

Determination of rhenium and osmium by ICP-MS for galena and sphalerite

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Received: 25 May 2015 / Revised: 16 July 2015 / Accepted: 8 October 2015 / Published online: 30 November 2015
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Abstract Digestion with *aqua regia* in a Carius tube and separation of Re with anion exchange resin is commonly employed for Re–Os dating of molybdenite and pyrite. However, the recovery of Re is extremely low when this routine anion exchange method is applied to galena, causing difficulty in Re–Os dating of galena. In this study, we investigated the mechanism of Re loss during sample preparation and tested a revised procedure for Re–Os dating of galena and sphalerite.

Keywords Galena · Sphalerite · Rhenium and osmium · Anion exchange resin · ICP-MS

1 Introduction

Galena, sphalerite, and pyrite are the major ore minerals in Pb–Zn sulfide deposits. Most pyrites in these deposits have multiple origins (Brill 1989), making it difficult or impossible to determine the timing of Pb–Zn mineralization. Re–Os dating of galena and sphalerite yield more reliable geochronological constraints on the timing of ore formation (Stein et al. 2000; Morelli et al. 2004). However, Re recovery from galena is extremely low when the

samples are processed as for molybdenite and pyrite, resulting in significant problems in Re–Os dating (Liu et al. 2015b).

Pre-concentration methods for Re in geological samples (Morgan et al. 1991; Tagami and Uchida 2000) have been reported intensively. Anion exchange chromatography (Morgan et al. 1991; Malinovsky et al. 2002; Meisel et al. 2003a; Qi et al. 2007, 2010) and extraction with organic solvent (Du et al. 1994, 2001; Birck et al. 1997; Yang et al. 2006; Li et al. 2009) are commonly used for separation of Re. However, high concentrations of different matrix metallic ions in sulfides sometimes affect the recovery of Re. For example, the recovery of Re decreases with increasing concentration of Fe^{3+} using anion exchange resin separation (Huang et al. 2012). Although our previous study showed that HNO_3 -based anion exchange separation is more suitable for Re purification of galena and sphalerite than HCl-based anion exchange (Liu et al. 2015b), how Pb^{2+} and Zn^{2+} affect the recovery and loss of Re during the HCl-based procedure is still unknown.

2 Experimental and analytical methods

2.1 Samples

The experimental galena sample was collected from the Fule Pb–Zn deposit and the sphalerite from the Laochang Pb–Zn deposit, both in Yunnan Province, southwest China (Liu et al. 2015a, b). The Pb–Zn sulfide ores were mechanically crushed and washed by ultrapure water. After being sieved through size 20–40 meshes, sphalerite and galena separates were hand-picked under a binocular microscope, and then grinded to pass through about 200

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mesh. Concentrations of Re in these galena and sphalerite samples were less than 1.0 ng/g.

2.2 Instrumentation

The instrument used for analysis of Re in this study is an ELAN DRC-e inductively-coupled plasma mass spectrometry (ICP-MS) instrument (Perkin Elmer, USA) in the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Background counts for 3 % HNO₃ solution are normally lower than 20 cps (counts per second) for Re. The sensitivity of the instrument was optimized to be more than 30,000 cps for 1 ng/mL of ¹⁰³Rh, in order to achieve the desired detection limits; the analytical uncertainty (RSD) was better than 3 %.

Osmium was determined by a Bruker Aurora M90 ICP-MS spectrometer. High sensitivity mode was used due to the low content of Os. In order to achieve the desired detection limits, the sensitivity of the instrument for high sensitivity mode was adjusted to more than 800,000 cps for 1 ng/mL of ¹¹⁵In and 300,000 cps for 1 ng/mL of ²³²Th. The RSD was better than 3 %.

Total analytical blanks were less than 6.0 pg for Re and 2.5 pg for Os.

2.2.1 Reagents and solutions

Rhenium spike solutions (US Services Inc) were enriched in ¹⁸⁵Re. Abundances of ¹⁸⁵Re and ¹⁸⁷Re were 94.36 and 5.64 %, respectively.

Re standard (std) solution 10 ng/mL (Perkin Elmer Pure Plus).

HCl was purified by sub-boiling distillation; HNO₃ was purified by bubbling clean air through the boiled HNO₃ with H₂O₂ in a 3000-mL glass beaker to remove possible volatile OsO₄, and then purified following routine sub-boiling distillation:

Ultrapure water was obtained from a Millipore purification system (18 MΩ cm⁻¹).

Anion resin Bio-rad AG 1-X8 (100–200 meshes).

Analytical reagents (ARs) FeCl₃ (99.8 %) and Pb(NO₃)₂ (99.0 %).

Zn(NO₃)₂ solution Concentration of Zn²⁺ was about 0.1 g/mL, prepared by zinc metal powders (95.0 %; AR) and sub-boiling HNO₃.

Carius tubes used in this study are reusable (Qi et al. 2013; Liu et al. 2014), and have an inner volume of about 200 mL, with a custom-made sealing system including a glass-lined PTFE stopper and a stainless steel screw cap. The reusable Carius tube is easy to clean, resulting in a lower Re blank.

2.3 Analytical procedure

The sulfides were precisely weighed and transferred into a reusable Carius tube with 6.0 ng Re spike and appropriate amount of reverse *aqua regia* (HNO₃: HCl ≈ 4:1). Each sealed Carius tube was placed into a stainless steel sheath and slowly heated to 150 °C for 5 h and then 200 °C for 12 h to dissolve the samples and reach isotopic exchange equilibrium.

After cooling down to about 40 °C, the content in the tube was transferred to a 50-mL centrifuge tube for centrifuging. After centrifuging, the upper solution was decanted into a 50-mL glass beaker and evaporated to dryness. The residue was then dissolved by 12 mL of 2 mol/L HCl, transferred into a 15-mL centrifuge tube, and centrifuged for 5 min. The upper solution was used for anion exchange separation of Re. Next, 12 mL of 2 mol/L HCl was used to wash the anion exchange resin and 15 mL of 9 mol/L HNO₃ was used to elute Re. The solution was evaporated to dryness and dissolved by 3 mL of 3 % HNO₃ for ICP-MS analysis (Qi et al. 2007).

3 Results and discussion

3.1 Re loss during routine chemical treatment

As mentioned in our previous study (Liu et al. 2015b), recovery of Re would be extremely low if we treated galena following the above described procedure (Table 1). For sphalerite, the rate of recovery of Re would decrease if the sample mass increased (Table 1). Low recovery of Re only occurred when large amounts of sphalerite (>1.0 g, 15 mL) were dissolved and treated following the above described procedure (Table 1). However, using 2 mol/L HCl as a blank without any matrix did not show any effect on the recovery of Re (Table 1). We therefore conclude that 2 mol/L HCl is not suitable for loading the sample onto the anion exchange column for separating Re from galena and sphalerite, and the routine procedure is not suitable for precise Re–Os dating of galena and sphalerite. The loss of Re should be investigated during sample preparation in order to enhance the recovery of Re.

3.2 Effect of Pb²⁺ and Zn²⁺ for recovery of Re during anion exchange separation

We first evaluated the effect of Pb²⁺ and Zn²⁺ on anion exchange separation of Re. For Pb²⁺, 0.2 to 1.0 g Pb(NO₃)₂ was weighed and placed into a 50-mL glass beaker. Water was used to dissolve the powder, then 10 ng Re std solution and 2 mL HNO₃ were added to the beaker and mixed with the Pb(NO₃)₂. The HNO₃ was used to

Table 1 Recovery of Re in galena and sphalerite during anion exchange

No.	Galena (g)	Sphalerite (g)	Add ^{185}Re spike (ng)	Volume (mL)	Recovery of ^{185}Re in 2 mol/L HCl medium (%)	Recovery of ^{185}Re in 0.8 mol/L HNO_3 medium (%)
1	0.5	–	6.0	15	2.4	93.2
2	1.0	–	6.0	15	2.1	88.3
3	2.0	–	6.0	15	1.8	95.6
4	–	1.0	6.0	15	30.8	87.9
5	–	1.5	6.0	15	26.6	90.6
6	–	2.0	6.0	15	15.3	91.5
7	–	–	6.0	15	97.6	99.5
8	–	–	6.0	15	98.3	96.8

This table is from Liu et al. (2015b)

oxidize all Re to +7, making it exist as $(\text{ReO}_4)^-$ in the solution. The mixture was evaporated to dryness. The residue was dissolved in 15 mL 2 mol/L HCl and centrifuged for 5 min. The upper solution was utilized for Re purification through anion exchange resin. For Zn^{2+} , an appropriate amount of $\text{Zn}(\text{NO}_3)_2$ solution was used as the matrix to evaluate the effect of Zn^{2+} .

The results show that Re in a $\text{Pb}(\text{NO}_3)_2$ matrix was quantitatively recovered (Table 2), indicating that Pb^{2+} did not affect Re recovery for anion exchange separation and that low recovery of Re for galena samples might not relate to column separation. However, Zn^{2+} showed different behavior from Pb^{2+} during anion exchange separation. Large amounts of Zn^{2+} (>1.0 g, 15 mL) in the matrix severely impacted recovery of Re (Tables 1, 3). Although Zn can form complex anions in an HCl medium (Harris et al. 2003; Akinfiev and Tagirov 2014) and may occupy the anion resin, the recovery was high in this study when the total mass of Zn^{2+} was less than 0.3 g (Table 3). That might be because Re has a higher affinity than Zn during anion resin exchange, and is preferentially exchanged. The low recovery of Re when large amounts of sphalerite sample were digested (>1.0 g, 15 mL) may have been due to the matrix effect.

3.3 Behavior of Re during sample pretreatment

It is noted that abundant white precipitates of lead salt formed during both stages of dissolving and medium change (from HNO_3 to HCl). In the former dissolving

stage, the precipitates were mostly PbSO_4 , $\text{Pb}(\text{NO}_3)_2$, and PbCl_2 (Fig. 1a, b). During digestion of galena using reverse *aqua regia*, the PbSO_4 precipitate results from the formation of SO_4^{2-} . Thus, the difference between Fig. 1a, b is probably due to a stronger oxidability of 10 mL reverse *aqua regia* compared to 5 mL. However, the precipitates formed in the later medium change stage were dominantly PbSO_4 and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (Fig. 1c, d). Therefore, it is necessary to distinguish the role of these precipitates in Re loss in galena samples.

As concentration of Re was as low as <1.0 ng/g in galena and sphalerite in this study, we added Re std solution into the sample to evaluate the recovery of Re following the procedure as follows:

Along with an appropriate amount of reverse *aqua regia*, 0.5 g galena powder and 10 ng Re were accurately weighed and placed into a Carius tube. The tube was sealed and heated to 150 °C for 5 h and then 200 °C for 12 h. After cooling, the solution and white precipitate (Fig. 1b) were transferred into a 15-mL centrifuge tube. The sample solution was centrifuged at 2500 rpm for 5 min. The upper solution was divided into three portions, which were transferred into three 50-mL beakers, and 6.0 ng ^{185}Re spike was added to each beaker.

After evaporating the solution to dryness in the first beaker, the residue was dissolved with 15 mL of 2 mol/L HCl and then transferred into a 15-mL centrifuge tube. New white precipitate formed during this stage (Fig. 1c, d). After centrifuging, the upper solution was used for purification of Re through anion exchange resin.

Table 2 Recovery of Re in $\text{Pb}(\text{NO}_3)_2$ during anion exchange in 2 mol/L HCl medium

No.	$\text{Pb}(\text{NO}_3)_2$ (g)	Add Re std solution (ng)	Volume (mL)	Recovery of Re (%)
1	0.19	10	15	95.4
2	0.49	10	15	81.3
3	0.77	10	15	85.1
4	1.07	10	15	84.8

Table 3 Recovery of Re in Zn solutions during anion exchange in 2 mol/L HCl medium

No.	Zn ²⁺ (g)	Add ¹⁸⁵ Re spike (ng)	Volume (mL)	Recovery of ¹⁸⁵ Re (%)
1	0.11	6.0	15	83.1
2	0.30	6.0	15	80.7
3	0.51	6.0	15	57.1
4	0.80	6.0	15	34.4
5	1.01	6.0	15	20.5
6	1.20	6.0	15	25.4
7	1.50	6.0	15	21.6

As for the second beaker, 1 mL of Zn(NO₃)₂ solution (about 0.1 g Zn²⁺) was added and then evaporated to dry. New white precipitate also formed during the dissolution with 15 mL of 2 mol/L HCl, but was much less than in the first procedure.

After evaporating the solution in the third beaker to dryness, about 15 mL of 0.8 mol/L HNO₃ was used to dissolve the residue (Tagami and Uchida 2000; Meisel et al. 2003b; Chu et al. 2007). Rhenium was separated and concentrated by anion exchange resin. In this procedure, only a few white precipitates formed.

Following the above procedures, the three eluted solutions of 15 mL of 9 mol/L HNO₃ were evaporated to dryness and then dissolved by HNO₃ and diluted to about 3 mL. All solutions were measured by ICP-MS. Intensity of ¹⁸⁵Re and ¹⁸⁷Re of the first sample are both in the range of tens of cps,

close to the background. Intensities of Re of the second and third samples are high enough to calculate the residual Re content in the dissolving solution by isotope dilution (ID). The recovery of Re during the former dissolving stage ranged from 84.0 to 89.1 % (Table 4), indicating that the added Re remained in the dissolving solution (reverse *aqua regia*) of galena in abundance (Fig. 1a, b). The precipitates of PbSO₄ and ZnSO₄·7H₂O (Fig. 1c, d) that formed at the second stage might have caused the loss of Re.

As a comparison, we used 0.1 g FeCl₃ instead of Zn(NO₃)₂ to evaluate the role of existence of Zn²⁺ in another set of parallel experiments (Table 4), in which 1.0 g galena was used. The recoveries of routine treatment, addition of FeCl₃, and 0.8 mL HNO₃ medium were 4.6, 96.1, and 100 %, respectively, similar to the experiment using Zn(NO₃)₂. Thus, addition of Zn(NO₃)₂ or FeCl₃

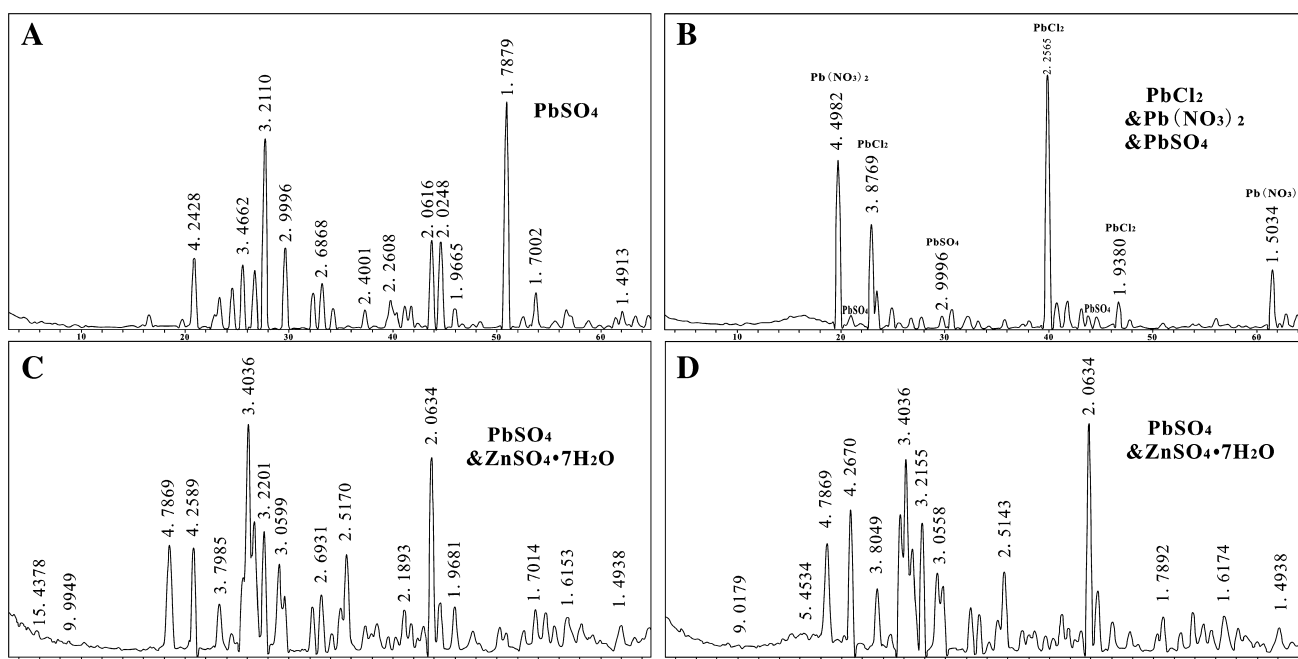


Fig. 1 X-ray powder diffraction (XRD) analysis spectra of white precipitates formed under different experimental conditions. **a** Precipitation formed under dissolving of 1.0 g galena by 10 ml reverse *aqua regia* (8 ml HNO₃ + 2 ml HCl), **b** precipitation formed under dissolving of 0.5 g galena by 5 ml reverse *aqua regia* (4 ml HNO₃ + 1 ml HCl), **c** precipitation formed when the dissolved solution of A is changed to HCl medium, **d** precipitation formed when the dissolved solution of B is changed to HCl medium

Table 4 Impact of the precipitation (formed at dissolving stage of galena) on recovery of Re

No.	Galena (g)	Added Re std solution (ng)	Re separation method	Recovered Re (ng)	Recovery (%)
1	0.5	10	Normal (2 mol/L HCl medium)	NA ^a	<1.0
2	0.5	10	Add ~0.1 g Zn ²⁺	8.91	89.1
3	0.5	10	0.8 mol/L HNO ₃ medium	8.40	84.0
4	1.0	10	(Same as No. 1)	NA ^a	<1.0
5	1.0	10	Add ~0.1 g FeCl ₃	9.61	96.1
6	1.0	10	(Same as No. 3)	10.0	100.0

^a NA not available

(0.5 g galena need about 0.1 g Zn(NO₃)₂ or FeCl₃) could significantly promote recovery of Re in HCl medium (Table 4). However, introduction of such reagents would enhance total procedure blank (Re concentrations of reagent FeCl₃ and zinc powders were 2.0 and 0.05 ng/g, respectively). Moreover, introducing a large amount of Fe³⁺ (Huang et al. 2012) and Zn²⁺ (Tables 1, 3) might also lower the recovery of Re. Thus, a relatively oxidized medium of 0.8 mol/L HNO₃ is more efficient for anion exchange of Re in galena (0.5–2.0 g) and sphalerite (>1.0 g) (Tables 1, 4). Previous experimental studies suggest that Re is mobile in Cl-rich oxidizing fluids (Xiong and Wood 1999, 2000; Widom et al. 2003), but immobile under reduced conditions (Colodner et al. 1995; Xiong and Wood 2001). Results in this study also indicate that Re precipitation cannot form at the oxidizing medium. Thus, an oxidized solution is necessary with anion exchange separation of Re for galena, and Re should be released at a higher rate in a medium of 0.8 mol/L HNO₃ than of 2 mol/L HCl. On the other hand, although Os is also immobile under reduced environments (Xiong and Wood 2000; Widom et al. 2003), the matrix effect would not affect the in situ distillation of Os.

3.4 A revised procedure of Re–Os isotope dating of lead–zinc ores

Samples of 1.0–2.0 g of galena/sphalerite and appropriate ¹⁸⁵Re and ¹⁹⁰Os spikes were precisely weighed and placed into a Carius tube with 10–20 mL reverse *aqua regia* in ice water bath. The sealed Carius tube was placed into a stainless steel sheath and slowly heated to 150 °C for 5 h and then 200 °C for 12 h. After cooling down to about 40 °C, the Carius tube was put into a refrigerator for 2 h for freezing. Then, 20 mL of water was added and the tube was connected to the in situ distillation equipment for in situ distillation of Os (Qi et al. 2010, 2013). After that, the residual solution was transferred to a 50-mL beaker and evaporated to dryness. The residue was then dissolved by 15 mL of 0.8 mol/L HNO₃ and transferred into a 15-mL centrifuge tube. After 5-min centrifuging, the upper

solution was used for anion exchange separation of Re. The anion exchange resin was washed with 12 mL 2 mol/L HNO₃ and 15 mL 9 mol/L HNO₃ was used to elute Re. The solution was evaporated to dryness and dissolved by 3 mL 3 % HNO₃ for ICP-MS measurement.

3.5 Results of reference materials

Because of the lack of international reference materials of galena and sphalerite for Re–Os dating, we used molybdenite, JDC, and HLP as reference material. To monitor the actual samples of galena and sphalerite, 0.1 g of JDC and HLP were added to 3.0 g of galena and sphalerite, respectively, as introduced by Qi et al. (2010). The same Pb–Zn ore samples were prepared as a blank without addition of molybdenite reference materials. The samples were digested following the procedure described in Sect. 3.4. To obtain the measured values, the calculated results were deducted from the blank of galena/sphalerite. As shown in Table 5, the results for JDC and HLP are in fairly good agreement with the certified values, demonstrating that the proposed method is a reliable means of determining Re and Os in galena and sphalerite. We also analyzed a galena sample and a sphalerite sample following the procedure described above. Despite very low concentrations of Re and Os, the samples yielded excellent repeatability. The precision and accuracy for Re- and Os-poor Pb–Zn ores are significantly improved.

4 Conclusions

This study systematically investigated the controlling factors of low recoveries of Re through the routine analytical method for Re–Os dating of typical galena and sphalerite samples. Our results show the following conclusions.

Abundant Pb²⁺ in galena matrix does not affect anion exchange of (ReO₄)⁻. The white precipitates (PbSO₄, Pb(NO₃)₂, and PbCl₂) formed during reverse *aqua regia* dissolving of galena are not responsible for the loss of Re.

Table 5 Analytical results for molybdenites (HLP and JDC), galena and sphalerite

	1	2	3	4	5	Average \pm SD ^a	Certified ^b
JDC							
Re ($\mu\text{g/g}$)	17.25	16.96	17.59	17.31	17.11	17.24 \pm 0.24	17.39 \pm 0.32
¹⁸⁷ Os (ng/g)	24.88	25.56	25.52	24.93	25.24	25.23 \pm 0.32	25.46 \pm 0.60
Age (Ma)	138.6	144.9	139.5	138.4	141.8	140.6 \pm 2.7	139.6 \pm 3.8
HLP							
Re ($\mu\text{g/g}$)	282.2	278.3	285.6	283.4	285.2	282.9 \pm 2.9	283.8 \pm 6.2
¹⁸⁷ Os (ng/g)	655.5	660.3	658.8	659.9	657.5	658.4 \pm 1.9	659 \pm 14
Age (Ma)	223.1	227.9	221.6	223.7	221.4	223.5 \pm 2.6	221.4 \pm 5.6
Galena							
Re (ng/g)	1.96	1.82	1.87	1.82	1.80	1.85	0.06
¹⁸⁷ Os (pg/g)	6.13	5.86	5.78	6.37	6.45	6.12	0.30
common Os (pg/g)	13.2	12.5	12.1	12.4	12.6	12.6	0.4
Sphalerite							
Re (ng/g)	4.75	4.52	4.26	4.39	4.25	4.43	0.21
¹⁸⁷ Os (pg/g)	16.1	14.6	15.2	14.8	14.3	15.0	0.7
common Os (pg/g)	16.7	18.1	17.2	17.6	16.8	17.3	0.6

^a SD Standard deviation^b Du et al. (2004)

The large amount of Zn²⁺ in sphalerite matrix (>1.0 g) severely reduces the recovery of Re during anion exchange separation. HNO₃-based anion exchange is more suitable for Re purification of galena and sphalerite, although the addition of Zn(NO₃)₂ or FeCl₃ could also significantly promote the recovery of Re. The revised procedure is reliable and can be applied for Re–Os dating of galena and sphalerite.

Acknowledgments This study was supported by the 12th Five-Year Plan Project of State Key Laboratory of Ore Deposit Geochemistry, Chinese Academy of Sciences (SKLOGD-ZY125-09; SKLOGD-ZY125-02) and the National Natural Science Foundation of China (Nos. 41373064; 41430315). Thanks are given to Prof. Sun Yali for useful discussions and suggestions.

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