

## Enrichment of Platinum-group Elements (PGE) and Re-Os Isotopic Tracing for Porphyry Copper (Gold) Deposits

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**Abstract:** Platinum-group elements (PGE) in PGE-rich porphyry copper (gold) deposits are mainly Pt and Pd, whereas the concentrations of other PGE (Ru, Rh, Os, Ir) are significantly low. Moreover, Pt and Pd mainly exist in sulfides in the forms of crystal lattice or tiny platinum-group mineral (PGM) inclusions. The present data show that there is a positive relationship between Pt and Pd concentrations and Cu (Au) in porphyry copper (gold) deposits. The comparison of chondrite-normalized PGE distribution patterns between the ore-bearing porphyry intrusions and ore-barren porphyry intrusions in arc setting,  $^{187}\text{Os}/^{188}\text{Os}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and S isotopes for porphyry copper (gold) deposits shows that PGEs were mainly derived from the mantle, and fluids from subduction zones devoted trivial PGE to the magma. The porphyry copper (gold) deposits associated with subducted events are most probably enriched in PGE, whereas those related to crustal thickening, lithospheric delamination or underplating rarely concentrate PGE. The osmium isotopic compositions in porphyry copper (gold) deposits reveal that ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values are highly variable and not lower than those of primitive upper mantle (PUM) and mantle peridotite, however, osmium concentrations are commonly lower than mantle peridotite, suggesting that parental magmas of some porphyry intrusions had experienced crustal contamination during magma evolution. Experimental investigations have proved that PGE exist in the forms of  $\text{Cl}^-$  and  $\text{HS}^-$  complexes during transportation and migration of the ore-forming fluids. This paper summarizes previous studies including crucial controlling factors and mechanisms for PGE enrichment, and points out that the mantle-derived magmas parental to porphyry intrusions are the prerequisite for PGE enrichment in porphyry copper (gold) deposits. Favorable physical and chemical conditions (including salinity, temperature, pressure, pH, and oxygen fugacity) in hydrothermal fluids crucially control the PGE enrichment, and sulfur concentrations of melts play important roles in this process as well.

**Key words:** PGE, Re-Os isotope, forms of migration, enrichment process, porphyry copper (gold) deposits.

### 1 Introduction

Porphyry copper (gold) deposit is an important type for its prominent position in copper resource worldwide. For decades, due to the progress of analytical techniques and further research, increasing researchers were interested in the enrichment of platinum-group elements (PGE) in porphyry copper (gold) deposits. PGE including Pt, Pd, Os, Ir, Ru, and Rh, are essential precious metal material for modern science, advanced technology, and industrial application, and are also very important and short mineral

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resource in China. On the basis of the order of melting point and compatibility, PGE are divided into IPGE (Ir-group platinum-group elements, including Os, Ir, and Ru) and PPGE (Pd-group platinum-group elements, including Rh, Pt, and Pd), which would segregate in mantle partial melting process because of different compatibility (Keays et al., 1981; Barnes et al., 1985; Barnes and Picard, 1993; Garuti et al., 1997; Xu et al., 2003). Previous studies had shown that Pt, Pd enriched in several locations of some porphyry copper (gold) deposits can be mined with Au as by-products. The observations are significant for improving the comprehensive utilization of this type of

ore deposit. PGE, Au, and Cu are all siderophile and chalcophile elements, which should be strongly distributed into sulfide phase compared with the silicate melts during partial melting of the mantle (Peach et al., 1990; Fleet and Stone, 1991; Bezmen et al., 1994; Fleet et al., 1996). Therefore, further study on PGE geochemical characteristics of porphyry copper (gold) deposits can provide new methods and ideas for revealing the ore-forming processes of copper and gold in porphyry systems, and has also very important implications for understanding crust-mantle interaction and evolution. After Eliopoulos and Economou-Eliopoulos (1991) firstly reported the PGE enrichment in the Skouries porphyry copper deposit of north Greece, several geologists have conducted more studies on PGE enrichment in similar ore deposits worldwide (Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Daltry and Wolson, 1997; Economou-Eliopoulos and Eliopoulos, 2000, 2005; Sotnikov et al., 2001; Tarkian et al., 2003; Kioussis et al., 2005; Auge et al., 2005; Berzina and Korobeinikov, 2007; Pašava et al., 2010; Economou-Eliopoulos, 2011). This paper summarizes the present studies concerning PGE enrichment in porphyry copper (gold) deposits mainly from the following several aspects: (1) existing forms or state of PGE and the relationship between PGE concentrations and Cu (Au); (2) origin of PGE; (3) Re-Os isotopic compositions; (4) migration forms of PGE; (5) enrichment process of PGE; (6) ongoing research prospect of PGE and Re-Os isotope in porphyry copper (gold) deposits.

In China, several geologists have studied PGE characteristics of volcanic rocks and mafic-ultramafic intrusions associated with Ni-Cu-PGE sulfide and Fe-Ti-V oxide ore deposits (Zhong et al., 2002, 2006, 2011; Qi and Zhou, 2008; Song et al., 2006, 2009; Bai et al., 2012; Gao et al., 2012; Zhu et al., 2012; Bai et al., 2013; Yan et al., 2013), however, little attention was paid to the PGE characteristics of porphyry copper (gold) deposits. We hope that this paper can help the researchers to better understand the issue.

## 2 The Existing Forms or State of PGE and the Relationship between PGE Concentrations and Cu (Au)

Previous researches show that PGE are mainly present in crystal lattice of sulfides (chalcopyrite, tetrahedrite, bornite), or in the form of tiny PGM inclusions in chalcopyrite (Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Pašava et al., 2010). PGM mainly include merenskyite, tellurium, and sperrylite (Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Tarkian et

al., 2003; Daltry and Wolson, 1997; Economou-Eliopoulos and Eliopoulos, 2000; Sotnikov et al., 2001; Xiao and Lzplante, 2004; Auge et al., 2005; Berzina, et al., 2005, 2007; Pašava et al., 2010; Lefort et al., 2011; Ackerman et al., 2013), generally having diameters of 2–20  $\mu\text{m}$  (Tarkian et al., 2003; Berzina et al., 2005). Others can exist as moncheite, kotulskite and other unknown PGM (Tarkian and Stribrny, 1999). Pašava et al. (2010) used in-situ LA-ICP-MS method to analyze PGE in chalcopyrite and tetrahedrite, and discovered that PGE are homogeneously distributed in crystal lattice of these minerals. However, more data are needed to confirm the observation. Regarding the geochemical behavior, PGE are siderophile and chalcophile, and strongly compatible in sulfide minerals and metal phases (Bezoz et al., 2004; Lorand et al., 2008a). PGE and Cu, Au have similar geochemical behaviors during the process of magma evolution. This may be the reason that PGE commonly exist in sulfide minerals including chalcopyrite, tetrahedrite, and bornite.

In PGE-rich porphyry copper (gold) deposits, Pt concentrations range between 1 ppb and 490 ppb and Pd are between 2 ppb and 3440 ppb (as shown in Table 1). For most PGE-rich porphyry copper (gold) deposits, Pd and Pt concentrations are above the analytical detection limit, and Pd is generally higher than Pt. However, other PGE including Ir, Ru, Rh, and Os are lower than the analytical detection limits. It may be affected by the following three reasons: (1) IPGE (Os, Ir, Ru) and Rh are mildly compatible elements, and generally remained in mantle source. In contrast, PPGE (mainly Pt, Pd) are strongly incompatible elements, tending to enter the silicate magma during partial melting of the mantle (Keays et al., 1981; Barnes et al., 1985; Barnes and Picard, 1993; Mungall and Naldrett, 2008); (2) Pt and Pd have consistently geochemical behavior during normal magma fractionation and crystallization process, however, they can be separated by the formation of Pt-enriched alloys under high-temperature mantle (Lorand et al. 1999; 2008b; 2010). The Pt-rich alloys remained in mantle source cause that Pt concentration is significantly lower than Pd in mantle-derived rocks (Brügmann et al., 1993; Mungall, 2002; Maier and Barnes, 2004; Park et al., 2013b); (3) In hydrothermal fluids, the mobility of Pt and Pd is highly greater than other PGE (Ir, Rh, Ru and Os). On the basis of experimental observation, Barnes and Liu (2012) pointed out that the solubility and mobility of Pd are greater than Pt in hydrothermal fluids. This also likely generates higher Pd concentrations compared with Pt in most porphyry copper (gold) deposits. In addition, PGE distribution in a same deposit is heterogeneous, and the concentrations are highly variable in different parts of the

Table 1 PGE, Cu and Au concentrations in the PGE-rich porphyry copper (gold) deposits worldwide

Deposit name	Country	Sample type	Main ore minerals	Ir	Ru	Rh	Pt	Pd	Au	Cu*	Data source
Skouries	Greece	Granite porphyry		40			1	65	1040	13000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Granite porphyry		36			2	52	1800	8000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Granite porphyry		41			5	260	2000	18000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Granite porphyry		18			10	480	7200	23000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Granite porphyry		32			8	2	250	7400	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Mineralized porphyry	cp,py,mt	8			5	200	1900	11000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Mineralized porphyry	cp,mt	12			10	110	3100	40000	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Beneficiated ore	cp	19			10	70	450	2500	Eliopoulos and Economou-Eliopoulos, 1991
Skouries	Greece	Granite porphyry					5	200	1900	11000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Granite porphyry					5	45	3500	39000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Granite porphyry					10	480	7200	23000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Chalcopyrite concentrate	cp				40	2400	22000	210000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Chalcopyrite concentrate	cp				20	75	8200	56000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Chalcopyrite concentrate	cp				40	2400	22000	210000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Granite porphyry					6	180	2700	18000	Economou-Eliopoulos and Eliopoulos, 2000
Skouries	Greece	Disseminated/veinlet ore	cp(M),py,bo,mt				8	160	7300	2400	Tarkian et al., 1999
Santo Tomas	Philippine	Diorite porphyry					11	160	4300	8292	Tarkian and Koopmann, 1995
Santo Tomas	Philippine	Diorite porphyry					11	27	3180	6870	Tarkian and Koopmann, 1995
Santo Tomas	Philippine	Diorite porphyry					8	15	3150	6756	Tarkian and Koopmann, 1995
Santo Tomas	Philippine	Diorite porphyry					3	20	1100	2031	Tarkian and Koopmann, 1995
Santo Tomas	Philippine	Diorite porphyry					38	22	510	1199	Tarkian and Koopmann, 1995
La Escondida	Chile	Flotation concentrates	cp,py(M),cc				8	44	2050	330000	Tarkian and Stribny, 1999
El Salvador	Chile	Flotation concentrates	cp,py(M),bo,cc,mt				8	16	1250	283000	Tarkian and Stribny, 1999
El Teniente	Chile	Flotation concentrates	cp(M),py,bo,cc				8	32	300	321000	Tarkian and Stribny, 1999
Alumbra	Argentina	Flotation concentrates	cp(M),py,cc,bo,mt				8	35	31000	295000	Tarkian and Stribny, 1999
Majdanpek	Serbia	Flotation concentrates	cp(M),py,mt				16	130	2250	301000	Tarkian and Stribny, 1999
Majdanpek	Serbia	Disseminated/veinlet ore	cp,py(M),mt,bo				24	240	7000	224000	Tarkian and Stribny, 1999
Medet	Bulgaria	Disseminated/veinlet ore	cp,py(M),mt,hm,mo				8	160	5600	149000	Tarkian and Stribny, 1999
Medet	Bulgaria	Granite porphyry	bo				14	17	290	9700	Economou-Eliopoulos and Eliopoulos, 2000
Medet	Bulgaria	Granite porphyry					26	50	340	21500	Economou-Eliopoulos and Eliopoulos, 2000
Assarel	Bulgaria	Flotation concentrates	cp,py(M),cc,bo,mo				14	54	4800	27900	Tarkian et al., 1999
Assarel	Bulgaria	Granite porphyry					12	29	140	32000	Economou-Eliopoulos and Eliopoulos, 2000
Assarel	Bulgaria	Granite porphyry					33	10	140	32000	Economou-Eliopoulos and Eliopoulos, 2000
Ryabinovoje	Russia	Disseminated/veinlet ore	bo(M),cc,cp,py,gn				88	32	720	588000	Tarkian and Stribny, 1999
Kadzharan	Armenia	Disseminated/veinlet ore	cp,bo,py(M),mo				84	24	3400	317000	Tarkian and Stribny, 1999
Grasberg	Indonesia	Flotation concentrates	cp(M),py,bo,cc,mt				15	58	18000	238000	Tarkian and Stribny, 1999
Mamut	Malaysia	Flotation concentrates	cp(M),py,mo,mt				490	1600	17000	207000	Tarkian and Stribny, 1999
Mamut	Malaysia	Flotation concentrates	cp(M),py,mo,mt				450	1180	13500	200000	Tarkian and Stribny, 1999
Ok Tedi	Papua new guinea	Flotation concentrates	cp(M),py,bo,cc,mo				24	980	28000	373000	Tarkian and Stribny, 1999
Panguna	Papua new guinea	Disseminated/veinlet ore	cp(M),mo,mt,py				8	40	520	352000	Tarkian and Stribny, 1999
Fissoka	Greece	Mineralized quartz vein					40	49	2E+05	600	Economou-Eliopoulos and Eliopoulos, 2000
Fissoka	Greece	Mineralized quartz vein					10	17	6900	510	Economou-Eliopoulos and Eliopoulos, 2000
Fissoka	Greece	Mineralized quartz vein					20	6	4700	300	Economou-Eliopoulos and Eliopoulos, 2000
Fissoka	Greece	Mineralized quartz vein					20	4	1600	150	Economou-Eliopoulos and Eliopoulos, 2000
Fissoka	Greece	Mineralized quartz vein					10	3	55	60	Economou-Eliopoulos and Eliopoulos, 2000
Fissoka	Greece	Diorite porphyrite					10	3	45	200	Economou-Eliopoulos and Eliopoulos, 2000

Continued Table 1

Deposit name	Country	Sample type	Main ore minerals	Ir	Ru	Rh	Pt	Pd	Au	Cu*	Data source
Pontokerasia	Greece	Granite porphyry		10			2		60	14000	Economou-Eliopoulos and Eliopoulos, 2000
Tsar Asen	Bulgaria	Granite porphyry		51			49		95	9300	Economou-Eliopoulos and Eliopoulos, 2000
Copper Mountain	Philippines	Chalcopryrite concentrate	cp	125			2735		5100	284000	Economou-Eliopoulos and Eliopoulos, 2000
Copper Mountain	Philippines	Chalcopryrite concentrate	cp	155			2800		4500	279000	Economou-Eliopoulos and Eliopoulos, 2000
Copper Mountain	Philippines	Chalcopryrite and bornite	cp,bo	50			3250		4200	400000	Economou-Eliopoulos and Eliopoulos, 2000
Allard, La Plana	Philippines	Chalcopryrite concentrate	cp	2880			1920		1230	180000	Economou-Eliopoulos and Eliopoulos, 2000
Allard, La Plana	Philippines	Chalcopryrite concentrate	cp	3935			2320		1740	270000	Economou-Eliopoulos and Eliopoulos, 2000
Copper King Mine	Philippines	Chalcopryrite concentrate	cp	3900			2060		250	200000	Economou-Eliopoulos and Eliopoulos, 2000
Copper King Mine	Philippines	Chalcopryrite concentrate	cp	912			2660		440	315000	Economou-Eliopoulos and Eliopoulos, 2000
Copper King Mine	Philippines	Chalcopryrite and bornite	cp,bo	13600			6430		190	220000	Economou-Eliopoulos and Eliopoulos, 2000
Aksug	Russia	Disseminated ore	py,cp(M),mo	17			11		30	1550	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py(M),cp	17			9		51	2090	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py(M),cp,mo	21			12		47	950	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py(M),cp,bo	21			12		204	2400	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py(M),cp,mo,bo	34			20		72	1010	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py,cp(M),mo	20			23		26	350	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py,cp,mo(M),bo	21			31		24	154	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore	py(M),cp,mo	24			12		36	3800	Sotnikov et al., 2001
Aksug	Russia	Disseminated ore		21			12		200	2400	Berzina et al., 2005b
Aksug	Russia	Granodiorite porphyry		20			23		26	350	Berzina et al., 2005b
Aksug	Russia	Granodiorite porphyry		29			17		178	10840	Berzina et al., 2005b
Aksug	Russia	Sulphide ore	cp,py,mo	96			62		5450	196500	Berzina et al., 2005b
Aksug	Russia	Flotation concentrate	cp	76			83		2740	102000	Berzina et al., 2005b
Aksug	Russia	Flotation concentrate	cp,mo	25			920		1210	53600	Berzina et al., 2005b
Aksug	Russia	Flotation concentrate	cp	10			18		21	490	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	py,mo(M),cp	10			12		17	15	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	py,mo(M),cp	10			17		16	1880	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	py,cp,mo(M)	10			13		19	133	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	py(M),cp,mo	10			10		16	240	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	py(M),mo,cp	10			9		12	14	Sotnikov et al., 2001
Sora	Russia	Disseminated ore	mt(M),py	10			9		12	14	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(M),cp,mo	28			12		18	2250	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(M),cp	25			16		19	2040	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(M),cp	32			17		37	1740	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(trace)	16			14		21	4050	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py,cp(M),mo	22			11		20	2690	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated/veinlet ore	py(M),cp	10			7		17	1110	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated/veinlet ore	py(M),mo,cp	18			11		17	190	Sotnikov et al., 2001
Erdenetuin	Mongolia	Breccia	py(trace)	28			11		17	43	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(M),cp,rt	20			13		21	125	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	py(trace)	15			23		23	100	Sotnikov et al., 2001
Erdenetuin	Mongolia	Disseminated ore	mo,py(M),cp	27			26		26	36	Sotnikov et al., 2001
Zhireken	Russia	Disseminated/veinlet ore	mo,py(M),cp	28			14		32	1000	Sotnikov et al., 2001
Zhireken	Russia	Disseminated/veinlet ore	cp,mo,py(M)	21			16		23	147	Sotnikov et al., 2001
Zhireken	Russia	Disseminated/veinlet ore	cp,mo,py(M)	37			21		29	113	Sotnikov et al., 2001
Zhireken	Russia	Disseminated/veinlet ore	py,mo(M),cp	32			13		60	27	Sotnikov et al., 2001
Zhireken	Russia	Disseminated/veinlet ore	py,mo(M),cp	31			11		19	53	Sotnikov et al., 2001
Elatstie	Bulgaria	Disseminated ore	py,mo(M),cp	11			43		9400	157000	Tarkian et al., 2003

Continued Table 1

Deposit name	Country	Sample type	Main ore minerals	Ir	Ru	Rh	Pt	Pd	Au	Cu*	Data source
Elatsite	Bulgaria	Ore	py, cp				4	10	235	4500	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				14	23	560	8700	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				22	500	4500	217000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				108	285	3500	148000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				8	64	900	28000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				24	295	1850	158000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				5	28	490	20000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				5	43	720	21000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				10	160	8200	232000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				68	215	16000	313000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				310	140	9000	266000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				7	23	12400		Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				18	60	2000	67000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				120	74	5000	107000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				21	54	3600	84000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				13	80	2200	48000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				33	230	10400	133000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				16	90	2850	45000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				1	14	540	5100	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				2	25	420	7400	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				1	6	580	8100	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				15	64	2050	48000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				9	130	5000	243000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				4	82	2700	93000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				10	155	6200	247000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				2	560	74000	518000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				39	92	14500	170000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				225	840	14500	192000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				40	580	8800	299000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				310	800	6800	109000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				310	780	8200	120000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				310	490	6400	56000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	mt, bn, cp				52	205	21500	160000	Tarkian et al., 2003
Elatsite	Bulgaria	Ore	py, cp				155	740	14000	256000	Tarkian et al., 2003
Elatsite	Bulgaria	Flotation concentrate	py, cp				19	1	31	7600	Economou-Eliopoulos and Eliopoulos, 2000
Elatsite	Bulgaria	Pyrite, chalcopyrite	cp, py				170	760	7600	19000	Tarkian and Stribrny, 1999
Elatsite	Bulgaria	Flotation concentrates	cp(M), py, bo, mo				72	1900	27000	25900	Tarkian and Stribrny, 1999
Elatsite	Bulgaria	Disseminated/veinlet ore	cp(M), py, mt, bo				4	2	1820	112000	Auge et al., 2005
Elatsite	Bulgaria	Ore	cp, bo	0.3			319	3440	1820	370000	Auge et al., 2005
Elatsite	Bulgaria	Ore	cp, bo	0.6			64	2070	34100	370000	Auge et al., 2005
Elatsite	Bulgaria	Ore	cp, bo	0.4			349	1980	7800	332000	Auge et al., 2005
Elatsite	Bulgaria	Ore	cp, bo	0.2			7	292	33000	490000	Auge et al., 2005
Elatsite	Bulgaria	Ore	cp, bo	0.2			1.1	9	400	5330	Auge et al., 2005
Elatsite	Bulgaria	Granodiorite porphyry					3.3	11	560	4500	Auge et al., 2005
Elatsite	Bulgaria	Granodiorite porphyry					38.3	7	531	5230	Auge et al., 2005
Elatsite	Bulgaria	Granodiorite porphyry					7.4	9	579	5830	Auge et al., 2005

Continued Table 1

Deposit name	Country	Sample type	Main ore minerals	Ir	Ru	Rh	Pt	Pd	Au	Cu*	Data source
Elaitsite	Bulgaria	Granodiorite porphyry				4	1.1	5	313	3990	Auge et al., 2005
Elaitsite	Bulgaria	Granodiorite porphyry				1.1	6.5	4	261	5720	Auge et al., 2005
Elaitsite	Bulgaria	Granodiorite porphyry				13.1	48	14	361	5480	Auge et al., 2005
Elaitsite	Bulgaria	Granodiorite porphyry				20	71	48	1350	10000	Auge et al., 2005
Elaitsite	Bulgaria	Granodiorite porphyry				45.6	78	71	1110	10000	Auge et al., 2005
Elaitsite	Bulgaria	Granodiorite porphyry				3.1	4.3	4.3	1825	12400	Auge et al., 2005
Kalmakyr	Uzbekistan	Ore	py,mo,cp	0.5		0.7	3.1	4.3	969	9600	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	cp,py,au	0.7		1.1	5.2	5.3	659	4900	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	py,mo,cp	0.3		0.3	0.4	1.7	986	2600	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	py,cp,au	0.3		0.2	1.7	17.3	7355	29700	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	py,mt,cp	0.3		0.6	9.1	73.1	16337	71000	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	py,cp	0.3		0.6	11.2	42	3912	56600	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	cp,py,mt	1.3		4.1	4.5	291.7	695	5100	Pašava et al., 2010
Kalmakyr	Uzbekistan	Ore	ga,sph,cp,py	0.3		0.2	8.9	6.3	4092	24000	Pašava et al., 2010
Kalmakyr	Uzbekistan	Average above ore(n=8)		0.5		1	5.5	55.2	600	600	Pašava et al., 2010
Kalmakyr	Uzbekistan	Mineralized porphyry	py,mo,cp,gn,sph	0.2		0.1	5.4	5.8	66	500	Pašava et al., 2010
Kalmakyr	Uzbekistan	Mineralized porphyry	py,sph	0.3		0.2	13.1	11.4	29	200	Pašava et al., 2010
Kalmakyr	Uzbekistan	Mineralized porphyry	py,sph,gn,cp	0.2		0.1	1.8	0.5			Pašava et al., 2010

Note: Ir,Ru,Rh,Pt,Pd,Au concentrations are in ppb; Cu concentration is in ppm

cp: chalcopyrite, py: pyrite, mt: magnetite, bo: bornite, mo: molybdenite, sph: sphalerite, gn: galena, cc: chalcocite, hm: hematite, M: main.

ore bodies. In general, PGE concentrations of wall rocks are lower than the mineralized porphyry intrusion (Economou-Eliopoulos and Eliopoulos, 2000), likely to be controlled by PGE geochemical characteristics and mineral assemblages.

Sotnikov et al. (2001) studied the distribution of Pt, Pd, and Au in typical porphyry copper (gold) deposits in Mongolia and Russia, and suggested that PGE distribution generally have no apparent relationship with alteration types, and PGE are not enriched or depleted in specific alteration zones. Furthermore, they proposed that the relatively constant PGE concentrations of different porphyry copper (gold) deposits in Mongolia and Russia might be due to similar source region and parental magma. Tarkian and Stribny (1999) summarized PGE concentrations in porphyry copper (gold) deposits from fifteen countries, and pointed out that the forming ages of intrusion, chemical compositions, and magma types seem to not affect PGE concentrations.

In contrast, it has been shown that Au and Cu concentrations display a positive correlation with Pt, Pd concentrations in the Santo Tomas porphyry Cu-Au deposit of Philippines (Tarkian and Koopmann, 1995). Tarkian and Stribny (1999) summarized PGE concentrations in thirty-three porphyry copper deposits, and revealed a very consistently positive relationship between Cu, Au and PGE, i.e., PGE contents increasing with increasing Cu and Au. Sotnikov et al. (2001) checked Pt, Pd and Cu, Au concentration in 34 samples from Aksug, Sora, Zhireken, and Erdenetuin, and also showed positive correlations between Pt, Pd and Cu, Au. On the basis of the published data, this paper plots the correlations for Pt, Pd, Cu, and Au (Fig. 1), and show that positive correlations occur between Pt, Pd and Cu, Au, especially between Au and Pt, Pd, indicating that Pt, Pd and Cu, Au are likely to be derived from an identical source.

Tarkian and Stribny (1999) suggested that Au-rich porphyries are promising exploration targets for Pd and Pt. As shown in the chondrite-normalized PGE-Au-Cu patterns for porphyry copper (gold) deposits and different end-members of the Earth (Fig. 2), the PGE-rich porphyry Cu deposits are generally characterized by obviously positive Au anomalies, and thus Au enrichment may be an important indicator for identifying PGE enrichment of porphyry copper deposits.

### 3 The Origin of PGE

PGE, enriched in the core and having a small amount in the mantle, are highly siderophile, and very low in the crust (Borisov and Palme, 1997; Xu et al., 2003; Dale et

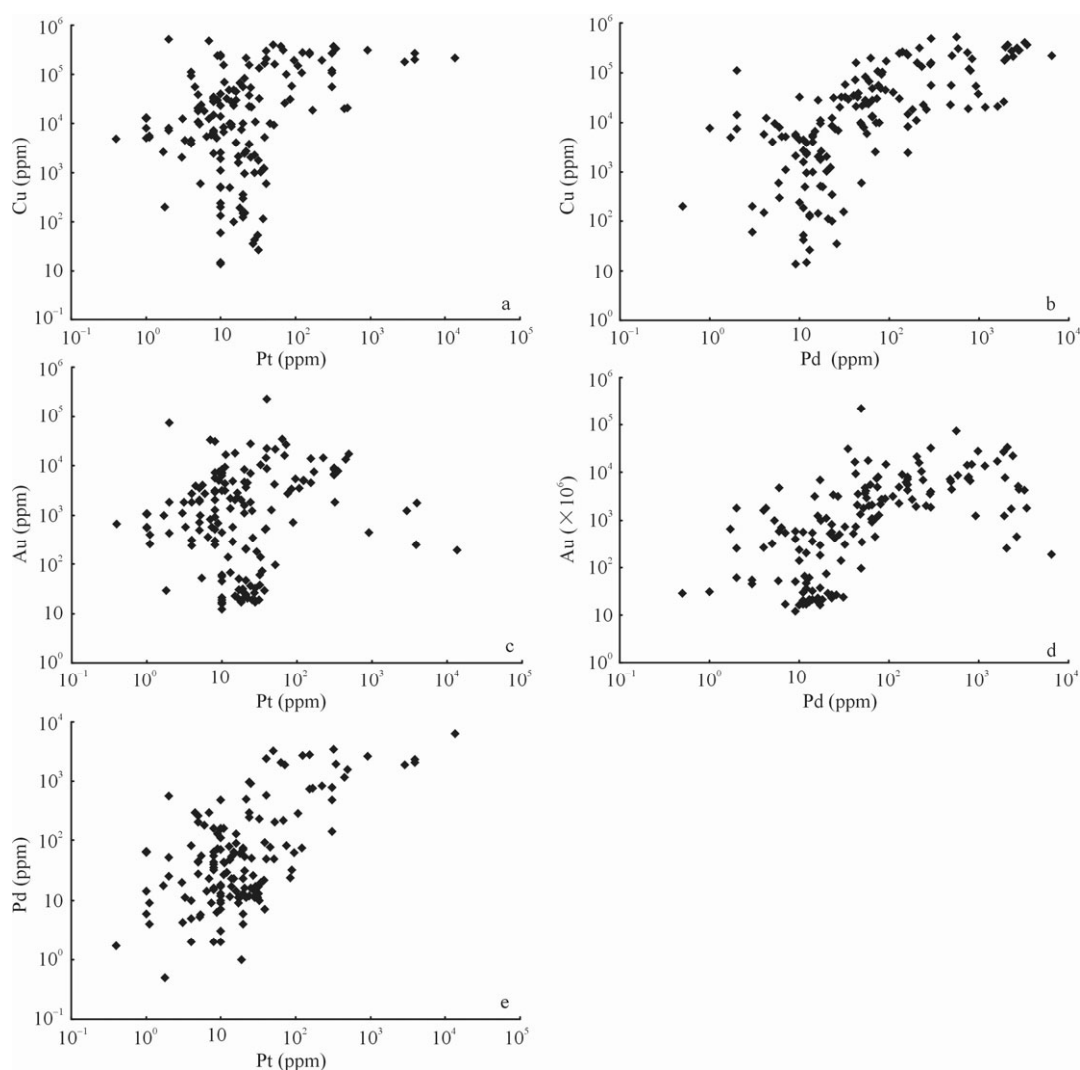


Fig. 1. Plots of correlations for Pt vs. Cu, Pd vs. Cu, Pt vs. Au, Pd vs. Au and Pt vs. Pd in the PGE-rich porphyry Cu (Au) deposits.

(a), Plot of correlations for Pt vs. Cu; (b), Plot of correlations for Pd vs. Cu; (c), Plot of correlations for Pt vs. Au; (d), Plot of correlations for Pd vs. Au; (e), Plot of correlations for Pt vs. Pd.

al., 2009; Wang et al., 2012). IPGE are compatible during partial melting process of the mantle, however, PPGE are incompatible and easily enter into melts (Keays et al., 1981; Barnes et al., 1985; Barnes and Picard, 1993; Maier and Barnes, 2004; Lorand et al., 1999, 2008a, 2010). The different compatibility of IPGE and PPGE can be used to distinguish the degree of partial melting of the mantle, magma crystallization and fractionation, and segregation of sulfide during magma evolution (Barnes et al., 1985; Brüggmann et al., 1993; Bezmen et al., 1994; Barnes and Francis, 1995; Garuti et al., 1997; Chazey and Neal, 2005). The formation of porphyry deposits is related to the magmatic source and the magma evolution process, thus making PGE to be good indicators for these factors.

As stated above, some porphyry copper (gold) deposits could concentrate PGE, whereas the others could not. PGE are generally rich in arc-island porphyry copper (gold)

deposits other than collision-related porphyry copper (gold) deposits. The arc-island porphyry copper (gold) systems are generated mainly in magmatic arc (including back-arc) environments subjected to a spectrum of regional-scale stress regimes (Sillitoe, 2010). The genetic model can be briefly described by the following processes according to plate tectonics theory. The mantle wedge would melt partially into magma when the oceanic plate subducted under the continental plate to a favorable depth. The low-density magma could arise up into the continental crust and then mixed with the magma generated by partial melting of the continental crust. The mixed magma characterized by abundant water and high oxygen fugacity ( $fO_2$ ) (Richards, 2003, 2009) finally formed the porphyry Cu deposits through complex processes of magma and hydrothermal evolution. Previous studies have shown that PGE are generally rich in arc-island porphyry copper

(gold) deposits, for examples, the giant porphyry copper (gold) deposits in west coasts of Chile and Argentina, Santo Tomas of Phillippines, Skouries of Greece (Tarkian and Koopmann, 1995; Tarkian and Stribny, 1999; Daltry and Wolson, 1997; Economou-Eliopoulos and Eliopoulos, 2000, 2005; Sotnikov et al., 2001; Tarkian et al., 2003; Kioussis et al., 2005; Auge et al., 2005; Berzina and Korobeinikov, 2007; Pašava et al., 2010; Economou-Eliopoulos, 2011).

Collision-related porphyry copper (gold) deposits include the porphyry deposits formed during continent-continent collision, collision after oceanic crust subduction (continent-arc collision), and extension after continent-continent collision. Because of crustal thickening mainly occurring during continent-continent collision and continent-arc collision, delamination, and underplating during extension after continent-continent collision (Richards, 2003, 2009; Hou et al., 2003, 2004, 2006, 2011; Hou, 2010; Hou and Cook, 2009), crust-mantle interaction and partial melting would happen in the crust-mantle transitional area (Stern and Kilian, 1996; Rapp et al., 1999; Thompson et al., 2001; Tsuchiya et al., 2005; Zhao et al., 2013; Ackerman et al., 2013). The magma formed from partial melting process of MASH (Melting, Assimilation, Storage, Homogeneous; Hildreth and Moorbath, 1988) and evolved finally into porphyries related to porphyry deposits systems and epithermal deposits systems. Until now, no reports about PGE enrichment in collision-related porphyry copper (gold) deposits have been presented. For example, no PGE enrichment data have been published in porphyry copper (gold) deposits from Tibet Plateau and Central Asian Orogenic Belt (CAOB).

A comparison of the PGE patterns for arc-island porphyry copper (gold) deposits with other ore-barren bodies under similar setting (see Fig. 3 and data from Table 2), indicates that PPGE (Pt, Pd) contents in porphyry copper (gold) deposits are obviously higher than those of the ore-barren lavas and intrusions formed in arc island, which is probably due to the existence of more sulfides in ore-bearing porphyries. Moreover, the observation suggests that most of PGE are hosted in sulfides of porphyry copper (gold) deposits. During the subducting process of oceanic plate, large amounts of fluids were brought into the subduction zone, which reduced greatly the melting point for mantle rocks, and caused higher degree of partial melting of the mantle, thereby dissolving more sulfides into melts (Naldrett et al., 1979; Crocket, 1979; Lorand et al., 1999, 2008a, 2010) and generating PGE-rich magma. Richards (2005) suggested that due to the emplacement of hot and oxidized magma derived from asenthosphere or lithospheric

thickening and thermal rebound, Au and PGE-rich sulfides remained in lithospheric mantle or lower continental crust re-melted, thus generating the Au and PGE-rich magma. Recent studies show that high-Mg andesites from south mid-Atlantic ridge (Kamenetsky et al., 2001; Michael and Kamenetsky, 2002) are highly enriched in PGE (46ppm Pt, 41ppm Pd, and 14ppm Au in sulfides; Kamenetsky et al., 2013), supporting the existence of Au and PGE-rich andesitic magma originated from the mantle.

In contrast to acr-island porphyry copper (gold) deposits, almost no PGE enrichments have been reported for collision-related porphyry copper (gold) deposits. The low-degree partial melting caused by thickening of the continental crust, underplating, and delamination in the lower continental crust (LCC) or the mantle, would leave sufficient sulfides containing PGE in LCC or mantle and generate relatively Au- and PGE-poor magma. McInnes et al. (1999) and Jagoutz et al. (2007) reported Fe-Ni sulfides with high concentrations of Au and PGE in xenoliths from mantle and LCC. If the residual PGE-rich sulfides were left in LCC and mantle, the parental magma would contain low PGE concentrations, and thus could not finally generate PGE enrichment in porphyry copper (gold) deposits.

Pašava et al. (2010) determined PGE concentrations in the Kalmakyr porphyry Au-Mo deposit, Uzbekistan, and suggested that PGE are crustal source because of similar shapes of chondrite-normalized PGE-Au pattern with the Kalmakyr continental crust. However, other researchers suggested that the parental magmas of the ore-forming bodies were dominantly derived from the mantle but experienced various degrees of crustal contamination, on the basis of Os isotopic compositions for porphyry copper (gold) deposits (Freydier et al., 1997; Mathur et al., 2000a, 2001; McBride et al., 2001; Dreher et al., 2005; Cardon et al., 2006, 2008). This possibly indicates that PGE in porphyry copper (gold) deposits originated from the mantle. Thompson et al. (2001) studied geochemical and isotopic compositions of the British Columbia alkaline porphyry copper (gold) deposit, and suggested PGE were derived from the mantle. Hattori and Keith (2001) proposed that mafic magma played an important role in the formation of the Mount Pinatubo porphyry copper deposit in Phillippines, and supplied large amounts of sulfur and chalcophile elements into felsic magma to generate the porphyry deposit. Maughan et al. (2002) noted that Cr, Ni, Ba, and PGE are enriched in the Bingham porphyry copper (gold, molybdenum) deposit, USA, and suggested that mafic magma mixed with felsic magma to form the parental magma of the Bingham porphyry copper deposit. Halter et al. (2005) proposed that the ore-forming fluids did not exsolve from the parental magma of dacitic



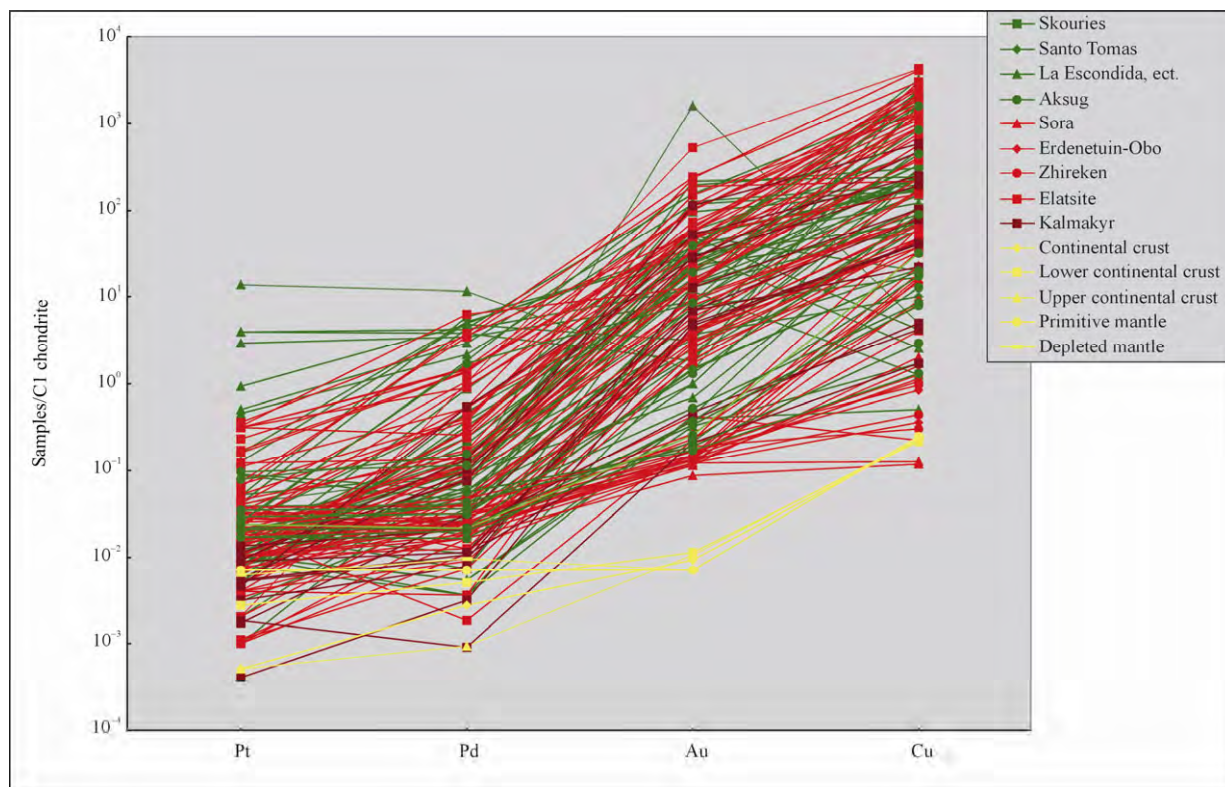


Fig. 2. C1 chondrite-normalized PGE-Au-Cu patterns in porphyry copper (gold) deposits and distinct units of the Earth. Data source: PGE in porphyry copper (gold) deposits from Table 1. continental crust (Rudnick and Gao, 2003); primitive mantle (McDonough and Sun, 1995); lower continental crust (Rudnick and Gao, 2003); upper continental crust (Rudnick and Gao, 2003); depleted mantle (Salters and Stracke, 2004); C1 chondrite (McDonough and Sun, 1995). La Escondida etc include: La Escondida, El Salvador, El Teniente, Alumbra, Majdanpek, Medet, Assarel, Ryabinovoje, Kadzharan, Grasberg, Mamut, Ok Tedi, Panguna, Fissoka, Pontokerasia, Tsar Asen, Copper Mountain, Allard La Plana, Copper King Mine.

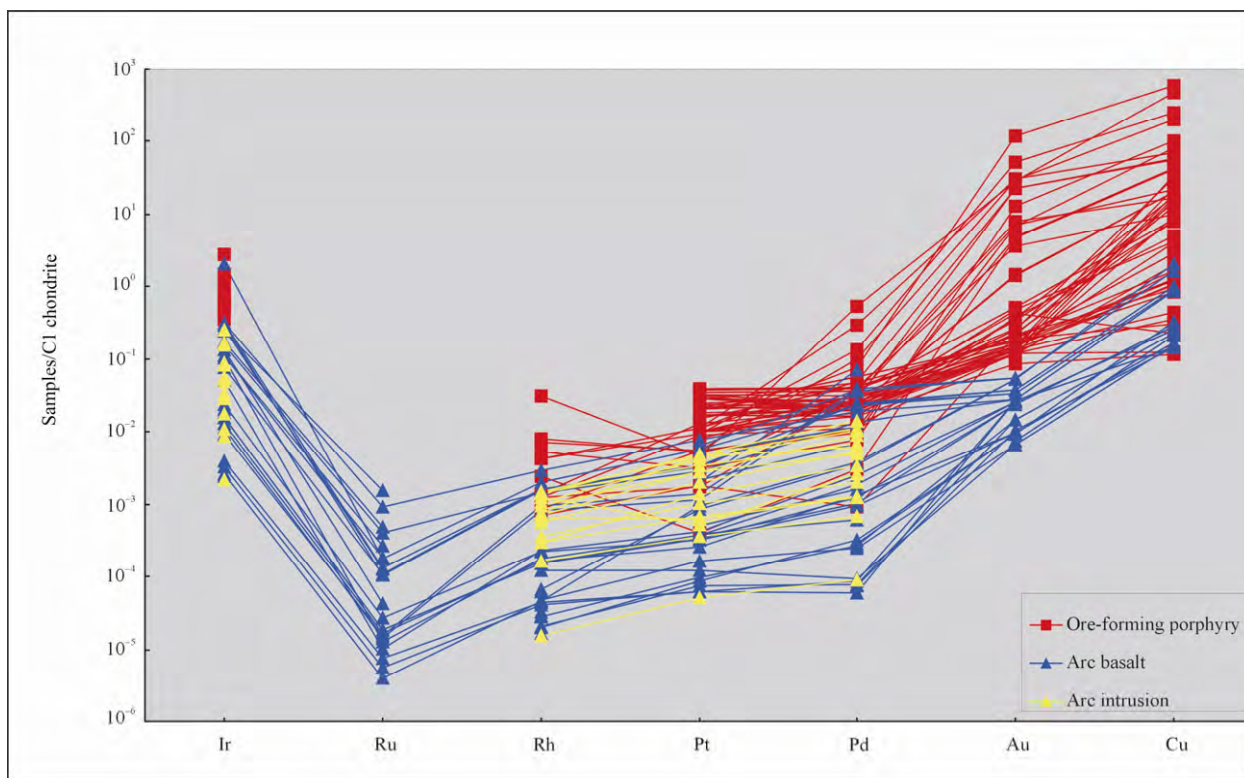


Fig. 3. PGE patterns of the volcanic rocks and plutons in arc island setting. Ore-forming porphyry from Table 1, Arc basalt and arc intrusion from Table 2. C1 chondrite from McDonough and Sun, 1995.

**Table 2 PGE concentrations of intrusions in island arc setting.**

	Rock type	Ir	Ru	Rh	Pt	Pd	Au	Cu*	Data source
Arc basalt	Arc basalt of Kamchatka	0.12	0.09		2.02	38.4			Ivanov et al., 2008
	Arc basalt of Kamchatka	0.05	0.19		6.26	20.4			Ivanov et al., 2008
	Arc basalt of Kamchatka	0.11	1.11		5.13	6.5			Ivanov et al., 2008
	Arc basalt of Kamchatka	0.08	0.35		0.39	0.33			Ivanov et al., 2008
	Arc basalt of Kamchatka	0.06	0.03		2.15	3.75			Ivanov et al., 2008
	Arc basalt of Kamchatka	0.05	0.13		0.49	0.88			Ivanov et al., 2008
	Arc basalt from Pual Ridge	0.07	0.288	0.187	2.8	7.61	3.84	103	Park et al., 2013a
	Arc basalt from Pual Ridge	0.146	0.639	0.385	7.61	10.4	3.84	103	Park et al., 2013a
	Arc basalt from Pual Ridge	0.146	0.092	0.207	3.4	13	4.73	109	Park et al., 2013a
	Arc basalt from Pual Ridge	0.94	0.125	0.265	5.71	12.7	4.73	109	Park et al., 2013a
	Arc basalt from Pual Ridge	0.136	0.073	0.198	3.2	13.7	5.2	122	Park et al., 2013a
	Arc basalt from Pual Ridge	0.035	0.076	0.208	3.32	12.9	5.2	122	Park et al., 2013a
	Arc basalt from Pual Ridge	0.005	0.01	0.105	1.13	20	7.52	196	Park et al., 2013a
	Arc basalt from Pual Ridge	0.004	0.011	0.126	1.36	21	7.52	196	Park et al., 2013a
Arc intrusion	Arc andesite from Pual Ridge			0.009	0.843	1.94	7.42	249	Park et al., 2013a
	Arc andesite from Pual Ridge	0.001	0.003	0.006	0.927	2.12	7.42	249	Park et al., 2013a
	Arc andesite from Pual Ridge	0.046	0.009	0.023	0.371	1.03	3.57	30	Park et al., 2013a
	Arc andesite from Pual Ridge	0.023	0.007	0.03	0.41	1.41	3.57	30	Park et al., 2013a
	Arc andesite from Pual Ridge			0.003		0.16	1.33	40	Park et al., 2013a
	Arc andesite from Pual Ridge			0.003	0.084	0.175	1.33	40	Park et al., 2013a
	Arc dacite from Pual Ridge	0.001		0.004	0.095	0.146	2.02	27	Park et al., 2013a
	Arc dacite from Pual Ridge			0.003	0.075	0.042	2.02	27	Park et al., 2013a
	Arc dacite from Pual Ridge	0.007	0.013	0.02	0.36	0.561	3.31	34	Park et al., 2013a
	Arc dacite from Pual Ridge	0.007	0.013	0.02	0.333	0.671	3.31	34	Park et al., 2013a
	Arc dacite from Pual Ridge	0.011	0.019	0.029	0.315	0.522	1.35	20	Park et al., 2013a
	Arc dacite from Pual Ridge	0.006	0.012	0.021	0.254	0.74	1.35	20	Park et al., 2013a
	Arc dacite from Pual Ridge	0.008		0.016	0.121	0.051	0.92	19	Park et al., 2013a
	Arc dacite from Pual Ridge	0.01		0.006	0.162	0.137	0.92	19	Park et al., 2013a
	Arc dacite from Pual Ridge			0.008			1.06	25	Park et al., 2013a
	Arc dacite from Pual Ridge			0.004			1.06	25	Park et al., 2013a
	Arc dacite from Pual Ridge	0.002	0.005	0.006	0.062	0.033	3.7	17	Park et al., 2013a
	Arc dacite from Pual Ridge	0.002	0.004	0.005	0.06	0.047	3.7	17	Park et al., 2013a
	Arc dacite from Pual Ridge			0.004		0.041	1.47	17	Park et al., 2013a
	Arc dacite from Pual Ridge			0.002			1.47	17	Park et al., 2013a
	Gabbro from Boggy Plain	0.04		0.181	4.86	7.87			Park et al., 2013b
	Gabbro from Boggy Plain	0.026		0.138	4.04	5.77			Park et al., 2013b
	Gabbro from Boggy Plain	0.077		0.1	4.5	6.22			Park et al., 2013b
	Gabbro from Boggy Plain	0.037		0.186	3.33	3.8			Park et al., 2013b
	Gabbro from Boggy Plain	0.116		0.196	4.58	3.42			Park et al., 2013b
	Gabbro from Boggy Plain	0.025		0.126	2.8	2.73			Park et al., 2013b
	Granodiorite	0.015		0.09	2.78	4.96			Park et al., 2013b
	Granodiorite	0.045		0.093	2.81	4.73			Park et al., 2013b
	Granodiorite	0.008		0.074	1.96	2.88			Park et al., 2013b
	Granodiorite	0.004		0.16	0.52	1.42			Park et al., 2013b
	Granodiorite	0.005		0.039	1.38	1.86			Park et al., 2013b
	Granite	0.022		0.047	1.02	1.09			Park et al., 2013b
	Granite	0.013		0.039	0.66	0.71			Park et al., 2013b
Granite	0.072		0.085	0.63	0.68			Park et al., 2013b	
Granite	0.013		0.021	0.36	0.37			Park et al., 2013b	
Aplite	0.001		0.002	0.05	0.05			Park et al., 2013b	

Note: Ir,Ru,Rh,Pt,Pd,Au concentrations are in ppb; Cu concentration is in ppm.

intrusion for the giant Bajo de la Alumbrera porphyry Cu-Au deposit, Argentina, and were derived from the andesitic magma of more mafic.

The summarized ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> and  $\delta^{34}\text{S}$  values of PGE-rich porphyry copper (gold) deposits in Table 3 show that the  $\delta^{34}\text{S}$  value range from  $-2.4\%$  to  $10.2\%$ , mostly close to  $0\%$ , and the ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> values are relatively low, implying that the parental magmas generating the ores were derived mainly from the mantle and experienced various degrees of crustal contamination. The observations also confirm that PGE in porphyry copper (gold) deposits are probably dominantly from the mantle.

#### 4 The Re-Os Isotopic Compositions

Following the improvement of precision and accuracy for analyses, the Re-Os isotopic system is progressively used to date the ore-forming age and trace the magmatic sources of porphyry copper (gold) deposits. Molybdenite is the most used mineral to determine the ore-forming ages and pyrite and chalcopyrite are also successfully utilized to obtain the ages (Ruiz et al., 1997; Freyrier et al., 1997; Stein et al., 1998; Wang et al., 2008). Rhenium easily substitutes molybdenum in the crystal lattice of molybdenite, whereas it is difficult for osmium. As a result, it is generally considered that no or minor common

**Table 3 The compositions of ( $^{87}\text{Sr}/^{86}\text{Sr}$ )<sub>i</sub> and  $\delta^{34}\text{S}$  in the PGE-rich porphyry copper (gold) deposits**

Country	Deposit name	Samples	( $^{87}\text{Sr}/^{86}\text{Sr}$ ) <sub>i</sub>	Data source
Russia	Aksug	Porphyry	0.70454–0.70496	Sotnikov et al., 2001
Russia	Sora	Porphyry	0.7040–0.7046	Sotnikov et al., 2001
Mongolia	Zhireken	Porphyry	0.70510–0.70642	Sotnikov et al., 2001
Mongolia	Erdenetuin	Porphyry	0.70406–0.70424	Sotnikov et al., 2001
Greece	Skouries	Porphyry	0.7079–0.7081	Frei, 1995
Bulgaria	ElatSITE	Porphyry	0.7042–0.7043	Sotnikov et al., 2001
Country	Deposit name	Samples	$\delta^{34}\text{S}$ (‰)	Data source
Russia	Aksug	Pyrite	(–1.2)–3.1	Berzina and Korobeinikov, 2007
Russia	Aksug	Chalcopyrite	(–1.8)–(–0.7)	Berzina and Korobeinikov, 2007
Russia	Aksug	Molybdenite	2.5–3.2	Berzina and Korobeinikov, 2007
Russia	Sora	Pyrite	6.6–9.6	Berzina and Korobeinikov, 2007
Russia	Sora	Chalcopyrite	7.4–8.5	Berzina and Korobeinikov, 2007
Russia	Sora	Molybdenite	8.3–10.2	Berzina and Korobeinikov, 2007
Mongolia	Erdenetiin	Pyrite	(–1.6)–1.5	Berzina and Korobeinikov, 2007
Mongolia	Erdenetiin	Chalcopyrite	(–1.3)–0.5	Berzina and Korobeinikov, 2007
Mongolia	Erdenetiin	Molybdenite	(–0.9)–1.4	Berzina and Korobeinikov, 2007
Greece	Skouries	Chalcopyrite	(–2.14)–(–0.62)	Frei, 1995
Greece	Skouries	Pyrite	(–0.23)–0.30	Frei, 1995

osmium exist in molybdenite and almost all the Os is the product of the decay of rhenium, thus can be used to date the ore-forming ages (Luck and Allegre, 1982; Suzuki et al., 1993; Takahashi et al., 2007; Li et al., 2012). Numerous successful cases of using molybdenite to obtain the ages of porphyry copper deposits have been reported (e.g., Stein et al., 1997, 1998; Selby and Creaser, 2001a, 2001b; Hou et al., 2006, 2011). This paper mainly discusses the implications of Re-Os system for tracing the porphyry deposits.

Recently, Re-Os system exhibits its unique advantage for demonstrating the source of magma parental to porphyry copper (gold) deposits, especially for those generated under convergent plate margin setting. Osmium, similar to other PGE in geochemical characteristics and behavior, belongs to PGE, and thus the osmium isotope is a good tracer for the origin of PGE. Rhenium and osmium are siderophile and chalcophile, however, during the process of magma differentiation, rhenium is mildly incompatible and osmium is strongly compatible (Shirey and Walker, 1998; Carlson et al., 2008; Suzuki et al., 2011; Widom, 2011). Therefore, rhenium is concentrated in the crust but osmium is in the mantle, producing large variations in Re/Os ratio between the crust and the mantle and significant difference in osmium isotope for the two end-members. The great contrast of osmium composition for the crust and subducted mantle wedge in an arc-island setting suggests that Re-Os isotopic compositions of the intrusions hosting porphyry copper (gold) deposits could be utilized to trace the origin of the ore-forming intrusions.

Previously published data show that most geologists focused on Re-Os system of sulfides (mainly including chalcopyrite, pyrite, bornite, and ore minerals or concentrates) from porphyry copper (gold) deposits, whereas little attention was paid to the studies on Re-Os isotopic characteristics of the ore-bearing intrusion

(Freydier et al., 1997; Mathur et al., 2000a, 2000b, 2000c; Barra et al., 2003). Rhenium and osmium are heterogeneously distributed in the ore minerals of porphyry copper (gold) deposits, with Re concentration much higher than Os, which are largely related to the source and origin of magma. Berzina et al. (2005a) studied the porphyry copper (molybdenium) deposits in Mongolia and Russia and suggested that rhenium concentrations are associated with the compositions of parental magma, differentiation and crystallization, source material and physicochemical conditions ( $f\text{O}_2$ , P, T). Ackerman et al. (2013) revealed that most rhenium exists in base-metal sulfides, and there is an obviously positive relationship between rhenium and sulfur concentrations.

The osmium isotopic ratios of different porphyry deposits shown in Table 4 are variable relative to those of present mantle (~ 0.13; Mathur et al., 2000a; Suzuki et al., 2011) and continental crust (>0.5, about 1.0–1.5, Suzuki et al., 2011), but not lower than primitive mantle. In Figure 4, the ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values for porphyry deposits exhibit a broad range, which is not lower than upper mantle and mantle peridotite, with lower osmium concentrations than peridotite. With the exceptions of few samples, low ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values close to present mantle and high osmium concentrations in the El Teniente giant porphyry copper deposit, indicate that the parental magma was dominantly derived from the mantle and subjected to minor crustal contamination. Low ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values and osmium contents near that of upper primitive mantle in two pyrite samples from Andacollo imply the mantle origin of parental magma as well. For other deposits such as the Bagdad, Quebrada Blanca, Chuquicamata, El Salvador, Cerro Colorado and Agua deposits, the ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values are highly variable, with few even higher than average crust, and their osmium concentrations are lower than those of oceanic basalts, basalts and picrites, implying

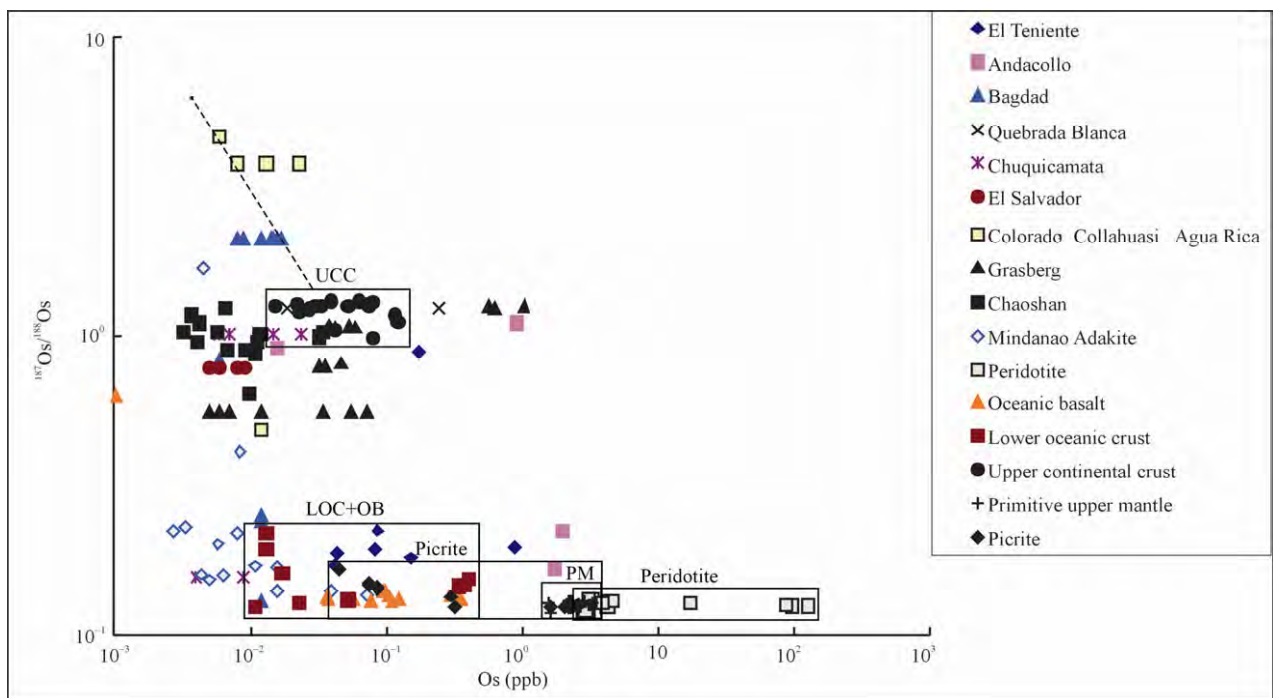


Fig. 4. Plot of  $^{187}\text{Os}/^{188}\text{Os}$  vs. Os for PGE-rich porphyry Cu (Au) deposits, mantle-derived rocks and average continental crust.

Data source: All  $^{187}\text{Os}/^{188}\text{Os}$  in the PGE-rich porphyry Cu (Au) deposits from Table 4; peridotite (Martin, 1991); oceanic basalts (Pegram and Allegre, 1992; Martin, 1991); lower oceanic crust (Blusztajn et al., 2000); upper continental crust (Esser and Turekian, 1993); primitive upper mantle (Meisel et al., 1996); picrites (Woodland et al., 2002; Zhang et al., 2008); all the  $^{187}\text{Os}/^{188}\text{Os}$  values except those for peridotites, oceanic basalts, upper continental crust, lower oceanic crust, primitive mantle, picrites are initial values. UCC: Upper Continental Crust, LOC: Lower Oceanic Crust; OB: Oceanic Basalt, PM: Primitive Mantle.

that the parental magmas of these deposits had been subjected to severely crustal contamination. Compared with the Mindanao adakites derived from the mantle, these deposits have similar osmium concentrations but higher  $(^{187}\text{Os}/^{188}\text{Os})_i$  values, possibly indicating that the parental magmas of ore-forming porphyries had experienced considerable crustal contamination during emplacement. In contrast to sulfide mineral samples from porphyry deposits mentioned above, porphyry rock samples have much lower osmium concentrations. The El Teniente and Andacollo giant porphyry copper deposits exhibit low  $(^{187}\text{Os}/^{188}\text{Os})_i$  values, suggesting that voluminous magmas predominantly originated from partial melting of the mantle with involvement of minor crustal material, thus generating huge storage of Cu. Mathur et al. (2000a) suggested that porphyry copper deposits with lower  $(^{187}\text{Os}/^{188}\text{Os})_i$  values have larger reserves. All the above observations imply that more compositions from the mantle for the parental magmas would produce larger copper deposits enriched in PGE.

With the exception of few up to 2.12, most  $(^{187}\text{Os}/^{188}\text{Os})_i$  values range from 0.13 to 1.69 in published data for porphyry copper (gold) deposits, indicating that the parental magmas were dominantly derived from the mantle (Mathur et al., 2000a; Cardon et al., 2006, 2008; Dreher et al., 2005) and experienced little crustal

contamination (Freydier et al., 1997; Mathur et al., 2000a; Dreher et al., 2005). Halter et al. (2005) checked the Farallón Negro andesitic volcanic complexes in northwestern Argentina, and found that the amphibole hosts melt inclusions with basaltic composition ( $\text{SiO}_2$ , 44 wt%), however, the plagioclase rhyodacitic inclusions ( $\text{SiO}_2$ , 71 wt%) in an andesitic rock containing amphibole and plagioclase, indicating that the parental magma was involved with felsic composition. Righter et al. (2002) studied Re, Os, and Cl contents in arc-type basalts and indicated that very minor Re, Os, and Cl were contained in subduction fluids, therefore could not significantly increase the  $^{187}\text{Os}/^{188}\text{Os}$  values in melts. They further proposed that radiogenic Os measured in many arc-type basalts is most likely due to crustal interaction rather than a subduction fluid with high and radiogenic Os concentrations. The interaction between plate melts and mantle wedge is a possible way of contaminating crustal material (Rapp et al., 1999; Tsuchiya et al., 2005), and of course, the parental magma could be also subjected to minor crustal contamination during ascending. Economou-Eliopoulos and Eliopoulos (2000) and Sotnikov et al. (2001) suggested that crustal contribution to a parental magma might be a common feature for porphyry copper intrusions and further detailed studies are required to define the degree of crustal contamination. The crust-

**Table 4 Os isotopic compositions of adakites and PGE-rich porphyry copper (gold) deposits**

Deposit name	Sample	Os (ppb)	( <sup>187</sup> Os/ <sup>188</sup> Os) <sub>i</sub>	Data source
El Teniente	Chalcopyrite	0.082	0.193	Freydier et al., 1997
El Teniente	Chalcopyrite	0.874	0.196	Freydier et al., 1997
El Teniente	Chalcopyrite	0.153	0.18	Freydier et al., 1997
El Teniente	Sphalerite	0.044	0.187	Freydier et al., 1997
El Teniente	Bornite	0.087	0.223	Freydier et al., 1997
El Teniente	Bornite	0.042	0.171	Freydier et al., 1997
El Teniente	Pyrite	0.176	0.884	Freydier et al., 1997
Andacollo	Pyrite	0.016	0.909	Freydier et al., 1997
Andacollo	Pyrite	0.915	1.11	Freydier et al., 1997
Andacollo	Pyrite	1.732	0.166	Freydier et al., 1997
Andacollo	Pyrite	1.982	0.221	Freydier et al., 1997
Bagdad	Pyrite	0.008	2.12	Barra et al., 2003
Bagdad	Pyrite	0.008	2.12	Barra et al., 2003
Bagdad	Pyrite	0.016	2.12	Barra et al., 2003
Bagdad	Pyrite	0.017	2.12	Barra et al., 2003
Bagdad	Pyrite	0.015	2.12	Barra et al., 2003
Bagdad	Pyrite	0.012	2.12	Barra et al., 2003
Bagdad	Pyrite	0.009	2.12	Barra et al., 2003
Bagdad	Pyrite	0.014	2.12	Barra et al., 2003
Bagdad	Chalcopyrite	0.006	0.83	Barra et al., 2003
Bagdad	Chalcopyrite	0.012	0.13	Barra et al., 2003
Bagdad	Chalcopyrite	0.012	0.25	Barra et al., 2003
Bagdad	Chalcopyrite	0.012	0.24	Barra et al., 2003
Quebrada Blanca	Pyrite	0.019	1.23	Mathur et al., 2000a
Quebrada Blanca	Pyrite	0.238	1.23	Mathur et al., 2000a
Quebrada Blanca	Pyrite	0.244	1.23	Mathur et al., 2000a
Chuquicamata	Pyrite	0.024	1.01	Mathur et al., 2000a
Chuquicamata	Pyrite	0.006	1.01	Mathur et al., 2000a
Chuquicamata	Pyrite	0.006	1.01	Mathur et al., 2000a
Chuquicamata	Pyrite	0.015	1.01	Mathur et al., 2000a
Chuquicamata	Pyrite	0.007	1.01	Mathur et al., 2000a
Chuquicamata	Pyrite	0.009	0.155	Mathur et al., 2000a
Chuquicamata	Pyrite	0.004	0.155	Mathur et al., 2000a
El Salvador	Pyrite	0.009	0.785	Mathur et al., 2000a
El Salvador	Pyrite	0.006	0.785	Mathur et al., 2000a
El Salvador	Pyrite	0.006	0.785	Mathur et al., 2000a
El Salvador	Chalcopyrite,pyrite	0.006	0.785	Mathur et al., 2000a
El Salvador	Chalcopyrite,pyrite	0.005	0.785	Mathur et al., 2000a
El Salvador	Pyrite	0.008	0.785	Mathur et al., 2000a
Cerro Colorado	Pyrite	0.008	3.8	Mathur et al., 2000a
Cerro Colorado	Pyrite	0.013	3.8	Mathur et al., 2000a
Cerro Colorado	Pyrite	0.023	3.8	Mathur et al., 2000a
Collahuasi	Pyrite	0.012	0.49	Mathur et al., 2000a
Agua Rica	Pyrite	0.006	4.68	Mathur et al., 2000a
Grasberg	Chalcopyrite,pyrite	0.636	1.24	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	1.024	1.26	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.571	1.26	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.053	1.08	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.038	1.09	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.042	1.07	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.06	1.07	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.036	0.79	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.032	0.79	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.047	0.81	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.007	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.005	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.006	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.056	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.034	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.071	0.56	Mathur et al., 2000c
Grasberg	Chalcopyrite,pyrite	0.012	0.56	Mathur et al., 2000c
Chaoshan	Pyrrhotite	0.03213	0.996	Wang et al., 2008
Chaoshan	Pyrrhotite	0.01109	0.951	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00577	1.032	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00325	1.033	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00364	1.184	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00971	0.644	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00678	0.895	Wang et al., 2008
Chaoshan	Pyrrhotite	0.03408	1.03	Wang et al., 2008
Chaoshan	Pyrrhotite	0.01184	1.016	Wang et al., 2008

Continued Table 4

Deposit name	Sample	Os (ppb)	( <sup>187</sup> Os/ <sup>188</sup> Os) <sub>i</sub>	Data source
Chaoshan	Pyrrhotite	0.00657	1.245	Wang et al., 2008
Chaoshan	Pyrrhotite	0.00403	0.955	Wang et al., 2008
Chaoshan	Pyrrhotite	0.0042	1.103	Wang et al., 2008
Chaoshan	Pyrrhotite	0.01066	0.87	Wang et al., 2008
Chaoshan	Pyrrhotite	0.0094	0.901	Wang et al., 2008
Mindanao adakite	Adakite	0.0085	0.4079	Dreher et al., 2005
Mindanao adakite	Adakite	0.011	0.1695	Dreher et al., 2005
Mindanao adakite	Adakite	0.0033	0.2262	Dreher et al., 2005
Mindanao adakite	Adakite	0.016	0.1676	Dreher et al., 2005
Mindanao adakite	Adakite	0.0045	1.6902	Dreher et al., 2005
Mindanao adakite	Adakite	0.0027	0.2201	Dreher et al., 2005
Mindanao adakite	Adakite	0.005	0.152	Dreher et al., 2005
Mindanao adakite	Adakite	0.0058	0.201	Dreher et al., 2005
Mindanao adakite	Adakite	0.0044	0.1587	Dreher et al., 2005
Mindanao adakite	Adakite	0.0082	0.219	Dreher et al., 2005
Mindanao adakite	Adakite	0.016	0.1405	Dreher et al., 2005
Mindanao adakite	Adakite	0.0063	0.1575	Dreher et al., 2005
Mindanao adakite	Adakite	0.071	0.1357	Dreher et al., 2005
Mindanao adakite	Adakite	0.04	0.1392	Dreher et al., 2005

mantle interaction caused by the subduction of oceanic crust may be one major way of experiencing crustal contamination (Stern and Kilian, 1996; Rapp et al., 2004; Tsuchiya et al., 2005; Dale et al., 2009; Ackerman et al., 2013). In summary, previous studies on Os isotopic compositions indicate that PGE in porphyry copper (gold) deposits were predominantly derived from the mantle.

## 5 The Migration Forms of PGE

Traditionally, PGE are considered to be not transported with hydrothermal fluids due to their insolubilities, and only magma process can complete the transport and enrichment of PGE (Xiong and Wood, 2000). The discovery of PGE and PGM enrichment in porphyry copper (gold) deposits (Eliopoulos and Economou-Eliopoulos, 1991; Tarkian and Koopmann, 1995; Daltry and Wolson, 1997; Tarkian and Stribrny, 1999; Sotnikov et al., 2001; Auge et al., 2005), and experimental investigations in hydrothermal geochemistry of PGE (Mountain and wood, 1988; Wood and Mountain, 1989; Wood et al., 1992; Wood and Normand, 2008; Sassani and Shock, 1990, 1998; Mckibben et al., 1990; Mernagh et al., 1994; Pan and Wood, 1994; Ganmmmons, 1995, 1996; Borisov et al., 1997; Mavrogenes and O'Neill, 1999; Middlesworth and Wood, 1999; Xiong and Wood, 1999, 2000; Halter et al., 2005; Hanley et al., 2005; Peregoedova et al., 2006; Berzina and Korobeinikov, 2007; Bell et al., 2009; Fonseca et al., 2009; Simon and Pettke, 2009; Blaine et al., 2011; Barnes and Liu, 2012) provide increasing evidence that Pt and Pd of PGE could be dissolved in hydrothermal fluids under appropriate geological conditions, favorable chemical composition and proper physical properties, and were transported by hydrothermal fluids to precipitate in available structural positions in porphyry copper deposits under favorable

physicochemical conditions.

On the basis of the geochemistry of mantle ultramafic xenoliths in the Kamchatka arc, Kepezshinskas et al. (2002) proposed that PGE exhibit mobility during sub-arc metasomatism. Lefort et al. (2011) studied fluid inclusions in the Mount Milligan porphyry copper (gold) deposit, Canada, and suggested PGE could migrate completely with hydrothermal fluids, and provided the possibility of migrating, transporting and finally precipitating PGE in epithermal deposits.

Figure 2 shows that Pt and Pd concentrations in PGE-rich porphyry copper (gold) deposits are apparently greater than primitive mantle, indicating that PGE in porphyry copper deposits system possibly experienced the process of transport and re-enrichment. Due to the chalcophile and siderophile behavior of PGE, they would prefer to enter into the crystal lattices of copper-bearing sulfides or form PGM during precipitation.

On the basis of experimental study on the complexes of PGE under different physical and chemical conditions, Mountain and Wood (1988) suggested that anion including OH<sup>-</sup>, Cl<sup>-</sup>, and HS<sup>-</sup> play an important role for PGE transporting in hydrothermal fluids. According to HSAB (Hard-Soft-Acid-Base) theory proposed by Pearson, Pt<sup>2+</sup> and Pd<sup>2+</sup> are soft acid cation, and easily combine with soft base anion including OH<sup>-</sup>, Cl<sup>-</sup>, and HS<sup>-</sup> into complexes, however, they are difficult to combine with hard base anion like as CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>2-</sup>, and F<sup>-</sup>. Even if they combine with hard base anion into complexes, but due to the poor stability, these complexes cannot play a significant role in PGE transporting. Further, they pointed that at a range of 25°C–250°C, the solubility of hydrosulfides increase with increasing temperature, but chlorides and hydroxides decrease accordingly. When the temperature is above 250°C, the trend will reverse. Wood and Mountain (1989, 1992) investigated physical and

chemical conditions ( $fO_2$ , pH) for stability of hydrosulfides, chlorides, hydroxides and amides containing Pt and Pd, and suggested that  $OH^-$  cannot play a role for Pt and Pd transporting under geological conditions. Mckibben et al. (1990) proposed that in hydrothermal fluids PGE can be migrated in the forms of hydrosulfides, and chlorides, which is supported by numerous later researches (Wood et al., 1992; Mernagh et al., 1994; Pan and Wood, 1994; Ganmmmons, 1995, 1996; Borisov et al., 1997; Sassani and Shock, 1998; Mavrogenes and O'Neill, 1999; Middlesworth and Wood, 1999; Xiong and Wood, 1999, 2000; Hanley et al., 2005; Peregoedova et al., 2006; Wood and Normand, 2008; Fonseca et al., 2009; Simon and Pettke, 2009; Blaine et al., 2011; Barnes and Liu, 2012). Barnes and Liu (2012) suggested that bisulfide complex is one of the existing forms of Pt and Pd in acidic-neutral solutions under reduced and moderate oxidation condition at 300°C, and chloride complexes are only important under extremely acidic or oxidized conditions. Xiong and Wood (2000) showed that Os concentrations are different at same  $fO_2$ , pH, temperature (500°C), and different levels of KCl solution, and up to 130 ppb in higher levels of KCl solution. The experiment exhibited that the higher oxygen fugacity in solution, Os concentration is greater (up to 1705 ppb in experimental conditions), indicating that Os exist in the form of chlorides and is affected by oxygen fugacity in hydrothermal fluid. The observation of hydrothermal geochemistry of Pt and Pd by Ganmmmons (1996) suggested that  $Pt^{4+}$  may be the dominant form in low temperature and high oxygen fugacity brine (e.g., seawater). Wood et al. (1992) investigated aqueous geochemistry of Pt, Pd and Au, suggesting that Pd exists in the form of  $PdCl_3^-$  but not  $PdCl_4^{2-}$  in most geological hydrothermal fluids at 300°C. Ganmmmons (1996) revealed that in oxidized, Cl-rich solutions, the solubility of Pt is extremely high at  $pH < 6$ , such that the mobility of this metal will most likely be limited by surface adsorption reactions and/or its abundance and rate of dissolution in the enclosing rock or soil.

Xiong and Wood (2000) applied their experimental results to porphyry copper systems having similar temperature, pH, salinity and oxygen fugacity to the

experimental parameters, and found that a typical porphyry system can transport at least 40 tons of Pd and about 3 tons of Os. Consequently, they proposed that porphyry systems have the capacity to transport sufficient PGE to form at least mid-sized PGE deposits. Numerous previous experiments show that the solubility of Pt and Pd is different in  $Cl^-$ -rich and  $HS^-$ -rich solution with distinct pH,  $fO_2$ , salinity, pressure, and temperature. Table 5 summarizes the temperatures and salinities of fluid inclusions in PGE-rich porphyry copper (gold) deposits, and show that most of them precipitated at medium-high salinities (4.2%–60% NaCl), medium-high homogenization temperatures (170–520°C), however, requiring more data to support the observation.

## 6 The Enrichment Process of PGE

The above demonstration indicates that PGE in porphyry copper deposits predominantly originated from the mantle. During partial melting process of the mantle, sulfur in magma played an important role for the enrichment of PGE and other chalcophile and siderophile elements in porphyry copper deposits (Thompson et al., 2001; Halter et al., 2005; Sotnikov et al., 2006; Simon and Ripey, 2011). Barnes and Liu (2012) proposed that Pt and Pd concentrations are lower in sulfide-poor environments compared to sulfide-rich environments, which might be the reason why Pt and Pd are widely present in sulfide ores but poor in country rocks with only minor sulfides. It has been shown that the solubility of Pt increases with increasing  $fS_2$  (Borisov and Palme, 1997, 2000; Ertel et al., 1999; Fonseca et al., 2009). Sulfur solubility is approximately 1000ppm in silicate magma from partial melting of the mantle (Mavrogenes and O'Neill, 1999), however, it is about 250ppm in upper mantle, thus requiring high degree (>25%) of mantle melting to reach sulfur saturation (Keays, 1995; Mungall, 2002), which generally rarely occurs. In contrast, the simulation results of Naldrett (2010) show that all sulfides are dissolved in melts, when the degree of partial melting up to 18%. Nevertheless, only picritic or basaltic-picritic magmas generated by high degree of partial melting can dissolve all or most sulfur in upper mantle, and carry more

**Table 5 Temperatures and salinities of fluid inclusions in the PGE-rich porphyry copper (gold) deposits**

Country	Deposit name	Salinity of inclusions (%, NaCl)	Homogeneous temperature of inclusions (°C)	Data source
Canada	Mount Milligan	4.2	170–270	Lefort et al., 2011
Philippines	Santo Tomas	35–>60	380–520	Tarkian and Koopmann, 1995
Malaysia	Mamut	35–55	300–450	Nagano et al., 1997
Serbia	Majdanpek		240–500	Tarkian and Stribny, 1999
Bulgaria	ElatSITE		320–350	Tarkian and Stribny, 1999
Bulgaria	ElatSITE	20–60	200–535	Von et al., 2005
Bulgaria	Medet	12	370–400	Tarkian and Stribny, 1999
Kazakhstan	Bozshakol		180–380	Tarkian and Stribny, 1999

chalcophile and PGE due to sulfide un-saturation in this magma. Borisov and Palme (1997, 2000) investigated the solubility of Pt in silicate melts, and suggested that with oxygen fugacity decreasing, Pt concentrations in three silicate melts reduce at temperature 1400°C, 1450–1500°C, 1450°C. Numerous researches have indicated that porphyry Cu-Au deposits related to felsic intrusions were generally formed under high oxygen fugacity condition (Blevin and Chappell, 1992; Candela, 1992; Hedenquist and Lowenstern, 1994; Ballard et al., 2002; Robb, 2004; Jugo, 2009; Sillitoe, 2010; Sun et al., 2013). During the formation of typical arc porphyry copper deposits, the involvement of large amounts of high oxygen fugacity fluids released from subducted oceanic slab caused high-degree partial melting of the overlying mantle wedge, thus generating highly oxidized magma. This is very favorable for the dissolution of PGE.

The basaltic magma generated by relatively high-degree partial melting could experience MASH process, following the exchange of material and energy with crust during ascent. The primitive basaltic magmas might stall at the base of lower crust due to density contrasts, and heat released from the mafic magma caused partial melting of crustal rocks to generate felsic melts. The two magmas would mix into intermediate, calc-alkaline, and low-density hybrid magma (Maughan et al., 2002; Richards, 2009). The mixed magma (andesitic) migrated up at a depth of 5–10 km and exsolved high-salinity fluids capable of carrying large amounts of metal (Fe, Cu, Au, and PGE) due to the magma cooling. The fluids were likely to further mix with fluids from shallow crust into mixed fluids to generate porphyry Cu-Au-Mo deposits at a depth of 1–4 km.

Previous studies suggested that high oxygen fugacity (generally > FMQ+2) and water-rich (> 4 wt%) andesitic magma is the key to generate magmatic hydrothermal deposits (Candela, 1992; Richards, 2003). High oxygen fugacity can restrain the formation of sulfides to prevent the escape of Au and PGE in magma (Hamlyn et al., 1985; Thompson et al., 2001; Auge et al., 2005; Richards, 2005). Water-saturated magma will ascend into upper crust, where chalcophile and siderophile can be redistributed (Candela and Holland, 1984). Candela (1989) suggested that Au and PGE-rich sulfides at magmatic stage may be oxidized or altered at later hydrothermal stage, and released metal into volatile phase. Nevertheless, PGE exist in the forms of chlorides and hydrosulfides in fluids at hydrothermal stage, can be transported by fluids via different fracture channels, and precipitate in enough space and physicochemical conditions (e.g.,  $fO_2$ , pH, salinity, temperature, pressure). At high oxygen fugacity state, magnetite precipitates in shallow crust, causing the decrease of sulfur solubility in

fluids and generating Au, Cu, Pt, Pd-rich sulfides, or resulting in the combination of PGE with Te, Sb, Bi, As to form PGM in hydrothermal fluids. It is possible that multi-stage mineralization occur during the above processes. As shown in Figure 2, PGE concentrations in porphyry copper (gold) deposits are obviously higher than those of lower continental crust, upper continental crust, primitive mantle, depleted mantle, indicating that during the transporting, precipitating processes, PGE were enriched in porphyry copper system. Economou-Eliopoulos and Eliopoulos (2000) observed Pt, Pd, Au concentrations in the Skouries porphyry copper deposit of Greece, and suggested that the redistribution-concentration by leaching process existed in this deposit, and Pd concentrations in the ores might be strongly controlled by the magmatic fluids of the hydrothermal system.

There are many factors affecting the PGE enrichment in porphyry copper (gold) deposits, however, which may be dominantly controlled by the following crucial factors summarized from previous studies:

(1) The parental magmas of the ore-bearing intrusions were mainly derived from the mantle, indicating that Cu and Au concentrations increase with the increasing contributions from the mantle, and thus the possibility of PGE enrichment in porphyry copper (gold) deposits is greater. Especially, Au-rich porphyry copper deposits may be an important target for exploring PGE enrichment in porphyry system. Therefore, the involvement of magma originated from the mantle during the ore-forming process is a prerequisite for the PGE enrichment in porphyry copper (gold) deposits and plays a crucial role.

(2) Sulfur concentration plays an important role for PGE enrichment at magmatic stage. Due to sulfur un-saturation at magmatic stage, PGE can be captured and preserved in magma, which is important for transportation and precipitation of PGE at later hydrothermal stage.

(3) At suitable pH, oxygen fugacity, salinity, temperature, and pressure, PGE can be transported by chlorides and hydrosulfides in hydrothermal fluids, and precipitate in favorable space. Thus, the pH, oxygen fugacity, salinity, temperature, and pressure in hydrothermal fluids are the key factors for the PGE precipitation and enrichment.

## 7 The Ongoing Research Prospect of PGE and Re-Os Isotope in Porphyry Copper (Gold) Deposits

The following conclusions are drawn from the above summaries:

(1) PGE are mainly present in the crystal lattices of sulfides, or in the forms of tiny PGM inclusions in



porphyry copper (gold) deposits.

(2) Generally, the PGE enrichment exist in arc-island porphyry copper (gold) deposits and PGE are dominantly derived from the mantle.

(3) PGE can be transported by chlorides and hydrosulfides in hydrothermal fluids.

(4) In porphyry copper (gold) deposits, the PGE enrichment process experienced magmatic and hydrothermal stages. Sulfur concentration plays a key role at magmatic stage, and pH, oxygen fugacity, salinity, temperature, and pressure play a crucial role at hydrothermal stage for PGE enrichment.

(5) ( $^{187}\text{Os}/^{188}\text{Os}$ )<sub>i</sub> values are highly variable due to different degrees of crustal contamination, and Os concentrations in related intrusions are much lower than those in sulfides.

As demonstrated above, PGE and Re-Os isotopic studies could help to further elucidate the genetic model for porphyry deposits and the evolution process of parental magma. Therefore, ongoing research concerning PGE and Re-Os characteristics of porphyry copper (gold) deposits could focus on the issues below:

(1) Following the improvement of analytical methods, more in-situ determinations of PGE concentrations in sulfides or other minerals could further distinguish the characteristics of PGE enrichment and distribution in porphyry system, which is important for thoroughly illustrating the origin, transport, and precipitation mechanism of PGE.

(2) Intensive studies on compositions from fluid inclusions and experiments of fluid simulation could help to further understand the transporting and precipitation mechanism of PGE, especially for the variations of PGE with the changes of pH, oxygen fugacity, sulfur fugacity, salinity, temperature, and pressure.

(3) Os, one of PGE, is significantly different from Re in their geochemical behavior. Thus, Re-Os isotopic system should play an important role in understanding the PGE enrichment process in porphyry copper (gold) deposits. In addition, comparative studies on Re-Os isotopic compositions between PGE-rich and PGE-poor porphyry copper (gold) deposits could gain further insight into the forming conditions and processes.

(4) It also needs to confirm whether all Au-rich porphyry copper deposits have elevated PGE concentrations and Au-poor porphyry copper deposits could enrich PGE, thus requiring more quantitative and qualitative studies on the relationship between PGE and Au in porphyry copper (gold) deposits.

(5) Comparative studies between PGE-rich and PGE-poor porphyry copper deposits and investigations in the sulfide differentiation history on the basis of PGE

geochemical characteristics of synchronous volcanic rocks, are highly desirable for recognizing the crucial factors controlling PGE enrichment and the differences in metallogenic model for porphyry copper (gold) deposits. This also has important implications for exploring new PGE resource.

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