

Original paper

Platinum-group elements (PGE) and their principal carriers in metal-rich black shales: an overview with a new data from Mo–Ni–PGE black shales (Zunyi region, Guizhou Province, south China)

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Lower Cambrian Mo–Ni sulfidic black shales from the Huangjiawan mine (Guizhou Province, south China) have anomalous platinum-group elements (PGE) concentrations (up to ~1 ppm in total). In order to identify principal PGE carriers, we used heavy mineral separates which were produced by innovative hydroseparation techniques. Subsequent detailed mineralogical study using electron microprobe did not result in the identification of discrete platinum-group minerals. Pyrite (grainy, not framboidal), millerite and gersdorffite that were found in our heavy concentrate were analyzed for PGE and Re. We found that they contain the following concentrations of PGE and Re: pyrite (up to 490 ppm Pt, 390 ppm Pd and 220 ppm Rh), millerite (up to 530 ppm Pt, 430 ppm Pd and 190 ppm Rh) and gersdorffite (up to 410 ppm Pt and 320 ppm Pd; no Rh detected). Rhenium was detected only in grainy pyrite (up to 1060 ppm). It was found that despite anomalous PGE concentrations, the Mo–Ni black shales do not contain any platinum-group minerals and that the PGE are bound to pyrite and Ni-sulfides (millerite and gersdorffite).

Keywords: Mo–Ni–PGE black shale, PGE concentrations in pyrite and Ni-sulfides, Re concentration in pyrite, hydroseparation, electron microprobe study, south China

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1. Introduction

Anoxic sediments and metasediments have been recently recognized as important host environments for the platinum group elements (PGE) (e.g., Pašava 1993; Sawlowicz 1993). Economically significant PGE concentrations have been reported from marine, metal-rich black shales in China, Yukon (Canada) and Poland (Kucha 1975; Chen et al. 1982; Hulber et al. 1992 and others). These ore-bearing horizons are characterized by extremely restricted vertical, and sometimes larger horizontal extents. They are associated with the evolution of intracontinental rifting structures without any magmatic activity, suggesting a possible driving mechanism for mineralization processes (Pašava 1993).

In metal-rich black shales with anomalous PGE concentrations, platinum-group minerals (PGM) have been identified from the so-called noble metal rich black shales within the Cu–Ag shales of the Kupferschiefer type (Kucha 1975, 1981, 1982; Piestrzynski et al. 1996; Pieczonka and Piestrzynski 1997 and others), in gold ores hosted by black shales at the Sukhoy Log deposit, Russia (Distler et al. 1998), metalliferous black shales of the Kursk magnetic anomaly (Rudashevsky et al. 1995), Neoproterozoic

U–V-rich black shales of the Onega trough, South Karelia, Russia (Polekhovskiy et al. 1991), Palaeoproterozoic U–Au–Pt–Pd black shale hosted Coronation Hill deposit, Australia (Carville et al. 1990) and sulfidic black shales in SW Catalonia (Canet et al. 2003).

The Early Cambrian marine black shales of south and southwest China host Mo–Ni–PGE–Au deposits that outcrop discontinuously throughout six provinces in a belt approximately 1600 km long (Chen et al. 1982; Fan 1983). The Mo–Ni ore contains more than 4 wt. % Mo, at least 2 wt. % Ni, up to 2 wt. % Zn, 2.5 wt. % As and 1–2 g/t of precious metals, primarily Au, Pt, Pd, and Os (Fan 1983). The deposits are important, particularly because they constitute a largely untested alternative to conventional sources of precious metals, especially PGE (Coveney and Chen 1991; Coveney et al. 1991 and others). Macroscopically, only pyrite can be recognized in ore samples. However, major ore minerals are vaesite, bravoite, jordisite and MoSC phase (Fan 1983; Kao et al. 2001; Orberger et al. 2007). Minor ore minerals include arsenopyrite, chalcopyrite, covellite, sphalerite, millerite, polydymite, gersdorffite, sulvanite, pentlandite, tennantite, tiemannite, violarite, and native gold (Fan 1983; Grauch et al. 1991). A highly porous matrix of the ore

bed is composed of organic matter or aluminosilicate-rich laminae or lenticular bodies that are intercalated with phosphate- or sulfide-rich lenses (Pašava et al. 2008). Various genetic models for the origin of these metal-rich facies were discussed by Coveney and Pašava (2005), including seawater origin of metals (e.g., Mao et al. 2002;

Lehmann et al. 2007; Xu et al. 2011), hydrothermal and/or multiple metal sources (Lott et al. 1999; Steiner et al. 2001; Orberger et al. 2003; Pašava et al. 2004; Emsbo et al. 2005; Jiang et al. 2006, 2007, 2009; Křibek et al. 2007; Pi et al. 2013 and others).

Despite anomalous PGE concentrations (Σ PGE \sim 1 ppm), no discrete PGE phases were identified to date. Using a special separation technique which was uniquely designed for the release and concentration of the PGM, in this paper we provide a new evidence that points to a close relationship between sulfides and PGE concentrations rather than the presence of individual discrete PGE phases.

2. Material and methods

For separation and concentration of heavy mineral fraction we used a representative sample which was collected

from fresh Mo–Ni–PGE ore-body at the Huangjiawan mine area, Zunyi region, northern part of the Guizhou Province (27°41'305"N; 106°40'069"E). The location and general geology of the sampling area is shown in Fig. 1.

The ore sample contains 7 wt. % Mo, 2 % Ni, 19 % S and 13 % C_{org}, 10 % CO₂, 14 % CaO, 1.2 % As, 2000 ppm Se, 5400 ppm Zn, 450 ppm U and V, and up to 1 ppm PGE (Orberger et al. 2007).

One representative sample (641 g) of Mo–Ni–PGE ore (Figs 2 and 3) was crushed down to a grain size <125 μ m by a RETSCH vibratory disc mill (RS 100), using an agate grinding set. The resulting fine fraction was carefully wet sieved by hand through a standard screen series following the methodology given by Aiglsperger et al. (2011). The finest size fraction (< 53 μ m) was processed by hydroseparation (HS-11) techniques (Ru-

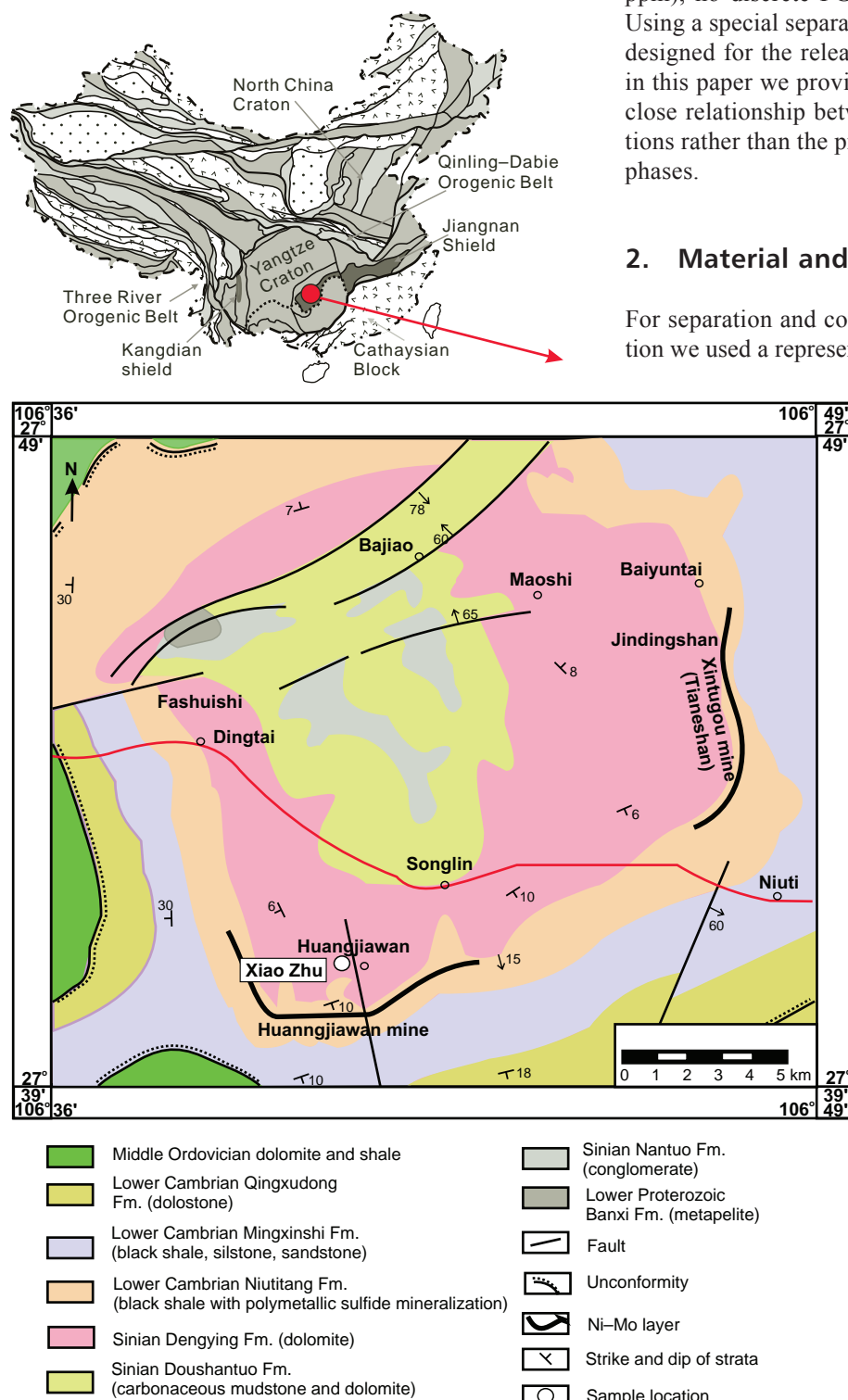


Fig. 1 Geological sketch map of the Zunyi region with black shale sampling location, the northern part of the Guizhou Province, southwest China (adapted from Mao et al. 2002, 2013).

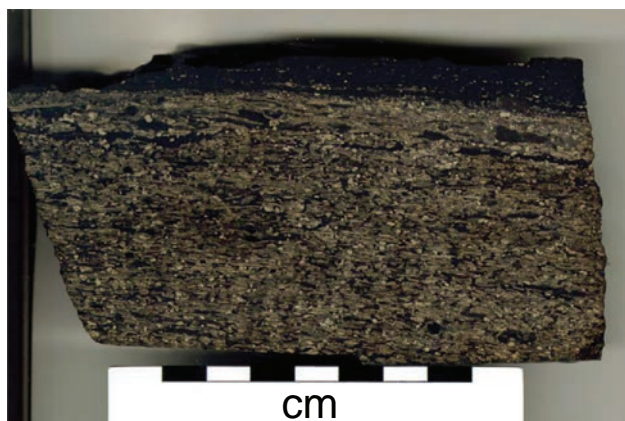


Fig. 2 Typical sample of Ni-Mo black shale showing the texture (photo by J. Pašava).

dashevsky et al. 2001a,b; Cabri et al. 2005; Rudashevsky and Rudashevsky 2006, 2007) at the hydroseparation (HS) laboratory in Barcelona. Monolayer polished sections were produced from 0.25 g final concentrate and subsequently studied using an electron microprobe (EMP) at the Eugen F. Stumpfl laboratory (University of Leoben, Austria).

Pyrite (493 analyses), millerite (248 analyses) and gersdorffite (66 analyses), (Figs 4 and 5) have been determined by a Jeol Superprobe JXA-8200 by wavelength dispersive systems (WDS) using 25 kV of accelerating voltage and 30nA of beam current. The counting times were 120 and 60 s for the peak and backgrounds, respectively. The beam diameter was *c.* 1 μm . The ore minerals were analyzed using pure metals as the reference material for PGE and Re, synthetic NiS, natural pyrite, chalcopryrite, skutterudite and nickeline for Fe, Ni, Cu, Co, As and S. The X-ray lines used were: K_{α} for S, Fe, Cu, Ni and Co; L_{α} for As, Ru, Rh, Pt and Pd; M_{α} for Re. The following diffracting crystals were selected: PETJ for S, PETH for Ru, Rh and Re, LIF for Cu, LIFH for Ni, Fe, Co and Pt and TAP for As. The detection limits of the trace elements are (in ppm) As = 70, S = 80, Fe = 70, Ni = 80, Co = 50, Cu = 90, Ru = 60, Rh = 50, Pd = 60, Pt = 80, Re = 110. Automatic

Fig. 4 Backscattered electron image of studied ore minerals (millerite, gersdorffite and pyrite), photo by F. Zaccarini.

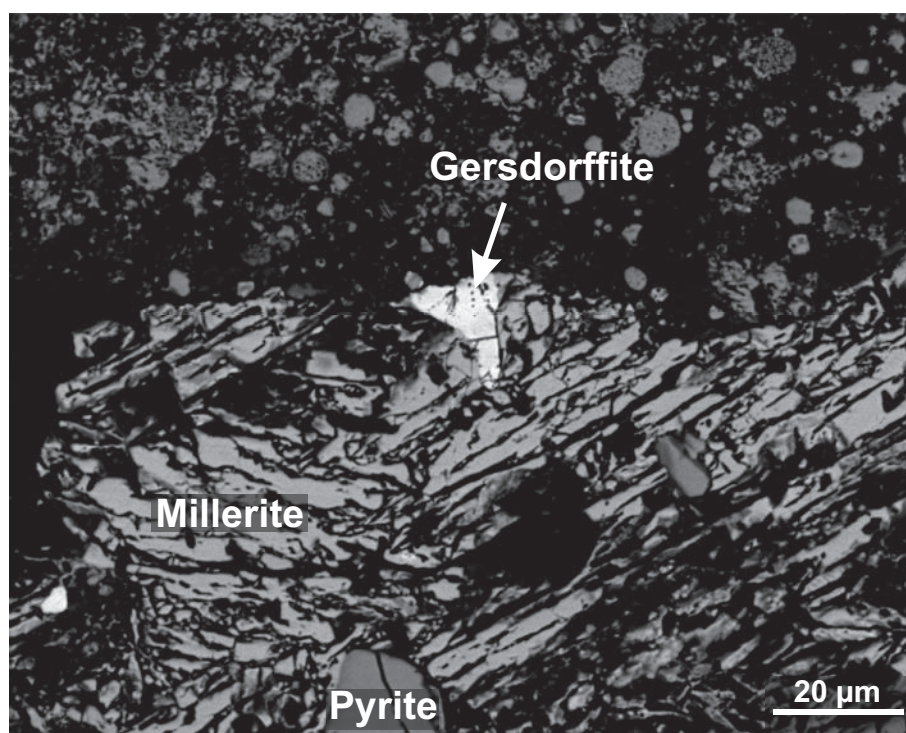


Fig. 3 Location of Ni-Mo horizon in the mine (placement of the hammer). Note near vertical white fracture quartz-carbonate fillings (photo by J. Pašava).

corrections were performed for interferences involving Ru-Rh and Rh-Pd. The results are listed in Tab. 1.

3. Results

Despite of the relatively high concentration of PGE in the studied samples ($\Sigma\text{PGE} \sim 1$ ppm), no specific PGM have been found. However concentrations of Rh, Pt, Pd and Re detectable with the electron microprobe, have been found in grainy pyrite, millerite and gersdorffite (Tab. 1, Fig. 6). Rhodium occurs in pyrite (up to 220 ppm) and in millerite

Tab. 1 PGE and Re concentrations in pyrite (grainy), millerite and gersdorffite from Mo–Ni–PGE black shale (Huangjiawan mine, Zunyi region, Guizhou Province, south China) (ppm)

Pyrite	n	NA	Mean	Std	Min	25%	Median	75%	Max
Rh	164	329	60	50	10	30	50	90	220
Pt	258	235	130	100	10	60	110	190	500
Pd	292	201	120	80	10	60	100	160	390
Re	205	288	140	120	10	50	110	180	1060
Millerite									
Rh	71	177	60	40	10	20	50	90	190
Pt	137	111	150	110	10	60	120	230	520
Pd	133	115	100	80	10	40	80	150	430
Gersdorffite									
Pt	33	33	150	110	10	60	130	200	410
Pd	39	27	130	80	10	80	120	190	320

Omitted are elements which were in the given mineral consistently below the respective detection limits. These were Pd – 60 ppm, Pt – 80 ppm, Rh – 50 ppm, Re – 110 ppm, Ru – 60 ppm

NA – not available

(up to 190 ppm), but not in gersdorffite. Platinum was found in all the minerals with concentration up to 500, 520 and 410 ppm in pyrite, millerite and gersdorffite, respectively. The highest concentration of Pd (430 ppm) was found in millerite, whereas pyrite and gersdorffite contain 390 and 320 ppm of Pd, respectively. Rhenium was found only in pyrite, reaching up to 1060 ppm. Ruthenium was always below detection limit of 60 ppm.

4. Discussion

In the following text we discuss the presence of PGM in different types of mineralizations associated with black shales worldwide and compare them with the studied

samples. Anomalous PGE concentrations of 10–370 ppm Pt and 10–120 ppm Pd (locally, up to 1000 ppm) were reported by Kucha (1982) from a thin noble metal-rich layer within the Polish Cu–Ag ores of the Kupferschiefer type. Kucha (1981) noted that Pt and Ir occur in the Kupferschiefer noble metal layer as admixtures in Au–Pt solid solutions and in other cases Pt and Ir form organometallic compounds – possibly metallocenes. Palladium is present in several minerals and phases: as native palladium, PdBi (sobolevskite), Pd₃As₅, PdAs₂, Pd₃As₂, (Pd,Au)₅As₂, Pd₃As (possibly vincentite), Pd₈As₂S, Pd₄As₃, palladium hydroxides of arsenic, PdNiAs (majakite), PdCu(As,S)₆, and Pd₈As₆S₃, and as Pd₂As palladoarsenide, Kucha 1975). Palladium is also concentrated in Ni and Co arsenides (up to 5.5 and 2.5 wt. %, respectively). The Pd content in organic matter is far lower than that of Pt and Ir and as a rule does not exceed 0.3 wt. %. In extreme cases, however, Pd reaches 2 wt. % and is associated with Bi, Pt, sometimes Sn, and up to 2 wt. % of S (Kucha 1982).

Mitrofanov et al. (1994) identified cooperite (PtS) as inclusions (in size of 0.3–0.5 μm) in pyrite of Au-ore hosted by black shales of Riphean age at the Sukhoy Log deposit (Russia). The study of ultraheavy concentrate from these Au-ore-bearing black shales resulted in the identification of native (?) Pt, isoferroplatinum (Pt₃Fe),

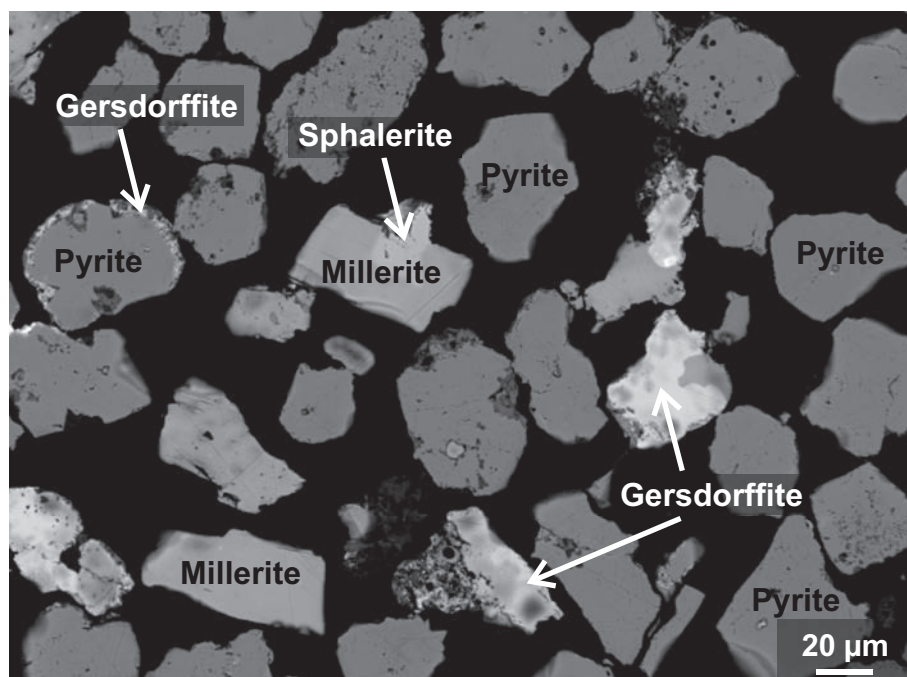


Fig. 5 Backscattered electron image of sulfide concentrate, photo by F. Zaccarini.

tetraferroplatinum (PtFe) and Pt–Fe–Cu inclusions in Au-bearing pyrite and a (Pd,Ag)(Te,Bi) phase, which was intergrown with galena and sphalerite (Distler et al. 1998).

New type of PGE mineralization was described by Chernyshov and Korobkina (1995) from Proterozoic black shales of the Voronezh Crystalline Massif. Rudashevsky et al. (1995) reported the presence of native Pd, Pt, Au–Pt–Pd, PdSn₂ and (Pd,Pt)₃Se₂ from the same occurrence.

A PGE mineralization was reported from U–V-rich black shales of the Onega Trough (South Karelia) by Polekhovskiy et al. (1991) who identified froodite (PdBi₂), sobolevskite (PdBi with Pt and Te), polarite Pd(Bi,Pb), insizwaite (PtBi₂), Pd,Pt selenides (padmaite PdBiSe and sudovikovite PtSe₂) and PGE sulfoselenides.

Discrete PGM (stibiopalladinite-Pd_{5+x}Sb_{2-x}, sudburyite – PdSb, native palladium, sudovikovite (Pt,Pd)Se₂, a Pt–Pd–Fe alloy, native platinum, milotaite (PdSbSe), palladseite (Pd₁₇Se₁₅) and rare bismuthian stibiopalladinite and Bi–Pd–Se phases were described by Gilbert (1987) and Carville et al. (1990) from Palaeoproterozoic U–Au–Pt–Pd black shale hosted Coronation Hill deposit, Australia.

Canet et al. (2003) studied Silurian sedex deposits in the Poblet area in southwestern Catalonia and found sulfidic black shales which are V- and Cr-rich and contain disseminated minerals bearing precious metals (e.g., spherulite and palladian löllingite).

Despite of anomalous PGE concentrations detected in our sample of Ni–Mo–sulfidic black shales from south China, no PGM were identified in HS concentrate. Maximum Pt and Pd concentrations (520 ppm and 430 ppm, respectively) were detected in millerite which also has Rh (Tab. 1). Maximum concentrations of Rh (220 ppm) and Re (1060 ppm) were found in pyrite, which contains on average 130 and 120 ppm of Pt and Pd, respectively. Gersdorffite is characterized by Ru, Rh and Re values below the detection limits of the electron microprobe and average Pt (150 ppm) and Pd (130 ppm).

Geological and experimental data show that some sul-

fides can incorporate significant amounts of PGE (up to several tens of percent) as solid solutions. For example, anomalous Pd concentrations were reported from native gold and pyrite at the Muruntau deposit in Uzbekistan (Rachmatullaev 1984). Similarly, Ermolayev et al. (1992) described anomalous Pd, Pt and Ir values in Au–REE–PGE ores hosted by the Cambro–Ordovician marine black shales and sandstones. The PGE are concentrated in the marginal parts of pyrite, arsenopyrite and löllingite but also in REE-phosphates, graphite and quartz. Close association of PGE and organic matter has been described from the Polish Kupferschiefer (Kucha 1981) and other metal-rich black shales worldwide mostly summarized in Pašava (1993). Orberger et al. (2007) reported increased Pd concentrations (up to 961 ppm) from a Mo–S–C phase and elevated Pt contents from pyrite (up to 98 ppm, Pd up to 66 ppm) and Ni-sulfides (up to 122 ppm Pt and up to 111 ppm Pd) in Mo–Ni–PGE black shales of South China. We found significantly higher Pt and Pd values (up to 500 ppm Pt and 390 ppm Pd) and newly also anomalous Rh and Re concentrations (up to 220 ppm and 1060 ppm, respectively) in pyrite. Similarly, PGE contents in Ni-sulfides obtained in course of the current study are significantly higher (up to 520 ppm Pt, 430 ppm Pd and 190 ppm Rh) than those reported by Orberger et al. (2007). These authors have proposed that Pd was preferentially incorporated with other biophilic

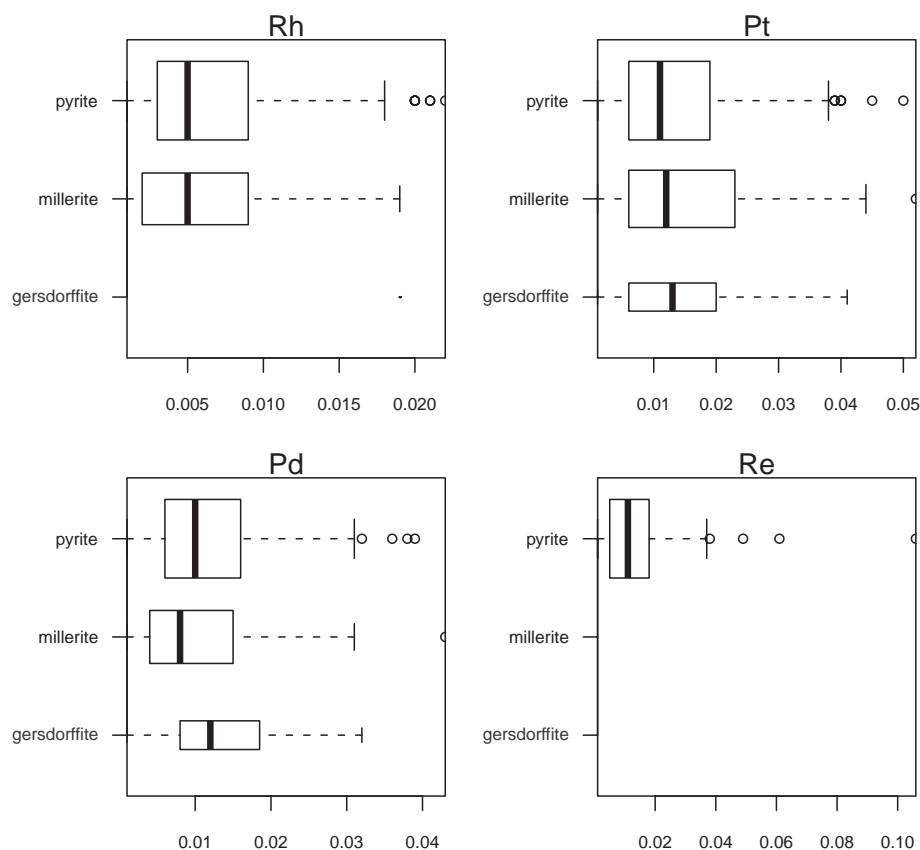


Fig. 6 Box plots showing distribution of Rh, Pt, Pd and Re in pyrite, millerite and gersdorffite separated from Ni–Mo–PGE black shale.

elements to Mo–S–C phase and that Pt was concentrated with less biophilic elements into pyrite and Ni-sulfides. Our data indicate that not only Pd but also Pt, Rh and Re were partitioned into pyrite and, besides Pt, also Pd and Rh were concentrated in Ni-sulfides. We suggest that the lack of specific PGM in our Chinese samples is related to the absence of these phases. We are aware that PGE can also occur in the form of non-traditional PGM that were reported by many authors from various occurrences. For example, oxygen-bearing compounds of Pt–Pd–Fe were described by Jedwab and Cassedanne (1998) from Minais Gerais in Brazil and Jedwab (2004) reported PGE oxides including several Ru–Ir–Pt–Ti–Cr–Fe oxide/hydroxide compounds from Ural. It is, however, very unlikely that PGE in Mo–Ni–PGE sulfide rich black shales would be associated with such phases as they originated under anoxic environment.

5. Conclusions

The special separation technique applied to a Mo–Ni–PGE black shale from the Huangjiawan mine (Guizhou Province, south China) produced a heavy separate consisting of grainy pyrite, millerite and gersdorffite. Subsequent detailed mineralogical study using electron microprobe resulted in the following findings:

1. Despite anomalous PGE concentrations (Σ PGE \sim 1 ppm) no specific platinum group minerals were identified through this study.
2. High concentrations of PGE were detected in grainy pyrite (up to 500 ppm Pt, 390 ppm Pd and 220 ppm Rh), millerite (up to 520 ppm Pt, 430 ppm Pd and 190 ppm Rh) and gersdorffite (up to 410 ppm Pt, 320 ppm Pd and without any Rh).
3. Newly, anomalous Re concentrations (up to 1060 ppm) were found in grainy pyrite.
4. We suggest that besides close association of Pd with organic matter (anomalous Pd concentrations previously reported from a Mo–S–C phase) Pt, Rh and also Re were incorporated into pyrite and also Ni-sulfides (millerite and gersdorffite).

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