Re-Os Dating of Galena and Sphalerite from Lead-Zinc Sulfide Deposits in Yunnan Province, SW China

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ABSTRACT: Dating of lead-zinc deposits is of critical importance for better understanding of ore genesis, but has long been a big challenge due to the lack of suitable minerals that can be unequivocally linked to the ore genesis and that can be used for tradition radiometric methods. This kind of deposits have simple mineralogy dominated by galena and sphalerite commonly associated with calcite and other gangue minerals. Both galena and sphalerite have low and high variable Re concentrations and thus Re-Os dating of these minerals have been less promising. In addition, the recovery of Re is extremely low for galena when conventional method was applied, lending additional difficulty in precisely dating galena. In this study, we investigate the recovery of Re using different media for anion exchange separation and reporte a revised preparation method for Re-Os dating of galena and sphalerite. By using the new protocol, two reliable Re-Os isochron ages of galena and sphalerite from the Fule (20.4±3.2 Ma) and Laochang (308±25 Ma) Pb-Zn deposits in Yunnan Province, SW China, are achieved.
KEY WORDS: lead-zinc sulfide deposits, Re-Os isotope dating, separation and concentration of Re, galena, sphalerite, Yunnan.

0 INTRODUCTION

Unlike lithophile isotope systems such as Rb-Sr and Sm-Nd, Re and Os are both siderophile and chalcophile elements mostly enriched in the Earth's core and sulfide minerals. Thus, Re-Os isotope system has been widely utilized to directly date (Ding et al., 2012; Gao et al., 2012; Zhong et al., 2011; Morelli et al., 2004; Mao et al., 2002; Selby et al., 2002; Stein et al., 2000) and constrain the origin of sulfide deposits (Gao et al., 2013; Zhao et al., 2013; Cheng et al., 2012; Wang et al., 2012; Gannoun et al., 2003). In previous studies, Re-Os isotope system is generally applied to sulfide minerals with relative high Re content and highly radiogenic Os isotopes, such as molybdenite (e.g., Liu and Liu, 2013; Zeng et al., 2012; Li W C et al., 2011), pyrite (e.g., Huang et al., 2013; Li N et al., 2011; Feng et al., 2009) and pyrrhotite (e.g., Lu et al., 2011; Wang et al., 2008). Although Re-Os isotope analytical method of these sulfides have been extensively studied (Liu et al., 2014; Qi et al., 2013, 2010; Jin et al., 2011; Sun et al., 2010; Malinovsky et al., 2002; Shirey and Walker, 1995), the analytical methods of Pb-Zn sulfide minerals are rarely investigated.

Galena, sphalerite and pyrite are the major minerals in Pb-Zn sulfide deposits. Pyrites from Pb-Zn deposits have multiple origins (Brill, 1989) making it difficult to link the pyrite deposition to the timing and genesis of Pb-Zn mineralization.

Conversely, Re-Os dating of galena and sphalerite would yield more reliable geochronological constraints on the timing of ore formation. Re-Os dating for sphalerite in Pb-Zn deposits has been pioneered by Morelli et al. (2004), however, no geologically meaningful age information was obtained from their study. In addition, Re concentrations of galena are relatively low (Stein et al., 2000) and the recovery of Re for galena is extremely low when the samples were processed using the procedures applied to molybdenites and pyrites, resulting in significant problem in Re-Os dating.

In fact, as Re is a highly dispersed element in the earth's crust, the crustal abundance of Re is less than 1.0 ng/g (Du et al., 2009). Therefore, except for molybdenite which has μg/g level of Re content, common sulfides such as pyrite, chalcopyrite, pyrrhotite, sphalerite and galena, have Re contents at pg/g to ng/g level and required separation and concentration for accurate determination of Re and Os.

The pre-concentration methods for both Os (Jin et al., 2013, 2011; Li et al., 2012; Paul et al., 2009; Hassler et al., 2000; Birck et al., 1997; Cohen and Waters, 1996) and Re (Tagami and Uchida, 2000; Morgan et al., 1991) in geologic samples have been extensively investigated. Anion exchange chromatography (Qi et al., 2010, 2007; Meisel et al., 2003a; Malinovsky et al., 2002; Morgan et al., 1991) and extraction with organic solvent (Li et al., 2009; Yang et al., 2006; Du et al., 2001, 1994; Birck et al., 1997) are usually used for separation of Re. However, the various concentrations of metallic ions in different sulfides would affect the recovery of Re. For example, the recovery of Re decreases with increasing abundance of Fe^{3+} for anion exchange resin separation (Huang et al., 2012).

The Fule and Laochang deposits are two major Pb-Zn de-

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poits in Yunnan Province. The Fule Pb-Zn ore deposit is a typ-ical carbonate-hosted sulfide deposit (Zhou et al., 2013a, b; Si et al., 2006; Fig. 1), whereas the Laochang Pb-Zn deposit (Ye et al., 2012) is one of the largest massive sulfide Pb-Zn deposits in China (Fig. 1). Due to lack of precise ages, the timing of Pb-Zn mineralization remains unclear, resulting the origin of these deposits is still controversial (Zhou J X, 2011; Xue, 2010, 2006; Long et al., 2007; Zaw et al., 2007; Si et al., 2006; Zhou et al., 2001; Chen et al., 2000; Xue, 1998; Zhou C X, 1998). In this study, we present an improved chemical and analytical protocol and Re-Os ages for the galena and sphalerite samples from the Fule and Laochang Pb-Zn deposits. The loss of Re during sample pre-treatment of typical galena and sphalerite samples was investigated and an improved sample preparation procedure was established for Re-Os dating. Additionally, the newly obtained precise Re-Os isochron ages provide significant information for the timing and genesis of Pb-Zn mineralization of the two studied deposits.

1 GEOLOGICAL SETTINGS
1.1 The Fule Pb-Zn Deposit

The Fule Pb-Zn deposit (Si et al., 2006), a dispersed elements-riched Pb-Zn sulfide deposit with 0.357 4 million tons (Mt) Zn, 0.023 7 Mt Pb, 7 200 t Cd, 749 t Se and 220 t Ge, is located in the Sichuan-Yunnan-Guizhou (SYG) Pb-Zn metal-logenic province (Zhou et al., 2013a, b), southwest Yangtze Block (Fig. 1). The province hosts more than four hundred carbonate-hosted epithermal Pb-Zn deposits and is an important producer of base metals in China (Zhou et al., 2014, 2013c, d; Liu and Lin, 1999).

In the Fule deposit, the major Pb-Zn ore bodies are hosted in limestone of Lower Permian Maokou Formation (Fig. 2a). Ore bodies are strata-bounded and lenticular vein in shape. Brecciated structure and coarse-grained texture are widely de-veloped (Figs. 2b and 2c). The ore minerals are mainly sphale-rite and galena (Figs. 2a–2f). Gangue minerals are mainly do-lomite and calcite (Figs. 2a–2c). The dolomite is the major gangue mineral mainly as assemblages of massive, lumpy, banded and vein (Figs. 2a–2c).

The sphalerite is mostly coarse-grained with euhedral grain sizes of 2.0–3.0 mm (Si et al., 2011, Figs. 2b–2f). The colors of the sphalerite are varied in this deposit (Figs. 2c–2d) including light yellow, brown and dark brown, of which the dark brown sphalerite is usually distributed in the central or bottom part of orebodies and was formed in the main ore-forming stage. The galena is mostly in massive, anhedral granular and banded textures with grain sizes of 0.5–30 mm (Figs. 2e–2f), closely associated with sphalerite. The dark brown sphalerite and associated galena samples were selected in this study, the isotopic age of which may represent the tim-ing of main Pb-Zn mineralization stage.

1.2 The Laochang Pb-Zn Deposit

The Laochang Pb-Zn deposit (Ye et al., 2012) in the south Sanjiang metallogenic belt, SW China, contains an estimated reserve of 0.866 Mt Pb, 0.336 Mt Zn, 1 736.84 t Ag, 0.116 Mt Cu and 2.836 Mt FeS_2 with appreciable amounts of Au, In, Cd, Se and Te as by-products. The country volcanic rocks of Lower

Carboniferous Yiliu Formation (Fig. 2g) are composed of tuffs, lavas, imandrite, diabase, pyroxene minette, tuffaceous sand-stone and limestone (Chen et al., 2010). Under the Pb-Zn-Ag ore bodies, a Himalayan (~44 Ma) Mo-Cu mineralized granite-porphyry has been found (Li et al., 2010). Thus, whether the Pb-Zn-Ag mineralization is related to the Carboniferous vol-canic rocks or the Himalayan granite-porphyry is controversial (Long et al., 2007; Chen et al., 2000; Xue, 1998). Wall rock alterations include ferromanganese carbonatation, meta-andesitization, carbonatization (Fig. 2g), silicification, pyritiza-tion and skarnization. The dominant ore minerals include gale-na, sphalerite, chalcopyrite and pyrite (Figs. 2h, 2j). Gangue minerals consist of quartz, calcite, dolomite and feldspar. Sphalerite is the dominant ore mineral, and occurs in anhedral to euhedral. It is coarse-grained with grain sizes from 0.05 to 2.0 mm (Figs. 2i, 2j). Sphalerite is dark brown or black in color (Fig. 2i), and co-exists with galena and/or pyrite (Figs. 2h, 2j). The associated galena in massive sulfide ores is also in anhe-dral to euhedral granular with grain sizes of 0.5–3.0 mm (Figs. 2h, 2j). The sphalerite and associated galena samples were selected for both methodological and isotope chronological studying of Re-Os isotope system.
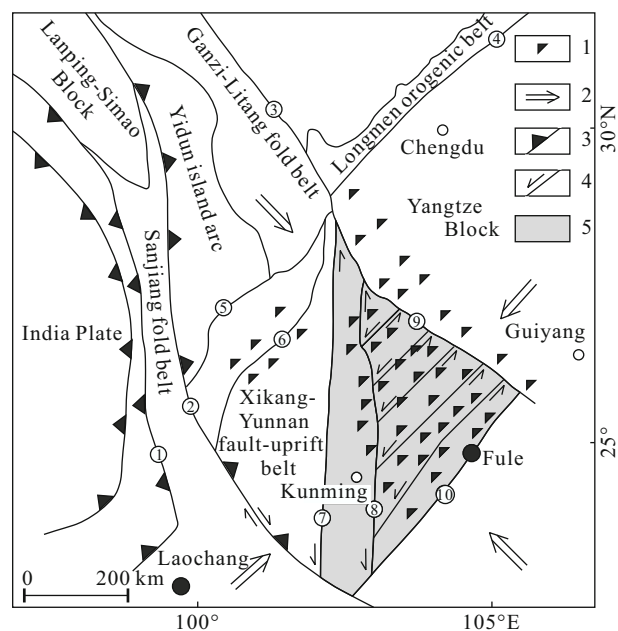
Figure 1. Scketch map showing geotectonic position of the southwestern margin of Yangtze Block (modified after Ma et al., 2004 and Luo and Yu, 2001). ① Nujiang fault; ② Jinshajiang-Honghe fault; ③ Xianshuihe fault; ④ Longmenshan fault; ⑤ Xiaojinhe-Zhongdian fault; ⑥ Qinghe-Chenghai fault; ⑦ Anninghe-Lüzhijiang fault; ⑧ Xiaojiang fault; ⑨ Kangding-Yiliang-Shuicheng fault; ⑩ Mile-Shizong-Shuicheng fault. 1. Emeishan basalt; 2. direction of tectonic stress; 3. plate junction belt; 4. strike fault; 5. SYG Pb-Zn metallogenic province.

## 2 EXPERIMENTAL STUDY
2.1 Samples

The galena and sphalerite samples were collected from the Fule and Laochang deposits. These ore samples were mechani-cally crushed and washed by ultrapure water. After sieved to

20–40 meshes, sphalerite and galena separates of each ore sample were selected by hand-picking under a binocular microscope without any other mineral inclusions under the naked eye. Selected galena and sphalerite grains were then grinded to about 200 meshes, with sufficient mixing.

2.2 Instrument

The instrument used for Re analysis in this study is an ELAN DRC-e ICP-MS (Perkin Elmer, USA) in the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The sensitivity
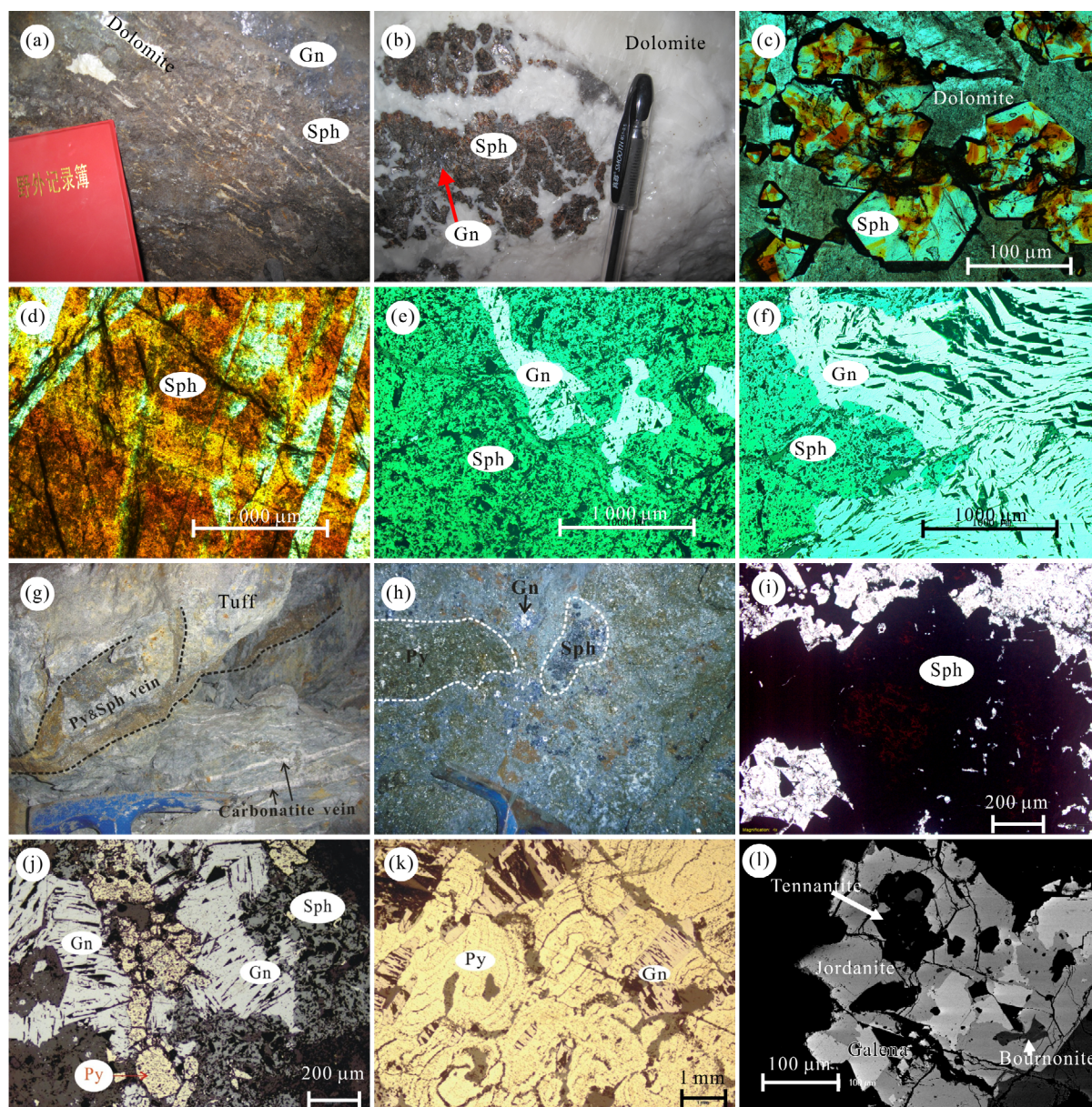
Figure 2. Field and microscopic pictures of the Fule and Laochang Pb-Zn deposits. (a) Field photograph showing the banded and vein dolomites and strata-bounded Pb-Zn ores in the Fule Pb-Zn deposit; (b) field photograph showing the massive and lumpy dolomites, lenticular vein Pb-Zn ores and the brecciated structure and coarse-grained texture of sphalerite in the Fule Pb-Zn deposit; (c)–(d) photomicrographs in diascopic lighting showing the color variation of colloform sphalerites from the Fule Pb-Zn deposit; (e)–(f) photomicrographs in reflected light showing the paragenic of sphalerite and galena in the Fule Pb-Zn deposit ((e) anhedral granular and banded textures of galena; (f) coarse grain galena); (g) field photograph showing the vein structures of Pb-Zn ores and wall rock alteration of carbonatization in the Laochang Pb-Zn deposit; (h) field photograph showing the paragenic of sphalerite, galena and pyrite in tuff from the Laochang Pb-Zn deposit; (i) photomicrograph in diascopic lighting showing the dark sphalerites from the Laochang Pb-Zn deposit; (j) photomicrograph in reflected light showing the paragenic of sphalerite, galena and pyrite in the Laochang Pb-Zn deposit; (k) recrystallized colloidal pyrite in the Laochang Pb-Zn deposit; (l) back-scatter electron image of mineral assemblages of galena with Sb-, As-Pb and Cu-sulfphosalts in the Laochang Pb-Zn deposit. Sph. sphalerite; Py. pyrite; Gn. galena.

of the instrument was optimized to be more than 30 000 cps (counts per second) for 1 ng/mL of ^{103}Rh.

Os was determined by a Bruker Aurora M90 inductively-coupled plasma mass spectrometry (ICP-MS). High sensitivity mode was used due to the low contents of Os. The sensitivity of the instrument for high sensitivity mode was adjusted to more than 800 000 cpsfor 1 ng/mL of ^{115}In and 300 000 cps for 1 ng/mL of ^{232}Th, in order to achieve the desired detection limits.

The analytical uncertainty (RSD) is better than 3%. Total analytical blanks were less than 4.7 pg for Re and 2.0 pg for Os.

2.3 Reagents and Solutions

Re and Os spike solutions (US Services Inc.) are separately enriched in ^{185}Re and ^{190}Os. In Re spike, abundances of ^{185}Re and ^{187}Re are separately 94.36% and 5.64%. In Os spike, abundances of ^{187}Os, ^{188}Os, ^{189}Os, ^{190}Os, and ^{192}Os are 0.014%, 0.055%, 3.57%, 91.53%, and 4.82%, respectively. Re and Os spike solutions were diluted to 20 and 10 ng/g in 10% HCl (v/v) solution, respectively.

HCl is purified by sub-boiling distillation; HNO$_3$ is purified by sub-boiling distillation twice. The first purification is treated by bubbling the clean air through the boiled HNO$_3$ with H$_2$O$_2$ in a 3 000 mL glass beaker to remove possible volatile OsO$_4$, and the second purification is following the routine sub-boiling distillation.

Ultrapure water was obtained from millipore purification system (18 MΩ·cm^{-1}).

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

Carius tubes used in this study are new design reusable Carus tubes (Qi et al., 2013), which have an inner volume of about 200 mL, with custom-made sealing system including a glass lined-PTFE stopper and a stainless steel screw cap. The reusable Carius tube is easy to clean so that it has lower Re and Os blanks.

3 METHODOLOGY

Variable acids have been used for anion exchange separation of Re. HCl (Palesskii et al., 2009; Qi et al., 2010, 2007; Meisel et al., 2003a), HNO$_3$ (Sun et al., 2010; Chu et al., 2007; Meisel et al., 2003b), *aqua regia* (Shirey and Walker, 1995) and H$_2$SO$_4$ (Malinovsky et al., 2002) media have all been used and could provide high recovery of Re. In this study, the common media, 2N HCl and 0.8N HNO$_3$, were used to investigate the recovery of Re on galena and sphalerite. The sphalerite in me-

thodological study is from the Laochang Pb-Zn deposit and galena is from the Fule Pb-Zn deposit, both of which have low concentrations of Re of <1.0 ng/g.

3.1 Analytical Procedure

About 0.5–2.0 g galena or 1.0–2.0 g sphalerite was precisely weighed and transferred into a reusable Carius tube with 6.0 ng Re spike and appropriate amount of reverse *aqua regia* (HNO$_3$: HCl≈4 : 1). 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 to 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 solution is then dissolved by 15 mL of 2N HCl (or 0.8N HNO$_3$) and transferred into a 15 mL centrifuge tube and then centrifuge for 5 minutes, the upper solution was used for anion exchange separation of Re. Twelve mL 2N HCl (or 2N HNO$_3$) was used to wash the anion exchange resin and 15 mL 9N HNO$_3$ was used to elute Re. The solution was evaporated to dryness and dissolved by 3 mL 3% HNO$_3$ for ICP-MS measurement (Qi et al., 2007).

3.2 Results and Discussion

In this study, we found that recovery of Re would be extremely low if the conventional method of Carius tube-reverse *aqua regia* was used to dissolve 0.5–2.0 g galena and 2N HCl (15 mL) was applied for anion exchange resin separation (Table 1). Following the procedure described above, the intensity (cps) of ^{185}Re for galena samples are much lower than other sulfides (e.g., pyrite) with same concentration of Re spike. The extremely low recovery of Re indicates that almost all of Re was lost during the sample treatment. On the other hand, low recovery of Re only occur when large amounts of sphalerite sample (>1.0 g, 15 mL) were dissolved (Table 1). The recovery decreases when the sample mass increases. But 2N HCl without any matrix do not show any effect on the recovery of Re (Table 1). Therefore, the 2N HCl medium is not suitable for precise Re-Os dating of galena.

However, the relatively oxidized matrix of 0.8N HNO$_3$ has been demonstrated to be very efficient for anion exchange of Re on galena (0.5–2.0 g) and sphalerite (>1.0 g) (Table 1). Thus, the HNO$_3$-based anion exchange separation is more suitable for Re purification of lead-zinc sulfide ore samples.

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 Re in 2N HCl medium (%)	Recovery of Re in 0.8N 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

3.3 A Revised Procedure of Re-Os Isotope Dating of Lead-Zinc Ores

Galena/sphalerite sample (1.0–2.0 g) and appropriate ^{185}Re and ^{190}Os 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 is put into a refrigerator for 2 h for freezing. Then, 20 mL of water was added and the tube was connected onto the in situ distillation equipment for in situ distillation of Os (Qi et al., 2013; 2010). After that, the residual solution was transferred to a 50 mL glass beaker and evaporated to dryness. The residue solution is then dissolved by 15 mL of 0.8N HNO_3 and transferred into a 15 mL centrifuge tube. After 5-minute's centrifuging, the upper solution was used for anion exchange separation of Re. Twelve mL 2N HNO_3 was used to wash the anion exchange resin and 15 mL 9N HNO_3 was used to elute Re. The solution was evaporated to dryness and dissolved by 3 mL 3% HNO_3 for ICP-MS measurement.

4 GEOCHRONOLOGICAL RESULTS AND DISCUSSION

Using the revised procedure described above, Re-Os isotope chronology was used for dating lead-zinc ores from the Fule and Laochang Pb-Zn deposits, Yunnan Province, SW China.

Decay constant (λ) used for ^{187}Re is 1.666×10^{-11} yr^{-1} (Smoliar et al., 1996). Model age is calculated according to equation: $t = 1/\lambda \ln(1 + {}^{187}Os/{}^{187}Re)$.

All uncertainties including in-run measurement precisions, standard reproducibility, blank variability, fractionation effects, weighing errors, spike calibration, and decay constant uncertainties are given at 2σ level.

Table 2 Re-Os isotope analyses of sulfide ores from the Fule and Laochang Pb-Zn deposit

Fule Sample No.	Mineral	Sample wt (g)	Total Re* (ng/g; ±2σ)	^{187}Re* (ng/g; ±2σ)	^{187}Re/^{188}Os* (±2σ)	^{187}Os* (pg/g; ±2σ)	Common Os* (pg/g; ±2σ)	Model age (Ma; ±2σ)
SBFL-01	Sph	0.503 2	398±5	249±3	55 618±8 504	87.0±7.2	34.4±5.2	21.1±1.7
SBFL-04	Sph	1.007 8	86.3±3.8	54.1±2.4	98 289±19 325	19.7±0.5	4.22±0.80	21.9±1.0
SBFL-21	Gn	2.008 9	3.52±0.98	2.20±0.06	3 902±404	0.68±0.16	4.34±0.44	20.0±1.4
SBFL-25	Gn	1.006 5	34.6±2.4	21.7±1.5	63 053±11 502	6.92±0.54	2.64±0.44	19.2±1.1
SBFL-29	Sph	2.003 2	7.21±0.42	4.51±0.27	4 876±448	1.50±0.10	7.11±0.50	20.1±1.2
SBFL-32	Sph	1.005 6	87.2±3.4	54.6±2.1	44 124±12 512	16.3±1.2	9.51±0.66	18.0±1.3
Laochang Sample No.	**Mineral**	**Sample wt (g)**	**Total Re* (ng/g; ±2σ)**	**^{187}Re/^{188}Os* (±2σ)**	**^{187}Os /^{188} Os* (±2σ)**	**^{187}Os* (pg/g; ±2σ)**	**Common Os* (pg/g; ±2σ)**	
LC-1850-03	Sph	2.005 6	6.82±0.10	1 046±50	6.23±0.40	21.1±1.4	31.3±2.4	
LC-1930-03	Sph	2.007 8	7.62±0.38	506±50	3.59±0.46	21.7±2.4	65.9±9.6	
LC-1930-04	Sph	2.001 2	2.81±0.18	765±62	5.06±0.22	8.77±0.80	16.7±1.2	
LC-1930-05	Sph	2.001 5	14.6±1.2	877±22	5.35±0.14	30.3±1.2	43.9±1.6	
LC-1930-07	Sph	2.004 5	3.29±0.20	581±32	3.53±0.36	8.52±1.00	26.5±1.4	
LC-1930-08	Sph	2.003 6	4.43±0.42	1 177±52	7.04±0.32	15.0±1.4	17.3±1.2	
LC-1930-11	Sph	2.008 9	5.28±0.42	1 101±56	6.83±0.34	17.1±1.2	22.5±1.6	
LC-1930-11	Gn	2.005 6	1.85±0.12	705±76	4.74±0.32	6.12±0.60	12.6±0.8	
LC-1800-06	Sph	2.004 2	40.7±1.8	1 436±62	8.18±0.16	143±2	136±6	
LC-1800-06 (duplicate)	Sph	2.006 2	35.3±1.9	1 537±74	8.60±0.46	117±4	109±6	

*All the data are blank corrected; Sph. sphalerite; Gn. galena.

4.1 The Fule Pb-Zn Deposit

The Re-Os isotope results of two galena and four sphalerite samples from the Fule Pb-Zn deposit (Table 2) show that they are typical low-level highly radiogenic (LLHR) sulfides (Stein et al., 2000) with relatively high and variable Re contents ranging from 3.52–398 ng/g. Common Os and radiogenic ^{187}Os contents are at ranges of 4.22–34.4 and 0.68–87.0 pg/g, respectively. The dating results showed that Re-Os model ages are from 18.0 to 21.9 Ma (Table 2), in good agreement with the ^{187}Re-^{187}Os isochron age of 20.4±3.2 Ma (Fig. 3).

Previous reported highly variable Pb isotopic model ages for the Fule Pb-Zn deposit range from 108 to 198 Ma (Si et al., 2006), Pb isotopic ages have been proved not to represent the timing of mineralization (Zhang, 1987; Zartman and Doe, 1981). Recent geochronological studies showed that the large scale Pb-Zn mineralization in the SYG provinces is during the Late Triassic (191–222 Ma; Wu, 2013; Zhou et al., 2013a, b; Mao et al., 2012; Lin et al., 2010; Yin et al., 2009; Li et al., 2007). On the other hand, some researchers considered that the Pb-Zn deposits in the metallogenic province have been reworked during Yanshanian (Xue, 2010, 2006; Zaw et al., 2007) or Himalayan (Zhou J X, 2011; Zhou et al., 2001; Zhou C X, 1998).

Our Re-Os isochron age (20.4±3.2 Ma; Fig. 3) is much younger than the previous reported Pb model ages of the Fule Pb-Zn deposit. The brecciated structure (Figs. 2b and 2c) and
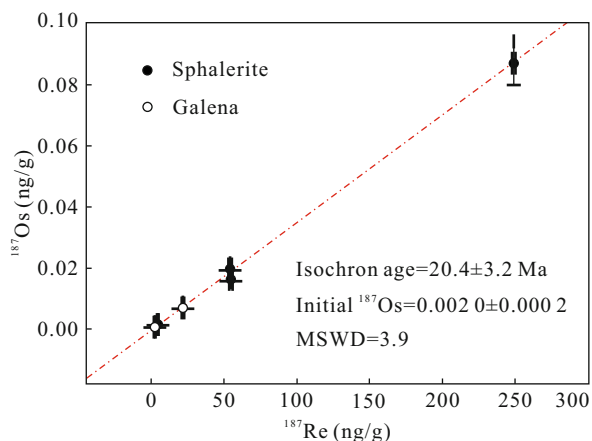
Figure 3. Re-Os isochron of galena and sphalerite from Fule Pb-Zn deposit, Yunnan Province, SW China.

colloform texture (Figs. 2c and 2d) of sphalerite in the deposit are indicative of multiple stages of mineralization. The Re-Os isochron age reveals that a Himalayan hydrothermal event has occurred in the Fule deposit. Geologically, at ca. 20 Ma, the E-W trending extension occurred (Mitsuishi et al., 2012; Wang et al., 2012), which might control the distribution of Pb-Zn deposits in Northeast Yunnan Province (Zhou et al., 2013b). The Re-Os isotopic system of the Fule Pb-Zn deposit may have recorded the possible hydrothermal event (Zhou J X, 2011; Zhou et al., 2001; Zhou C X, 1998) at this period.
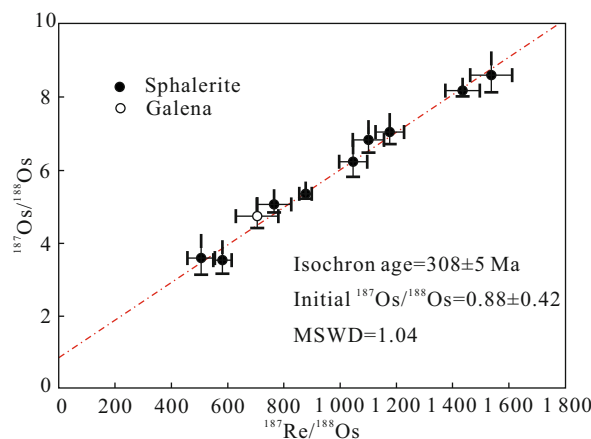
4.2　The Laochang Pb-Zn Deposit

One galena and nine sphalerite samples (Table 2) from the Laochang Pb-Zn deposit have relative lower concentrations of Re ranging from 3.29 to 40.7 ng/g. Common Os and radiogenic ^{187}Os contents are at ranges of 12.6–136 and 6.12–143 pg/g, respectively. The Re-Os isotopic data yield a $^{187}Re/^{188}Os$-$^{187}Os/^{188}Os$ isochron age of 308±25 Ma (2σ, MSWD=1.04), with initial $^{187}Os/^{188}Os$ ratio of 0.88±0.42 (Fig. 4). The age is consistent with U-Pb age of the hosting volcanic tuff (323.6±2.8 Ma; Chen et al., 2010) and the country basalt (312±4 Ma; Ye Lin unpub. data), but is much older than the underneath Mo-Cu mineralized granite-porphyry which has a zircon U-Pb age and a molybdenite Re-Os age of 44.6±1.1 Ma and 43.78±0.78 Ma, respectively (Li et al., 2010). This age supports that Pb-Zn mineralization is not related to the porphyry system but regional volcanism, and the Laochang deposit is supposed to be VHMS-type.

Such a hypothesis is also well supported by some geological features. Firstly, the Pb-Zn ore bodies occur mostly along strata as bands approximately parallel to bedding in the host rocks (Fig. 2g), consistent with a syngenetic origin of the Pb-Zn mineralization. Secondly, the abundant occurrences of recrystallized colloidal pyrites (Fig. 2k; Ye et al., 2012, 2011) indicate a turbulent sedimentary environment. Thirdly, mineral assemblages of galena with Sb-, As-Pb and Cu-sulfphosalts (e.g., jordanite, bournonite-seligmannite, tetrahedrite-tennantite, duftite and gratonite; Ye et al., 2011) exist extensively in Laochang deposit (Fig. 2l). Such assemblages also generally occur in remobilized ores from many Caledonian VHMS and SEDEX type deposits in the world (e.g., Sulitjelma, Bleikvassli; Nor-

way; Cook et al., 1998; Cook, 1996). Moreover, in-situ trace elements measurement by LA-ICP-MS for sphalerites from the Laochang deposit also showed the characteristics of VHMS Pb-Zn deposits (Ye et al., 2012).

The calculated initial $^{187}Os/^{188}Os$ ratio of 0.88±0.42 (Fig. 4) indicates a mixed source involving both mantle and crustal materials, a conclusion which is also supported by S, C, H, O, Pb isotope (Long et al., 2009, 2007) and trace element (Ye et al., 2012) data.

Figure 4. Re-Os isochron of galena and sphalerite from Laochang Pb-Zn deposit, Yunnan Province, SW China.

5　CONCLUSION

The medium of 0.8N HNO_3 is more efficient than 2N HCl for anion exchange separation of Re for galena and can be used for Re-Os dating of galena and sphalerite.

Using the revised method, galena and sphalerite samples from the Fule and Laochang Pb-Zn deposits in Yunnan Province, SW China, yield Re-Os isochron ages of 20.4±3.2 and 308±25 Ma, respectively. These two Re-Os isotopic ages have significant geological implications for the two studied deposits.

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