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Re–Os dating of molybdenite *via* improved alkaline fusion

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This study describes an improved alkaline fusion technique for the Re–Os dating of molybdenite. The molybdenite sample was digested in a zirconium crucible with NaOH and carbonized flour at 700 °C. The flour can reduce Os from a high oxidation state to a lower oxidation state during the high-temperature digestion so that isotope equilibration can be reached between the spike and the sample. Less amount of NaOH was used compared with the previously reported technique, lowering the procedure blank. Rhenium was separated by kinetic absorption with an anion exchange resin, and Os was purified by distillation with aqua regia and H_2O_2. Both Re and Os isotope compositions were measured *via* inductively coupled plasma mass spectrometry. The results obtained for the molybdenite reference material, JDC, were in good agreement with certified values, demonstrating that the proposed method is efficient for the Re–Os dating of molybdenite. Compared with Carius tube and high-pressure asher sealed acid digestion methods, the improved alkaline fusion method yields comparable Os blanks but has a more simple, quick, and secure procedure.

Introduction

Sample digestion is an essential step for elemental and isotopic compositional analysis with mass spectrometry techniques, which converts solid samples to soluble salt-bearing solutions that are suitable for element separation and purification. Commonly used sample digestion methods include open or closed vessel acid digestion, microwave digestion, partial dissolution, dry ashing, alkaline fusion, fire assay, Carius tube, and high-pressure asher (HPA-S).[1–3] Molybdenite (MoS_2) commonly occurs in high-temperature porphyry-related deposits and is a key source of Mo and Re metals.[4] Similar to most sulfides, molybdenite can be dissolved by acids with a strong oxidizing ability, such as HNO_3 and aqua regia, which are prepared by concentrated HNO_3 and HCl with a volume ratio of 1 : 3.[3] The dissolution of molybdenite by concentrated H_3PO_4 alone is slow and incomplete at 290 °C for 3 h, but a mixture of concentrated H_3PO_4 and $HClO_4$ can completely dissolve molybdenite within 45 min due to its higher oxidation potential.[2,5] Perchloric acid is not commonly used because of its relatively high boiling point (203 °C for 71.6% acid), whereas the involvement of H_3PO_4 will cause mass spectrometry interferences related to phosphate ions.[2] Molybdenite cannot be decomposed by other mineral acids such as HF and H_2SO_4.[2] The fusion of molybdenite by NaOH at 500–700 °C and by Na_2O_2 at about 480 °C can reach complete decomposition, and the amount of these alkaline reagents should be four to five times the sample mass.[3]

The Re–Os dating of molybdenite is a traditional method for the geochronological study of hydrothermal ore deposits.[6] The most commonly employed techniques for the Re and Os analysis are the Carius tube[7–18] and HPA-S.[19–25] Because samples are dissolved by aqua regia in a sealed glass or quartz tube under high temperatures (220–240 °C for the Carius tube, 300 °C for HPA-S), Re and Os are in their highest oxidation states with complete equilibration between spikes and samples. These two acid digestion techniques have very low procedural blanks due to small volumes of reagents and have been proved to be efficient in dissolving molybdenite for measuring Re and Os. The disadvantages of these techniques are the relatively complex operation and explosion risk of glass or quartz tubes.

The alkaline fusion technique is very effective in dissolving all kinds of geological samples.[13,26–33] However, it may have a relatively high procedure blank because reagents such as NaOH and Na_2O_2 are hard to purify. Moreover, the complete equilibration between spikes and samples is not stable. Markey *et al.* (1998)[29] reported a relatively complex procedure for dissolving molybdenite with alkaline fusion, which was modified from Morgan and Walker (1989).[26] Their procedure are roughly described as follows. The Re and Os spikes were first weighed into a 35 ml Zr crucible and evaporated to dryness at 50 °C. The molybdenite sample, 1 g of NaOH, and 1 ml H_2O were then added to the crucible and evaporated to dryness to ensure that Re and Os in the spike and sample smoldered in NaOH. About 3.3 g of NaOH was added and heated to 350 °C. The crucibles

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were removed from the furnace and vigorously swirled until the contents froze every 20 min during the 1 h fusion. Also, the temperature was increased in 25 °C increments twice during this hour to a final temperature of 400 °C. After cooling, 4 g of Na_2O_2 was added and then heated to 550 °C in order to ensure the equilibration between spikes and samples, during which the crucibles were swirled, and the temperature was increased in 25 °C increments for every 20 min for 1 h until a final temperature of 600 °C was reached. Because this technique has a relatively complex procedure and the equilibration between spikes and samples sometimes depends on the experience of the operator,[32] most researchers would prefer to select the technique of the Carius tube acid digestion.

Du *et al.* (2002)[32] evaluated the method of Markey *et al.* (1998)[29] and investigated the effect of ways of spike addition on the Re–Os isotope results. Their studies have demonstrated that mixed spikes were better than a single spike and that the spikes should be added before the high-temperature alkaline fusion.[32] No further modification of alkaline fusion technique was reported for molybdenite digestion in the later years.

In this study, we further improved the previous alkaline fusion procedure and achieved the accurate determination of Re and Os isotopes for molybdenite dating. The mixed Re and Os spikes were added to the 50% alkaline solution. No spike loss was observed during the sample heating. The carbonized flour was added to the sample, which can reduce Os in the spike and sample at the same lower chemical state. Isotope equilibration could be reached during the sample digestion at 700 °C. The analytical results of the molybdenite reference material, JDC, were in good agreement with the certified values, indicating the reliability of the proposed method.

Experimental

Instrumentation

The instrument used in this study is a Plasma Quant MS ICP-MS from Jena company in the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. Background counts for 2% HNO_3 solution (V/V) are normally <10 cps (counts per second) for Re and Os. The sensitivity of the instrument was adjusted to about 300 000 cps for 1 ng ml^{-1} of ^{115}In and 200 000 cps for 1 ng ml^{-1} of ^{232}Th. The instrument settings are outlined in Table 1.

Table 1 Instrument operating parameters

Parameter	Value	Parameter	Value
RF power	1300 W	Mirror lens left	90
Plasma flow	9.0 L min^{-1}	Mirror lens right	50
Aux gas	1.35 L min^{-1}	Mirror lens bottom	60
Nebulizer gas	1.00 L min^{-1}	Entrance lens	8
First extraction lens	−290	Entrance plate	−85
Second extraction lens	−680	Fringe bias	−3.0
Third extraction lens	−550	Pole bias	1
Corner lens	−490		

Table 2 Isotopic abundances of the spike

Isotope	Abundance (%)	Isotope	Abundance (%)
^{187}Os	0.014	^{192}Os	4.82
^{188}Os	0.055	^{185}Re	94.36
^{189}Os	3.57	^{187}Re	5.64
^{190}Os	91.53		

Reagents and solutions

HCl and HNO_3 were purified *via* double sub-boiling distillation. Water was obtained from an 18 MΩ cm^{-1} grade Millipore purification system.

Spike solutions with enriched stable isotopes, ^{185}Re and ^{190}Os, were prepared from pure metals (U.S. Services Inc., Oxbow, N.J.). The concentrations of the stock spike solutions were 100 μg ml^{-1} for ^{185}Re and 10 μg ml^{-1} for ^{190}Os with a 10% HCl solution and kept in a 100 ml glass flask in a refrigerator. Isotopic abundances of the spike are listed in Table 2. The mixed spike solution contains 700 ng ml^{-1} ^{185}Re and 20 ng ml^{-1} ^{190}Os.

The anion exchange resin was Bio-Rad AG1X8 (200–400 mesh). Approximately, 30 g of fresh resin was cleaned in a custom-made 20 mm inner diameter glass column and eluted with 200 ml of 9 mol L^{-1} HNO_3. Then, the resin was eluted with 30 ml of 6 mol L^{-1} HCl for the reconversion of the resin into the chloride form. Finally, the resin was conditioned with 10 ml of 1 mol L^{-1} HCl and kept in a 50 ml centrifuge tube for use.

A corundum crucible has a volume of about 18 ml with a 60 mm height and 20 mm inner diameter.

A Zr crucible has a volume of about 14 ml with a 37 mm height and 25 and 20 mm of upper and bottom inner diameter.

Carbonized flour: about 20 g of wheat flour was put in a porcelain crucible. Then, the covered crucible was placed in a muffle furnace and heated to 500 °C for about 15 min. After that, the cold carbonized flour was ground to fine particles for use.

50% NaOH (W/V): 50 g of NaOH was dissolved in 100 ml water.

Analytical procedure

About 20 to 50 mg of molybdenite and 30 mg of carbonized flour were weighed into the Zr crucible. 1 ml of 50% NaOH (W/V) was added to the crucible, followed by the addition of appropriate amounts of the enriched isotope spike solution containing ^{185}Re and ^{190}Os to the alkaline solution in the Zr crucible. Next, the crucible was heated at 200 °C in a muffle furnace for about 30 min to remove the water, followed by further heating to 700 °C for about 60 min. Then, 3 ml of water was added to the cooled crucible and heated on a hot plate for 10 min to dissolve the alkaline cake. After cooling, 3 ml of concentrated HCl was added to the crucible to acidize the alkaline solution, and the whole mixture was transferred to a 50 ml re-usable Carius tube.[34] Before connecting the distillation system, 5 ml of HNO_3 was added. The tube was put in an 80 °C water bath for Os distillation for 15 min.

Table 3 Analytical results (ng g^{-1}) for the molybdenite reference material, JDC, for different fusion reagents

	Re	^{187}Os	Age (Ma)
JDC	This study (mean ± SD[a]) $N = 5$[b]	This study (mean ± SD[a]) $N = 5$[b]	This study (mean ± SD[a]) $N = 5$[b]
Certified[c]	17 360 ± 320	26.46 ± 0.60	139.6 ± 3.8
NaOH	17 258 ± 298	30.64 ± 0.65	170.0 ± 3.6
NaOH	17 815 ± 172	34.32 ± 0.73	184.4 ± 3.9
NaOH + flour	16 676 ± 261	24.40 ± 0.45	140.1 ± 2.6
NaOH + flour	17 925 ± 172	25.91 ± 0.34	138.4 ± 1.8

[a] SD = standard deviation. [b] Five times the measurement of the same solution. [c] Certified values are from Du *et al.* (2004).[41]

Table 4 The added and measured ^{190}Os spike in the alkaline solution at 200 °C

Group	Added (ng)	Measured (ng)
1	0.20	0.21
2	0.20	0.19
3	0.20	0.20
4	0.20	0.21
5	0.20	0.19

About 2 ml of H_2O_2 was added to the solution during the distillation. The procedure for Os distillation was the same as our previously reported work.[34] Rhenium was separated by an anion exchange resin with kinetic absorption.

Rhenium in ~0.9 mol L^{-1} HNO_3 solution and Os in water solution were measured by ICP-MS. Osmium was collected in water because Os(VIII) in water solution is relatively stable and gives high sensitivity during the ICP-MS measurement.[35] In order to correct mass discrimination, Ir was added to the Re-bearing solution before measurement, as proposed by Schoenberg *et al.* (2000).[36] The same correction technique was also used for Os because the common Os contents of molybdenite were too low to allow us to perform accurate internal fractionation corrections using the measured ^{192}Os/^{188}Os ratios. The sample solution was introduced by a PTFE tube of ~10 cm long to the nebulizer system. 2% HNO_3 (v/v) and 2% HCl (v/v) was used to clean the sample introduction system after each analysis to avoid cross-contamination. Commonly, the background counts of ^{187}Re and ^{187}Os were reduced to 1% counts of the previous sample, which is ready for the measurement of the next sample.

Results and discussion

Alkaline fusion and isotope equilibration

Markey *et al.* (1998)[29] used about 4 g of NaOH and 4 g of Na_2O_2 to dissolve 10 to 200 mg of the molybdenite sample. The relatively large amount of NaOH and Na_2O_2 used may increase the procedure blank, and a large amount of HCl has to be used to neutralize the alkaline solution. Also, using a substantial amount of Na_2O_2 during the high-temperature fusion may increase the corrosion risk for the Zr crucible.[37] In this study, we demonstrated that only about 0.5 g of NaOH was enough to dissolve 20–50 mg of molybdenite. Because NaOH absorbs water quickly in the air; thus, it is not easy to weigh solid NaOH. Here, 1 ml of 50% NaOH solution was piped to the molybdenite sample by a transfer liquid gun as it is easy to mix the spike and sample in the NaOH solution.

To let Re and Os completely equilibrate between the spike and the sample by alkaline fusion, Markey *et al.* (1998)[29] used 4 g of Na_2O_2 to oxidize Re and Os to their highest states. In this study, a molybdenite reference material, JDC, was used as a sample and digested using two methods, NaOH and NaOH combined with carbonized flour, to investigate the isotope equilibration between the spike and the sample. First, 0.03 g of JDC and the mixed spike solution containing 200 ng of ^{185}Re and 1 ng of ^{190}Os was digested with 1 ml of 50% NaOH by following the procedure described above. The results listed in Table 3 indicate that the concentration of ^{187}Os and the age of JDC were higher than the respective certified values. Thus, fusion with only NaOH cannot yield the isotope equilibration between the spike and the sample.

Both the oxidant and reducer can make Os and Re in the spike and sample reach the same chemical state, higher or lower. As a food ingredient, wheat flour is very convenient to obtain and has been used as a reducing agent in fluxes used in the fire assays/assay processes for the determination of platinum-group elements and gold in geological samples.[38–40] In this study, 30 mg of JDC and the spike were digested with 1 ml 50% NaOH combined with carbonized flour, as described above. The purpose of adding the carbonized flour is to avoid the sputtering of volatile organic materials during high-

Table 5 Procedural blank (ng) and detection limit (DL, ng g^{-1}) for Re and Os

Elements	Blank-1	Blank-2	Blank-3	Blank-4	Blank-5	Blank-6	Average	DL (3σ)
Common Os	0.0016	0.0011	0.002	0.0018	0.0017	0.0015	0.0016	0.0009
^{187}Os	0.00054	0.00034	0.00042	0.00036	0.00047	0.00037	0.00042	0.0002
Re	0.052	0.041	0.065	0.049	0.064	0.098	0.062	0.060

Table 6 Analytical results (ng g^{-1}) for molybdenite reference material, JDC

	Re	^{187}Os	Age (Ma)
JDC	This study (mean ± SD[a]) $N = 5$[b]	This study (mean ± SD[a]) $N = 5$[b]	This study (mean ± SD[a]) $N = 5$[b]
Certified[c]	17 360 ± 320	26.46 ± 0.60	139.6 ± 3.8
JDC-1	16 676 ± 261	24.40 ± 0.45	140.1 ± 2.6
JDC-2	17 925 ± 172	25.91 ± 0.34	138.4 ± 1.8
JDC-3	17 786 ± 328	25.83 ± 0.33	139.1 ± 1.8
JDC-4	17 407 ± 174	25.77 ± 0.55	141.8 ± 3.0
JDC-5	17 115 ± 284	25.36 ± 0.35	141.9 ± 2.0
JDC-6	17 867 ± 230	25.76 ± 0.76	138.1 ± 4.0

[a] SD = standard deviation. [b] Five times the measurement of the same solution. [c] Du *et al.* (2004).[41]

Table 7 Comparison of blank levels (pg) for the alkaline fusion, Carius tube, and HPA-S methods

Digestion method	Reference	Re	Os
Alkaline fusion	This study	62	2.02
	Markey *et al.* (1998)[29]	100	18
	Stein *et al.* (1998)[45]	125	10
	Du *et al.* (2002)[32]	200–700	18.9–28.6
Carius tube	Shirey and Walker (1995)[7]	10	5
	Du *et al.* (2001)[44]	20	7
	Sun *et al.* (2010)[18]	2.8	0.7
	Qi *et al.* (2010)[17]	6.4	2
	Qi *et al.* (2013)[34]	6	2
HPA-S	Meisel *et al.* (2001)[19]	5	4
	Meisel *et al.* (2003)[20]	2	2

temperature fusion. About 0.03 g of the carbonized flour was added to reduce Re and Os at their lower chemical states. The Re–Os ages obtained by the NaOH + flour fusion were consistent with certified values, indicating that the addition of the carbonized flour can achieve the full isotope equilibration between the spike and the sample (Table 3).

The addition of spike

Markey *et al.* (1998)[29] added the Re and Os spikes into the Zr crucible at the beginning of the experiment and evaporated slowly to dryness on a 50 °C warm hot plate to avoid the loss of Os. In this study, in order to investigate the loss of the Os spike during the alkaline fusion, 0.2 ng of ^{190}Os spike, and 1 ml of the 50% NaOH solution were added to a re-usable Carius tube with 0.03 g of the carbonized flour at the bottom. The open tube was put in an electric oven and heated to 200 °C for about 1 h. After cooling, the tube was cooled in an ice-water bath. Next, 0.6 ng of the Os standard, 2 ml of HCl and 6 ml of cooled HNO_3 (cooled at the freezer part in a refrigerator) were added. The sealed tube was digested at 200 °C for about 5 h, and Os was distilled as described above and measured by ICP-MS. The results listed in Table 4 indicate that no ^{190}Os was lost during heating of the alkaline solution at 200 °C. Our results of molybdenite samples also indicate that no Os was lost during the water evaporation at 200 °C and the fusion at 700 °C (Table 3).

The selection of the crucible

In this study, the Ag, Zr and corundum crucibles were tested for fusion. The metal crucible of Ag and Zr have very smooth inner walls that can protect the spike solution from creeping into the wall of the crucibles. Thus, Ag and Zr crucibles can be used effectively to digest molybdenite samples, and all the alkaline cake can be easily washed out to avoid cross-contamination. However, the dissolved Ag may co-preconcentrate with Re during the separation with the anion exchange resin.[42] Also, the relatively high concentration of Ag may contaminate the instrument of ICP-MS. The corundum crucible was also tested in this study. To avoid the alkali creep to the upper side of the crucible and cross-contamination, a 60 mm high and 20 mm inner diameter crucible was selected. After about three times of fusion, some of the Al_2O_3 powder stripped from the corundum crucible. The porous structure of the corundum material makes it easy for acid and spike to penetrate, resulting in cross contamination.[32] Thus, the Zr crucible was used for fusion in previous studies due to its strong corrosion resistance towards acids, alkalis and strong oxidants.[29,32,37] Moreover, the Zr crucible is stable when the temperature reaches 700 °C during the alkaline fusion,[3] but the temperature of the silver crucible must be controlled precisely at 510–520 °C in order to avoid excessive corrosion of the crucible.[3]

The separation of rhenium

Column chromatography with anion exchange resin was often used for Re separation in most previous studies.[17,34,42] It was indicated that Re was very difficult to elute from the resin and a substantial amount of mineral acids need to be used for eluting the resin in order to obtain a very low blank level if the resin was used for another separation.[42,43] Thus, the resin was commonly disposable. To simplify the procedure and save reagents, adding the resin in a solution for kinetic absorption was used for Re separation in this study. After Os distillation, the filtrate was evaporated to dryness and dissolved with 10 ml of 15% HCl. The resultant mixture was transferred to a 15 ml centrifuge tube. About 0.1 ml of the slurried AG1X8 anion exchange resin was pipetted into the solution. The sealed tubes were shaken in a horizontal position on a shaker for about 10 min. After standing for about 5 min, the upper portion of the solution was discarded. 10 ml of 15% HCl (v/v) was added to the resin to elute the matrix. 0.3 ml of concentrated HNO_3 was added to elute Re for about 10 min, and then 5 ml of water was added. The solution was measured by ICP-MS after the resin precipitation. The disposable used resin can avoid cross-contamination, and only 0.3 ml of concentrated HNO_3 is used for eluting Re, which simplifies the procedure of Re pre-concentration.

Blank and detection limits

The total procedural reagent blank was prepared by adding 0.1 ng of Re and 0.005 ng of Os spikes following the same procedure described above. The average compositions of six individual procedural blanks are shown in Table 5. The procedure blank ranges from 1.1 to 2.0 pg for common Os, 0.34 to 0.54 pg for ^{187}Os and 41 to 98 pg for Re. The blank levels for this study were significantly lower than the content of Re and Os in molybdenite. The detection limits for common Os, ^{187}Os and Re were 0.9, 0.2, and 60 pg g^{-1}, respectively.

The results of reference materials

The molybdenite reference material, JDC, was selected to test the reliability of the improved alkaline fusion method. Six individual weights (0.03 g) of JDC and the mixed spike solution containing 200 ng of ^{185}Re and 1 ng of ^{190}Os were digested following the procedure described above. The results are shown in Table 6. The ages of JDC were in good agreement with the certified values.[41] Therefore, our results demonstrated that the proposed method is a reliable technique for the Re–Os dating of molybdenite samples.

Main merits of the improved alkaline fusion method

The proposed method improved the classical alkaline fusion method of Markey *et al.* (1998)[29] in the following aspects. First, the improved alkaline fusion method has simplified the analytical procedure. Only a two-step fusion was used, and the sample decomposition time reduces from more than 3 h to less than 2 h. Second, the procedure blanks for Re and Os were reduced due to less NaOH (0.5 g) was used compared to 4 g NaOH and 4 g Na_2O_2 used by Markey *et al.* (1998)[29] (Table 7). The lowered Re blank was ignorable for molybdenite with a high Re concentration (*e.g.*, reference material JDC), but it is significant for molybdenite with a low Re (ppb level) concentration. The lowered Os blank is also important for low-Os molybdenite samples. Third, carbonized flour transfers Re and Os in the solution to more reducing states, avoiding the volatile loss of Re and Os in molybdenite and spikes. However, in the study of Markey *et al.* (1998),[29] Re and Os may be lost during the evaporation of spikes to dryness in the Zr crucible with continued heating in the absence of stabilizing alkali.

Compared to the Carius tube closed digestion with aqua regia, the proposed alkaline fusion method also has its advantages. The most important is the simplified procedure and the shortened sample digestion time from about 12 h[7,17,44] to 2 h. Moreover, the sealing and opening of the Carius tube need a professional operation.[7] The Carius tube also has the risk of burst during heating, and thus caution should be taken when moving the Carius tube containing reacted sample solution.[7] The open dissolution in the muffle furnace also has no explosion risk for the operator. The total Os blank of the improved alkaline fusion method is comparable to that of the Carius tube and HPA-S methods (Table 7). Although the Re blank of the improved method is higher than other two acid digestion methods (Table 7), the pg level Re blank is insignificant for hundreds of ppb to a few ppm Re in molybdenite. Therefore, the improved alkaline method is more time-saving and economical than the Carius tube and HPA-S methods.

Conclusions

The alkaline fusion method for the Re–Os dating of molybdenite was improved by reducing the use of chemical reagents, adding the carbonized flour to guarantee the isotope equilibrium between the spike and the sample, and changing the ways of spike addition and Re separation. Also, the zirconium crucible in place of the Ag and corundum crucibles was used to avoid cross-contamination. The proposed method has a low procedural blank and detection limits and has been proved to be reliable for the Re–Os dating of molybdenite. This method is simple, quick, and green because of its simplified procedure and less usage of chemical reagents, which are the main merits over Carius tube and HPA-S acid digestion methods.

Conflicts of interest

There are no conflicts to declare.

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