Talanta 81 (2010) 954–958

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of rhenium content in molybdenite by ICP–MS after separation of the major matrix by solvent extraction with N-benzoyl-N-phenylhydroxalamine

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ARTICLE INFO

Article history:
Received 16 October 2009
Received in revised form 18 January 2010
Accepted 20 January 2010
Available online 25 January 2010

Keywords:
Re–Os dating
Molybdenite
N-Benzoyl-N-phenylhydroxylamine
Solvent extraction
ID–ICP–MS

ABSTRACT

A simple and rapid analytical method for determining the concentration of rhenium in molybdenite for Re–Os dating was developed. The method used isotope dilution–inductively coupled plasma–mass spectrometry (ID–ICP–MS) after the removal of major matrix elements (e.g., Mo, Fe, and W) from Re by solvent extraction with N-benzoyl-N-phenylhydroxylamine (BPHA) in chloroform solution. The effect on extraction efficiency of parameters such as pH (HCl concentration), BPHA concentration, and extraction time were also assessed. Under the optimal experimental conditions, the validity of the separation method was accessed by measuring ^{187}Re/^{185}Re values for a molybdenite reference material (JDC). The obtained values were in good agreement with previously measured values of the Re standard. The proposed method was applied to replicate Re–Os dating of JDC and seven samples of molybdenite from the Yuanzhuding large Cu–Mo porphyry deposit. The results demonstrate good precision and accuracy for the proposed method. The advantages of the method (i.e., simplicity, efficiency, short analysis time, and low cost) make it suitable for routine analysis.

1. Introduction

The ^{187}Re–^{187}Os isotopic system based on the β^- decay of radioactive ^{187}Re to stable ^{187}Os is thought to be highly suitable for the directly dating of sulfide minerals [1]. As a chronometer, the Re–Os isotopic system has proven particularly useful analyses of molybdenite (MoS_2), because of its extremely high Re/Os ratio, which results in Os isotopic compositions that are close to 100% radiogenic ^{187}Os [2–5]. Consequently, molybdenite is ideally suited to geochronological applications using the ^{187}Re–^{187}Os isotope system.

Recent advances in various mass spectrometric techniques and chemical procedures have enabled easier access to Re–Os isotope measurements [6–19]. Using laser ablation–multiple collector–inductively coupled plasma mass spectrometry (LA–MC–ICPMS), it is now possible to date microscale samples of molybdenite [4]; however, this method is not routinely used for molybdenite because of large analytical uncertainty and the great expense of the analytical equipment.

Inductively coupled plasma–mass spectrometry (ICP–MS) is widely used to determine Re–Os concentrations because of its high sensitivity and relatively simple chemical treatment process; however, ICP–MS performance in analyses of geological materials is commonly affected by interface effects, matrix effects (suppression and/or enhancement), polyatomic and isobaric interference, signal drift, and memory effect. When bulk solutions of geological samples are analyzed, high levels of salt content cause plugging of the sampling orifice, with a concomitant decrease in signal intensity; the salt also causes severe matrix effects and many potential spectral interferences [20].

For the measurement of Re in molybdenite by ICP–MS, the simplest way to reduce the matrix and salt effects is to use large dilution factors; however, this approach is not feasible in the case of high levels of Mo and relatively low levels of Re in molybdenite. Therefore, separation of the analytes of interest from the matrix elements prior to ICP–MS measurement remains the most efficient way to avoid matrix effects, polyatomic and isobaric overlap interferences, and clogging problems. In this regard, ion-exchange technology has been developed for the separation of Re from molybdenite since the 1980s [15]. However, in some cases, two columns using anion-exchange resins were employed to separate the major elements; consequently, the complex and time-consuming nature of the ion-exchange procedure has become a major disadvantage in routine analysis. Du et al. [10] used an acetone extraction method to separate Re from the other matrix elements. Although acetone extraction is a simpler procedure than anion exchange, it is difficult to distinguish the acetone phase from the aqueous phase.

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doi:10.1016/j.talanta.2010.01.043

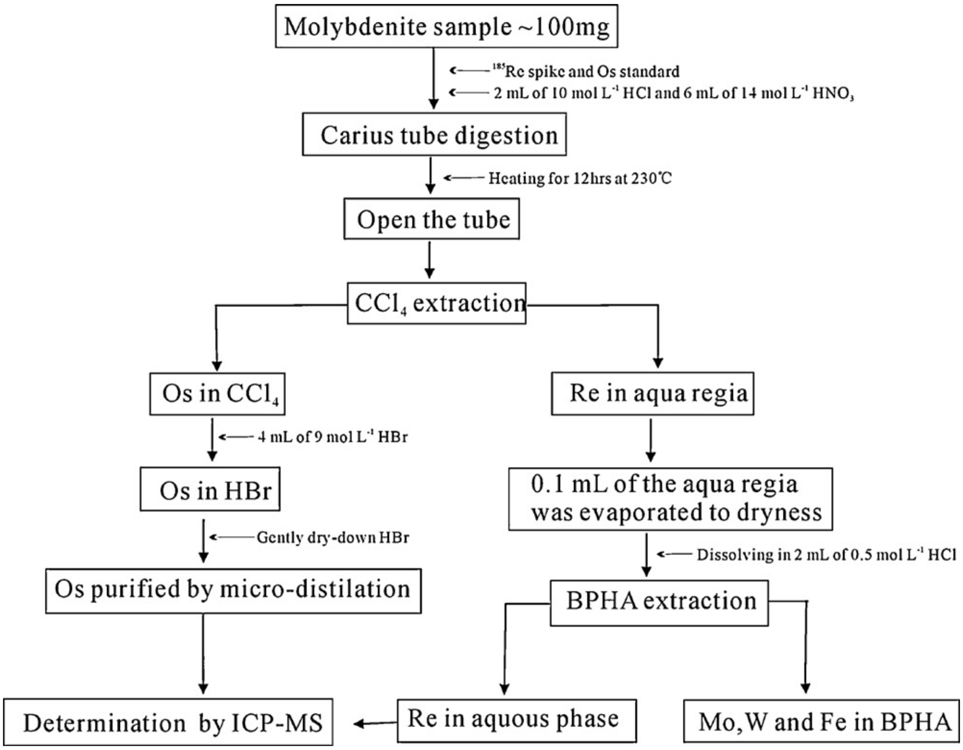

Fig. 1. Separation scheme of Re and Os from molybdenite matrices.

Recently, Shinotsuka and Suzuki [21] used N-benzoyl-N-phenylhydroxylamine (BPHA) in chloroform solution to separate platunim group elements (Pt, Pd, Ru and Ir) and Re from interfering elements (i.e., Zr, Mo, Hf, and W). Because BPHA acts as a typical chelating agent, even under high concentrations of acid, it selectively extracts tetra-, penta- and hexavalent group ions from strongly acid solutions into $CHCl_3$ with BPHA [22–27]; hence, it is suitable for removing the above matrix elements and interferents. This method is simple, rapid, and effective in removing Zr, Mo, Hf, and W from PGEs and Re. Encouraged by the results obtained by Shinotsuka and Suzuki, a solvent extraction method using BPHA for the separation of Re from Mo-rich molybdenite prior to ICP–MS measurement was investigated. To the best of our knowledge, this is the first report to describe the purification of Re in molybdenite samples. Combined with Carius tube digestion and Os extraction using CCl_4 solvent, a simple and effective procedure for the determination of Re and Os concentrations in molybdenite was established. The potential of the procedure is demonstrated by analyses of molybdenite reference material (JDC).

2. Material and methods

2.1. Sample and reagents

To test the proposed method, molybdenite reference material (JDC) obtained from the Jinduicheng porphyry molybdenum deposit in the east Qingling molybdenum belt, Shaanxi Province, China was used [5,10]. The molybdenite for analysis was obtained using the floatation method and ground to 200 mesh and blended to assure homogeneity. The contents of major and minor components in JDC, including Re and Os, have been determined previously [5,10,17–19]. ^{185}Re-enriched Re metal was purchased from Oak Ridge National Laboratory. This material was dissolved in concentrated nitric acid. The ^{185}Re content of the spikes was determined using isotope dilution method by calibration against a Re standard which concentration was obtained by gravimetric method. This Re standard was a natural Re standard solution prepared by dissolving high purity Re ribbon (99.999%, Niloco Co., Japan) with concentrated nitric acid. A commercial Os standard solution with common isotopic abundances (Johnson Matthey Corporation) was used to determine the ^{187}Os content by the isotope dilution method. Common Os can be employed as a type of isotopic internal standard because molybdenite contains only pure radiogenic ^{187}Os, according to its structure during formation [16,17,19]. In the present analyses, pure water from a Milli-Q system (Millipore Ltd.) and acids (HCl, HNO_3 and HBr) from a sub-boiling distillation system was used. Osmium extraction was performed with HPLC-grade carbon tetrachloride (Tianjing Kermel Chemical Reagent Co., Ltd.). N-Benzoyl-N-phenylhydroxyl-amine (BPHA) was obtained from Aladddin Reagent Inc. China, and was purified by recrystallization via aqueous solution, solubility 5 g L^{-1} at 95 °C, 0.3 g L^{-1} at 4 °C. BPHA solution in chloroform (0.2 mol L^{-1}) was prepared by dissolving 4.26 g of purified BPHA in 100 mL of chloroform (Tianjing Kermel Chemical Reagent Co., Ltd.). Absolute alcohol was purchased from Tianjing Kermel Chemical Reagent Co., Ltd.

2.2. Separation method

The proposed separation procedure for Os and Re is shown in Fig. 1F. The proposed analytical procedure for determining Os concentrations is based on Carius tube digestion [11] combined with carbon tetrachloride extraction [13,14] and micro-distillation [28]. The Carius tube method is an effective decomposition technique for achieving complete isotopic equilibration of sample-derived Os with the enriched spike in a wide range of geological materials [17]. Between 50 and 100 mg of sample powder was weighed and transferred, together with ^{185}Re spike (typically 0.05 mL of 4.672 μg mL^{-1}) and common Os standard (0.06 mL of 0.912 μg mL^{-1}) solutions and inverse aqua regia (6 mL of 14 mol L^{-1} HNO_3, 2 mL of 10 mol L^{-1} HCl) to Carius tubes chilled in a bath mixture of liquid nitrogen and ethanol. The Carius tubes were sealed and heated at 230 °C for at least 12 h. After cooling, the tubes were frozen in a bath mixture of liquid nitrogen and ethanol and opened carefully with a propane torch. The solution was transferred into a 20 mL PFA vessel, and 4 mL of chilled carbon tetrachloride was added. This mixture was allowed to warm, and was shaken for 2 min. The organic fraction containing Os was then transferred into another 20 mL PFA vessel. Carbon tetrachloride extraction from the aqua regia fraction was performed twice more, to ensure consistent Os recovery. A total of 9 mol L^{-1} HBr was added to the CC1$_4$ and the mixture was tightly capped in a PFA vessel, allowed to warm to room temperature, and shaken for 2 min. Subsequently, the vessel was placed under a heat lamp for 2 h. After cooling in a freezer, the mixture of Os-bearing HBr and carbon tetrachloride was separated. The Os-bearing HBr fraction was gently evaporated and then further purified by micro-distillation. The purified Os was then ready for analysis by mass spectrometry.

The inverse aqua regia fraction after CCl$_4$ extraction was ready for analyses of Re. Because of the high concentration of Re in molybdenite, only a small aliquot of this solution is needed to provide enough Re for measurement by mass spectrometry. Consequently, only about 0.1 mL of the solution was evaporated to dryness at 135 °C, and the residue was dissolved in 2 mL of 0.5 mol L^{-1} HCl, and then transferred to a centrifugal tube. Next, 1 mL BPHA solution (0.2 mol L^{-1}) was added to the centrifugal tube. The tube was tightly capped and vigorously shaken for about 15 min. Molybdenum, tungsten, and iron were extracted into the organic phase which was then completely separated from the aqueous phase by centrifugation and discarded. Finally, the resulting aqueous phase was clean enough for analysis by mass spectrometry.

2.3. Measurements

All isotope measurments were performed using an ICP–MS instrument (Elan 6000, PerkinElmer, America). The sample injection system used conventional solution nebulization with a concentric glass nebulizer (Glass Expansion, Australia).

The memory effect is a well-known problem in Os measurement by ICP–MS [29,30]. The main source of Os memory is the nebulizer; however, the use of a glass nebulizer can reduce the Os memory effect compared with a Teflon nebulizer. Os memory is readily eliminated by washing the inlet system using 5% (v/v) HCl and ethanol mixed solution, this solution was made from 5 mL of 10 mol L^{-1} HCl and 5 mL of absolute alcohol diluted in 90 mL of water [30].

Mass bias correction was performed using the standard bracketing method for the determination of Re in samples. The Re isotopic ratios obtained for the sample/spike mixtures were corrected using the factors between the average ratios observed in the bracketed standards and those obtained from IUPAC values [31]. The mass bias correction for Os was estimated on-line throughout each measuring session. The mass bias factor for ^{190}Os/^{187}Os was calculated by normalization to ^{192}Os/^{189}Os, which depended on the employed Os standard. Variation in the correction factors between the results of the initial and final standard runs was ~2%.

2.4. Data processing

Re and Os concentrations were determined by the isotope dilution method [32]:

$$C_s = C_{sp}\frac{W_{sp}M_m A_{sp}^{a}(R_m - R_{sp})}{W_s M_{sp} A_s^{b}(1 - R_m R_s)} \qquad (1)$$

where C_s is the unknown concentration of the metal (Re or Os) in the sample(s); C_{sp} is the concentration of the metal (Re or Os) in the spike (sp); W_s and W_{sp} are the weight of the sample and spike, respectively; M_s and M_{sp} are the relative atomic masses of Re or Os in the sample and spike, respectively; A_{sp}^{a} is the isotopic abundance of reference isotope a (^{190}Os or ^{185}Re) in the spike; A_s^{b} is the isotopic abundance of the reference isotope b (^{187}Os or ^{187}Re) in the sample; R_m and R_{sp} are the atomic ratios (isotope b/isotope a) in the mixture and spike, respectively; and R_s is the atomic ratio (isotope a/isotope b) in the sample.

Table 1

Extraction percentages of Fe, Mo and W from 0.1 mol L^{-1} BPHA in chloroform using different concentrations of HCl.

HCl concentration (mol L^{-1})	Extraction percentage (%)		
	Fe	Mo	W
0.05	85.9	98.3	100.0
0.1	85.6	99.6	100.0
0.5	84.6	99.8	100.0
1	64.2	99.6	100.0
2	11.7	99.2	100.0

Molybdenite Re–Os ages were calculated according to the following equation:

$$T = \frac{1}{\lambda}\ln\left(1 + \frac{^{187}\mathrm{Os}}{^{187}Re}\right) \qquad (2)$$

The measured concentrations of Os and Re were converted to atoms of ^{187}Os and ^{187}Re based on the Re and Os isotopic composition of the molybdenite (100% and 62.6% [26], respectively). The ^{187}Re decay constant $\lambda_{\times} = 1.666 \times 10^{-11}$ a^{-1} was employed [33].

Rhenium and Os concentrations, and uncertainties in Re–Os molybdenite dating are presented at the 2σ (standard error) level, which includes uncertainties in mass spectrometer measurements of Re and Os. The uncertainties in weighing the samples and spikes, or uncertainty in the ^{187}Re decay constant were not considered.

3. Results and discussion

3.1. Optimization of separation conditions

The optimum conditions (e.g., HCl concentration, BPHA concentration in the organic phase) for the selective extraction of the major matrix elements (e.g., Mo, W, Fe, and Re) in molybdenite were investigated. In these analyses, the selective extraction efficiencies for these elements were determined by ICP–MS analyses of the aqueous phase before and after extraction.

3.1.1. HCl concentration

The effect of HCl concentration on the selective extraction of Mo, Fe, W, and Re with the BPHA–chloroform system was assessed, testing concentrations in the range of 0.05–2 mol L^{-1}. To avoid the use of synthetic solution, the molybdenite reference material JDC was prepared. About 50 mg of JDC powder was dissolved in 4 mL inverse aqua regia in a sealed Carius tube. After extraction of Os by CCl$_4$, 0.1 mL of aqueous phase was dried-down at 135 °C and then diluted with 2 mL of variable HCl concentrations (for preparation details, see Section 2.2). The extraction was performed using 0.1 mol L^{-1} BPHA solution. The signals of Re, Mo, W, and Fe in an aliquot of the aqueous phase were measured by ICP–MS and compared with those in the control solution.

Table 1 and Fig. 2 show the effect of HCl concentration (in the range of 0.05–2 mol L^{-1}) combined with 1 mL 0.1 mol L^{-1} BPHA solution on the extraction of Mo, Fe, W, and Re from JDC. Almost no Re was extracted in the HCl range of 0.05–2 mol L^{-1}, whereas Mo and W were almost completely extracted, especially at an HCl concentration of 0.5 mol L^{-1}. In addition, about 85% of the Fe was extracted into the BPHA-chloroform phase at an HCl concentration of 0.5 mol L^{-1}. Based on these results, 0.5 mol L^{-1} HCl concentration was used in the present study.

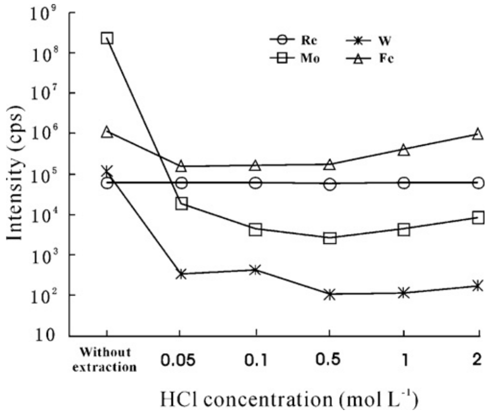

Fig. 2. The effect of the concentrations of HCl in the range of 0.05–2 mol L^{-1} combined with 1 mL 0.1 mol L^{-1} BPHA in chloroform on extraction of Mo, Fe, W and Re from molybdenite reference smaple JDC.

Table 2
Extraction percentages of Fe, Mo and W from different concentrations of BPHA in chloroform using 0.5 mol L^{-1} HCl.

BPHA concentration (mol L^{-1})	Extraction percentage (%)		
	Fe	Mo	W
0.025	21.3	96.5	100.0
0.05	90.7	99.5	100.0
0.1	86.2	99.8	100.0
0.2	97.3	99.4	100.0

3.1.2. BPHA concentration

The effect of BPHA concentration on the extraction efficiencies of Mo, W, Fe and Re was investigated. Samples of the standard JDC were prepared as described in Section 3.1.1. The extraction was carried out using 1 mL BPHA solution in the range of 0.025–0.2 mol L^{-1}. Table 2 and Fig. 3 show the experimental results. The Re signal remained constant with changing BPHA concentration. The extraction efficiencies of Mo and W increased with increasing BPHA concentration from 0.025 to 0.1 mol L^{-1}, but decreased slightly with a further increase to 0.2 mol L^{-1}. The extraction of Fe increased with increasing BPHA concentration. A BPHA concentration of 0.2 mol L^{-1} was chosen for further experiments because it was most effective in decreasing the level of total dissolved solids (TDS) in the Re solutions, and because of its competitive complexation with other metal ions in the samples.

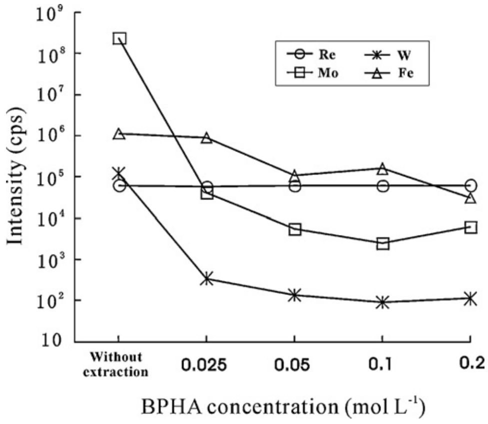

Fig. 3. The effect of the concentrations of BPHA in chloroform in the range of 0.025–0.2 mol L^{-1} on extraction of Mo, Fe, W and Re from molybdenite reference smaple JDC.

3.1.3. Extraction time

The effect of extraction time on the extraction efficiency of Mo, W, and Fe was examined in the range of 5–20 min. The obtained results showed that the extraction percentages of Mo, W and Fe increased with the increase of extraction time from 5 to 15 min. Maximum extraction was attained at 15 min, further shaking had no effect on extraction efficiency. So, the extraction time of 15 min was selected for all subsequent analysis.

From the above results it follows that 0.2 mol L^{-1} BPHA solution was sufficient for the separation of molybdenum, iron and tungsten from rhenium in 0.5 mol L^{-1} HCl medium. After separation under these conditions, more than 97% of Mo, W and Fe were extracted into organic phase, while Re was remained in aqueous phase and can be directly determined by ID–ICP–MS.

3.2. Interferences and matrix effect

The mass interferences of ^{169}Tm^{16}O^{+} on ^{185}Re and ^{171}Yb^{16}O^{+} on ^{187}Re are unavoidable under the present extraction conditions using BPHA [34]; however, molybdenite contains very low Tm and Yb contents, and the oxide yields of these elements are low in ICP–MS analyses (<0.1%). Hence, the contributions of Tm and Yb to Re isotope measurements are considered negligible. The overlap of ^{187}Os on ^{187}Re is avoided because all the Os is removed in the solvent extraction step. Any residual Os in the aqueous phase is almost lost in subsequent dry-down at 135 °C. No Os signal was detected in the molybdenite samples during the measurements.

To investigate the validity of the proposed method, the ^{187}Re/^{185}Re isotopic ratios of Re standard solution and JDC (after separation of the major matrix by BPHA) were measured alternately by ICP–MS. The average ^{187}Re/^{185}Re values obtained for the JDC and Re standard solution were 1.695 (n = 8, RSD = 0.34%) and 1.704 (n = 6, RSD = 0.49%), respectively. This good agreement demonstrated that the employed method was effective in precisely measuring Re concentrations using isotope dilution.

3.3. Accuracy and precision

Replicate analyses of the molybdenite reference powder (JDC) and unknown samples were performed to evaluate the overall precision of the proposed analytical method. Table 3 lists the obtained Re and Os concentrations and ages for JDC. The precision of concentration results for Re and ^{187}Os were 1.1% and 1.2% relative standard deviation (RSD), respectively. The mean and standard deviation of the calculated ages were 140 ± 4 Ma (n = 8, 2σ). These values were in excellent agreement with the certified values [10] and previ-

Table 3
Replicate analyses for the homogeneous molybdenite powder JDC. Uncertainties on concentration data and individual age determinations are 2σ standard deviations.

Sample (JDC)	Re (μg g^{-1})	^{187}Os (ng g^{-1})	Age (Ma)
1	17.6 ± 0.5	26 ± 2	138 ± 3
2	17.7 ± 0.4	26 ± 1	142 ± 3
3	17.7 ± 0.6	26 ± 2	140 ± 3
4	17.5 ± 0.6	26 ± 3	140 ± 3
5	17.3 ± 0.6	26 ± 2	143 ± 3
6	17.7 ± 0.3	26 ± 2	139 ± 2
7	17.9 ± 0.3	26 ± 2	139 ± 2
8	17.4 ± 0.8	25 ± 2	139 ± 3
Average	17.6 ± 0.4	25.8 ± 0.6	140 ± 4
Ref. [5]	17.4 ± 0.4	25.2 ± 0.7	138.4 ± 0.5
Ref. [11]	17.4 ± 0.3	25.5 ± 0.6	140 ± 4
Ref. [20]	17.7 ± 0.2	26.2 ± 0.4	141 ± 4

Re–Os age calculations were based on the ^{187}Re decay constant of 1.666 × 10^{-11} a^{-1} [33]. Errors in all Re–Os ages do not include the 1.2% uncertainty of the decay constant.

Table 4
Analyses for molybdenites from the Yuanzhuding large Cu–Mo porphyry deposit, Southern China. Stated errors for each analysis are 2σstandard deviations.

Sample	Re ($\mu g\,g^{-1}$)	^{187}Os ($ng\,g^{-1}$)	Age (Ma)
112-1	4.69 ± 0.08	7.7 ± 0.2	155.9 ± 0.7
112-2	5.7 ± 0.1	9.1 ± 0.2	151 ± 1
112-3	2.71 ± 0.04	4.3 ± 0.1	151.5 ± 0.2
112-4	4.85 ± 0.08	7.7 ± 0.2	151.9 ± 0.7
112-6	2.69 ± 0.08	4.2 ± 0.1	149.8 ± 0.4
112-7	3.63 ± 0.07	5.9 ± 0.1	154.7 ± 0.5
112-8	4.70 ± 0.08	7.6 ± 0.2	153.1 ± 0.7

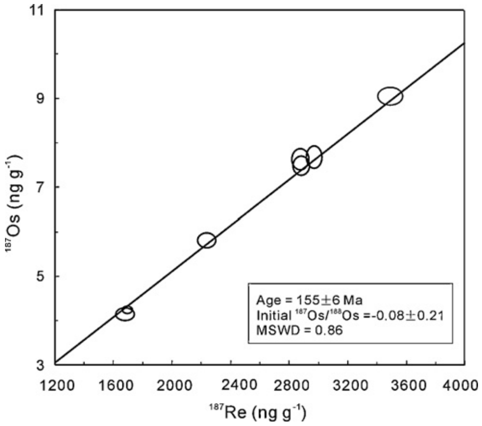

Fig. 4. Re–Os isochron plot for molybdenite samples from Yuanzhuding large Cu–Mo porphyry deposit, Southern China. Regression was performed in ISOPLOT [35] and the age was calculated using ^{187}Re decay constant $\lambda_{\times} = 1.666 \times 10^{-11}$ a^{-1} [33].

ously reported data [5,19], thereby demonstrating the fitness of the proposed method for Re–Os dating of molybdenite.

Seven samples of molybdenite from the Yuanzhuding large Cu–Mo porphyry deposit were selected as unknown molybdenite samples. This deposit, discovered in 2008, is located at the boundary between Guangdong and Guangxi provinces, China, and is the first large Cu–Mo deposit to be discovered in south China. Tectonically, the deposit straddles the Dayaoshan and Tiantangshan tectonic belts. The exposed strata in the vicinity of the ore are Cambrian in age and to a lesser degree Devonian.

The seven molybdenite samples used for Re–Os isotopic dating were selected from drill core ZK12-112 at depths of 54.0–54.5 m. The molybdenite occurred as ore within quartz veins. The core was divided into 10 segments, and the seven molybdenite analytes were picked out by hand.

Table 4 lists the obtained Re and ^{187}Os concentrations and corresponding apparent ages, following the analytical methods described above. An isochron age of 155 ± 6 Ma was obtained (Fig. 4F). This age datum suggests that the Yuanzhuding Cu–Mo porphyry deposit formed during the mid-Jurassic, consistent with the regional geological setting and the ages of voluminous granites in south China. This age datum is important in terms of understanding the regional geology and exploring for similar deposits. We are currently preparing another manuscript that considers the detailed geologic setting of the Yuanzhuding Cu–Mo porphyry deposit and relevant age data, and that discusses the origin of the molybdenite.

4. Conclusion

The described method using the solvent extraction with N-benzoyl-N-phenylhydroxylamine (BPHA) has a good potential for the removal of the major matrix ions (Mo, Fe and W) from Re in the molybdenite samples, and Re determinations by ID–ICP–MS. The main benefits of the method were: simplicity, low cost and rapid analysis time. The results acquired from the analyses of the JDC molybdenite reference material confirmed the reliability of the method. The proposed technique can be successfully applied to molybdenite samples for Re–Os dating.

Acknowledgements

This paper benefited from valuable comments by Dr. Ya-Li Sun. The authors are grateful to the two anonymous reviewers for their thorough review and helpful comments. Wang Bao-di is thanked for assistance with sample preparation and ICP–MS analyses. This is contribution No. IS-1159 from GIGCAS. Financial support for this research was provided by NSFC projects (40903007, 40806049, 40930316, 40721063).

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