

Revisiting platinum group elements of Late Permian coals from western Guizhou Province, SW China

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ARTICLE INFO

Article history:

Received 13 January 2008

Received in revised form 25 April 2008

Accepted 5 May 2008

Available online 16 May 2008

Keywords:

Coal

Platinum group elements (PGEs)

ICP-MS

SW China

ABSTRACT

Twenty five coal samples from the Late Permian coal-bearing strata in Weining, Nayong, and Zhijin, western Guizhou Province, SW, China, were analyzed for platinum group elements (PGEs). The coal ashes were digested by the Carius tube technique and accurately measured by isotope dilution-inductively coupled plasma mass spectrometry (ID-ICP-MS) for all PGEs. The results are much lower than the previous reported values. Our study suggested that the previously reported PGE values are incorrect and may due to the polyatomic interferences in ICP-MS measurements. In our study, samples from the Weining coalfield have the lowest PGE contents (from 0.019 Ir to 0.42 ng/g Pd), which represent the PGE background value in coal in western Guizhou province. Some of the coals have Pt and Pd contents about 20-times higher than the background value, indicating PGEs are concentrated. We also reported new and reliable PGE data and background value of coal in western Guizhou province, SW, China, and suggested to rework the PGE background values of Chinese coals.

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1. Introduction

Platinum group elements (PGEs), also known as noble metals, include Os, Ir, Ru, Rh, Pt, and Pd. They have strong affinity for iron (siderophile) and sulfur (chalcophile) and significant economic values because of their nobility and catalytic features. This coherent group of highly siderophile elements are known to be sensitive indicators for understanding several fundamental aspects of the origin and evolution of the earth and mantle-derived rocks (e.g. Rehkämper et al., 1999; Ely and Neal, 2003; Crocket and Paul, 2004; Lightfoot and Keays, 2005).

PGEs occur mostly as Cu–Ni–PGE sulfides ore. Although few high PGE coalfield were reported before 1982 (Goldschmidt and Peters, 1933; Goldschmidt, 1954; Chyi, 1982), additional work about PGEs in coals were not available until recently. Swaine (1990) summarized PGEs in coals, but the results for Ru and Os were not reported. Coals are widely spread in Guizhou province, SW, China. Recently, some researchers reported high PGE contents in these coals (Dai et al., 2003, 2004, 2005a; Yang, 2006). The concentrations of Pd range from 30 to 4240 ng/g and Pt from 10 to 2430 ng/g. If these coals contain such high PGEs as they reported, the coals in SW China may be the new Pt and Pd resource in the world. Thus, it is very important to confirm if their data are reliable.

The PGE analytical method they reported was reported by Xie et al. (2001). The samples are digested by HF, HNO₃, HCl, and HClO₄ and directly measured by high-resolution (HR) ICP-MS without pre-concentration and separation of the matrix and interference elements,

such as Cu, Ni, Zn, Sr, Y, Rb, Zr and Hf. These elements have significant interference on PGEs when measured by ICP-MS, even in high resolution mode. Such interferences cannot be avoided and ignored. Thus, a pre-concentration procedure must be used to obtain high quality PGE results in coals. Furthermore, they did not report any international certified reference materials values.

In this paper, we reported a reliable analytical method to determine the PGEs in coal ashes. The PGE contents of 25 coal samples collected from same area are much lower than the previous reported values (Dai et al., 2003, 2004, 2005a; Yang, 2006) and the background values of coals in China as reported by Dai et al. (2003).

2. Geological background and samples collection

The strata of Weining, Nayong, and Zhijin in the western Guizhou province, (Fig. 1), including the Dengying Formation of Precambrian to Quaternary except the strata of mid-upper Ordovician and upper Silurian. From the early Paleozoic to late Triassic, the strata are mainly composed of marine carbonates, whereas post-Triassic strata mainly consist of continental clastic rocks. Late Permian Emeishan flood basalts are widespread in Yunnan, Sichuan, and western Guizhou provinces in SW China and lie between the Middle Permian Maokou Formation and the early Late Permian Longtan Formation or Triassic sedimentary rocks (Song et al., 2001).

In western Guizhou Province, coal-bearing strata mainly occurred in late Permian, including the Emeishan Formation, the Longtan Formation, the Changxin Formation, and the Dalong Formation. The 300-m thick Longtan Formation is the main coal-bearing formation

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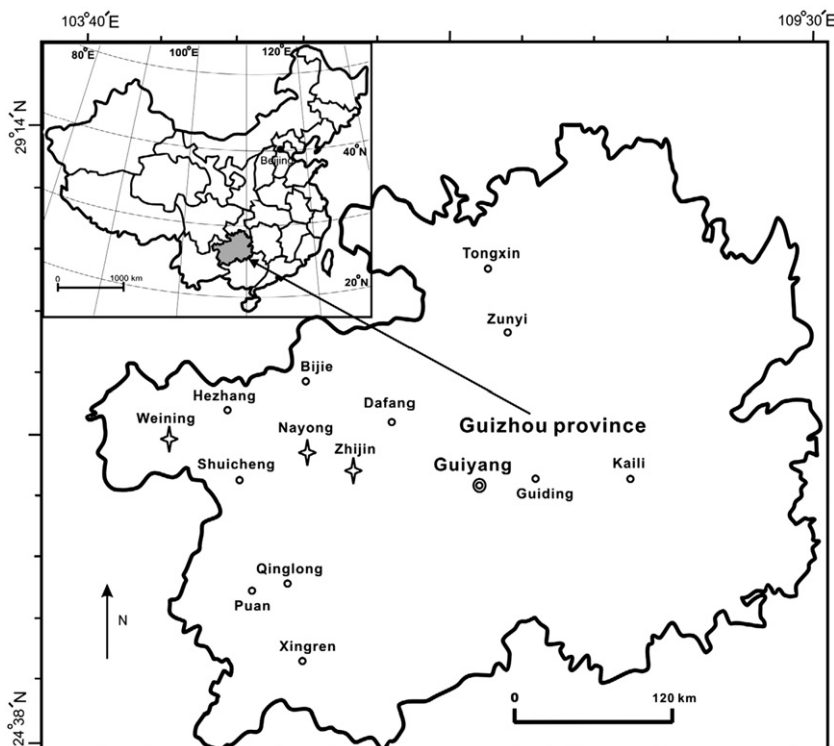


Fig. 1. Study area in western Guizhou Province.

and is composed of sandstone, siltstone, mudstone, limestone, and over 30 coal seams. The units formed from lagoons and tidal flats to lower delta plains to tidal flats and carbonate subtidal flats. The 130-m thick Changxin Formation is the sediments from shallow marine and paralic delta. The 51-m thick Dalong Formation mainly consists of interbanded silica rocks and mudstones. There are more than 50 coal seams, including both minable and un-minable seams, within the coal-bearing strata in the study area.

Twenty five coal and carbonaceous shale samples were collected in Weining, Nayong and Zhijin, western Guizhou province in this study (Fig. 1). The coal ashes of these samples range from 9.04% to 93.9%.

3. Analytical methods

3.1. Instrumentation and reagents

The instrument used in this study is an ELAN DRC-e ICP-MS in the State Key Lab of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Background counts for 2% HNO₃ solutions are normally <5 cps (counts per second) for all PGEs. The sensitivity of the instrument was adjusted to >40,000 cps for 1 ng/ml of ¹¹⁵In, in order to achieve the desired detection limits.

HCl and HNO₃ were purified by sub-boiling distillation. Water was obtained from 18 MΩ.cm grade Millipore purification system.

Te solution (about 2 mg/ml) and SnCl₂ solution (20%, w/v) were purified by Te-coprecipitation following the procedure described by Qi et al. (2004).

The Carius tubes, custom-made high-pressure autoclave, and Os distillation system are the same as that described by Qi et al. (2007).

Spike solutions with enriched stable isotopes, ¹⁹⁰Os, ¹⁰¹Ru, ¹⁰⁵Pd, ¹⁹³Ir, and ¹⁹⁴Pt were prepared from pure metals (US Services Inc., Oxbow, N J). An ICP multi-element standard solution of 100-μg/ml Pt, Pd, Rh, Ru, Ir, and Au (AccuStandard, USA) was used and diluted as needed for calibrating the spike solutions and the concentrations of mono-isotopic element, Rh.

3.2. Analytical procedure

In this study, 10 g of powdered coal sample was accurately weighed and placed in a porcelain crucible and ignited in a muffle furnace at 750 °C to completely remove organic and inorganic carbon, the resultant ash was then transferred to a 75 ml Carius tube. Appropriate amounts of enriched isotope spike solution containing ¹⁹⁴Pt, ¹⁰⁵Pd, ¹⁰¹Ru, ¹⁹³Ir, and ¹⁹⁰Os were accurately added and mixed with 25 ml *aqua regia*. The sealed Carius tube was placed in a custom-made high-pressure autoclave filled with water to prevent explosion of the tube when heated to about 250 °C (Qi et al., 2007). After 10 h, the Carius tube was cooled and the contents were

Table 1
Blank (ng) and analytical results (ng/g) of reference materials, WGB-1, TDB-1 and WPR-1

Elements	Blank	WGB-1 (gabbro)			TDB-1 (diabase)			WPR-1 (peridotite)	
		Average N=5	Meisel	Certified	Average N=5	Meisel	Certified	Average N=5	Certified
Os	0.0026	0.35±0.02	0.544		0.14±0.01	0.117		14.2±0.6	13
Ir	0.025	0.15±0.02	0.211	0.33	0.088±0.01	0.075	0.15	13.2±0.9	13.5
Ru	0.017	0.15±0.01	0.144	0.3	0.21±0.02	0.198	0.3	22.8±1.5	22
Rh	0.026	0.21±0.02	0.234	0.32	0.51±0.02	0.471	0.7	12.5±0.8	13.4
Pt	0.18	6.55±0.65	6.39	6.1	5.55±0.32	5.01	5.8	292±11	285
Pd	0.37	13.5±1.2	13.9	13.9	23.8±1.3	24.3	22.4	225±15	235

Meisel=(Meisel and Moser, 2004); Certified=(Govindaraju, 1994).

Table 2
Platinum group elements abundance (ng/g) for coal in western Guizhou Province, SW, China

Sample number	Sample locations	GPS locations	Ash%	Os	Ir	Ru	Rh	Pt	Pd		
WN-1	Weining coalfield	26°41'35"N 104°38'50"E	90.5	0.028	0.023	0.026	0.016	0.26	0.23		
WN-2			83.1	0.042	0.022	0.028	0.027	0.45	0.24		
WN-4			93.9	0.096	0.024	0.025	0.018	0.42	0.65		
WN-7			26°51'34"N 104°17'00"E	77.8	0.141	0.01	0.008	0.012	0.15	0.42	
WN-8				24.8	0.101	0.017	0.056	0.028	0.58	0.18	
WN-9			26°45'26"N 104°11'15"E	90.5	0.014	0.016	0.038	0.016	0.31	0.58	
WN-10					82.2	0.007	0.021	0.032	0.017	0.41	0.67
Average						0.061	0.019	0.030	0.019	0.37	0.42
NY-1			Nayong coalfield	26°42'34"N 105°15'04"E	13.2	0.005	0.012	0.007	0.044	0.77	0.43
NY-2					19.0	0.137	0.039	0.079	0.078	6.43	1.01
NY-3	32.1	0.05			0.018	0.031	0.052	1.07	0.32		
NY-4	26°43'49"N 105°17'59"E	29.3			0.05	0.025	0.027	0.09	2.18	1.98	
NY-5		12.2			1.749	0.071	0.343	0.159	9.26	3.31	
ZJ-1	Zhijin coalfield	26°49'31"N 105°40'32"E	75.8	0.028	0.095	0.056	0.302	5.74	7.87		
ZJ-2			86.3	0.034	0.023	0.019	0.082	1.68	2.73		
ZJ-3			26°49'31"N 105°40'55"E	16.9	0.015	0.025	0.015	0.038	0.75	0.54	
ZJ-4				38.0	0.026	0.016	0.023	0.105	2.18	2.79	
ZJ-5			85.3	0.002	0.012	0.003	0.01	0.33	0.52		
ZJ-6			12.1	0.047	0.088	0.037	0.109	3.68	3.84		
ZJ-7			26°46'26"N 105°43'17"E	52.6	0.017	0.007	0.007	0.029	0.55	0.62	
ZJ-8				23.8	0.022	0.013	0.021	0.046	1.23	2.77	
ZJ-9			26°46'15"N 105°43'25"E	79.9	0.056	0.083	0.094	0.118	3.38	1.24	
ZJ-10				9.04	0.024	0.01	0.012	0.013	0.38	0.52	
ZJ-11			26°40'24"N 105°57'59"E	90.9	0.021	0.016	0.013	0.009	0.21	0.4	
ZJ-12				69.7	0.229	0.086	0.275	0.377	7.9	0.56	
ZJ-13				68.8	0.302	0.06	0.316	0.422	7.63	0.6	

transferred to a 50-ml centrifuge tube. After centrifuging, the upper solution was transferred to a distillation system for Os distillation (Qi et al., 2007). The collected Os solution was used for measuring the Os concentration by isotope dilution. After distillation, the remaining solution was used to pre-concentrate PGE by Te-coprecipitation and all the interference elements are removed by using a cation exchange resin and P507 extraction chromatography resin combined in the same column as described by Qi et al. (2004). Platinum, Pd, Ru, and Ir were measured by isotope dilution, whilst ^{194}Pt was used as the internal standard to calculate the concentration of the mono-isotope element Rh (Qi et al., 2004).

3.3. Quality controls

The CCRMP (Canadian Certified Reference Materials Project) certified reference materials, WGB-1 (gabbro), TDB-1 (diabase), and WPR-1 (peridotite) were used in this study for quality controls, because of the lack of international PGE coal reference materials. Analytical results are shown in Table 1. The PGE concentrations for Ru, Rh, and Ir in WGB-1 and TDB-1 are lower than the certified values, but agree well with reported values (Meisel et al., 2003; Meisel and Moser, 2004). The results for WPR-1 are in excellent agreement with the certified values. The total procedural blanks

Table 3
The interference of molecules, selected isotope, resolution needed and interference ratios

Interference of molecules	PGE Isotope	Resolution needed	Interference ratios
$^{65}\text{Cu}^{40}\text{Ar}^+$	^{105}Pd	7042	0.15%
$^{64}\text{Zn}^{40}\text{Ar}^{1}\text{H}^+$	^{105}Pd	18340	0.28%
$^{88}\text{Sr}^{16}\text{O}^{1}\text{H}^+$	^{105}Pd	31983	0.11%
$^{89}\text{Y}^{16}\text{O}^+$	^{105}Pd	24373	0.56%
$^{179}\text{Hf}^{16}\text{O}^+$	^{195}Pt	8108	1.86%
$^{177}\text{Hf}^{16}\text{O}^+$	^{193}Ir	7782	1.64%
$^{61}\text{Ni}^{40}\text{Ar}^+$	^{101}Ru	8312	1.01%
$^{63}\text{Cu}^{40}\text{Ar}^+$	^{103}Rh	7609	0.08%

were lower than 0.0003 ng/g for Os; 0.003 ng/g for Ru, Rh and Ir, 0.04 ng/g for Pd, and 0.02 ng/g for Pt.

4. Results and discussion

4.1. The PGE results of this study

Dai et al. (2003) used a muffle furnace to ignite the coal samples at 750 °C for 5 h to completely remove organic and inorganic carbon. Although PGEs may be lost during the ignition (Mitkin et al., 2000; Mitkin, 2006; Seredin, 2007), for comparison, in this study, samples were also ignited at 750 °C in a muffle furnace and then prepared as described above. The results are listed in Table 2. Samples from Weining have the lowest PGE contents ranging from 0.15 to 0.58 ng/g for Pt and 0.18 to 0.65 ng/g for Pd and the average values (ng/g) are Os (0.061), Ir (0.019), Ru (0.030), Rh (0.019), Pt (0.37) and Pd (0.42). In Nayong and Zhijin, the PGE contents are much higher than Weining which ranged from 0.21 to 9.26 ng/g for Pt and 0.32 to 7.87 ng/g for Pd (Table 2). The highest Pt and Pd contents of the 25 samples analyzed in this study are lower than the lowest values previously reported and 200–400-times lower than the highest previous reported values (Dai et al., 2003, 2004, 2005a; Yang, 2006). As reported by Mitkin et al. (2000), up to 14% of Pt, 40% of Pd, 40% of Ru, and 10% of Ir may be lost as gaseous reaction products during high-temperature ashing, thus, the results obtained in this study may lower than the actual values.

4.2. The previously reported PGE results

Dai et al. (2003) reported high PGE background values in Chinese coals (Pd 150 ng/g, Pt 30 ng/g, Ru 5 ng/g, Rh 14 ng/g, and Ir 1 ng/g). They also reported high PGE contents (Pt 10–110 ng/g and Pd 30–540 ng/g) in coal seams in western Guizhou Province. Dai et al. (2004) reported Pt (30–2430 ng/g), Pd (82–4240 ng/g), Ir (2–64 ng/g), Ru (3–52 ng/g) and Rh (4–30 ng/g) in some coal seams in Zhijin coalfield, especially for No. 30 coal seam which has high concentration of Pt (2430 ng/g) and Pd (2100 ng/g). Dai et al. (2005a) also reported Pt (40–150 ng/g) and Pd (100–1570 ng/g) in

Table 4
Comparing the results (ng/g) of direct measurement and isotope dilution

Sample	Sample type	Method used	¹⁰⁵ Pd	¹⁹⁵ Pt
G-2	Granite	DM	636	71
GSR-1	Granite	DM	988	45
QL-99	Coal ash	DM	3200	164
QL-99	Coal ash	ID	11.0	12.8

DM=Direct measurement; ID=isotope dilution.

Dafang coalfield in western Guizhou province. Yang (2006) reported Pt (18–98 ng/g) and Pd (90–640 ng/g) in Puan coalfield in Guizhou province.

4.3. The validity of previously reported PGE results

The previously used analytical method (Dai et al., 2003, 2004, 2005a; Yang, 2006) for PGE analyses in coals was reported by Xie et al. (2001). They used HCl, HNO₃, HF, and HClO₄ to decompose the sediments from Tunguska explosion site, Russia, and measured directly by VG Plasma Quad II ICP-MS without pre-concentration. The instrument they used was high-resolution (HR) ICP-MS, but the exact resolution was not reported (Dai et al., 2003, 2004, 2005a; Yang, 2006). Although the PGE isotopes they selected can avoid the interference of isobaric spectral overlap, the polyatomic interferences cannot be avoided. For example, the atomic interferences of Cu, Zn, Sr, Y, and Hf combined with H, O, and Ar can significantly interfere the determination of Pd and Pt even in high resolution mode (Table 3). Normally, the concentrations of Cu, Zn, Sr, Y, and Hf are about 3–4 orders-of-magnitude higher than PGEs. So, the concentrations of PGEs will be much higher than the actual values when the direct-measurement technique is used.

In our study, 100 ng/ml of single Cu, Zn, Sr, Y, Hf, and Ni standard solutions were used to investigate the interferences. Table 3 shows the interference of molecules to PGE isotopes, the resolution required to separate the interference and the interference ratios. The interference ratios are the intensity ratios of selected PGE isotopes and the isotopes of interference elements. The selected isotopes were referred to Dai et al. (2003, 2004, 2005a) and Yang (2006). The Interference ratios of Cu, Zn, Sr, and Y on ¹⁰⁵Pd range from 0.11 to 0.56% and Hf on ¹⁹⁵Pt is 1.86% (Table 3), indicating the interferences of atomic molecules are serious and will result in high concentrations of Pd and Pt. Because the concentrations of Cu, Zn, Sr, and Y are much higher than Hf in coals, especially with a hydrothermal fluid origin (Dai et al., 2005a,b), the interferences of ¹⁰⁵Pd for coal samples are much higher than ¹⁹⁵Pt. That may be the reason why the previous reported values have higher Pd than Pt in coals from western Guizhou province (Dai et al., 2003, 2004, 2005a; Yang, 2006).

To demonstrate the interference for direct measurement of PGEs by ICP-MS, two international granite reference materials and a coal ash sample were dissolved by using HF and HNO₃ following the method as described by Liang et al. (2000), and measured directly by ICP-MS. The results for direct measurement and isotope dilution technique are shown in Table 4. The concentrations of PGEs for granite are normally less than 1 ng/g (Chi and Yan, 2006), but the results we obtained with direct measurement technique are ranged from 636 to 988 ng/g for Pd and 45 to 71 ng/g for Pt. The Pd contents in coal ashes with direct measurement are 3-orders-of-magnitude higher than isotope dilution technique. These facts suggested that the previous results may be incorrect with the direct measurement technique.

Considering the samples we collected are from the same area with the previous reported samples, the large differences between PGE contents indicate that previous reported data are incorrect. The sample mass (10 g) used in this study is much larger than the previous reported method (200 mg) (Dai et al., 2003), such that the nugget effect can be reduced. The digestion technique we used was the Carius tube, which is the recommended method for PGE digestion (e.g. Shirey and Walker,

1995; Pretorius et al., 2003). We used Te-coprecipitation and a mixed resin column to separate PGE from the matrix and all the interference elements, so that we can analyze the PGEs without interference (Qi et al., 2004). The isotope dilution technique we used is considered to be the best technique for PGE measurement (e.g. Meisel et al., 2003; Meisel and Moser, 2004; Qi et al., 2004). We also obtained excellent results for three CCRMP certified reference materials as described above. On the contrary, the previous used method is not suitable to the measurement of PGEs and cannot avoid the interference. From all above, we consider that the previous results may incorrect.

Dai et al. (2003) reported PGE background values (ng/g) in Chinese coals Ru (5), Rh (14), Ir (1), Pd (150) and Pt (30) which are much higher than the PGE abundance of crust in eastern part of China (Ru 0.028 ng/g, Rh 0.023 ng/g, Pd 0.28 ng/g, Os 0.046 ng/g, Ir 0.017 ng/g, and Pt 0.26 ng/g) (Chi and Yan, 2006) and all coal samples we collected in western Guizhou province (Table 2). So, we suggested that the PGE background values for Chinese coals are wrong and the PGE background values should be reworked. Because of the large amount of coal reserves in China, it may be the biggest source of Pt and Pd in the world if the PGE contents in coals are as high as the previous reported values.

5. Conclusions

The concentrations of PGEs in coals from western Guizhou province are much lower than the previous reported values. The interference of Cu, Zn, Sr, Y, and Hf generate prominent interference on Pd and Pt with the direct-measurement technique. The previous reported analytical method is not suitable for PGE analysis in coal and the previous reported PGE values in coal from western Guizhou province may be incorrect. The analytical method used in this study is suitable for PGE determination in coal ash and the results are reliable. The PGE background values in Chinese coals should be reworked.

Acknowledgements

This study was supported by “CAS Hundred Talents” Project from Chinese Academy of Sciences to Qi Liang, the National Natural Science Foundation of China (NSFC 40573049), and the Research Grant Council of Hong Kong (HKU7057/05P).

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