NOTE

Precise determination of PGE in a GSJ reference sample JP-1 by ID-ICPMS after nickel sulfide fire assay preconcentration

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All platinum group element (PGE) abundances of a standard rock JP-1 are determined by isotope dilution method (for Ru, Pd, Os, Ir and Pt) and external calibration method (only for Rh) using ICP-MS combined with a fire assay preconcentration technique. The errors range 13–25% (2σ ; $n = 5$), which are comparable with those by the similar methods combined with chemical separation of PGE (Pearson and Woodland, 2000; Meisel *et al.*, 2001).

Large deviations between our data and preferable values proposed by the Geological Survey of Japan (GSJ) are observed for Os and Ir. The scattered Os data might be indicative of heterogeneity of Os in JP-1. From various viewpoints, it seems likely that our Ir data are much more reliable than the preferable values proposed by GSJ.

INTRODUCTION

The platinum group elements (PGE) include six transition metals, i.e., Ru, Rh, Pd, Os, Ir and Pt. On the earth, due to the nature of chemical partitioning, these elements are distinctively depleted in the crust material. On the other hand, most meteorites are enriched in the PGE compared with the crust. Consequently, PGE abundances have been utilized for the index of the cosmic input signature (Alvarez *et al.*, 1980; Esser and Turekian, 1988; Ebihara and Miura, 1996) to surface of the earth. Recently, PGE abundances are also utilized for testifying “late veneer” accretion (Snow and Schmidt, 1998). However, before 90’s, the application of PGE to geochemical studies had been quite limited because of analytical difficulties due to their extremely low concentration (mostly in ppb or lower).

The recent progress in mass spectrometer

opens the door for the “PGE geochemistry”. Due to the development of the negative thermal ionization mass spectrometry (NTIMS) (Creaser *et al.*, 1991; Volkening *et al.*, 1991), Os emerged as a versatile isotopic tracer in various geochemical and cosmochemical issues. As for the other PGE, ICP-MS combined with fire assay technique is one of the most convenient methods for abundance determination. This method has a potential for the simultaneous determination of all PGE in a single measurement. One of the most popular preconcentration procedures along this method is Te coprecipitation after the NiS fire assay (Jackson *et al.*, 1990; Oguri *et al.*, 1999; Gros *et al.*, 2002). However, since this method usually does not use any stable isotope spikes, the complete recovery is required. If isotope dilution technique (ID) is employed, the NiS fire assay technique is expected to give high quality PGE data regardless of chemical recovery. Ravizza and Pyle (1997) did the pio-

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neering work to combine the fire assay and ID-ICP-MS for determining PGE (Os, Ir, Pt and Rh) in geological samples.

However, so far, there have been few available data sets covering all six PGE using ICP-MS. Data on Os and Rh are generally missing because of analytical difficulties (for instance, insufficient achievement of isotope equilibrium and incomplete chemical separation etc. for Os and inability to apply ID due to mono-isotopic element nature and low abundance for Rh). With Os and Rh data, we could further go into the details of mutual fractionation of PGE during various geological processes, such as weathering and planetary differentiation, and of identifying the group of meteorites, which impacted during the K-T period. Namely, the geochemical/cosmochemical application of PGE abundances must be extended as a "fingerprint" like REE. Actually, based on PGE data, McDonald *et al.* (2001) recently reported that the projectile, which stuck at the Morokong impact crater formed at the Jurassic-Cretaceous boundary, was probably an ordinary chondrite (McDonald *et al.*, 2001). However, as pointed out by Schmidt *et al.* (1997) and Schmitz *et al.* (2001), the problem in uncertainties of PGE abundances in meteorites still remains.

The aim of this paper is to report whole PGE data including Os and Rh of JP-1, a reference sample issued from the Geological Survey of Japan (GSJ), by ICP-MS (ID-ICP-MS for five multi-isotope elements and calibration line method for Rh) to evaluate the quality of our data. We employ the fire assay preconcentration technique developed by Li *et al.* (1996), which was initially employed in neutron activation analysis.

ANALYTICAL METHOD

The sample used in this study is a standard rock sample JP-1, which is distributed from GSJ. JP-1 is a peridotite collected at Horoman in the Hokkaido Island in Japan and expected to show high PGE concentration (1–10 ppb) (Imai *et al.*, 1995). Recently, Suzuki and Tatsumi (2001) reported Os concentration and isotopic ratio data of

JP-1. As for Ir, Pd, Ru and Pt, only the preferable values based on two data sets are proposed (Imai *et al.*, 1995), and none for Rh.

The fire assay technique for PGE preconcentration is almost identical with that of Li and Ebihara (2003), a modified technique of Li *et al.* (1996). A fusion mixture of the following composition is added to 5 g of JP-1 powder: sodium tetraborate 10 g, sodium carbonate 5 g, nickel powder 0.5 g, sulphur 0.3 g, silica 1 g and mixture of PGE enriched spike (^{100}Ru , ^{105}Pd , ^{189}Os , ^{191}Ir and ^{196}Pt). The fusion mixture and sample are thoroughly mixed and then transferred into a china crucible. The fusion is carried out for 20 minutes at 850°C followed by 20 minutes at 1000°C in an electrical furnace. After the fusion is done, the NiS button is separated from the slag. The button is crushed and heated with 6M HCl to dissolve NiS. Subsequently, the solution is passed through a 0.2 μm PTFE membrane filter to separate a precipitate, which contains PGE. The precipitate is dissolved in 6M HCl with hydrogen peroxide. After the complete dissolution, internal standards (In and Tl) for Rh measurement are added. The final solution is prepared by diluting to 25 ml and afforded for the isotopic analysis.

Every set of analysis (typically four samples), we prepare procedure blanks, which are processed identically with the samples.

The isotopic analyses are performed by ICP-MS (VG Plasma Quad3). For isotope dilution method, we determine following isotopic ratios: $^{100}\text{Ru}/^{101}\text{Ru}$, $^{105}\text{Pd}/^{106}\text{Pd}$, $^{189}\text{Os}/^{190}\text{Os}$, $^{191}\text{Ir}/^{193}\text{Ir}$ and $^{196}\text{Pt}/^{195}\text{Pt}$. As for Rh, a mono-isotopic element (^{103}Rh), we use an external calibration method using Rh standard solutions with In and Tl internal standards for abundance determination. We also apply the calibration method for the other PGE to monitor recovery of each element (calibration method data/ID data).

Several possible isobaric interferences are summarized in Table 1 (Pb solution analysis indicates that there is no ^{206}Pb double charge ion interference on mass number 103). Based on Table 1, we correct the isobaric interferences for Ru, Rh and Pd isotopes, measuring Ni, Cu, Zn, Zr, Mo

Table 1. Isobaric interferences on PGE isotopes

Isotopes	Interferences
^{100}Ru	^{100}Mo , $^{65}\text{Cu}^{35}\text{Cl}$, $^{63}\text{Cu}^{37}\text{Cl}$, $^{60}\text{Ni}^{40}\text{Ar}$, $^{62}\text{Ni}^{38}\text{Ar}$, $^{64}\text{Ni}^{36}\text{Ar}$, $^{64}\text{Zn}^{36}\text{Ar}$
^{101}Ru	$^{64}\text{Ni}^{37}\text{Cl}$, $^{64}\text{Zn}^{37}\text{Cl}$, $^{66}\text{Zn}^{35}\text{Cl}$, $^{61}\text{Ni}^{40}\text{Ar}$, $^{63}\text{Cu}^{38}\text{Ar}$, $^{65}\text{Cu}^{36}\text{Ar}$
^{103}Rh	$^{66}\text{Zn}^{37}\text{Cl}$, $^{68}\text{Zn}^{35}\text{Cl}$, $^{63}\text{Cu}^{40}\text{Ar}$, $^{65}\text{Cu}^{38}\text{Ar}$, $^{67}\text{Zn}^{36}\text{Ar}$
^{105}Pd	$^{68}\text{Zn}^{37}\text{Cl}$, $^{70}\text{Zn}^{35}\text{Cl}$, $^{65}\text{Cu}^{40}\text{Ar}$, $^{67}\text{Zn}^{38}\text{Ar}$
^{106}Pd	^{106}Cd , $^{90}\text{Zr}^{16}\text{O}$, $^{66}\text{Zn}^{40}\text{Ar}$, $^{68}\text{Zn}^{38}\text{Ar}$, $^{70}\text{Zn}^{36}\text{Ar}$
^{189}Os	non
^{190}Os	^{190}Pt
^{191}Ir	non
^{193}Ir	non
^{195}Pt	non
^{196}Pt	non

and Cd standard solutions during sample analysis. The corrections of isobaric interferences are performed for both samples and procedure blanks. The contributions of isobaric interferences to the samples are ^{100}Ru , 10–25% (mainly ^{100}Mo); ^{101}Ru ; less than 1%; ^{103}Rh ; less than 1%; ^{105}Pd , less than 1%; ^{106}Pd ; 5–40% (mainly $^{90}\text{Zr}^{16}\text{O}$). Then, the real counts of samples are obtained by subtracting the procedure blanks from the samples. Relative procedural blank corrections for PGE are Ru, less than 2%; Rh, less than 1%; Pd, 2–4%; Os, less than 3%; Ir, less than 1%; and Pt, 2–5%. Finally, the calculated isotopic ratios are further corrected for the mass discrimination using the PGE standard solutions.

The Rh data are corrected for recovery, which is assumed to be same as the averaged recovery of Ru, Pd, Pt and Ir (more than 85% in most cases). As for Ru, Pd and Pt, we have tried cross-checking of data using various sets of isotopic ratios obtained by reanalyzing JP-1 (3) and (4): Ru, $^{100}\text{Ru}/^{101}\text{Ru}$, $^{100}\text{Ru}/^{99}\text{Ru}$; Pd, $^{105}\text{Pd}/^{106}\text{Pd}$, $^{105}\text{Pd}/^{108}\text{Pd}$; Pt, $^{196}\text{Pt}/^{194}\text{Pt}$, $^{196}\text{Pt}/^{195}\text{Pt}$, and $^{196}\text{Pt}/^{198}\text{Pt}$. All the elements show good internally consistent results, which agree within 4%. Further detailed analytical procedure will be reported elsewhere.

RESULTS AND DISCUSSION

The PGE concentrations of JP-1 are shown in Table 2 together with the previously reported data. The average and error of replicate analyses are

also shown. The errors of each measurement are less than 5% in most cases.

The 2sigma-error/average (%) of PGE range 13–25%, which are comparable with those for the PGE analyses of reference materials reported by Pearson and Woodland (2000) and Meisel *et al.* (2001), both of which are employing solvent extraction/anion exchange separation techniques after acid digestion. Taking into the consideration that we do not separate any coexisting elements, such as Zr and Hf, we believe that the reproducibility of our analyses is satisfactory.

Only few data are available for PGE in JP-1 and do not necessarily show good agreement with our data. Between our data and the GSJ preferable values, Ru and Pd show good agreement, but Os and Ir do not.

Suzuki and Tatsumi (2001) recently reported the Os isotopic ratio and concentration of JP-1. Although the duplicate isotopic analyses show almost identical values, the duplicate concentration analyses differ in 10%. They suggested that the heterogeneous distribution of Os in sample resulted in such difference in concentration. Our data are 40 to 60% higher than those of Suzuki and Tatsumi (2001).

One of the possible explanations for the difference between our data and those by Suzuki and Tatsumi (2001) is the preferential loss of spike Os. The fire assay technique used in this study might be more prone to the loss of spike Os than the Carius tube method employed by Suzuki and

Table 2. PGE concentrations of JP-1 (ppb)

	Os	Ir	Ru	Rh	Pt	Pd
JP-1(1)	3.49 ± 0.05	3.05 ± 0.10	5.62 ± 0.05	0.844 ± 0.019	3.67 ± 0.12	1.28 ± 0.03
JP-1(2)	3.95 ± 0.16	3.56 ± 0.21	5.95 ± 0.14	0.775 ± 0.005	3.79 ± 0.09	1.21 ± 0.02
JP-1(3)	4.03 ± 0.06	3.12 ± 0.05	6.31 ± 0.08	0.819 ± 0.009	3.80 ± 0.11	1.35 ± 0.06
JP-1(4)	3.75 ± 0.16	3.35 ± 0.05	6.00 ± 0.07	0.926 ± 0.026	4.25 ± 0.14	1.28 ± 0.06
JP-1(5)	4.82 ± 0.10	3.48 ± 0.07	7.00 ± 0.09	1.010 ± 0.020	4.44 ± 0.07	1.51 ± 0.03
average ($n = 5$)	4.01	3.31	6.18	0.875	3.99	1.33
error (1sigma)	0.50	0.22	0.52	0.093	0.33	0.11
2sigma/average (%)	24.9	13.4	16.9	21.4	16.8	17.2
GSJ preferable value	7.9	2.0	6.5	—	4.9	1.3
Suzuki and Tatsumi (2001)	2.44, 2.71	—	—	—	—	—

Fig. 1. CI-normalized PGE patterns of JP-1. The concentrations of CI chondrites are from McDonough and Sun (1995).

Tatsumi (2001). If the preferential loss of spike solution could occur, it would result in erroneous high Os concentration. From following reasons, however, we will deny a possibility of the preferential loss of spike Os in our sample. PGE in the Allende meteorite of different samples amounts (5–20 mg) were determined by using the same procedure and Os concentration, 892 ± 14 ppb ($n = 3$; Nishino, 2002) was found to be consistent with literature values (830–860 ppb) (Jochum, 1996; Wolf *et al.*, 1983). Recently, Lee (2002)

compared the Os concentration data of peridotite xenoliths determined by acid digestion and by fire assay and found that most of the data agrees within 25%. These facts support the reliability of our method and suggest that the difference is not due to the analytical artifacts. Although further intensive studies are required, we think that Os is highly heterogeneous in JP-1 as suggested by Suzuki and Tatsumi (2001).

The CI chondrite-normalized PGE patterns for JP-1 are plotted in Fig. 1 together with that of the

Fig. 2. Diagram of CI chondrite-normalized Pt/Ir vs. Ru/Ir. Note that the GSJ preferable data point clearly deviates from the other data.

GSJ preferable values. We arrange PGE (x -axis) in the order of melting point (high to low), following Pattou *et al.* (1996). The clear differences in Os and Ir concentrations are observed between our data and the GSJ preferable values. First, we would like to evaluate the Ir concentrations. Rehkamper *et al.* (1999) reported Ir, Ru, Pt and Pd concentrations of peridotites from Horoman, Japan, which is the same sampling location as that of JP-1. Figure 2 is a diagram of CI chondrite-normalized Pt/Ir vs. Ru/Ir of JP-1 and the Horoman peridotites analyzed by Rehkamper *et al.* (1999). The GSJ preferable value point clearly deviates from both our data and the Horoman data. Although the Horoman data are scattered, Fig. 2 suggests that $(\text{Ru/Ir})_N$ of the peridotites (both Horoman and JP-1) should be less than 1.5. So, our data seem to be compatible with the data of Rehkamper *et al.* (1999). Therefore, the GSJ preferable value seems to show too high Ru concentration or too low Ir concentration. We think that the high Ru concentration is improbable because the Ru concentration shows good agreement with our data. Furthermore, Shinozuka *et al.* (2003) recently report the PGE data (except for Os) of JP-1 by NiS fire assay preconcentration with Te coprecipitation technique and found that their Ir

concentration is 3.4 ppb, which is almost identical with our data. Consequently, we conclude that the GSJ preferable Ir concentration must be lower than the true value. At now, our data determined by ID method seem to be the most reliable ones.

It is not easy to evaluate whether Rh data are reliable or not due to lack of any reference value. Aforementioned above we arrange the PGE as the same manner as Pattou *et al.* (1996) and found a smooth decrease trend from Ru to Pd. This implies that Rh data fall on this trend and supports the reliability of our Rh data.

SUMMARY

We determined all the PGE of JP-1 issued from GSJ using ID-ICP-MS combined with fire assay technique. Compared our data with the preferable data proposed by GSJ, the large deviations are observed for Os and Ir. The Os data also deviate from those reported by Suzuki and Tatsumi (2001). These observations suggest that Os is highly heterogeneous in JP-1. On the other hand, as for Ir, various evidences indicate that our data are much more reliable than the preferable value. The smooth PGE patterns from Ru to Pd might verify our Rh data.

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