Electronic Supplementary Information (ESI)

Development of Sulfide Reference Materials for
\textit{in situ} Platinum Group Elements and S-Pb isotopes
analyses by LA-(MC)-ICP-MS

Yantong Feng,\textsuperscript{a} Wen Zhang,\textsuperscript{*a} Zhaochu Hu,\textsuperscript{a} Yongsheng Liu,\textsuperscript{a} Kang Chen,\textsuperscript{a} Jiali Fu,\textsuperscript{a}

\textit{Junyi Xie,\textsuperscript{a} Quanhui Shi}\textsuperscript{a}

\textsuperscript{a}State Key Laboratory of Geological Processes and Mineral Resources, China

University of Geosciences, Wuhan, 430074, PR China

*Corresponding author

E-mail: tuyaken@hotmail.com

Tel: 86-27-67885096

Fax: 86-27-67885096

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A. Scheme for element analyses using solution ICP-MS

(1) Quantitative analysis of trace elements

Trace element analyses of four synthetic samples were conducted on Agilent 7900 ICP-MS (Agilent Technology, Tokyo, Japan) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. The detailed sample-digesting procedure was as follows: (1) Sample powder were placed (2) 50 mg sample powder was accurately weighed and placed in a Teflon bomb; (3) 1 mL HNO$_3$ and 1 mL HF were slowly added into the Teflon bomb; (4) Teflon bomb was putted in a stainless steel pressure jacket and heated to 190 ℃ in an oven for > 24 hours; (5) After cooling, the Teflon bomb was opened and placed on a hotplate at 140 ℃ and evaporated to incipient dryness, and then 1 mL HNO$_3$ was added and evaporated to dryness again; (6) 1 mL of HNO$_3$, 1 mL of MQ water and 1 mL internal standard solution of 1 ppm Lu were added, and the Teflon bomb was resealed and placed in the oven at 190 ℃ for > 12 hours; (7) The final solution was transferred to a polyethylene bottle and diluted to 100 g by the addition of 2 % HNO$_3$.

Experiments were carried out by ICP-MS equipped with a Micro Flow nebulizer (0.10 mL·min$^{-1}$, PFA) and a double-path spray chamber. The spectrometer was optimized to obtain good signal intensities for Li, Y, Ce, and Tl, while keeping the CeO$^{+}$/Ce$^{+}$ and Ce$^{2+}$/Ce$^{+}$ ratios below 1.2 %. The working curve method was combined with Lu internal standard for the ICP-MS analysis. Calibration of the instrument was done on five standard solutions with 0, 5, 10, 25, and 50 ppb concentrations. Referring the analytical method of PGEs from Gilbert et al.$^1$ A pyrite sample was digested by the methods above and spiked with single element solutions of PGEs and Au. This pyrite solution was used to correct the matrix effect. Detail description same with Gilbert et al.$^1$

(2) Quantitative analysis of Ru, Pd, Ir and Pt by dilution method

Analyses of Ru, Pd, Ir and Pt in four synthetic samples were conducted on Element XR (Thermo Fisher Scientific, Bremen, Germany) at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. About three grams of powder were spiked with appropriate amounts of $^{99}$Ru, $^{105}$Pd, $^{191}$Ir and $^{194}$Pt enriched isotopes prior to digestion. Digestion was conducted in sealed Pyrex borosilicate Carius tubes heated to 270 ℃ for 96 hours. Upon opening the cooled tubes, take out and dilute the solution. The chemical separation of Ru-Pd-Ir-Pt fraction from matrix was performed on columns filled with 10 mL of precleaned Eichrom 50W-X8 (100-200 mesh) cation exchange resin.$^2,^3$ The isotope ratio of each element was tested with Element XR, and then calculated the concentration by the dilution formula.
B. **Scheme for S and Pb isotope analyses using IR-MS and MC-ICP-MS**

(1) **Determination of S isotope using IR-MS**

The S isotopic compositions of four synthetic samples were determined at the State Key Laboratory of Biogeology and Environmental Geology in China University of Geosciences, Wuhan. Four synthetic samples were carried out by using the chromium reduction method described in Canfield *et al.*[^4] with zinc acetate and silver nitrate traps for analyses of $S_{py}$ and $\delta^{34}S_{py}$, respectively. The $\delta^{34}S_{py}$ was measured by online combustion of $Ag_2S$ precipitates with an excess of $V_2O_5$ on a Thermo Instruments Delta V Plus isotope ratios mass spectrometer coupled with a Costech elemental analyzer. Sulfur isotopes are reported in standard $\delta$-notation relative to Vienna Canon Diablo Troilite (VCDT). Analytical precision for $\delta^{34}S_{py}$ of the sample set from replicate analyses of IAEA standards (IAEA S1, S2 and S3) is better than ±0.1 ‰ (1σ, SD). Detail description same with Feng *et al.*[^5]

(2) **Determination of Pb isotope using solution MC-ICP-MS**

The Pb isotopic compositions of four synthetic samples were determined at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan. First, ~50 mg of the sample was weighed into in a homemade, PTFE-lined stainless steel bomb (consisting of a 10- mL PTFE inner vessel with lid, which fitted tightly into an outer stainless steel pressure jacket). After the addition of 0.5 mL of HF (40 % v/v, GR grade) and 2.0 mL of HNO$_3$ (68 % v/v, GR grade), the sealed bomb was heated to 190 °C in an electric oven for 48 hours. Pb was separated using standard ion exchange procedures (Bio-Rad AG1-X8, 200-400 mesh resin) in HBr-HCl media. The total procedural blank was less than 20 pg. Pb isotopic compositions were determined using static mode on a Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) using Faraday cups. After chemical separation, NBS 981 (NIST SRM 981) Pb standards and sample solutions were spiked with NIST-SRM 977 Tl. The samples and standards were adjusted to a consistent Pb/Tl ratio of 3:1 to reach appropriate ion currents in the range of 10-15 V total Pb. A modified Tl normalization technique[^1] was used to correct for the mass bias. In this method, the natural Tl-isotopic composition was assumed, and a series of reference samples were then run to define the mathematical relationship between Tl and Pb mass bias. This relationship could then be applied to the unknowns, providing a robust correction for any mass bias related to either instrument drift or matrix effects. The ion beam intensities for $^{202}$Hg were always below 0.17 mV for all runs, corresponding to a correction of less than 0.1 mV in mass for $^{204}$Hg. The samples were analyzed with the reference material NBS 981 run every two samples. The results for NBS 981 of $^{208}$Pb/$^{204}$Pb = 36.7228 ± 0.0038, $^{207}$Pb/$^{204}$Pb = 15.4986 ± 0.0015 and $^{206}$Pb/$^{204}$Pb = 16.9403 ± 0.0015 (n=6) were obtained.
References

Fig. S1 The signal intensities of line scans in 10th-01, 11th-01, 11th-02 and 11th-03. The laser spot of 60 μm was used with the influence of ~5 J cm⁻², the frequency of 6 Hz and the scan speed of 10 μm s⁻¹.
Fig. S2 Relationship between ablation signal ratios (Fe normalized) and mass fraction ratios (Fe normalized) for Ru, Pd, Re, Ir and Pt in the four synthetic sulfide reference materials.