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Palladium, platinum and gold distribution in porphyry Cu ± Mo deposits of Russia and Mongolia

Vitaliy I. Sotnikov [a,*], Anita N. Berzina [a,1], Maria Economou-Eliopoulos [b], Demetrios G. Eliopoulos [c]

[a] Institute of Geology, Koptyug ave., 3, Novosibirsk 630090, Russia
[b] Department of Geology, University of Athens, Panepistimiopolis, Ano Ilissia, GR-15784 Athens, Greece
[c] Institute of Geology and Mineral Exploration, 70 Messoghion Street, GR-11527 Athens, Greece

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Abstract

The porphyry Cu–Mo deposits in the southern Siberian craton and Northern Mongolia including subduction-, collision-, and rift-related igneous series of early Paleozoic to Mesozoic age, are all characterized by varying crustal contribution to their parent magmas and the presence of explosive breccias. Precious metal and associated element contents are reported for mineralized samples, sulphide concentrates, and chalcopyrite–molybdenite flotation concentrates from porphyry Cu ± Mo intrusions of Russia (Sora, Aksug and Zhireken) and Mongolia (Erdenetiun-Obo). Average PGE contents in rocks are 17 ppb Pd and 22 ppb Pt in the Aksug deposit, 13 ppb Pd and <10 ppb (detection limit) Pt in the Sora, 14 ppb Pd and 21 ppb Pt in the Erdenetuin-Obo and 18 ppb Pd and 28 ppb Pt in the Zhireken deposit. Average gold content in rocks is 61 ppb in the Aksug deposit, 17 ppb in the Sora, 21 ppb in the Erdenetuin-Obo, and 30 ppb in the Zhireken deposit. The highest average 2.3 ppm Ag was recorded in the rocks of the Sora deposit. In general, the precious metal distribution in the studied deposits has no apparent relationship with the alteration types. The molybdenum content in rocks ranges between <1 and 128 ppm Mo in the Aksug deposit, from <1 to 5400 ppm Mo in the Sora deposit, from 2 to 755 ppm Mo in the Erdenetuin-Obo deposit, and from 3 to 1530 ppm Mo in the Zhireken deposit. The average copper content in rocks is 1540 ppm in the Aksug deposit, 460 ppm in the Sora deposit, 1460 ppm in the Erdenetuin-Obo deposit, and 220 ppm in the Zhireken deposit. The Cu–Mo ratios are highest in the Aksug and Erdenetuin-Obo deposits and lowest in the Sora and Zhireken deposits. The correlation matrix for selected major and trace element data on mineralized samples and sulphide concentrates (34 samples) indicates that precious metals are associated with either chalcopyrite or molybdenite. Copper shows a strong positive correlation with Au and Pd ($r \geq +0.91$) while Mo shows a strong positive correlation with Pt ($r = +0.98$). In addition, Mo

* Corresponding author. Fax: +7-3832-332792.
E-mail addresses: berzina@uiggm.nsc.ru (V.I. Sotnikov), berzina@uiggm.nsc.ru (A.N. Berzina), meconom@geol.uoa.gr (M. Economou-Eliopoulos), eliopoulos@igme.gr (D.G. Eliopoulos).
1 Fax: +7-3832332792.

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exhibits a strong positive correlation with W ($r = +0.94$). An interelement positive correlation between precious metals is 0.57 (Ag–Au). The Pd and Pt contents of both chalcopyrite and molybdenite in flotation concentrates are low, varying from 9 to 83 ppb Pd and from <10 to 110 ppb Pt. The highest values recorded are 924 ppb Pd in sulphide concentrates from the Aksug deposit, and 684 ppb Pd and 299 ppb Pt in sulphide concentrate from breccia of the Zhireken deposit. The highest gold content, 5450 ppb Au, is in chalcopyrite flotation concentrate from the Aksug deposit, whereas in the majority of concentrates the gold content is in the order of a few hundreds parts per billion. The relatively low contents and limited variation of the precious metal contents in the individual deposits of Russia and Mongolia point to the essential role of the composition of the source and composition of parent magmas.

Keywords: Platinum; Palladium; Porphyry Cu ± Mo; Chalcopyrite; Molybdenite; Concentrates; Russia; Mongolia

1. Introduction

Platinum/or palladium enrichment in porphyry Cu systems is well documented in a number of hydrothermal systems, such as those of British Columbia connected with high alkali magmatism (Werle et al., 1984; Mutschler et al., 1985), in the porphyry Cu deposits of Skouries (2400 ppb Pd, and up to 21 wt.% Cu) (Eliopoulos and Economou-Eliopoulos, 1991; Economou-Eliopoulos and Eliopoulos, 2000), the Elacite deposit in Bulgaria, the Mamut deposit in Malaysia and the Grasberg deposit in Indonesia (Rubin and Kyle, 1997; Tarkian and Stribrny, 1999).

The PGE data on porphyry Cu systems of Russia are limited (Faramazyan et al., 1970; Filimonova, 1984; Kochetkov, 1984, 1993; Sotnikov and Tsimbalist, 1992; Kovalenker et al., 1996; Sazonov et al., 1997, 1998; Tarkian and Stribrny, 1999). In this study, for the first time, precious metal and associated element contents are investigated in mineralized samples representative of all alteration types, including chalcopyrite–molybdenite concentrates from porphyry Cu ± Mo intrusions of Russia (Sora, Aksug and Zhireken) and Mongolia (Erdenetiun-Obo).

2. Characteristic features of porphyry Cu ± Mo systems in Russia and Mongolia

Porphyry Cu–Mo deposits of the fold belts in the southern part of the Siberian Craton (Fig. 1) comprise magmatic segments of the Central Asian belts, including subduction-, collision-, and rift-related igneous series of early Paleozoic and late Paleozoic to Mesozoic age (Berzina et al., 1999b). Large plutonic intrusions that host porphyry systems, and the porphyry ore-bearing complexes themselves, have been interpreted as having formed in different geodynamic environments. More specifically, the former are surmised to have formed during collisional (Kuznetsk Alatau, Tuva, Transbaikalia) or in a continental margin settings (Mongolia), while smaller porphyry stocks (up to 1 km^2) and numerous dikes are attributed to the beginning of rifting (Berzina et al., 1994, 1999b).

The Cu–Mo mineralization is associated in time and space with the porphyry stocks and dikes, hosted within granitoid plutons. The host and porphyry complexes are represented by compositionally variable mafic to felsic rocks; evolved rocks are more abundant in the porphyry complexes, as demonstrated by their rare element contents. Representative chemical analyses of the rare element contents of the major host plutons and porphyry rock types of the deposits studied are given by Berzina et al. (1999c).

The porphyry intrusions are accompanied by well-developed hydrothermal alteration and disseminated or vein-stockworks of pyrite, chalcopyrite and molybdenite, with temperatures of formation varying from early potassic (700–500°C) to late sericitization, silicification and argillization (400–200°C) (Sotnikov et al., 1977). A common feature of the studied porphyry copper–molybdenum systems is the presence of explosive breccias, which are considered to be related in space and time to the porphyry stocks; furthermore, a crustal contribution to the parent magmas of the porphyry intrusions is apparent (Berzina et al., 1999a; Sotnikov et al., 1999). The Sora, Erdenetuin-Obo and Aksug deposits are char-

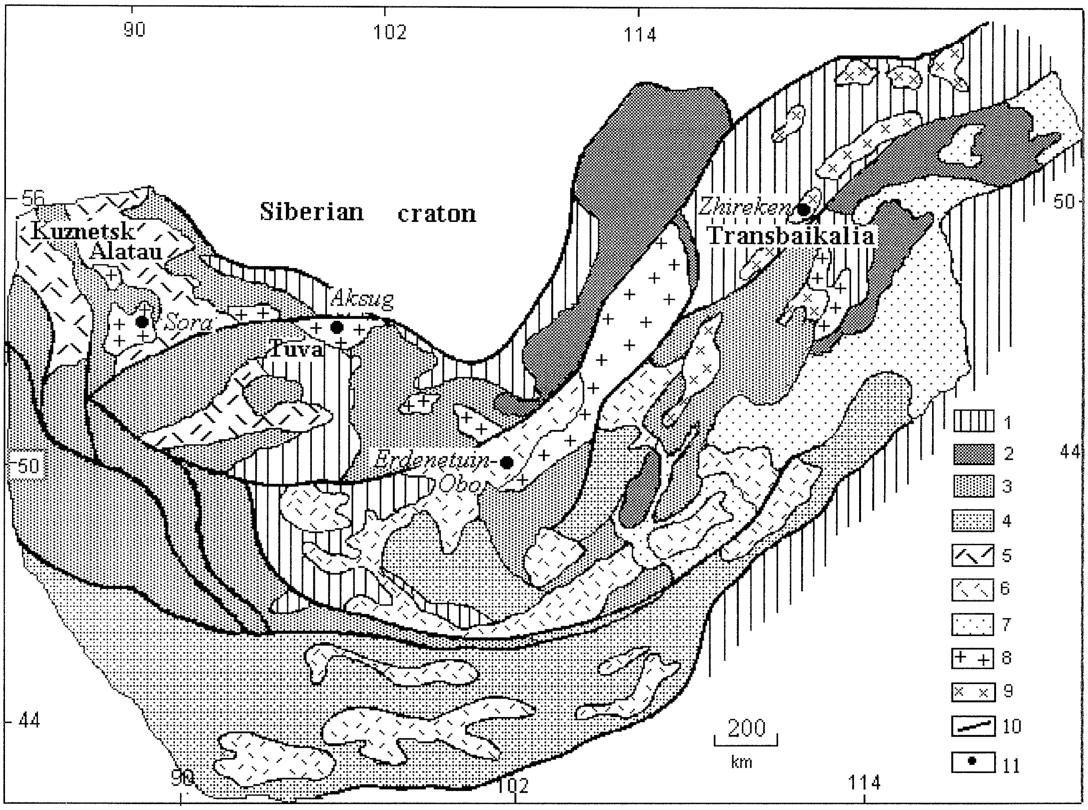

Fig. 1. Simplified geological map showing the location of the studied Cu ± Mo porphyry deposits (according to Peive and Yanshin, 1980). Basement: 1—pre-Riphean, 2—Riphean, 3—Caledonides, 4—Hercynides; including magmatic arcs: 5—Devonian, 6—Upper Paleozoic, 7—Mesozoic; including collisional granitoids: 8—Paleozoic, 9—Mesozoic; 10—lineaments, 11—location of the deposits.

acterized by a dominant mantle component in their parent magma, in contrast to the Zhireken deposit, characterized by an elevated crustal component (Table 1).

2.1. Aksug Cu–Mo deposit, Northeastern Tuva

The Aksug deposit of Northeastern Tuva, is of early Paleozoic (Devonian (?)) age, and is located in the Tuvinian terrane. This terrane comprises an island-arc complex, including an Early Cambrian, low Na content basalt–andesite–rhyolite series, followed by Middle Cambrian collisional-related plutons of gabbro-diorite–tonalite affinity that host the porphyry Cu-bearing complex (Berzina et al., 1999b,c). The porphyries consist of diorite and tonalite, with rare granodiorite. The chemical compositions of the porphyries are similar to that of the host granitic plutons. The Aksug porphyries belong to the calc-alkaline series and represent an andesitic parental magma (Kuzmin, 1985). They are characterized by low Rb, Cs, Th, Ta, and REE contents, high K/Rb ratios (Berzina et al., 1999b,c), and low F/Cl in magmatic fluids compared to the deposits studied, based on the chemical composition of halogen-containing minerals, such as titanite, amphibole, biotite and apatite (Berzina and Sotnikov, 1995; Sotnikov et al., 2000). In addition, the deposit is dominated by a mantle source component, with $(^{87}Sr/^{86}Sr)_0$ varying from 0.70458 to 0.70496.

Hydrothermal alteration is represented by early propylitization and widespread quartz-sericite metasomatism. K-silicates, in the form of quartz-K-feldspar veinlets, occur in the peripheral zones of the deposit.

Table 1
Characteristics of the deposits studied

Deposit, location	Average Cu/Mo in ores	Age	Age (Ma) ^{40}Ar– ^{39}Ar	Age (Ma) Rb–Sr	$(^{87}Sr/^{86}Sr)_0$	Host intrusive rock	Magma type
Aksug, Northeastern Tuva, Russia	40–70	Devonian (?)	400 ± 380		0.70458–0.70496	Diorite, tonalite porphyries	calk-alkaline
Sora, Kuznetsk Alatau, Russia	2–4	Early Devonian	402–386		0.70400–0.70460	Monzodiorite, diorite, syenite, subalkaline granite porphyries	K-calc-alkaline
Erdenetuin-Obo, Northern Mongolia	30–50	Triassic	225 ± 3.5	252–220	0.70406–0.70424	Diorite, granodiorite, granite porphyries	calc-alkaline
Zhireken, Eastern Transbaikalia, Russia	1	Late Jurassic	160–165	156 ± 23	0.70510–0.70642	Diorite, granodiorite, subalkaline granite porphyries	K-calc-alkaline

Sulphide mineralization occurs as veins, stockworks, and disseminated grains within the porphyries and host diorites and tonalites, consisting of chalcopyrite and pyrite with subordinate molybdenite, bornite, chalcocite, and trace tetrahedrite, sphalerite, and native copper.

2.2. Sora Mo–Cu porphyry deposit, Kuznetsk Alatau

The Mo–Cu porphyry Sora deposit of Early Devonian age, is located in the Kuznetsk Alatau terrane, an island-arc complex of Vendian–Early Cambrian age, consisting of trachyrhyolite–trachyandesite subvolcanics and monzonite–diorite-gabbro intrusions. In general, these rocks are characterized by relatively high Na contents. Collisional plutons of Cambrian–Ordovician age are represented by a monzodiorite–granosyenite–leucogranite association. Mineralization is related to subvolcanic stocks including monzodiorite, diorite, syenite- and subalkaline granite-porphyries. The Sora porphyries have a K-calc-alkaline affinity, and although host granitoids and porphyries are similar in composition, a significant time gap of about 20–30 Ma between them is suggested by Sotnikov et al. (1995b).

Strontium isotope data $(^{87}Sr/^{86}Sr)_0 = 0.70400$–0.70460 suggest that porphyry the emplacement coincided with the beginning of rift magmatism. Sora porphyries are characterized by increased REE, Nb, and Ta contents, high K/Rb (Berzina et al., 1999b,c), and elevated F/Cl in halogen-containing minerals, highest among the deposits studied (Berzina and Sotnikov, 1995; Berzina et al., 1997a; Sotnikov et al., 2000). The Sora deposit is essentially characterized by Mo mineralization, consisting of molybdenite accompanied by pyrite, chalcopyrite and small amounts of sphalerite, galena, and tetrahedrite. The porphyry stock is characterized by potassic alteration (biotite, K-feldspar) and strong albitization, with minor subsequent sericitization and silicification.

2.3. Erdenetuin-Obo Cu–Mo porphyry deposit, Northern Mongolia

The Triassic Erdenetuin-Obo Cu–Mo deposit is located in the Selenga-Vitim belt of northern Mongolia, formed above the subduction zone of the Mongolo-Okhotsk and Paleo-Tethys plates under the Siberian continent. Granites and andesites are the most volumetrically important rock types, with minor quartz diorites and granodiorites. Mineralization is most closely related to diorite and granodiorite porphyries with minor copper associated with the granite porphyries. The Erdenetuin-Obo porphyries belong to calc-alkaline series characterized by relatively high Na content, like the host granitoids, although the time gap between them is about 30 Ma (Sotnikov et al., 1995a). Isotope data suggest that, the host granitoids formed synchronously with that of early volcanism of a continental margin, whereas the ore-bearing porphyries are coeval with bimodal rift-related volcanism.

The Erdenetuin-Obo deposit comprises strontium isotope signatures $(^{87}Sr/^{86}Sr)_0$ value (0.70406–0.70424) for porphyry-generating magmas, which suggest a mantle source. These porphyries are characterized by high Sr and Ba content, and moderate HFSE and REE contents (Berzina et al., 1999c).

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.

2.4. Zhireken Mo–Cu porphyry deposit, Eastern Transbaikalia

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 granodiorites, granosyenites and granites. The Zhireken subvolcanic stocks are of K-calc-alkaline affinity, mainly diorite-, granosyenite- and subalkaline granite-porphyries. Geologic and isotopic data suggest that these high REE porphyry genesis was related to the beginning of rifting during Late Jurassic–Cretaceous time. Among the other deposits discussed, the Zhireken subvolcanic stocks exhibit the highest Rb, Cs, Li, and Th contents and the lowest K/Rb ratios. Zhireken porphyry intrusions also have very high Rb/Sr ratios (Berzina et al., 1999c). Halogen-containing minerals are characterized by elevated F contents, although F/Cl ratios are generally lower than those of Sora deposit (Sotnikov et al., 2000).

Table 2
Description of samples analysed for PGE

Sample	Ore type	Ore minerals	Alteration type / silicates
Aksug, Russia			
s-0463b	Diss.	py, cp (M), mo (Mi), sl, fa (Tr)	Sericitic / ser-qz
s-0464	Diss.	py (M), cp (Mi)	Potassic / K-feldspar, qz, ab
s-0468	Diss.	py, (M), cp, mo (Mi)	Silicification-sericitic / ser, qz
s-0474	Diss.	py (M), cp, bo, rt (Tr)	Silicification-sericitic / ser, qz, ab
s-0486	Diss.	py (M), cp, mo, bo, rt (Tr)	Silicification-potassic / K-feldspar, ser, qz, ab
s-0487	Diss.	py, cp (M), mo, rt (Tr)	Potassic / K-feldspar, qz, ab, bi
s-0488	Diss.	py, cp, mo (M), bo, rt, fa (Tr)	Silicification-sericitic / ser, qz, ab
s-0497a	Diss.	py (M), cp, rt, mo (Tr)	Potassic / K-feldspar, qz, ab
s-2392b	Sf.C	cp (M), py (Mi), bo, fa, rt, mo (Tr)	Propylitic / chl, carb, ser, qz
4T / 1	F.C.	cp, (M), mo(Mi), py, sl, fa, bo, Cu (Tr)	
4T / 2	F.C.	cp (M), mo, sl, fa, (Mi), py, bo, cc, gal, Cu (Tr)	
4T / 3	F.C.	mo (M), cp, fa (Mi), py, bo, sl, gal, (Tr)	
Sora, Russia			
K-64a	Diss.	py, mo (M), cp, fa, sl (Tr)	Albitization / ab, K-feldspar, qz
K-64b	Diss.	py, mo (M), cp, sl (Tr)	Potassic / K-feldspar, qz, bi, ab
K-65a	Diss.	py, cp, mo (M), sl, rt, fa (Tr)	Silicification-K-silikate / qz, bi, K-feldspar
K-70a	Diss.	py (M), cp, mo, sl (Tr)	Potassic-albitization / K-feldspar, ab, ser, kaol
K-79	Diss.	py (M), mo, cp (Tr)	Sericitic / ser, qz
K-95e	Diss.	mt (M, py, rt (Tr)	relatively unaltered
C-1	F.C.	mo, cp (M), py, sl (Mi), gal (Tr)	
C-3	F.C.	mo (M), cp, py, sl (Mi), fa (Tr)	
C-4	F.C.	cp (M), sl, mo, py, gal,(Mi), fa (Tr)	
C-5	F.C.	py (M), cp, mo, sl, (Mi), gal, fa (Tr)	
Erdenetuin-Obo, Mongolia			
s-0404	Diss.	py (M), cp, mo, rt, sl (Tr)	Silicification / qz, ser
s-0404a	Diss.	py (M), rt, cp, sl, fa (Tr)	Silicification-sericitic / qz, ser, kaol
s-0413	Diss.	py (Tr)	relatively unaltered
s-0414	Diss.	py, cp (M), fa, mo (Tr)	Sericitic / ser, qz, kaol
s-0424	Diss. / veinlet	py (M), cp, sl, rt (Tr)	Chloritization / chl, qz, ser, carb
s-0424a	Diss. / veinlet	py (M), mo (Mi), cp (Tr)	Argillic / kaol, qz
s-0873	Breccia	py (Tr)	relatively unaltered
s-0923d	Diss.	py (M), cp, rt (Tr)	Chloritization / chl, qz, ser
s-0943v	Diss.	py (Tr)	Potassic / K-feldspar, qz, bi
s-0946g	Diss.	mo, py (M), cp, sl, rt (Tr)	Sericitic / qz, ser, ab
s-0572g	Sf.C.	cp (M), mo, py, sl (Mi)	Sericitic-silicification / qz, ser
Zhireken, Russia			
s-0508a	Diss. / veinlet	mo, py (M), cp, sl, fa (Tr)	Potassic / K-feldspar, qz, tm, cab
s-0511b	Diss. / veinlet	cp, mo, py (M)	Silicification-potassic / qz, K-feldspar, ab, ser
s-0515	Diss. / veinlet	py, mo, (M), cp, rt, sl, (Tr)	Sericitic / qz, ser
s-0515a	Diss. / veinlet	py, mo (M), cp (Tr)	Sericitic / qz, ser, K-feldspar, ab
s-0516b	Diss.	py, mo (M), cp, rt (Tr)	Argillic / kaol, montm, qz
K-11	Diss. / veinlet	mo, py (M), cp (Tr)	Potassic / K-feldspar
s-0508g	Sf.C. (breccia)	mo (M), cp (Mi), py, sl (Tr)	Silicification-argillic / qz, kaol, montm

F.C.—flotation concentrate, Sf.C.—sulphide concentrate, Diss.—disseminated, M—major, Mi—minor, Tr—trace, ab—albite, bi—biotite, bo—bornite, carb—carbonate, cc—chalcocite, chl—chlorite, cp—chalcopyrite, Cu—native copper, fa—fahlore, gal—galena, kaol—kaolinite, mo—molybdenite, montm—montmorillonite, mt—magnetite, py—pyrite, qz—quartz, rt—rutile, ser—sericite, sl—sphalerite, tm—tourmaline.

The most salient feature of the Zhireken deposits is elevated $(^{87}Sr/^{86}Sr)_0$ 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.

3. Analytical methods

Platinum, palladium and gold were determined at both X-ray Assay Laboratories (XRAL), Ontario, Canada, the National University of Athens, using ICP/MS and atomic absorption spectroscopy (heated graphite atomizer), respectively, after preconcentration by the Lead Fire Assay technique from large (30 g) samples of mineralized rocks and sulphide con-

Table 3
Precious metal and associated trace element content in rocks from porphyry Cu–Mo deposits of Russia and Mongolia

Sample	Concentration (ppm; * ppb)												Pt/Pd	Cu/Mo
	Ag	Au*	Ba	Cr	Cu	Mo	Ni	Pb	Pd*	Pt*	W	Zn		
Aksug, Russia														
s-0463b	< 0.2	30	1360	34	1550	8	3	< 2	11	17	73	8	0.65	194
s-0464	0.3	51	660	23	2090	10	4	< 2	9	17	< 10	22	0.53	209
s-0468	< 0.2	47	430	3	950	55	3	< 2	12	21	88	78	0.57	17
s-0474	0.5	204	400	11	2400	55	4	< 2	12	21	88	78	0.57	44
s-0486	0.3	72	830	10	1010	72	4	< 2	20	34	170	17	0.59	14
s-0487	0.2	26	1100	27	350	43	3	< 2	23	20	36	58	1.15	8
s-0488	< 0.2	24	1250	28	154	128	4	< 2	31	21	30	13	1.48	1
s-0497a	0.3	36	660	11	3800	< 1	5	< 2	12	24	< 10	26	0.5	> 1800
Sora, Russia														
K-64a	0.8	21	1410	15	490	56	3	5	18	< 10	30	100	> 1.8	9
K-64b	< 0.2	17	1070	9	15	4	5	< 2	12	< 10	88	67	> 1.2	4
K-65a	2.1	16	880	61	1880	5400	20	< 2	17	< 10	120	880	> 1.7	0.4
K-70a	3.7	19	1300	36	133	3	4	5	13	< 10	68	81	> 1.3	44
K-79	6.9	16	1280	15	240	14	7	5	10	< 10	< 10	61	> 1.0	17
K-95e	< 0.2	12	800	23	14	< 1	3	5	9	< 10	< 10	44	> 0.9	> 14
Erdenetuin-Obo, Mongolia														
s-0404	10	18	400	21	2250	9	4	124	12	28	144	140	0.43	250
s-0404a	< 0.2	19	1320	19	2040	21	4	< 2	16	25	168	16	0.64	97
s-0413	0.6	37	800	25	1740	21	10	5	17	32	177	36	0.53	83
s-0414	0.6	21	940	33	4050	23	14	4	14	16	156	42	0.88	176
s-0424	0.5	20	2340	46	2690	2	30	18	11	22	< 10	113	0.5	1345
s-0424a	0.3	17	1250	12	1110	10	6	627	7	< 10	68	130	> 0.7	111
s-0873	< 0.2	17	960	40	490	18	6	< 2	11	18	80	46	0.61	27
s-0923d	< 0.2	17	780	43	43	5	12	23	11	28	42	59	0.39	9
s-0943v	< 0.2	21	830	28	125	3	8	< 2	13	20	100	36	0.67	42
s-0946g	< 0.2	23	1500	19	100	755	5	< 2	23	15	74	32	1.53	0.1
Zhireken, Russia														
s-0508a	< 0.2	26	790	24	36	1530	5	2	26	27	110	15	0.96	0.02
s-0511b	< 0.2	32	500	18	1000	210	7	< 2	14	28	156	44	0.5	4.8
s-0511d	< 0.2	23	720	32	147	225	7	4	16	21	106	24	0.76	0.6
s-0515	< 0.2	29	420	26	113	1220	3	53	21	37	182	9	0.57	0.1
s-0515a	< 0.2	60	350	5	27	136	3	20	13	32	61	6	0.41	0.2
s-0516b	< 0.2	19	760	30	53	3	6	17	11	31	153	19	0.36	18
K-11	< 0.2	21	900	60	174	573	8	10	24	22	156	60	1.1	0.3

Table 4
Precious metal and associated trace element content in flotation concentrate (F.C.) and sulphide concentrate (Sf.C.) samples from Cu–Mo porphyry deposits

Sample	Description	Concentration (ppm, * ppb)															
		Ag	As	Au*	Ba	Cr	Cu	Mo	Ni	Pb	Pd*	Pt*	Se	Te	W	Zn	Pd/Pt
Sora, Russia																	
C-1	F.C.	1	< 3	12	254	13	610	490	10	10	9	< 10	1.2	< 0.1	< 10	200	> 0.9
C-3	F.C.		< 3	120	< 1	17	11 500	290 000			48	94	20.9	0.1	640	960	0.51
C-4	F.C.	> 100	< 3	110	8	7	143 500	780	43	800	52	110	15.6	< 0.1	10	> 10 000	0.47
C-5	F.C.	28.4	< 3	74	6	12	20 000	660	90	240	46	60	12.5	0.3	< 10	2830	0.77
Aksug, Russia																	
4T/1	F.C.	1.7	277	178	527	6	10 840	224	10	10	17	29	5.9	0.2	< 10	70	0.59
4T/2	F.C.	26	5700	5450	21	12	196 500	980	5	244	62	96	109	< 0.1	< 10	1100	0.64
4T/3	F.C.	19.6	4100	2740	26	67	102 000	14 080	15	222	83	76	97	0.2	18	860	1.1
s-2392b	Sf.C.	10	< 3	1210	400	40	53 600	85	7	2	924	25			100	72	37
Erdenetuin-Obo, Mongolia																	
s-0572g	Sf.C.	2.9	70	74	40	22	620	250	13	10	20	33	16.2	< 0.1	48	160	0.61
Zhireken, Russia																	
s-0508g	Sf.C.	0.2	< 3	139	5	160	27 350	240 000			684	299	108	0.6	992	10	2.29

centrates. Detection limits are 1 ppb for Pd and Au, 10 ppb for Pt. Platinum and Pd in molybdenites were determined at the analytical center of the United Institute of Geology, Geophysics and Mineralogy, Novosibirsk, Russia, using heated graphite atomizer—Perkin Elmer HGA-600, after preconcentration. Detection limits are 1 ppb for Pd and 5 ppb for Pt.

Copper, Mo and trace elements were determined using AAS method at the National University of Athens. Se and Te were analyzed using the atomic absorption/hydride system. Detection limits are 0.1 ppm for Te, Se, 0.2 ppm for Ag, 1 ppm for Cu, Mo, Zn, Ni, 2 ppm for Pb, Cr, 3 ppm for As and 10 ppm for W, Ba.

Isotope analyses were carried out at the United Institute of Geology, Geophysics and Mineralogy, Novosibirsk, Russia, by Mr. V.A. Ponomarchuk.

4. Precious metal and associated element contents

The precious metals platinum, palladium, gold and silver, and associated elements (such as Ba, Cr, Cu, Mo, Ni, Pb, W, Zn) were determined in 43 total representative samples from Aksug, Sora, Zhireken and Erdenetuin-Obo porphyry systems. Description of samples is given in Table 2. Samples analyzed include intrusive mineralized rocks with veinlets of sulphides accompanied by quartz, and disseminated

Table 5
Precious metal content in molybdenites from Cu–Mo porphyry deposits

Sample	Ore type	Alteration type	Concentration, ppb			
			Pt	Pd	Au	Ag
Zhireken, Russia						
G-104	Diss.	Sericitic	300	260	320	60
G-147	Diss.	Potassic	88	50	4.6	74
G-6	Diss.	Relatively unaltered	210	17	2	13
S-0511a	Diss.	Silicification-potassic	n.d.	n.d.	8	35
S-0512	Diss.	Silicification-potassic	n.d.	100	12	47
S-0512a	Diss.	Silicification-potassic	59	26	17	62
S-0512v	Diss.	Argillization	n.d.	18	15	11
S-0513/1	Diss.	Silicifation-potassic	57	25	9.8	52
S-0513/2	Diss.	Silicification-potassic	120	37	34	72
S-0517	Diss.	Relatively unaltered	34	7	9.6	22
G-117	Diss.	Silicification-albitization	n.d.	n.d.	9	58
S-762	Diss.	Potassic	120	51	36	110
G-133	Veinlet	Chloritization	295	53	15	77
G-140	Veinlet	Silicification	94	19	3.3	90
S-0519e	Veinlet	Potassic	100	82	32	52
S-0502a	Breccia	Potassic	n.d.	110	6.8	48
S-0518	Breccia	Argillization	40	22	8	64
S-0518a	Breccia	Potassic	380	270	15	43
Sora, Russia						
2047	Breccia	Potassic-albitization	36	92	40	860
2032	Breccia	Potassic-albitization	19	11	31	65
2033	Veinlet	Potassic-albitization	5	16	1.4	43
2034	Veinlet	Potassic-albitization	10	8	0.5	1
Erdenetuin-Obo, Mongolia						
S-280v	Veinlet	Silicification-sericitic	10	27	1.4	1.2
CM-2	Veinlet	Sericitization-potassic	15	n.d.	30	40

n.d.—not detected.

sulphides from various alteration types (Table 3), sulphide concentrates from highly mineralized samples, as well as chalcopyrite and molybdenite flotation concentrates (Table 4) and molybdenites (Table 5).

Pd and Pt contents in the mineralized rocks representing all alteration types (Table 2) range between 7 and 31 ppb, and from < 10 (detection limit) to 37 ppb, respectively (Table 3, Fig. 2). Average PGE contents in mineralized rocks are 17 ppb Pd/22 ppb Pt in the Aksug deposit, 13 ppb Pd/< 10 ppb Pt in the Sora, 14 ppb Pd/21 ppb Pt in the Erdenetuin-Obo and 18 ppb Pd/28 ppb Pt in the Zhireken deposit. Gold contents in mineralized rocks are generally low, ranging from 16 to 72 ppb, with an average gold content of 61 ppb Au in the Aksug deposit, 17 ppb in the Sora, 21 ppb in the Erdenetuin-Obo, and 30 ppb in the Zhireken deposit. Silver values are generally 10–20 times that of gold, with greatest Ag values characterizing the Sora deposit (Table 3). These preliminary data on the precious metal distribution in the studied deposits do not establish any relationship with the alteration types (Tables 2 and 3). Hence, average contents of PGE and trace elements in rocks including different alteration types were used in this study.

Copper and molybdenum contents are qualitatively consistent with the sulfide mineral assemblages present in each sample (Tables 2 and 3). Molybdenum content in samples studied ranges between < 1 and 128 ppm Mo in rocks of the Aksug deposit, from < 1 to 5400 ppm Mo in the Sora deposit, from 2 to 755 ppm Mo in the Erdenetuin-Obo deposit, and from 3 to 1530 ppm Mo in rocks of the Zhireken deposit. Average copper contents in our samples are 1540 ppm in rocks of the Aksug deposit, 460 ppm in the Sora deposit, 1460 ppm in the Erdenetuin-Obo deposit, and 220 ppm in rocks of the Zhireken deposit. Cu/Mo ratios in mineralized rocks are highest in the Aksug and Erdenetuin-Obo deposits and lowest in the Sora and Zhireken deposits (Table 3).

Table 6
Correlation matrix for selected major and trace elements from porphyry Cu–Mo deposits of Russia and Mongolia ($n = 34$)

	Ag	Au	Cu	Mo	Pd	Pt	W
Ag	1						
Au	0.57	1					
Cu	0.51	0.91	1				
Mo	−0.07	0.06	0.42	1			
Pd	0.44	0.84	0.98	0.58	1		
Pt	−0.08	0.08	0.43	0.98	0.58	1	
W	−0.07	0.07	0.41	0.94	0.56	0.95	1

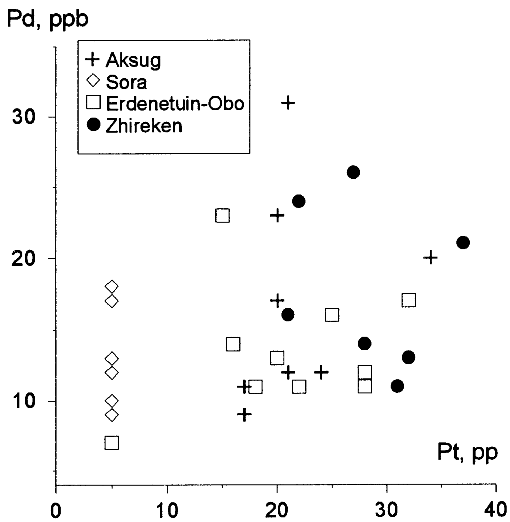

Fig. 2. Correlation between Pd and Pt contents in mineralized rocks (data from Table 3).

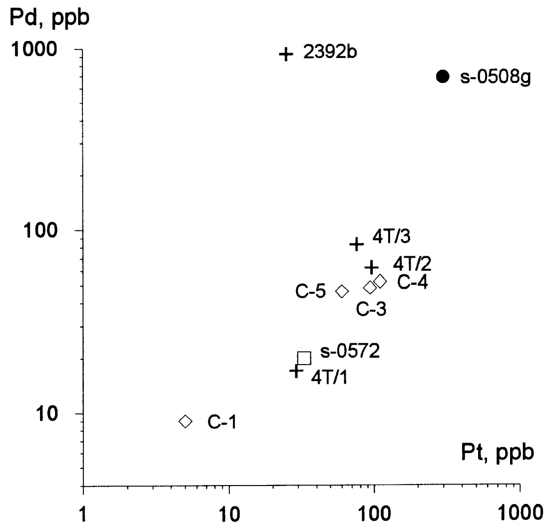

Fig. 3. Correlation between Pd and Pt contents in flotation and sulphide concentrates (data from Table 4).

The correlation matrix for selected major and trace element data on mineralized samples and sulphide concentrates (34 samples) (Tables 3 and 4) indicates that precious metals are associated with either chalcopyrite or molybdenite (Table 6). Copper shows a strong positive correlation with Au and Pd ($r \geq +0.91$) while Mo shows a strong positive correlation with Pt ($r = +0.98$). In addition, Mo exhibits a strong positive correlation with W ($r = +0.94$). An interelement positive correlation between precious metals is 0.57 (Ag–Au).

The Pd and Pt contents of both chalcopyrite and molybdenite in flotation concentrates are low, varying between 9–52 ppb Pd and < 10–110 ppb Pt in the Sora deposit, 17–83 ppb Pd and 29–96 ppb Pt in the Aksug deposit, 20 ppb Pd and 33 ppb Pt in the Erdenet deposit (Table 4, Fig. 3). The highest values recorded are 924 ppb Pd in concentrate sulphides from the Aksug deposit, and 684 ppb Pd and 299 ppb Pt in concentrate sulphides from breccia, Zhireken deposit (Table 4). The high content of Pd in sample s-2392b from the Aksug deposit probably reflects the presence of the PGE mineral. Distinct platinum group minerals have been identified as inclusions in chalcopyrite from several Cu-porphyry deposits (Tarkian et al., 1991; Tarkian and Stribrny, 1999). The highest gold content, 5450 ppb Au, is in chalcopyrite flotation concentrate from the Aksug deposit, whereas in the majority of concentrates the gold content is in the order of a few hundreds parts per billion (Table 4).

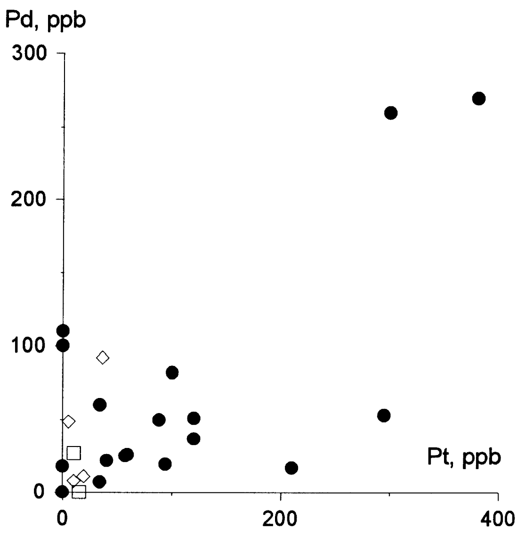

Fig. 4. Correlation between Pd and Pt contents in molybdenites (data from Table 5).

Thus, the average Pd content in flotation concentrates from the Russian systems is low (39 ppb Pd to 4.3 wt.% Cu in the Sora deposit and 54 ppb Pd to 10.3 wt.% Cu in the Aksug deposit). If calculated to 100% chalcopyrite (or 33 wt.% Cu), this would amount to about 293 (Sora) and 173 (Aksug) ppb Pd. However, certain concentrates, in particular pure molybdenites (Table 5, Fig. 4) and sulphide concentrate from the breccias of the Zhireken deposit, exhibit a significant enrichment in both Pt and Pd.

5. Comparison of the porphyry Cu deposits of Russia and Mongolia with those of other geologic provinces

Porphyry-type ore deposits range from copper–gold, like Grasberg (Indonesia) and Mamut (Malaysia) to copper–molybdenum deposits such as those of the southwest US or western South America. Molybdenite in porphyry Cu–Au type deposits is commonly of low concentration and occurs in low-grade peripheral zones outside the principal copper ore body, while in porphyry Cu–Mo deposits molybdenite usually occurs within and beneath the copper-bearing rock volumes.

Porphyry Cu–Mo deposits of Siberia and Mongolia, which are of Caledonian and Hercynian to Mesozoic age, are characterized by relatively small stocks and dikes (Berzina et al., 1997b). 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 mineralized samples contain 10 to 80 ppb Pd, and up to 18 ppb Pt. Molybdenum concentrates contain 5 to 220 ppb Pd and 12 to 390 ppb Pt, and copper concentrates contain from 9 to 160 ppb Pd and up to 20 ppb Pt (Faramazyan et al., 1970).

Many porphyry-Cu deposits hosted in calc-alkaline or alkaline intrusions are widespread in the Cordillera Province of the Western Hemisphere. Batholiths contain major intrusive phases including porphyry stocks, which may be apophyses of the

Table 7
Geochemical data on porphyry Cu ± Mo deposits of Russia and Mongolia—a comparison to other intrusions

Location	Type of associated intrusion	Age	Sample	Concentration							Pd/Pt
				ppb			ppm		wt.%		
				Pd	Pt	Au	Se	Te	Cu	Mo	
Russia											
Sora	K-calc-alkanine	Devonian	C-3	48	94	120	20.9	0.1	1.15	29	0.51
Sora			C-4	52	110	110	16	< 0.1	14.4	0.08	0.05
Aksug	calc-alkaline	Devonian	4T/2	62	96	5450	109	< 0.1	19.65	0.1	0.65
Aksug			4T/3	83	76	2740	97	0.2	10.2	1.4	1.09
Zhireken	K-calc-alkanine	L. Jurassic	S-0508g	684	299	139	108	0.6	2.7	24	2.29
Ryabinovoje[a]				32	88	720	n.d.		58.8		0.36
Mongolia											
Erdenetuin-Obo	calc-alkaline	Triassic	S-0572	20	33	74	16	< 0.1	0.06	0.03	0.61
Armenia											
Kadzharan[a]				24	84	3400			31.7		0.29
Palladium-enriched concentrates											
Greece[b]											
Skouries		Miocene	C.Sk.Po.F	2400	40	22 000	190	18.5	21	0	60
Burgaria[c]											
Elacite		Cretaceous	$n = 1$	1900	72	27 000			26.4		26.4
Elacite			$n = 1$	760	170	7600			19		4.5
Malaysia[c]											
Mamut				13 190	470	15 250			20.35		3
British Columbia. Cordillera[d]											
Allard, La plana	highly alkaline		$n = 3$	2320	3935	1740		0.4	27		0.6
Copper King Mine	highly alkaline		$n = 2$	2660	912	440		7	31.5		0.7

n.d. = no data.
[a] After Cabri (1981).
[b] Economou-Eliopoulos and Eliopoulos (2000).
[c] After Tarkian and Stribrny (1999).
[d] After Mutschler et al. (1985).

batholiths. PGE concentrations are very low, although very minor PGEs are recovered from copper refining in the USA (Cabri, 1981).

Porphyry-Cu systems associated with high alkali magmatism seem to be the most prospective source of PGE. Among them, the Copper Mountain deposit is hosted in a Mesozoic suite composed by highly alkaline potassic rocks, similar to the Allard stock syenites, La Plata Mountains, Colorado. The most salient feature in both the Allard and Copper Mountain deposits are their geochemically (not economically) high concentrations of Ba, Sr, Cu, Ag, Au, Pt and Pd, and low Mo, Pb and Zn content. The Pd and Pt contents in copper sulphide concentrates (18–40 wt.% Cu) from these deposits range from 1.9 to 3.2 ppm Pd and from 0.05 to 3.9 ppm Pt (Werle et al., 1984; Mutschler et al., 1985).

The Mamut Cu deposit (with ore reserves 179 million tons) of upper Miocene age, is located on the northern end of the island of Borneo. The deposit is linked to a high-K adamellite porphyry intrusion, with alteration characterized by strong silicification. The ore mineral assemblage is dominantly chalcopyrite accompanied by pyrite, pyrrhotite, magnetite, and hematite with minor molybdenite and sparse galena and sphalerite (Kosaka and Wakita, 1978). The significant content in precious metals (up to 17 ppm Au, 1600 ppb Pd and 390 ppb Pt) in flotation concentrates (20.7 wt.% Cu) is characteristic feature of the Mamut deposit (Tarkian and Stribrny, 1999).

In general, the Russia and Mongolia porphyry systems show lower Pd and Au contents than those in geochemically similar porphyry-Cu deposits (Table 7). For example, mineralized samples representing the main vein type mineralization at Skouries (Greece) show average Pd (110 ppb) and Au (3000 ppb) contents (Economou-Eliopoulos and Eliopoulos, 2000). In addition, assuming that Pd is mainly associated with chalcopyrite, calculating the measured Pd contents in chalcopyrite (measured contents are normalized to 100% chalcopyrite or 33 wt.% Cu), then the Pd values in the mineralized samples from Skouries (3300 ppb Pd), are comparable to that in the flotation concentrates (2400 ppb Pd at 21 wt.% Cu). Although the Pd content in flotation concentrates may attain relatively high values (Fig. 3), the average Pd content in the flotation concentrates from Russia is much lower (51 ppb Pd at 8.1 wt.% Cu) (Table 4), even calculated to 100% chalcopyrite (210 ppb Pd).

6. Factors controlling the precious metal concentration in porphyry Cu $\pm$ Mo deposits

The study of the contribution of mantle, oceanic and crustal wall rock to the parent magmas of porphyry-Cu intrusions, compared to subsequent petrogenetic processes still continues (Titley and Bean, 1981; Griffiths and Godwin, 1983; Lang and Titley, 1998). Further detailed studies are required to contribute to the delineation of processes critical to the formation of porphyry Cu $\pm$ Mo mineralization. Crustal contribution to a parent magma may be a common feature for porphyry Cu $\pm$ Mo porphyry intrusions (Jancoviv, 1980; Sillitoe, 1980; Berzina et al., 1997b; Sotnikov et al., 1998, 1999).

Given the oxidized (high fO_2/fS_2), salinity (30 to >75 wt.% alkali chlorides) and high temperature (400°C to >700°C) nature of the magmatic-hydrothermal fluids in porphyry Cu–Au deposits, it has been suggested that gold, like copper, must have been introduced as chloride complexes and underwent precipitation within the K-silicate alteration assemblage (Kosaka and Wakita, 1978; Seward, 1984; Cameron and Hattori, 1987; Cox and Singer, 1992; Sillitoe, 1993). The cooler, more dilute and more oxidized character of meteoric water-dominated fluids may permit the outward transport of Au as bisulphide complexes. Chloride complexes of gold ($AuCl_2^-$) have been favored as the dominant transport mechanism in mineralized solutions of the Skouries porphyry Cu deposit characterized by high temperature, salinity, and oxidation state alteration assemblages (Tompouloglou, 1981; Eliopoulos and Economou-Eliopoulos, 1991; Frei, 1992, 1995). Among the studied deposits within Siberia and Mongolia, the Aksug deposit is characterized by relatively high contents of Au and Cu and Cu/Mo ratio (Table 3), elevated Cl in minerals and relatively high oxidized character, as indicated by the presence of abundant anhydrite ($CaSO_4$) (Berzina and Sotnikov, 1995; Sotnikov et al., 2000).

The mineralogy of RGEs in porphyry systems indicates that palladium often occurs as merenskyite; for example, at grain boundaries of chalcopyrite II and bornite of the Skouries deposit (Tarkian et al., 1991), or exclusively as inclusions in chalcopyrite and bornite in the Santo Tomas II occurrence, Philippines, (Tarkian and Koopmann, 1995). These textural relations between base metal sulphides and Pd- and Au-telluride minerals suggest a deposition temperature of between 350°C and 490°C (Cabri, 1965; Nyman et al., 1990; Eliopoulos and Economou-Eliopoulos, 1991). Frei (1992, 1995), based on isotopic data, concluded that in the case of the Skouries deposit, the deposition of most of Cu is related to a major vein stage ($\sim$480°C to $\sim$380°C).

In addition, on the basis of fluid inclusion and isotopic data, most of the copper in the Sungun porphyry Cu deposit, Iran, has been interpreted to have deposited during the waning stages of the hydrothermal activity at temperatures of 300°C to 400°C (Hezarkhani et al., 1999). They calculated the Cu solubility to have been $>50\,000$ ppm during early potassic alteration (>450°C), whereas the Cu content of the initial fluids responsible for the ore deposition was estimated to have been 1200–3800 ppm. Copper solubility drops rapidly with decreasing temperature, and at 400°C it is approximately 1000 ppm, and at 350°C it is only 25 ppm. Furthermore, they emphasized that initially the fluid was highly undersaturated with respect to chalcopyrite, which is consistent with the presence of molybdenite (only occasionally chalcopyrite) in veins formed at $T>$ 400°C.

Our ongoing study indicates a small correlation between Cu and Mo ($r=0.42$), a strong positive correlation ($r=+0.98$) between Pd and Cu, and Pt–Mo (Table 6). The lack of a strong Cu–Mo correlation may confirm the precipitation of the molybdenite and chalcopyrite during different stages, and that the bulk Mo mineralization has probably taken place from fluids undersaturated with respect to chalcopyrite, at relatively higher temperature (Hezarkhani et al., 1999).

A limited variation of the Pd/Pt ratio, seems to be characteristic of the studied porphyry Cu–Mo deposits of Russia and Mongolia. The greater Pd and Pt contents in sulphide concentrates from the Aksug and Zhireken deposits may be related to their Na- and high-K-calc-alkaline parent magmas, respectively. Molybdenite concentrate from the Zhireken deposit (24 wt.% Mo and 2.7 wt.% Cu) shows high contents of Pd (684 ppb) and Pt (299 ppb) (Fig. 3, Table 4, sample s-0508g). Molybdenites from this system exhibit a significant enrichment in both Pt and Pd, especially in breccia-hosted samples (Fig. 4, Table 5). However, molybdenites and molybdenum flotation concentrate from the Sora deposit, which is related to high-K (and elevated F) calc-alkaline magmatism, show low Pt and Pd contents (Table 4, sample C-3; Fig. 4, Table 5). This difference between the Zhireken and Sora molybdenites seems to be consistent with the higher values of the Sr isotope data in the former than in the latter (Table 1), suggesting a major contribution of crustal rocks at depth prior the final emplacement. Recently, Xiong and Wood (2000) conducted a series of experiments on the solubility of Pd in hydrothermal systems. They concluded that in the earlier stages of porphyry copper systems fluids are fully capable of transporting at least 10 ppb Pd if sources for PGE are available.

Geotectonic setting appears to be one of substantial (but not decisive) factors for higher contents of Au, Pd and Pt in copper porphyry deposits. Island-arc porphyry copper deposits might host more Pd and Pt than the continental margin types ones (Tarkian and Stribrny, 1999). All copper–molybdenum porphyry deposits discussed are attributed to the beginning of rifting (Berzina et al., 1994, 1999b), but large plutonic intrusions that hosts porphyry systems have been interpreted as having formed in different geodynamic environments. Ore-bearing porphyry systems apparently inherited geochemical features of preceding magmatism (Berzina et al., 1999c). The Aksug ore-bearing porphyry complex occurred within preceding collisional-related plutons associated with island-arc basalt–andesite–rhyolite series and is characterized by highest Pd content and Pd/Pt ratio in sulphide concentrate as well as the highest Au contents in flotation and sulphide concentrates among the deposits studied. The Zhireken ore-bearing porphyry complex was formed with significant crustal contribution. In the Late Triassic–Middle Jurassic period, northern parts of Eastern Transbaikalia (where the Zhireken deposit is located) were formed in continental-margin setting with subduction of oceanic crust (Zonenshain et al., 1990). The mantle source was partially changed under the influence of subduction processes. Sedimentary rocks possibly participated in these processes, which could be reflected by elevated PGE contents of the Late Jurassic ore-bearing porphyry complex. This is, however, only our assumption, as PGE data for these sedimentary rocks are not presently available.

The wide range of Pt (34–380 ppb) and Pd (7–270 ppb) contents recorded in Zhireken molybdenites (Fig. 4, Table 5), the abundance of Pt over Pd ($Pt/Pd > 1$), and the association of the highest values in molybdenites from breccia (Sotnikov and Tsimbalist, 1992; Sazonov et al., 1997, 1998; Table 4, sample s-0508g) may suggest the role of magma fractionation and volatile concentration as important factors in breccia formation and Pt concentration.

Thus, in addition to crustal rock contributions, the volatile content of magma during its fractionation history and a high oxidation state of magma chemistry in calc-alkaline magmas seem to strongly control the nature of any evolved phases and their potential to partition metal from the melt (Burnham and Ohmoto, 1980). Since anhydrite is predominantly observed in the potassic zone of porphyry Cu systems (Beane, 1982), the common presence of anhydrite in the Aksug deposit may reflect a relatively high oxidized character. The geochemical features of porphyry Cu intrusions in cordillera settings, especially their alkali contents and the common occurrence of high concentration of REE and F along with high Pt and Pd content of Cu-sulphides have been attributed to the concentration of fluid phases (volatile component) at shallow intrusive levels (Mutschler et al., 1985).

7. Conclusions

Compilation of some data on the precious metal and associated trace element content in porphyry Cu–Mo systems of Russia and Mongolia combined with published data lead to the following conclusions:

1. There is a strong positive correlation between Cu–Pd ($r = 0.98$) and Mo–Pt ($r = 0.98$), and a good correlation between Cu and precious metals ($r \geq 0.51$).
2. Mineralogical and geochemical data indicate that both Pd and Pt were deposited during the major vein stage of molybdenum and copper.
3. The low Pd, Pt and Au concentrations are probably connected with the availability of source material and composition of the parent magma.
4. Relatively high contents of Pt and Pd in the Zhireken molybdenites associated with breccia may be caused by the assimilation of crust rocks and the magma fractionation (volatile component).

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