Palladium, Platinum and Gold Concentrations in Fengshan Porphyry Cu–Mo Deposit, Hubei Province, China

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Abstract: The Fengshan porphyry-skarn copper–molybdenum (Cu–Mo) deposit is located in the south-eastern Hubei Province in east China. Cu–Mo mineralization is hosted in the Fengshan granodiorite porphyry stock that intruded the Triassic Daye Formation carbonate rocks in the early Cretaceous (~140 Ma), as well as the contact zone between granodiorite porphyry stock and carbonate rocks, forming the porphyry-type and skarn-type association. The Fengshan granodiorite stock and the immediate country rocks are strongly fractured and intensely altered by hydrothermal fluids. In addition to intense skarn alteration, the prominent alteration types are potassic, phyllic, and propylitic, whereas argillation is less common. Mineralization occurs as veins, stock works, and disseminations, and the main ore minerals are chalcopyrite, pyrite, molybdenite, bornite, and magnetite. The contents of palladium, platinum and gold (Pd, Pt and Au) are determined in nine samples from fresh and mineralized granodiorite and different types of altered rocks. The results show that the Pd content is systematically higher than Pt, which is typical for porphyry ore deposits worldwide. The Pt content ranges from 0.037 to1.765 ppb, and the Pd content ranges between 0.165 and 17.979 ppb. Pd and Pt are more concentrated in porphyry mineralization than skarn mineralization, and have negative correlations with Au. The reconnaissance study presented here confirms the existence of Pd and Pt in the Fengshan porphyry-skarn Cu–Mo deposit. When compared with intracontinent and island arc geotectonic settings, the Pd, Pt, and Au contents in the Fengshan porphyry Cu–Mo deposit in the intracontinent is lower than the continental margin types and island are types. A combination of available data indicates that Pd and Pt were derived from oxidized alkaline magmas generated by the partial melting of an enriched mantle source.

Key words: porphyry, skarn, copper–molybdenum, palladium, platinum, gold, Fengshan, China

1 Introduction

Platinum and/or palladium enrichment in porphyry systems is well documented in a number of hydrothermal systems, such as those of British Columbia that are 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% weight Cu) (Eliopoulos et al., 1991; Economou-Eliopoulos and Eliopoulos, 2000), the Elasite deposit in Bulgaria, the Mamut deposit in Malaysia, the Grasberg deposit in Indonesia (Rubin and Kyle, 1997; Tarkian and Stribrny, 1999), the Aksug deposit in Russia, and the Erdenetiin Ovoo deposit in Mongolia (Sotnikov et al., 2001; Berzina and Korobeinikov, 2007) (Fig. 1). Platinum group minerals (PGM) have been identified in samples from Scouries (Greece), Elasite (Bulgaria), Majdanpek (Serbia), Kalmakyr (Uzbekistan), Boshekul (Kazakhstan), Santo Tomas and Biga (Philippines), Mamut (Malaysia), and Ryabinovoye and Askug (Russia) porphyry Cu deposits (Filimonova, 1984; Tarkian et al., 1991; Petrunov, et al., 1992; Tarkian and Koopmann, 1995; Tarkian and Stribrny, 1999; Kozlov et al., 2000; Berzina et al., 2005; Berzina et al., 2007). There are sparse data on the background contents of Pd and Pt in non-mineralized magmatic rocks, hosting Cu–Mo porphyry deposits.

Although platinum-group elements are a subject of intense investigation, many questions concerning the level of their concentration in various ore-forming environments still remain. The published data on platinum group element (PGE) content and its distribution in the ores of these deposits are limited, in particular, for deposits from

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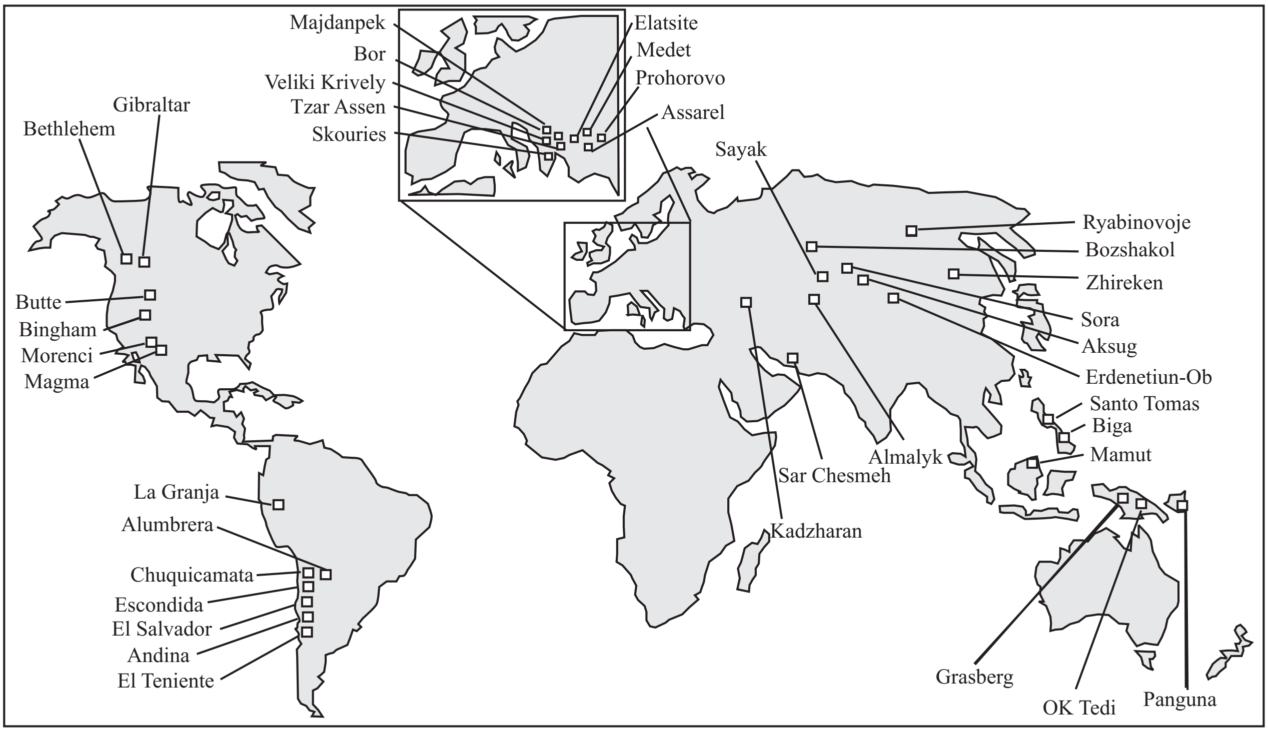

Fig. 1. Location map of platinum group element (PGE) mineralization in world's porphyry copper deposits.

China (Wang et al., 2009; Fu et al., 2009). The Pd, Pt, and Au enrichment in porphyry Cu deposits has been ascertained as the result of hydrothermal transport related to these systems (Finch et al., 1983; Mountain and Wood, 1988; Fleet et al., 1999; Xiong and Wood, 2000).

In this paper, the precious metal concentrations and other important components of the mineralized porphyry stock of the Fengshan porphyry-skarn deposit are given, and their implications to the metallogenesis of the deposit are discussed. Compilation of these new data with published mineralogical and geochemical data may contribute to the establishment of the factors controlling the precious metal enrichment in the porphyry Cu systems. The comparison between porphyry Cu deposits in the intracontinent (Fengshan deposit) and island arc (Elatsite deposit) geotectonic setting has been studied. The results of the present study are being applied to other porphyry-type occurrences in the region.

2 Sampling and Analytical Methods

Nine hand specimens from the Fengshan porphyry deposit were analyzed for their precious metal content. More specifically, the samples analyzed include representative ones from the main vein-type mineralization, consisting mainly of veinlets of sulfides accompanied by quartz and stringers of magnetite, the altered host rock, and porphyry intrusion.

Platinum, palladium, and gold were determined at both the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, and the Australian Laboratory Services (ALS) CHEMX, Guangzhou, China using isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) after preconcentration by Carious tube and inductively coupled plasma atomic emission spectrometry (ICP-AES) after preconcentration by the lead fire assay technique from large (30 g) samples, respectively. Detection limits were: 1 ppt for Pt and Pd, and 1 ppb for Au.

3 Geological Setting

The Fengshan porphyry-skarn Cu–Mo deposit is located in the south-eastern Hubei Province in east China and belongs to the Middle–Lower Yangtze River belt (MLYRB). The MLYRB extends ~450 km from south-eastern Hubei eastward to the Zhejiang Province over an area of ~30,000 km^2, and represents one of the most important economic mineral districts in China (Pan and Dong, 1999; Hou et al., 2007), containing seven magmatic regions, which are, from southwest to northeast, the Daye, Jiurui, Anqing, Luzong, Tongling, Ningwu, and Ningzhen (Fig. 2).

The MLYRB is located on the northern margin of the Yangtze Craton and runs along the south-eastern margin

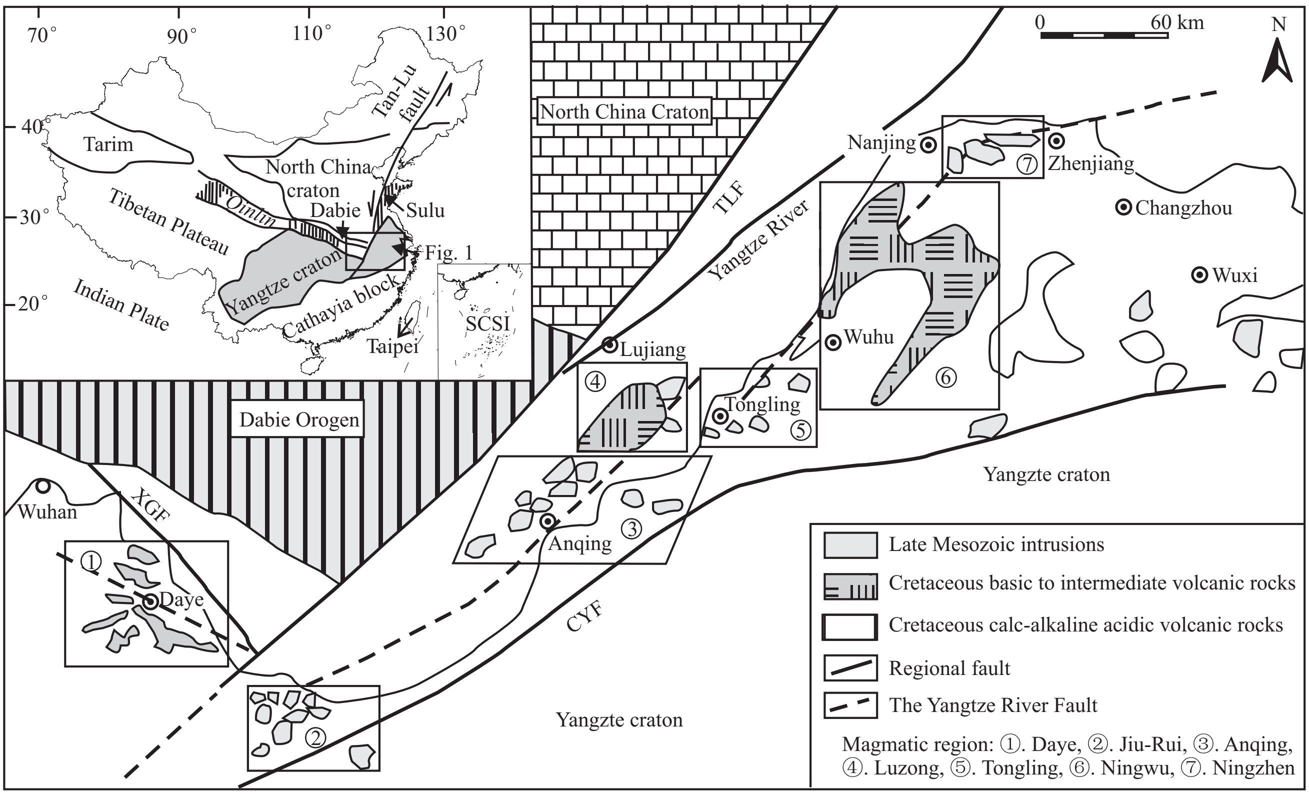

Fig. 2. Schematic illustration of the seven magmatic regions from the Eastern Yangtze Craton (based on Zhai et al., 1992).
CYF, Changzhou–Yangxin Fault; TLF Tan–Lu Fault; XGF Xiangfan–Guangji Fault.

of the North China Craton and Dabie orogenic belt. It is bound by the Xiangfan–Guangji Fault to the northwest, the Tan-Lu regional strike-slip fault to the northeast, and the Yangxing–Changzhou Fault to the south (Fig. 2).

Basement rocks of the Yangzi Craton include biotite–hornblende gneisses, tonalites, trondjhemites, granodiorites, and supracrustal rocks all metamorphosed to amphibolite and granulite facies conditions with pervasive migmatization. Zircon U–Pb and whole-rock Sm–Nd geochronological analyses revealed that these basement rocks were Paleo-Proterozoic to Archean in age (1895–2900 Ma) (Chang et al., 1991). The basement rocks are overlain by a Paleo- to Neo-Proterozoic (990–1850 Ma) (Chang et al., 1991) volcanic-sedimentary suite of calc-alkaline basalts, rhyolitic eruptives, and shallow marine carbonate and clastic sedimentary rocks that are moderately metamorphosed to schists and gneisses. The Jinning tectono-magmatic event caused extensive folding, granitoid magmatism, and metamorphism in these Precambrian formations, and resulted in the stabilization of the Yangtze Craton at approximately 850 Ma.

The Fengshan porphyry Cu–Mo deposit is situated in the Jiurui region, which is part of the Eastern Yangtze Craton, belonging to the intracontinent geotectonic setting. The porphyry stock in the Fengshan deposit is of Early Cretaceous age (Zhai et al., 1992) and consists of granodiorite. Geochemical analyses exhibit calc-alkaline characteristics (Chang et al., 1991; Zhai et al., 1992).

4 Mineralization and Associated Wall-Rock Alteration

The typical alteration types of the porphyry Cu intrusions described by Lowell and Guibert (1970) are more or less present in the Fengshan intrusion with potassic and phyllic alterations being the predominant types, whereas the surrounding propylitic and argillation alteration is limited (Shu et al., 1992). However, they tend to overlap, and thus do not occupy clearly-defined zones. As shown in Fig. 3a, the potassic alteration zone is characterized by K-feldspar, biotite, and quartz. Sericite and chlorite are less abundant. Biotite is the dominant alteration mineral in the potassic zone. Quartz forms numerous small veinlets, and is mostly associated with sulfides. Chlorite replaces primary hornblende, and primary and secondary biotite. It also occurs commonly in veinlets with quartz and sulfides. Chlorite, epidote, and calcite are the typical alteration minerals found in the phyllic alteration, which was superimposed on the potassic zone. Highly-mineralized rocks occur in the potassic and

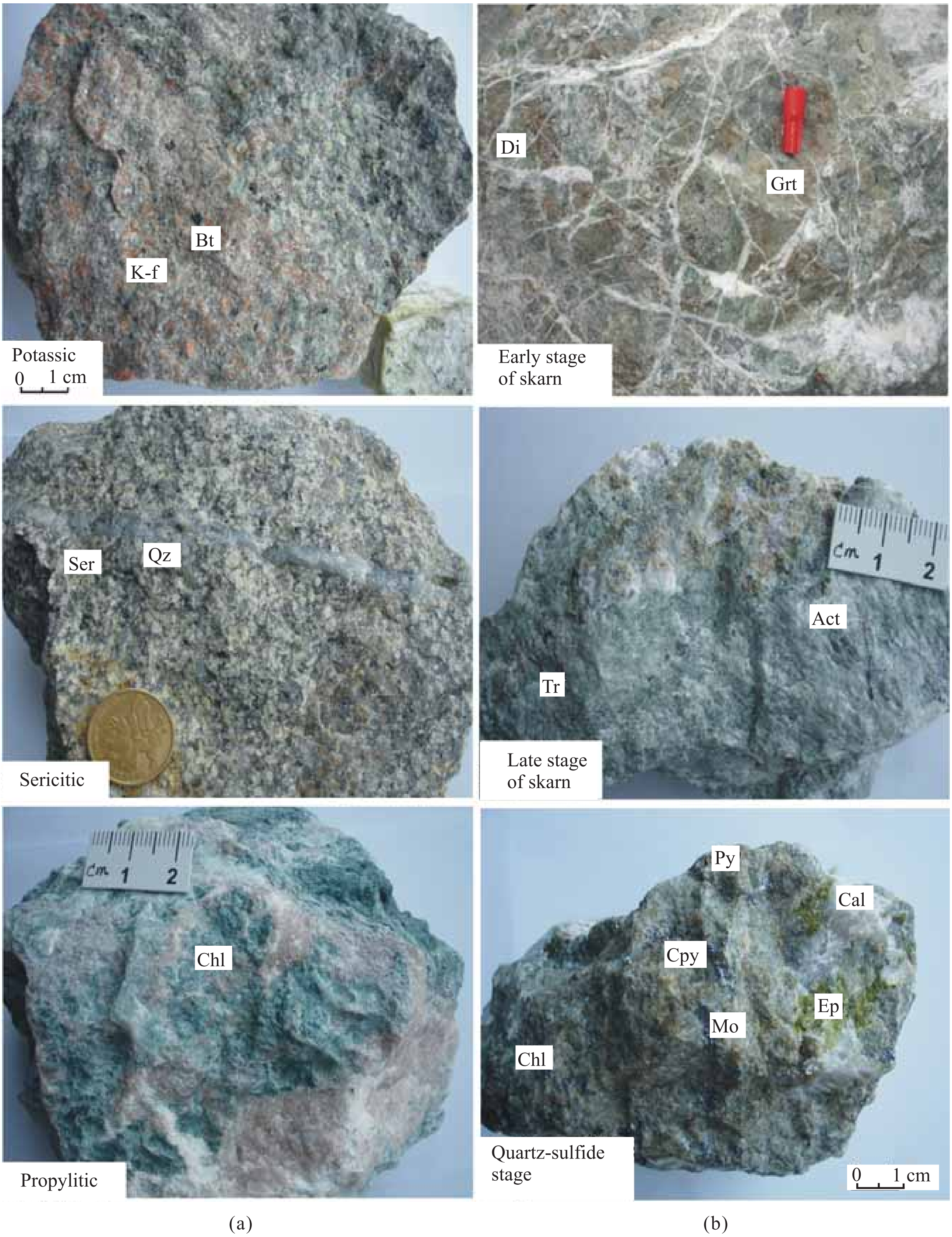

Fig. 3. Mineralization and associated wall-rock alteration. (a) porphyry; (b) skarn.
Abbreviations: Act-actinolite; Bi-biotite; Cal-calcite; Chl-chlorite; Cpy-chalcopyrite; Di-diopside; Ep-epidote; Grt-garnet; K-f- potassic feldspar; Mo-molybdenite; Py-pyrite; Qz-quartz; Ser-sericite; Tr-tremolite.

phyllic zone, consisting of veinlet and less abundant disseminated sulfides. Cu–Mo sulfides in veinlets are commonly accompanied by quartz and chlorite.

The skarn mineralization is spatially and temporally related to the early Cretaceous (~140 Ma) granodiorite porphyry stock emplaced into the Triassic Daye Formation carbonate rocks. As described in text book, the typical alteration types are obvious in the Fengshan deposit, which are the early stage of skarn, the late stage of skarn, the oxidation stage, and the quartz–sulfide stage (Fig. 3b). The early stage of skarn is characterized by anhydrous silicate minerals, such as garnet and diopside. The late stage of skarn is characterized by the presence of hydrous silicate minerals, such as tremolite, epidote, actinolite, and minor magnetite.

5 Palladium, Platinum, and Gold Concentrations

The precious metals, platinum, palladium, and gold, were determined in nine total representative samples in the Fengshan deposit. A description of samples is given in Table 1. The samples analyzed include intrusive mineralized rocks with veinlets of sulfides accompanied by quartz and disseminated/massive sulfides from various alteration types (Table 2).

Pd and Pt contents in the mineralized rocks representing all alteration types (Table 2) range between 0.037 and 17.979 ppb. The average PGE content in the mineralized rocks is 5.969 ppb Pd and 0.372 ppb Pt in the Fengshan deposit. Gold content in the mineralized rocks is relatively higher than Pd and Pt, ranging from 4 to 1480 ppb, with an average gold content of 373 ppb Au in the Fengshan deposit. These preliminary data on the precious metal distribution in the studied deposits do not establish any relationship with the alteration types. Thus, the average PGE content in rocks, including different alteration types, were used in this study.

Table 1 Description of samples analyzed for palladium, platinum, and gold content

Sample	Type	minerals	Alteration type/ silicates	Ore type
FS-50	Intrusive rock	-	-	
FS-57	Altered wall rock	-	K-f, qz, ab, bi	Porphyry
FS-94	Altered wall rock	-	K-f, qz, ab, bi	Porphyry
FS-4	Ore sample, massive	py, cpy, mt	chl, qz, ser, carb	Skarn
FS-8	Ore sample, massive	mo, py, cpy	ser, qz, ab	Porphyry
FS-9	Ore sample, disseminated	py, cpy	chl, qz, carb	Skarn
FS-36	Ore sample, veinlet	cpy, py	Relatively unaltered	Porphyry
FS-45	Ore sample, massive	cpy, py	chl, qz	Skarn
FS-64	Ore sample, disseminated	cpy, py	chl, qz	Skarn

Abbreviations: ab-albite; bi-biotite; carb-carbonate; chl-chlorite; cpy-chalcopyrite; K-f- potassic feldspar; mo-molybdenite; mt- magnetite; py-pyrite; qz-quartz; ser-sericite.

Table 2 Platinum group element (PGE) and Au contents in the Fengshan porphyry skarn Cu–Mo deposit

Sample	Au	Pt	Pd	Pt+Pd	Pd/Pt
FS-50	11	0.137	0.165	0.302	1.2
FS-57	10	0.389	3.907	4.296	10.0
FS-94	4	0.234	0.288	0.522	1.2
FS-4	1480	0.037	3.095	3.132	83.6
FS-8	28	1.765	13.888	15.653	7.9
FS-9	531	0.204	17.979	18.183	88.1
FS-36	220	0.175	6.877	7.052	39.2
FS-45	310	0.099	0.403	0.502	4.1
FS-64	402	0.070	1.314	1.384	18.8

Abbreviations: Au-gold; Pd-palladium; Pt-platinum. Unit: (ppb)

According to the alteration types and field studies, the ore samples can be divided into porphyry ore samples and skarn ore samples. The porphyry ore samples include FS-57, FS-94, FS-8, and FS-36, and the skarn ore samples include FS-4, FS-9, FS-45, and FS-64. As shown in Fig. 4a, the Pd, Pt, and Pd+Pt contents are fairly higher in porphyry ore samples than in skarn porphyry ore samples, and in intrusive rock, the PGE content is fairly low. The

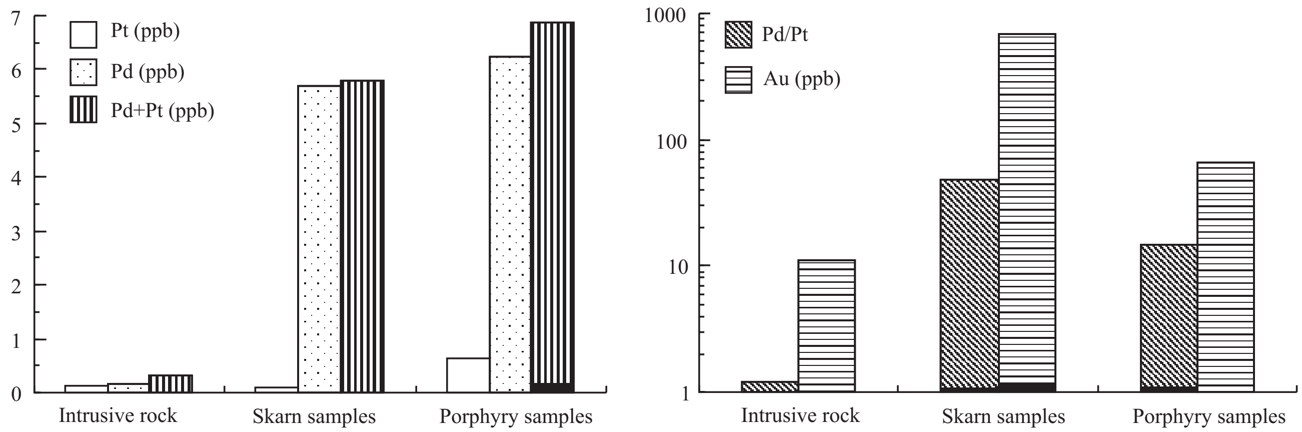

Fig. 4. Pt, Pd, and Pd+Pt contents shows higher concentrations in the porphyry samples than in the skarn samples, while the Au content and Pd/Pt ratio shows higher concentrations in the skarn samples than in the porphyry samples.
Abbreviations: Au-gold; Pd-palladium; Pt-platinum.

Au content and Pd/Pt ratio show contrary features in porphyry and skarn ore samples, whereas they are higher in the skarn ore samples than in the porphyry ore samples (Fig. 4b).

Generally, the Pt concentration is approximately one order of magnitude lower than Pd. The other PGE in the hand specimens is extremely low, with osmium (Os), ruthenium (Ru), and rhodium (Rh) below the detection limit (<1 ppb), and iridium (Ir) between 0.004 and 0.008 ppb.

6 Comparison with Other PGE Porphyry Cu Deposits

Mutschler et al. (1985) indicate that the PGE content is <0.025–13.6 ppm Pt and <0.003 to 6.4 ppm Pd in rocks, ores, and concentrates of Cordilleran alkaline suite porphyries containing Cu and precious metals, for example, the Allard stock (Colorado), Copper King mine (Montana), Comstock mine (Washington), and some Cordilleran porphyries in British Columbia. Moreover, elevated PGE contents are reported by Eliopoulos and Economou-Eliopoulos (1991, 2000) and Tarkian and Koopmann (1995) from Skouries in Greece with 480 ppb Pd, and from Santo Tomas II in the Philippines with 160 ppb Pd and 38 ppb Pt (the maximum values of whole-rock samples). Tarkian et al. (1999, 2003) report the PGE content in concentrates of island arc and continental margin porphyries, and fluid-inclusion petrography of the Elatsite porphyry Cu deposit. Thompson et al. (2001) report the presence of PGE, particularly Pd and Pt, in heavy mineral concentrates prepared from samples from the alkaline suite of porphyry Cu–Au deposits in British Columbia. Auge et al. (2005) represent the Elatsite model for PGE concentration and evolution. Berzina et al. (2005, 2007) undertook research on the PGE concentration in porphyry Cu–Mo deposits in Russia and Mongolia.

Porphyry-type ore deposits range from Cu–gold, like Grasberg (Indonesia) and Mamut (Malaysia), to Cu–Mo deposits, such as those of southwest USA or western South America. The 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., 2005). The Cu–Mo deposits in Armenia are considered to be similar in age and genesis to those in Andes and western Cordillera of North America (Sotnikov et al., 2001). Highly-mineralized samples contain 10–80 ppb Pd, and up to 18 ppb Pt.

Many porphyry Cu deposits hosted in calc-alkaline or alkaline intrusions are widespread in the Cordillera Province of North American. Batholiths contain major intrusive phases, including porphyry stocks, which may be apophyses of the batholiths. PGE concentrations are very low, although very minor PGE are recovered from Cu that are refined 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, USA. The most salient feature in both the Allard and Copper Mountain deposits are their geochemically, not economically, high concentrations of barium (Ba), strontium (Sr), Cu, silver (Ag), Au, Pt, and Pd, and low Mo, lead (Pb), and zinc (Zn) contents. The Pd and Pt contents in the Cu sulfide concentrates (18%–40% weight 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, 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 majority of porphyry Cu deposits, as summarized by Sillitoe (1993) and Lang and Titley (1998), reveal common features of their geotectonic setting. They have been formed at convergent plate margins, above zones of active subduction, ranging from primitive through mature island arcs to continental margins. They are also characterized by the properties of a sequence of shallowly-emplaced igneous rocks rather than a single intrusion.

The Fengshan porphyry Cu–Mo deposit is located in the north-east margin of the Eastern Yangtze Craton, belonging to intracontinent geotectonic setting. In general, the Fengshan porphyry deposit shows lower Pd, Pt, and Au contents than those in other porphyry Cu deposits (Table 3).

7 Discussion

The study of the contribution of mantle and oceanic and crustal wall rock to the parent magmas of porphyry Cu intrusions, compared to subsequent petrogenetic processes, still continues (Titley and Beane, 1981). Further detailed studies are required to contribute to the delineation of processes critical to the formation of porphyry Cu±Mo mineralization. Crustal contribution to a parent magma may be a common feature for porphyry Cu±Mo intrusions (Sillitoe, 1979; Sotnikov et al., 2001).

A larger variation of the Pd/Pt ratio seems to be

Table 3 Nobel metal content of porphyry copper deposits under investigation

Country	Deposit	Geotectonic setting	Au	Pd	Pt	Pd+Pt
USA	Bingham	Continental margin	1350	8.	n.d.	8
Peru	La Granja	Continental margin	760	10	n.d.	10
Greece	Skouries	Continental margin	7300	160	8	168
Armenia	Kadzharan	Continental margin	3400	24	84	108
Serbia	Bor	Island arc	1700	40	19	59
	Majdanpek	Island arc	7000	240	24	264
Bulgaria	Elasite	Island arc	27,000	1900	72	1972
	Medet	Island arc	5600	160	8	168
	Tzar Assen	Island arc	130	8	n.d.	8
Kazakhstan	Bozshakol	Island arc	1080	245	n.d.	245
The Philippines	Santo Tomas	Island arc	40,000	1500	400	1900
	Biga	Island arc	2350	56	8	64
Papua New Guinea	Panguna	Island arc	520	40	8	48
China	Fengshan	Intracontinent	495	7	0.4	7.4

n.d, not detected. Abbreviations: Au-gold; Pd-palladium; Pt-platinum. Unit: ppb

characteristic of the Fengshan porphyry Cu–Mo deposit. The greater Pd and Pt contents may be related to the porphyry ore samples. Geotectonic settings appear to be a substantial (but not a decisive) factor for higher contents of Au, Pd, and Pt in Cu porphyry deposits. Island arc porphyry Cu deposits might host more Pd and Pt than the continental margin types (Tarkian and Stribrny, 1999). As shown in Table 3, the Fengshan porphyry Cu–Mo deposit in the intracontinent is lower than the continental margin types and island arc types. Although the database is relatively small, it seems likely that a higher Pd or Pt content in all of the samples correlates negatively with Au (“mirror-image” symmetry) (Fig. 5), which is contrary to the other porphyry Cu deposits in island arc geotectonic settings. Thus, the intracontinent geotectonic setting also might host Pd and Pt, and be characteristic of a negative relation with Au.

8 Conclusions

The compilation of some new data on the precious metals in the porphyry Cu systems of Fengshan, compared with published data of other porphyry Cu deposits, leads to the following conclusions:

(1) In the Fengshan porphyry-skarn Cu–Mo deposit, Pd, Pt, and Au are exclusively higher in porphyry ore samples than in skarn ore samples and those contained in Cu–Mo sulfides. Generally, the Pt concentration is approximately one order of magnitude lower than that of Pd. The other PGE in the hand specimens are extremely low, with Os, Ru, and Rh below the detection limit (<1 ppb), and Ir between 0.004 and 0.008 ppb.

(2) Differing from the other porphyry Cu systems in the continental margin and island arc geotectonic settings, a decrease of the Pd and Pt contents with an increasing Au content may indicate the unique characteristics in the Fengshan deposit, which is different from the other porphyry Cu deposits in the intracontinent geotectonic setting.

(3) Compared with intracontinent and island arc geotectonic settings, the Pd, Pt, and Au contents in the Fengshan porphyry Cu–Mo deposit in the intracontinent is lower than the continental margin types and island arc types.

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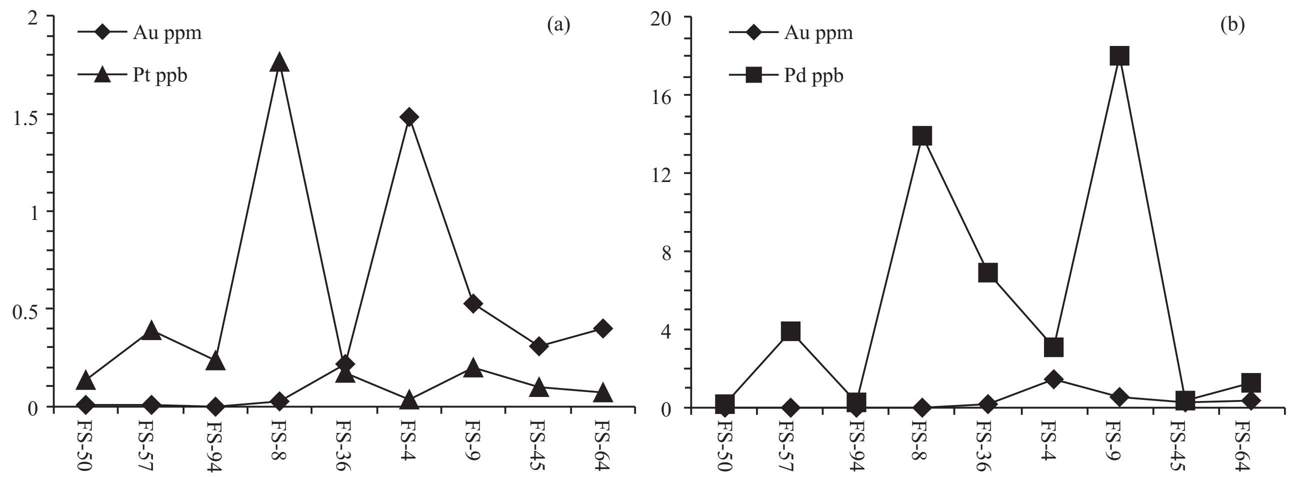

Fig. 5. Pt–Au (a) and Pd– Au (b) correlation diagrams for various samples from the Fengshan deposit, showing the“mirror-image” symmetry between Pd, Pt, and Au .
Abbreviations: Au-gold; Pd-palladium; Pt-platinum.

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