Inclusions of merenskyite (me) intergrown with hessite (hs) in chalcopyrite; Majdanpek

Gold and silver

According to the analytically determined high gold contents, about one third of the occurrences investigated (including the Mamut, Ok Tedi, Majdanpek, Elacite and Skouries deposits) carry native gold or electrum (Table 1). They mostly occur as rounded, single inclusions of maximum 40 μm diameter, mostly in chalcopyrite and occasionally, also in bornite. Rarely are they intergrown with PGM (Fig. 7). Hessite (Ag_2Te) is comparatively widespread and occurs in samples from Majdanpek, Elacite, Ryabinovoje, Kadzharan, Panguna occasionally in the intergrowth with merenskyite (Fig. 6d), while petzite (Ag_3AuTe_2) and stuetzite ($Ag_{5-x}Te_3$) have been identified in one occurrence each (Sayak and Kadzharan, respectively).
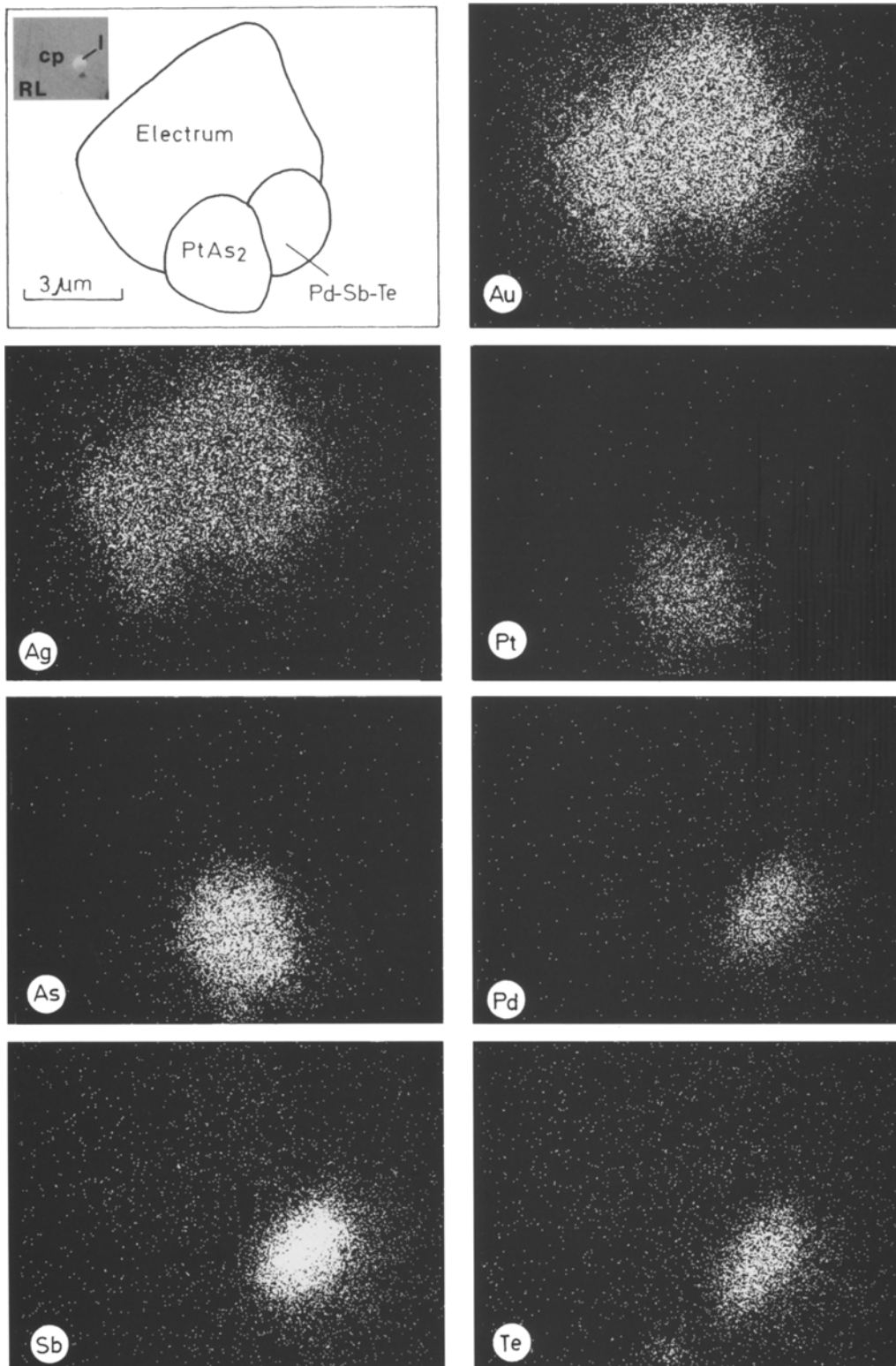
Fig. 7. Complex intergrowth of electrum, sperrylite and an unidentified Pd-Sb telluride as inclusions in chalcopyrite; Mamut. Single element scans for Au, Ag, Pt, As, Pd, Sb and Te

Table 4. *Characteristics of the deposits with elevated levels of PGE*

Deposit	Geotectonic setting	Age	Host instrusive rock	Magma type	Au (ppm)	Pd (ppb)	Pt (ppb)	Au/Pd
Mamut/Malaysia*	IA	Upper Miocene	adamellite porphyry	calc-alkaline	13.5–17.0	1180–1600	450–490	10–11
Ok Tedi/PNG*	IA	Plio-to Pleistocene	latite porphyry	calc-alkaline	16.2–28.0	650–980	24	25–28
Majdanpek/Serbia*	IA	Upper Cretaceous	diorite-granodiorite	calc-alkaline	2.2–7.0	130–240	16–24	17–29
Elacite/Bulgaria*	IA	Upper Cretaceous	syeno-diorite	calc-alkaline to subalkaline	7.6–27.0	760–1900	72–170	10–14
Medet/Bulgaria⁺	IA	Upper Cretaceous	granodiorite porphyry	calc-alkaline	5.6 (9.3)ᶜ	160 (270)ᶜ	8 (15)ᶜ	35
Skouries/Greece⁺	C	Miocene	syenite-diorite porphyry	sub-alkaline	7.3 (36)ᶜ	160 (800)ᶜ	8 (40)ᶜ	45
Bozshakol/Kasakhst.*	IA	Cambrium	tonalite	calc-alkaline	1.1	245	n.d.	4

IA island arc; *C* continental margin; *n.d.* not detected; * flotation- and sulphide concentrate; ⁺ore samples; ()ᶜ calculated to 100% sulphide

Deposits with elevated PGE levels

In the following we discuss relevant characteristics of those deposits which carry exceptionally high PGE contents (Table 4).

Mamut, Malaysia

The deposit is situated at the northern end of Borneo and represents one of many mineralised areas along a NW-SE striking tectonic zone in Sabah. The Cu mineralisation is linked to an isolated, K-rich monzonitic to granodioritic porphyry stock of Upper Miocene age; it exhibits calc- alkaline characteristics and island arc affinity. About 40% of the production, however, are from a serpentinite body related to an ultramafic intrusion which predates the monzonite. Country rocks are Paleocene-Eocene siltstones and pyroclastics. The ore mineral association includes chalcopyrite accompanied by pyrite, pyrrhotite, magnetite, hematite and small amounts of molybdenite. The instrusive stock reveals distinct potassic alteration, with biotite, orthoclase and quartz, and strong silicification (*Kosaka* and *Wakita*, 1978). Fluid inclusions have salinities of 35–55 wt.% NaCl equiv. Homogenisation temperatures are between 300 and 450°C. (*Nagano* et al., 1977). This deposit is part of a group of Au-rich porphyry deposits (*Sillitoe*, 1979). This is confirmed by Au contents in flotation concentrates, which also carry high Pd and Pt-contents (Table 4). Ore reserves of the deposit are 179 million tons with 0.476% Cu and 0.66 g/t Au (*Kosaka* and *Wakita*, 1978).

Ok Tedi (Fubilan), Papua New Guinea

Plate tectonic models for the evolution of central and western New Guinea involve a collision between the Australian continental plate and an island arc located on the southern margin of the Pacific plate (*Dewey* and *Bird*, 1970; *Bamford*, 1972). Although the subduction history of Papua New Guinea is not as clear as that of the neighbouring islands, the Ok Tedi porphyry copper deposit appears to be related to a young southward-directed subduction along the New Guinea trench (*Solomon*, 1990). The deposit is very likely of island arc type. Copper mineralisation at Ok Tedi is associated with a latite porphyry stock of calc-alkaline character of Plio-Pleistocene age (1.2 Ma); (*Page* and *McDougall*, 1972). The country rocks are Upper Cretaceous to Miocene siltstones, limestones and sandstones. Copper mineralisation consists of chalcopyrite, with subordinate bornite, chalcocite, covellite, pyrite, marcasite and little molybdenite and native copper. It forms part of an intensive potassic alteration zone, characterised by biotite, K-feldspar and quartz. Magnetite is absent in the porphyry body, it does, however, occur in peripheral skarns (*Bamford*, 1972). Ore reserves have originally been estimated at 275 million tons with average copper contents of 0.75% and gold contents of 0.5 g/t (*Gilmour*, 1982). Supergene zones carry Au contents of up to 3 g/t and in skarns Au contents of 1.8 g/t are widespread (*Titley*, 1978). Flotation concentrates investigated within the framework of this study reveal Au as well as high Pd contents (Table 4). PGM have not been identified. Pd is probably located in the lattice of native Au or in chalcopyrite; these contents are, however, below the detection limit of the

microprobe (< 500 ppm). *Rubin* and *Kyle* (1997) report Pd-contents of up to 3500 ppm in native gold from the Grasberg porphyry Cu-Au deposit, Indonesia.

Majdanpek, Serbia

Cu-mineralisation is linked to a calc-alkaline volcano-intrusive complex of Upper Cretaceous age, which shows volcanic are affinity similar to the other magmatic rocks in eastern Serbia (*Karamata* et al., 1997). The country rocks of the mineralised dioritic-granodioritic porphyry stocks are Cretaceous-Paleogene andesites as well as Paleozic gneisses and phyllites. The main ore mineral is chalcopyrite, with subordinate pyrite, magnetite and hematite. Bornite and molybdenite occur in traces only. The intrusive rock as well as the associated volcanic rocks show potassic alteration with K-feldspar, biotite and quartz. In pyrite-rich zones there is argillic alteration with kaolinite and quartz (*Spasov*, 1965). According to *Jankovic* (1972) chalcopyrite and quartz have been deposited at temperatures of 240 to 500 °C. Ore reserves at Majdanpek are not known. Average copper contents are 0.8%. Au contents of the mineralised rocks vary from 0.1 to 0.3 g/t (*Vakanjak*, 1993). Pd-contents of the concentrates investigated are remarkably high (Table 4), but a sulphide concentrate separated from an ore sample of the silicification-argillic zone displays higher values than the flotation concentrate (Table 1 and 2, samples Majdanpek/2 and Majdanpek/1).

Elacite, Bulgaria

Elacite is one of six porphyry copper deposits in the Srednogorie volcano-intrusive zone, of which another four deposits (Medet, Prohovoro, Tzar Assen, Assarel) have been investigated for PGE-contents (Fig. 8). The magmatic rocks of the Srednogorie zone developed in an Upper Cretaceous island arc system (*Dabovski* et al., 1991)

Mineralisation at Elacite is linked to a syenodiorite porphyry stock of calc-alkaline to subalkaline character, which was emplaced into Cambrian greenschists during the Upper Cretaceous (*Bogdanov*, 1986). The intrusive stock shows typical potassic alteration with K-feldspar and biotite. Copper mineralisation comprises chalcopyrite with more or less bornite, pyrite, magnetite and traces of molybdenite. The formation temperature of the quartz-chalcopyrite association is 320–350 °C (*Bogdanov*, 1986). Ore reserves of the deposit are 185 million tons with 0.45% Cu and 0.3 g/t Au. Concentrates investigated in this study revealed high Au, Pd and Pt contents (Table 4). Au and Pd contents in a sulphide concentrate separated from an ore sample of the K-silicate zone are significantly higher than in the flotation concentrate (Table 1 and 2, samples Elacite/2 and Elacite/1).

Medet, Bulgaria

This deposit occurs in the northern part of the Panagyurishte ore district (Fig. 8). Copper mineralisation is associated with a calc-alkaline granodiorite porphyry stock of Upper Cretaceous age (75–77 Ma), which was emplaced into Precambrian gneisses and into Paleozoic granites. Mineralisation consists mainly of chalcopyrite,
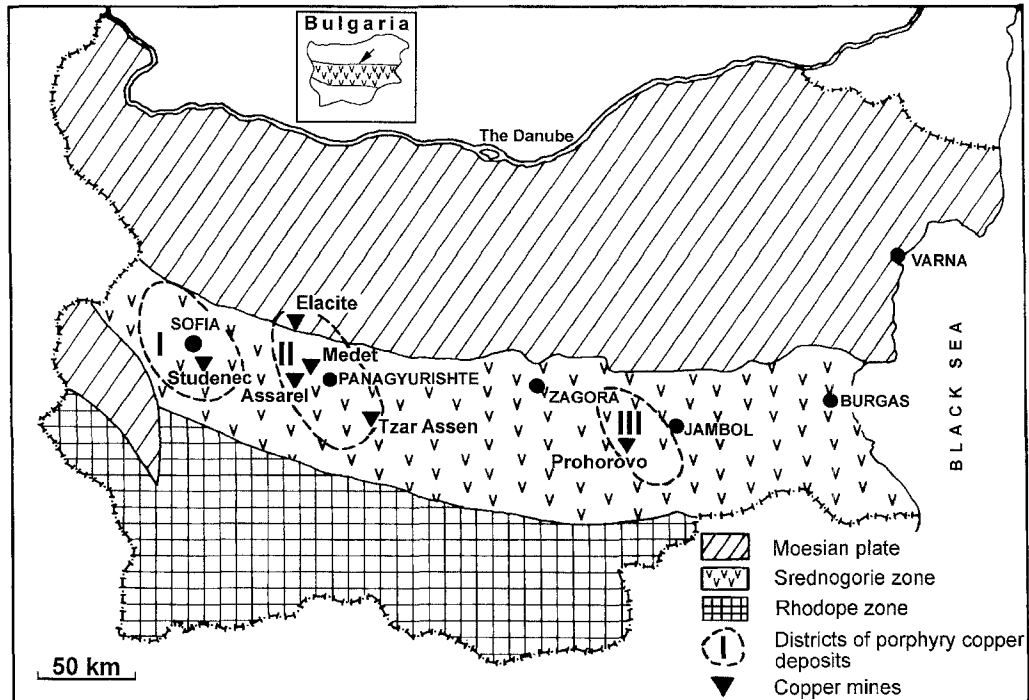
Fig. 8. Sketch map showing location of the porphyry copper deposits Studenenec, Elacite, Medet, Assarel, Tzar Assen and Prohorovo in the Srednogorie zone (simplified after *Bogdanov*, 1986)

with subordinate pyrite, and traces of molybdenite. Hydrothermal alteration is mainly of potassic and propylitic type (*Angelkov*, 1974; *Bogdanov*, 1982, 1986). Investigation of fluid inclusions in quartz from the potassic zone (with K-feldspar, biotite, magnetite and hematite) reveal homogenisation temperatures of 370–400 °C and salinities of 12 wt.% NaCl equiv.

Mining activities at the Medet deposit have recently been discontinued. The sulphide concentrate analysed for PGE has been separated from an ore sample of the silicification zone. Although it is heavily contaminated with silicate minerals, the Pd content is high (Table 2). In an ore sample from Medet containing 2.15 wt. % Cu *Eliopoulos* et al. (1995) determined a Pd content of 50 ppb. In contrast samples from other Bulgarian porphyry copper deposits (Assarel, Tzar Assen and Prohorovo), which have also been derived from silicification zones, are Pd-poor (Tables 1 and 2).

Skouries, Greece

This deposit is situated in the Chalkidiki Peninsula, Northern Greece. It is a porphyry stock of syenitic-dioritic composition with subalkaline character. It was emplaced into metamorphic rocks (gneisses, micaschists, amphilbolites) of the Servomacedonian Massif during the Miocene and it has an age of 18 Ma (*Kockel* et al., 1975; *Kalogeropoulos*, 1986; *Eliopoulos* and *Economou-Eliopoulos*, 1991).

The geotectonic setting of the subvolcanic intrusions which cut through the crystalline basement in Chalkidiki along NW-SE striking deep faults of which the Skouries intrusion forms a part, is continental (*Veranis*, 1994). The copper mineralisation is largely of veinlet type, consisting of chalcopyrite, bornite, pyrite and magnetite. Dominant hydrothermal alteration is potassic (characterised by K-feldspar and biotite) and silicific. The deposit is presently being explored and known ore reserves are 26 million tons with 0.78% Cu and 1.4 g/t Au (*Kalogeropoulos*, 1986).

Pd contents in the range of 2–480 ppb have been reported by *Eliopoulos* and *Economou-Eliopoulos* (1991) from ore samples (Cu: 0.25–4 wt. %) of the Skouries deposit. The sample investigated in the present study carries 2.4 wt. % Cu and has been derived from the transition zone between potassic and propylitic alteration (Table 1). Considering that this sample contains 80 vol.% silicates (Table 2), the Au contents are very high and Pd contents are above average. If calculated to 100% sulphide, this would amount to about 36 ppm Au and 800 ppb Pd in concentrates.

Bozshakol, Kazakhstan

The deposit is situated in the NE-part of Kazakhstan, about 90 km west of the town of Eqibastuz. The copper mineralisation is associated with Middle Cambrian porphyry intrusions of tonalitic composition and calc-alkaline character, which form part of an island arc volcanic complex (*Kudryavtsev*, 1996). The country rocks are sedimentry and volcanic units of Middle Cambrian age. The ore bodies are linear stockworks, extending over a total length of about 3 km and a thickness of up to 500 m. Potassic (K-feldspar-biotite-quartz-hematite-magnetite) and propylitic (quartz-sericite-carbonate-chlorite) alteration zones extend over considerable distances in the porphyry body. Mineralisation consists mainly of chalcopyrite, with subordinate pyrite and molybdenite. Ore reserves are 176 million tons with 0.72% Cu and 0.28 g/t Au. Copper- and pyrite concentrates carry 1.04 and 0.59 ppm Pt, and 0.37 and 0.28 ppm Pd, respectively (*Kudryavtsev*, 1996) Inclusions of merenskyite and kotulskite in pyrite and chalcopyrite have been reported by *Filimonova* and *Terekhovich* (1972). According to *Kudryavtsev* (1996) quartz-K-feldspar and quartz-sulphide veinlets have been deposited at temperatures of 380–320 °C and 320–180 °C, respectively.

The sulphide concentrate investigated in this study has been separated from an ore sample of the propylitic-sericitic alteration zone (Table 1). Its Pd content is relatively high (Table 4).

Discussion and conclusions

The results presented show that about half of the investigated island arc (6 out of 14) but only one out of 17 continental margin porphyry copper deposits reveal high contents of Pd. (Table 4). In five of them (Mamut, Majdanpek, Elacite, Skouries, Bozshakol) discrete PGM have been identified in accordance with elevated levels of Pd. For the deposits with the highest PGE grades, potential reserves are calculated (Table 5).

Table 5. *Tonnage and grade of Cu, Au, and PGE*

Deposit	Ore (mt)	Cu (t)	Grade (%)	**Au** **(t)**	Grade (g/t)	**Pd** **(t)**	Grade (g/t)	**Pt** **(t)**	Grade (g/t)
Mamut	179	852.000	0.476	**118**	0.66	**8.2**	0.046	**2.7**	0.015
Ok Tedi	275	2000.000	0.75	**137**	0.5	**7.4**	0.027	**0.5**	0.002
Elacite	185	832.000	0.45	**55**	0.3	**4.6**	0.025	**1.0**	0.0055

Further deposits with increased Pd and Pt contents are Santo Tomas II, Philippines (*Tarkian* and *Koopmann*, 1995), and the alkaline porphyry deposits in British Columbia (*Thompson* et al., 1999). The Santo Tomas II deposit is linked to a Pliocene quartz diorite of island arc setting. Ore samples from the potassic zone, respectively from the potassic-prophylitic transition zone, have Pd and Pt contents of up to 160 and 38 ppb respectively and Au contents of 1.8 ppm in average. They carry discrete PGM. Pd and Pt contents in sulphide concentrates are estimated at 1.5 ppm, and 0.5 ppm, respectively (*Tarkian* and *Koopmann*, 1995). The porphyry deposits in British Columbia are also of island arc type. They are linked to Jurassic-Triassic diorites, monzodiorites and syenites of alkaline character. The Pd and Au-contents of heavy mineral concentrates (*Thompson* et al., 1999) are partly high and comparable with those obtained during the present study. These results suggest that higher concentrations of Au, Pd and Pt may be expected in island arc rather than in continental margin porphyries. However, there is no straightforward relationship between PGE contents and geotectonic setting. All five Bulgarian deposits investigated form part of an island arc setting, but only two (Elacite and Medet) show high PGE contents. The other three are PGE-poor. Other aspects of intrusive rocks, such as geological age, chemical composition and magma type do not seem to influence PGE-contents. Similar observations have been reported by *Sillitoe* (1979) as regards the Au-contents.

Solomon (1990) suggested, that Au-rich porphyries in island arcs may form by two-stages melting, i.e. re-melting of previously molten mantle material due to arc (subduction) reversal, so that Au and PGE are relatively enriched during the second stage. However, the geotectonic setting does not appear to be the determining factor for Au contents of porphyry copper deposits, since several occurrences of continental margin type also form part of the Au-rich porphyry group (*Sillitoe*, 1979, 1993). Other factors which are not yet understood may play a role in this context. However, from the results of the present study a trend is obvious, suggesting that higher Pd and Pt contents are associated with high Au-contents. Thus Au-rich porphyries are promising exploration targets for Pd and Pt. The geochemical correlation of Au, Pd and Pt points towards a common origin. Although porphyry copper deposits of different geotectonic settings may have some common features, their mechanisms of formation may be different as regards derivation, place of formation and development of source magmas. Several factors may be responsible for Au- and PGE enrichment in porphyry copper deposits, e.g. sulphur undersaturation in the magma so that the Au and PGE remain in the silicate melt, silicate fractionation before final emplacement, high oxidation potential so that sulphur solubility is relatively high. However, an evaluation of these factors is

not possible on the basis of the reconnaissance dataset presented here. Comprehensive mineralogical and geochemical investigations of individual deposits are required to clarify the role of these parameters for Au and PGE concentration in porphyry copper ores. The primary derivation of PGE, however, must be attributed to the chemical composition of the upper mantle or the subducted oceanic crust the partial melting and differentation of which lead to the formation of intermediate host intrusive rocks of copper porphyries. The primary concentration of PGE depends mainly on the fractionation and differentiation processes in the magma. An important condition would have to be fullfilled and this is the absence of early fractionation of magmatic sulphides and, accordingly, availability of PGE for the later hydrothermal transport and concentration in the porphyry system. *Thompson* et al. (1999) postulate high oxygen fugacity in the magma as an explanation for the high PGE contents of alkaline island arc porphyries in British Columbia. Similar conditions may well have existed in the calc-alkaline-subalkaline magmas of the seven porphyry deposits with relatively high PGE contents presented here. The fact that 43% of the island arc porphyries, but only 6% of the continental margin porphyries investigated here, carry high Pd contents might be attributed to the reduced likelihood of PGE "dilution" by crustal contamination of magmas in island arcs, because the sialic crust tends to be thin or absent in these settings. Magma contamination by crustal material may add sulphur and cause sulphide precipitation, thereby withdrawing Au and PGE from the remaining silicate melt. Early sulphide precipitation might also be caused by magma mixing processes. These assumptions must, however, be considered speculative at the present stage of the investigations.

Hydrothermal metal transport during late stages of magmatic evolution is significant for PGE concentration in porphyry systems. Fluid inclusion data reported from Cu-Fe-sulphide bearing K-silicate alteration zones of many porphyry copper deposits show homogenisation temperatures between 350 and 725 °C and salinities of 30 to > 60 wt.% NaCl equiv. (*Roedder*, 1971; *Batchelder*, 1977; *Eastoe*, 1978; *Wilson*, 1978; *Bodnar* and *Beane*, 1980; *Ahmad* and *Rose*, 1980). Temperatures in the 350 to 550 °C range are most widespread.

PGM identified in this study are minerals of Pd and Pt. Textural evidence suggests that they have formed simultaneously or slightly later than the Cu-Fe sulphides. Santo Tomas II (Philex) is, so far, the only porphyry deposit where fluid inclusions in PGM (Pd-Pt telluride) bearing bornite-chalcopyrite-magnetite assemblages of the potassic zone have been investigated. They are characterised by high salinity (35- > 60 wt.% NaCl equiv.) and trapping temperatures between 380 and 520 °C. (*Tarkian* and *Koopmann*, 1995). Ore samples from potassic-propylitic zones in this deposit display high Au, Pd and Pt contents (*Tarkian* and *Koopmann*, 1995). This is supported by results from the Elacite and Skouries deposits investigated here. Systematic studies would be required to clarify whether this applies to other deposits as well.

The results discussed above are in agreement with experimental data and support the concept of joint transport of Au, Pd and Pt as chloride complexes in high salinity hydrothermal solutions (*Henley*, 1973; *Seward*, 1984; *Mountain* and *Wood*, 1988; *Gammons* et al., 1992; *Wood* et al., 1992). At temperatures of up to 300 °C solubilities of more than 10 ppb for Pd and Pt as chloride complexes can be

obtained only under highly oxydizing and acidic conditions (*Wood* et al., 1992). At higher temperatures (>400 °C) solubilities increase significantly (*Mountain* and *Wood*, 1988; *Sassani* and *Shock*, 1990; *Wood* et al., 1992). The PGE contents in sulphides determined in this study can, however, easily be accounted for by solubilities of 10 ppb in hydrothermal solutions. The high Pd/Pt-ratios in the sulphides suggest that in most cases considerably more Pd was transported than Pt. The other PGE (Os, Ir, Ru and Rh) have not been mobilised.

Acknowledgements

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