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Development of sulfide reference materials for *in situ* platinum group elements and S–Pb isotope analyses by LA-(MC)-ICP-MS†

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The platinum group elements and sulfur-lead isotopes in sulfide minerals are important geochemical tracers in the earth sciences. However, *in situ* analyses of PGEs and S–Pb isotope compositions in natural sulfides using laser-ablation (multicollector) inductively coupled plasma mass spectrometry (LA-(MC)-ICP-MS) are limited by a lack of suitable sulfide reference materials. A new synthetic method to produce sulfide reference materials was reported in this study. The hydrothermal synthesis technique was used to prepare the initial nano-FeS₂ particles. Trace elements were added to the reaction medium and then entered into the lattice of the nano-FeS₂ particles during the crystal growth process. The powder-pressed pellets prepared by the nano-FeS₂ particles (500–600 nm) exhibited excellent cohesion and were suitable for laser ablation microanalysis. Using this method, we synthesized four sulfide reference materials with different mass fractions of trace elements. Repeated measurements using LA-(MC)-ICP-MS demonstrated good homogeneity for most of the trace elements (RSD <3% for PGEs, Au and Pb) and S isotope compositions (<0.23‰, 2SD) in the four sulfide reference materials, and Pb isotope compositions in two of these materials (<0.06% and <0.17%, 2RSD). Four sulfide reference materials were used as external standards to certify two commercial sulfide standards, MASS-1 and STDGL3#35. Accurate results from the analysis for trace elements were obtained, indicating that the synthesized sulfide reference materials are appropriate matrix-matched materials available for calibration in sulfides using LA-ICP-MS. The results also indicated that the hydrothermal synthesis of the nanoparticles can serve as a potentially effective approach for the preparation of microanalysis reference materials.

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1. Introduction

The platinum group elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt) and sulfur (S)–lead (Pb) isotopes in sulfide minerals are excellent geochemical tracers. PGEs are powerful tools to understand magmatic-hydrothermal processes in ore-genesis studies.^{1–7} In addition, the S and Pb isotope compositions provide sensitive chemical fingerprinting to identify ore formation processes, including the sources of metals, magma evolution and fluid sources.^{8–12}

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) allow for *in situ* analysis of the mass fraction of PGEs and S–Pb isotope compositions in sulfide minerals at high spatial resolution.^{2,8,13–16} LA-(MC)-ICP-MS techniques can reveal grain and

subgrain-scale elemental and isotopic variations, which may be critical given the complex textural relationships observed in ore systems. In addition, no complex chemistry process is required for LA-(MC)-ICP-MS, which can avoid blank and time-consuming problems and achieve high sample throughput. However, the lack of reference materials is one of the important factors limiting the development of LA-(MC)-ICP-MS techniques for natural sulfides analysis.^{13,17,18} Suitable reference materials are advisable for the calibration of instrument mass discrimination and the evaluation of the measurement results.

Recently, the development of sulfide reference materials has received increasing attention.^{18–21} Natural minerals are the best choice because complete matrix matching can be achieved during the laser ablation process. However, suitable natural sulfide minerals with homogenous distributions of trace elements are rare, especially for the PGEs, which are well-known to exhibit a nugget effect. Therefore, synthesizing reference materials is inevitable for the quantitative analysis of PGEs using LA-ICP-MS.

Many LA-ICP-MS laboratories have independently conducted methodological studies on the synthesis of sulfide reference materials for the quantitative analysis of PGEs, including the

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pressed powder pellet,^{22–24} fire assay,^{25,26} and high temperature melting methods.^{13,24,27,28} Tabersky *et al.*¹⁸ pointed out that the synthetic products after a high temperature process could suffer from losses of volatile elements (*e.g.*, Au, Ag, Ru and Tl). Therefore, the fire assay and high temperature melting methods would be not suitable for the synthesis of Pb isotope reference materials, although they have been successfully used in the synthesis of PGEs reference materials. The pressed powder pellet method is a conventional solid sample preparation method. The United States Geological Survey (USGS) used this method to synthesize reference materials for the quantitative analysis of trace elements in sulfides (MASS-1) and carbonates (MACS-3). MASS-1 is an Fe–Zn–Cu–S matrix sulfide reference material and was prepared by precipitating amorphous metal sulfide from solution.²² This sample is currently one of the few commercially available sulfide reference materials, and it has been demonstrated that the S and Pb isotopes are homogeneous.^{29,30} However, MASS-1 only contains Ir and Pt and lacks other platinum group elements.

Preparing the initial material is considered a critical step in the pressed powder pellet method. The nano powders have been proposed as the initial material, as this material can provide a more uniform distribution of elements and isotopes and significantly improve the cohesion of the pressed powder pellets. For example, Onuk *et al.*²⁴ developed a sphalerite reference material (MUL-ZnS-1) for the calibration of *in situ* trace elements. In this case, nanocrystal powders of ZnS and FeS were used as the initial materials and mixed with single-element standard solutions. The mixture was ground in a planetary ball mill and showed a particle size distribution of $D_{90} < 0.7 \mu\text{m}$. Homogeneity tests of MUL-ZnS-1 showed that most of the elements are homogeneously distributed for spot sizes = 50–60 μm with RSDs mostly <10%. Fu *et al.*²⁹ used a mixer mill to grind natural minerals (pyrite, chalcopyrite and sphalerite) to prepare matrix-matching sulfide reference materials for *in situ* S isotope ratios analysis. These nano powders (<1 μm) were pressed to pellets and analyzed by LA-MC-ICP-MS. Repeated analysis results showed that external precisions of $\delta^{34}\text{S}_{\text{V-CDT}}$ were better than 0.3‰, which satisfied the needs of *in situ* S isotope ratios analysis. Afterward, other researchers have carried out works similar to Fu *et al.*²⁹ to prepare sulfide reference materials for *in situ* S, Pb and Os isotope analyses.^{19,31,32} In addition to the use of mechanical grinding methods to obtain ultrafine powder, Tabersky *et al.*¹⁸ used a flame spray technique to yield 10–50 nm nanoparticles to synthesize a new reference material with the same matrix as the NIST SRM 610 glass standard. The manufactured material was homogeneous in terms of its major elements and had REEs similar to those of NIST glass (<5% RSD). However, the distribution of the PGE showed a slightly larger spatial variation on the order of <7.5% (RSD).

Hydrothermal synthesis has been widely used to synthesize nanomaterials for the applications of special materials, rechargeable batteries and solar cell devices.^{33–35} Ke *et al.*²⁰ has attempted to use nanosulfide powders prepared by hydrothermal synthesis as the initial material to develop an in-house PGE-bearing sulfide reference material. The synthetic sulfide

powders of FeS₂, NiS, CuS, and ZnS were mixed with standard solutions and fused by an in-house high temperature furnace. The synthetic sulfide reference materials contained only Ru, Rh, Pd and Pt. Homogeneities assessed by comparing the RSD of repeat analyses for Ru, Rh, Pd and Pt were 3.78–9.22%, 1.61–11.36%, 8.37–14.69% and 6.06–20.59%, respectively, which showed heterogeneity for Pd and Pt. In this study, a new hydrothermal synthesis method for the preparation of sulfide reference materials is developed. An important improvement is that trace elements are not spiked into the initial material by mechanical grinding, while the multielement standard solution is added to the reaction medium at the first step of the hydrothermal synthesis. Trace elements would enter the synthetic sulfide lattice in the isomorphic form during the crystal growth process. In this way, we synthesized a series of iron sulfide powder-pressed pellets with different mass fractions of trace elements, including Ru, Rh, Pd, Os, Ir, Pt, Au and Pb. The morphology of nanosulfide particles and the homogeneity of trace elements and S–Pb isotope compositions were investigated. The analytical results indicate that four synthetic sulfide reference materials were homogenous for PGEs, Au, Pb and S–Pb isotope compositions. The results indicate that the hydrothermal synthesis can serve as a potentially effective approach for the preparation of *in situ* sulfide reference materials.

2. Experiment

2.1 Reagents and reference materials

Ultrapure water with a resistivity of 18.0 M Ω cm^{−1} was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Commercially available nitric acid (HNO₃, 68%, GR grade) and hydrofluoric acid (HF, 40%, GR grade) were further purified in a sub-boiling distillation system. The single-element standard solutions of Ni, Cu, Zn, Ru, Rh, Pd, In, Re, Os, Ir, Pt, Au and Pb (1000 $\mu\text{g ml}^{-1}$) were purchased from Alfa Aesar (China) Chemical Co. Ltd. and used to prepare a multielement solution using a gravimetric serial isotope dilution method. The sulfur powder (325 mesh, 99.5%) and the iron(II) chloride tetra hydrate (FeCl₂·4H₂O, 98%) were also purchased from Alfa Aesar. The ethylene glycol (C₂H₆O₆, 99%), carbon disulfide (CS₂, AR grade) and sodium hydroxide (NaOH, AR grade) were purchased from Sinopharm Chemical Reagent Co., Ltd.

The USGS reference materials MASS-1 and the ARC Centre of Excellence in Ore Deposits reference material STDGL3#35 were used in this study. MASS-1 is one of the few commercially available sulfide reference materials and is primarily used for the determination of trace elements by LA-ICP-MS. STDGL3#35 is a new commercially available fused glass based on a flux of Li-tetraborate, Na-nitrate and Li-nitrate, which contain a mixture of sulfide minerals (RTS-4 and CZN-3; 2.5 : 1) doped with a range of trace elements. A nature pyrite PPP-1 and a nature sphalerite Sph-HYLM were used as the external standards for the *in situ* S and Pb isotope analyses, respectively. The chemical and isotopic compositions of PPP-1 and Sph-HYLM were reported by Gilbert *et al.*²¹ and Zhang *et al.*,³⁰ respectively.

2.2 Instruments

The experiments were performed mainly in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences in Wuhan. An Agilent 7900 quadrupole ICP-MS (Q-ICP-MS or ICP-MS, Agilent Technology, Tokyo, Japan) in combination with a GeoLas HD laser ablation system (Coherent Inc, Göttingen, Germany) was used for the quantitative analysis of PGEs in this study. The standard ablation cell in the GeoLas HD system, which is a closed-design cell and consists of a cylindrical volume (approximately 40 cm³) with an inlet nozzle (i.d. < 0.5 mm) and a wide outlet (i.d. 1.5 mm), was used. A wire signal smoothing device was used to produce the smooth signal.³⁶ Helium was applied as a carrier gas. Argon was used as the make-up gas and mixed with the carrier gas *via* a T-connector before entering the ICP. Nitrogen was added into the central gas flow (Ar + He) of the Ar plasma to decrease the detection limit and improve precision.³⁷

A NEPTUNE Plus MC-ICP-MS instrument (Thermo Fisher Scientific, Bremen, Germany) was employed using the aforementioned LA system for the *in situ* S–Pb isotope analyses. The NEPTUNE Plus is a double focusing MC-ICP-MS equipped with seven fixed electron multiplier ion counters and nine Faraday cups fitted with 10¹¹ Ω resistors. In addition, a large dry interface pump (100 m³ h^{−1} pumping speed) and newly designed X skimmer cone and Jet sample cone were used to increase the instrumental sensitivity. Helium was used as the carrier gas for the ablation cell. For S isotope analysis, signals of ³²S, ³³S and ³⁴S were collected in the L3, center and H3 Faraday cups, respectively. The amount of the additional nitrogen was controlled by a mass flow controller (Aalborg DFC 26 mass flow controller), which was then merged with the argon makeup gas flow and the carrier gas by a simple Y junction. For Pb isotope analysis, the ion beams of ²⁰²Hg, ²⁰³Tl, ²⁰⁵Tl, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb were collected by Faraday cups. A signal-smoothing and mercury-removing device was used downstream from the sample cell to efficiently eliminate the short-term variation of the signal and remove the mercury from the background and sample aerosol particles.³⁸ The CETAC Aridus II™ desolvation nebulizer system (CETAC Technologies, Omaha, USA) was used to introduce the Tl solution for the mass bias correction.

An Element XR (Thermo Fisher Scientific, Bremen, Germany) ICP-SF-MS was used to determine mass fractions of Ru, Pd, Ir and Pt elements in synthetic sulfide reference materials using the isotope dilution method. In addition, the measurements of mass fractions for other elements (Fe, Ni, Cu, Zn, Rh, In, Re, Os, Au and Pb) were carried out using an Agilent 7900 quadrupole ICP-MS instrument.

The referenced values of S and Pb isotope compositions in synthetic sulfide reference materials were determined by an isotope ratio mass spectrometry (IR-MS, DELTA V Plus, Thermo Fisher Scientific, Bremen, Germany) and the NEPTUNE Plus MC-ICP-MS, respectively.

A scanning electron microscope (SEM, Quanta 450, Field Electron and Ion Company, USA) was used to observe the particle size. A mixer mill (MM400, Retsch, Germany) was used to mill the synthetic products.

Details of the LA-(MC)-ICP-MS instrumental operating conditions and measurement parameters for *in situ* trace elements and S–Pb isotope analyses are summarized in Table 1.

2.3 Analytical methods

In LA-ICP-MS analysis, the carrier and make-up gas flows were optimized to obtain the maximum signal intensity for ²³⁸U⁺ while keeping a low ThO⁺/Th⁺ ratio (0.1–0.3%). The ion-signal intensity ratio measured for ²³⁸U and ²³²Th (²³⁸U/²³²Th ≈ 1) was used as an indicator of complete vaporization.³⁹ Samples were ablated in single spot mode with a spot size of 60 μm, a repetition rate of 5 Hz and a laser energy density of 5 J cm^{−2}. Each analysis incorporated a background acquisition of approximately 20–30 s followed by 50 s of data acquisition from the sample. All analyses were acquired using time-resolved software. The excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction and quantitative calibration for trace element analysis.⁴⁰ The element mass fractions of the synthetic sulfide reference materials were calculated and normalized by an internal standardization method. Fe was determined by solution ICP-MS and used as the internal standard. The main spectral interferences on PGEs are transition metal argides for *in situ* analyses in sulfides.^{21,28,41,42} In this study, the mass fractions of Ni, Cu, and Zn in synthetic sulfide reference materials are less than 50 μg g^{−1}, while the mass fractions of Ru, Rh and Pd are from ~4.0 to ~35 μg g^{−1}. Due to the low mass fractions of Ni, Cu and Zn, the influence of their interference was ignored in this study.

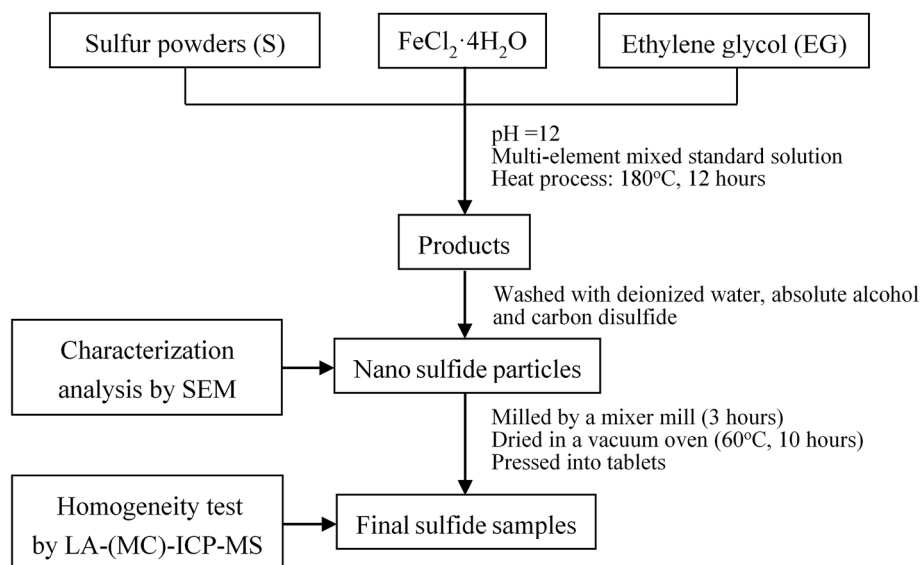
In situ S isotope measurements of the synthetic sulfide reference materials were conducted using LA-MC-ICP-MS. The isotopes of ³²S, ³³S and ³⁴S were measured at mass resolving power (R_{power} (5, 95%)) of 4996 (calculated *via* the difference between *m/z* on 5% and 95% of the peak height). Samples were ablated in single spot mode, with a spot size of 90 μm, a repetition rate of 2 Hz and a laser energy density of 5 J cm^{−2}. Each measurement was performed in static mode consisting of one block of 200 cycles with an integration time of 0.262 s per cycle. Total acquisition time for each measurement was approximately 52 s. An integration time of 18 s was used to acquire the gas background signal followed by a time of 34 s for ablation signal acquisition. The standard-sample bracketing method was applied to correct instrumental mass bias by repeatedly measuring the standard PPP-1 before and after every five samples. All of the data were reported relative to (³⁴S/³²S)_{V-CDT} = 0.044163.⁴³ More detail of the *in situ* S isotopic ratios analysis was described by Fu *et al.*²⁹

In situ Pb isotope analysis of the synthetic sulfide reference materials were performed using LA-MC-ICP-MS. Samples were ablated in the single spot mode, with a spot size of 120 μm, a repetition rate of 6 Hz and a laser energy density of 5 J cm^{−2}. The routine data acquisition consisted of one block of 180 cycles (0.524 s integration time per cycle): the first 70 cycles for background collection (no laser ablation) and the remaining 110 cycles for signal collection. The mass discrimination factor for Pb was determined using a Tl solution nebulized at the same

Table 1 LA-(MC)-ICP-MS instruments and data acquisition parameters for the test of trace elements and S–Pb isotopes

Agilent 7900 ICP-MS	
RF power	1350 W
Cool gas flow	14.0 L min ⁻¹
Auxiliary gas flow	1.0 L min ⁻¹
Argon make-up gas flow	0.9 L min ⁻¹
Helium carrier gas flow	0.65 L min ⁻¹
Sampling depth	5.0 mm
Dwell time per isotope	10 ms
Monitor isotopes	⁵⁷ Fe, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁹⁹ Ru, ¹⁰³ Rh, ¹⁰⁵ Pd ¹¹⁵ In, ¹⁸⁵ Re, ¹⁸⁹ Os, ¹⁹³ Ir, ¹⁹⁵ Pt, ¹⁹⁷ Au and ²⁰⁸ Pb
Neptune plus MC-ICP-MS	
RF power	1250 W
Cool gas flow	16.0 L min ⁻¹
Auxiliary gas flow	0.9–1.0 L min ⁻¹
Argon make-up gas flow	0.5–0.95 L min ⁻¹
Helium carrier gas flow	0.5–0.7 L min ⁻¹
Interface cones	X skimmer cone + Jet sample cone
Collectors	(³² S) L3, (³³ S) C, (³⁴ S) H3 for S (²⁰² Hg) L3, (²⁰³ Tl) L2, (²⁰⁴ Pb–Hg) L1, (²⁰⁵ Tl) C, (²⁰⁶ Pb), (²⁰⁷ Pb) H2, (²⁰⁸ Pb) H3 for Pb
Laser ablation system	
Wave length	193 nm, excimer laser
Pulse length	15 ns
Spot size	60–120 μm
Pulse frequency	2–6 Hz
Pulse energy	~5 J cm ⁻²
Aridus II desolvation nebulizer system	
Membrane temperature	160 °C
Spray chamber temperature	110 °C
Sweep gas flow	2.5 L min ⁻¹ Ar
Sample uptake rate	50 mL min ⁻¹ PFA nebulizer
Nebulizer flow	0.95 L min ⁻¹

time as the sample using an Aridus II desolvating nebulizer. The mass fractionation of Pb isotopes was corrected by ²⁰⁵Tl/²⁰³Tl with the exponential law. Note that the optimized values of ²⁰⁵Tl/²⁰³Tl, which were calibrated from measuring two Pb isotope standards MASS-1 (USGS) and Sph-HYLM (sphalerite, in-house standard), replaced the natural Tl isotopic

Fig. 1 Flow chart showing details of synthesizing nano-FeS₂ particles.

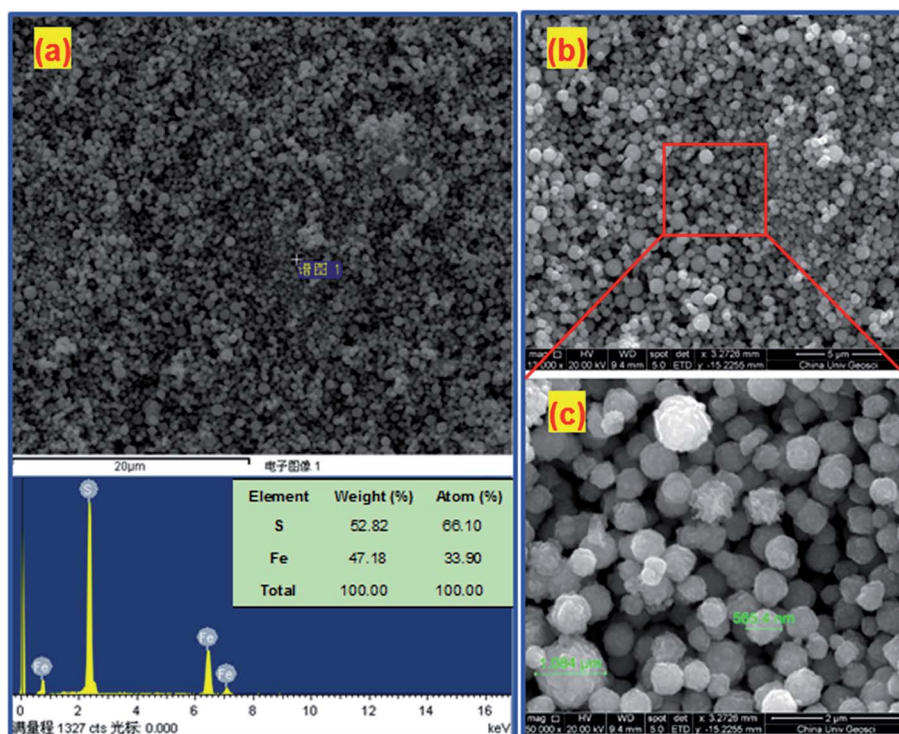


Fig. 2 Scanning electron microscope images of synthesized nano-FeS₂ particles.

composition for the mass fractionation correction of Pb isotopes. The ²⁰²Hg signal was used to correct the remaining ²⁰⁴Hg interference on ²⁰⁴Pb using the natural ²⁰²Hg/²⁰⁴Hg ratio (0.2301). In addition, the mass fractionation of ²⁰⁴Hg/²⁰²Hg was corrected by the ²⁰⁵Tl/²⁰³Tl normalization. In this case, we assumed identical mass fractionation factors for ²⁰⁴Hg/²⁰²Hg and ²⁰⁵Tl/²⁰³Tl. Sph-HYLM was used to monitor the precision and accuracy of the measurements after ten sample analyses, over the entire period of analysis. The greater detail of the *in situ* Pb isotopic ratios analysis was described in Zhang *et al.*³⁰

In addition, the determination of reference values for trace elements and S–Pb isotopes in synthetic materials was completed using solution ICP-MS (Element XR and Agilent

7900), IR-MS (DELTA V Plus, Thermo Fisher Scientific, Germany) and MC-ICP-MS (NEPTUNE Plus, Thermo Fisher Scientific, Germany), respectively. Detailed operating conditions and data reduction are given in the ESI.†

2.4 Synthesis of FeS₂ particles

The hydrothermal synthesis technique has been used in the synthesis of nanomaterials, including pyrite (FeS₂) due to its unique optical, magnetic and electrochemical properties in the scientific and industrial fields. Several approaches for synthesizing micro- and nanostructures of iron sulfide materials have been reported.^{44,45} The choice of iron and sulfur sources is a key

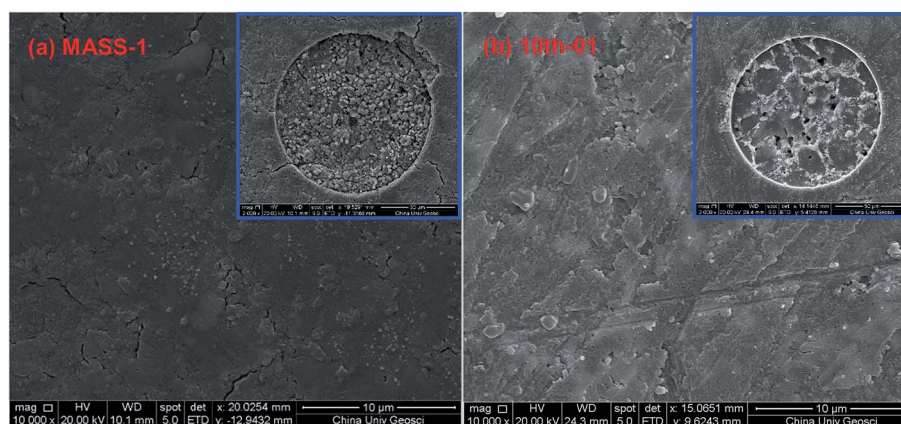


Fig. 3 Scanning electron microscope images of the surface and laser ablation crater (a spot size of 120 μm) on MASS-1 (a) and 10th-01 (b).

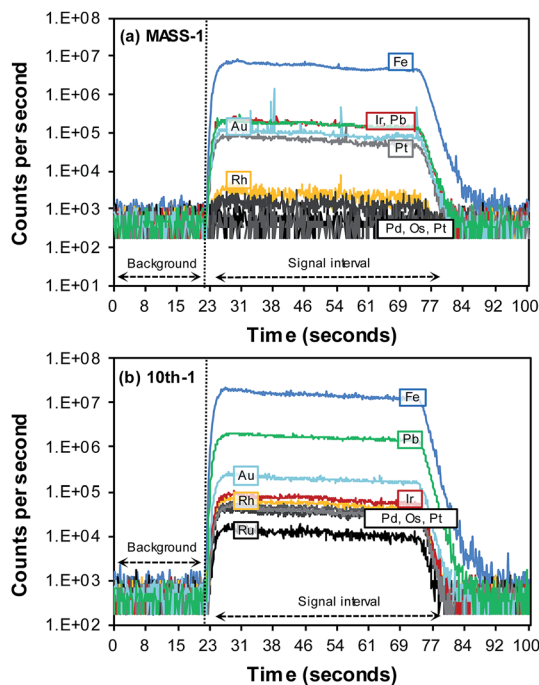


Fig. 4 LA-ICP-MS time-resolved signals for the analyses of MASS-1 (a) and 10th-01 (b) with a spot size of 120 μm , a repetition rate of 4 Hz and a laser energy density of 5 J cm^{-2} .

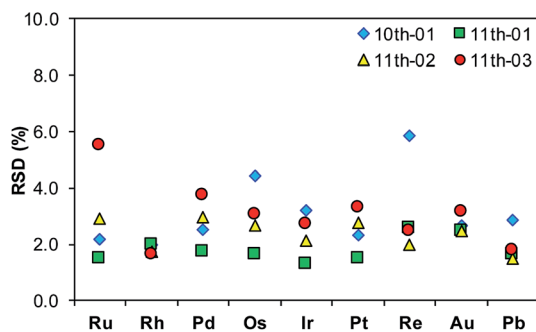


Fig. 5 Homogeneity of trace elements in 10th-01, 11th-01, 11th-02 and 11th-03 based on repeated LA-ICP-MS analyses expressed as relative standard deviation (RSD%).

parameter. After many attempts, ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and sulfur powder were used as the iron source and sulfur source, respectively, which refer to the synthesis method of FeS_2 particles reported by Wang *et al.*⁴⁶ The synthesis process was slightly modified, including adding reagent dosage, abandoning surfactant and washing by carbon disulfide. The details of our synthesis process are shown in Fig. 1.

(1) The PTFE-lined stainless-steel bombs were used as reactors, which consisted of a 150 mL PTFE inner vessel with lid and an outer stainless-steel pressure jacket. 3.8 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ particles and 4.0 g of sulfur powders were carefully and accurately weighed into hydrothermal reactors with 90 mL of ethylene glycol (EG). After stirring for 30 minutes, different amounts of multi-element solution were added slowly. Then, sodium hydroxide solution (NaOH) was added to adjust the pH to 12.

(2) Nitrogen was passed into the reactor to avoid oxidation. Then, sealed bombs were heated at 180 $^\circ\text{C}$ in an electric oven for 12 hours. After cooling to room temperature naturally, the synthetic products were collected by centrifugation, then washed with deionized water and absolute alcohol alternately several times. Due to some remaining sulfur powders, a carbon disulfide solution (CS_2) was used to soak the synthetic products and remove the residual sulfide powders.

(3) The cleaned synthetic products were ground using a Mixer Mill (MM400) for 3 hours. ~ 3 mL of absolute alcohol was pipetted into the grinding vials to avoid oxidation. Then, the synthetic products were completely dried at 60 $^\circ\text{C}$ in vacuum oven for 10 hours. The final sample powders were measured using solution ICP-MS, IR-MS and solution MC-ICP-MS for the determination of their trace elements and S-Pb isotope compositions.

Four FeS_2 samples with different mass fractions of trace elements were synthesized. The S, Fe and Pb isotope compositions should be consistent in the four FeS_2 samples because of the same initial element reagents. Four FeS_2 samples are denoted as 10th-01, 11th-01, 11th-02 and 11th-03, respectively. A portion of the sample powders were pressed to form tablets with an ~ 12 mm diameter without any binder using a manual presser that applied 10 tons of pressure for 5 min. LA-(MC)-ICP-MS were used to characterize the homogeneity of the elements and isotope compositions in the pressed powder pellets.

3. Results and discussion

3.1 Characteristics of synthetic FeS_2 particles and pressed powder pellets

The synthetic products after soaking by the CS_2 solution were directly investigated using a scanning electron microscope. As shown in Fig. 2, most synthetic products are spherical particles and approximately 500 to 600 nm in diameter. A few particles have a large particle size to ~ 1 μm . The elemental compositions of synthetic products were analyzed by SEM and consist of pure FeS_2 . These results indicate that the optimized hydrothermal synthesis method can be used to prepare nanosized FeS_2 particles.

The synthetic FeS_2 particles were pressed to form tablets without any binder for the laser ablation analysis. Fig. 3 shows the SEM images of the surface, and the ablation crater in a sulfide reference material (MASS-1) and a pressed pellet of 10th-01. The smooth surface can be observed in both samples. The process of ablation, which depends significantly on the mechanical strength of the solid against a highly energetic laser beam, has a direct impact on the quality of the results.⁴⁷ We used a 193 nm laser beam to ablate MASS-1 and 10th-01 with a spot size of 120 μm , a repetition rate of 4 Hz and a laser energy density of 5 J cm^{-2} . For MASS-1, there are obvious cracks on the edges of the ablation crater, which may be caused by the shock waves generated by the laser ablation, and some large fragments are also present in the crater. In contrast, no cracks appear in the ablation crater of 10th-01, and fine and homogeneous deposits are observed. The better ablation behavior in 10th-01 could be due to the stronger cohesive force of the

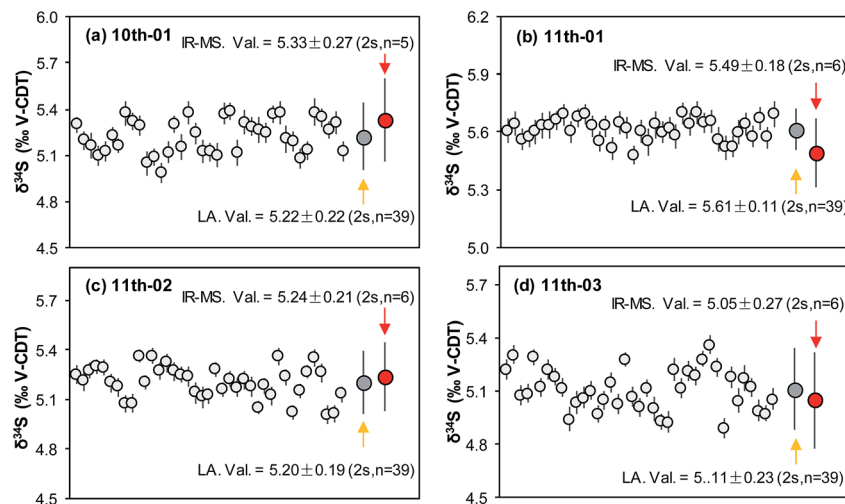


Fig. 6 Homogeneity test of S isotope compositions in 10th-01 (a), 11th-01 (b), 11th-02 (c) and 11th-03 (d) based on repeated LA-MC-ICP-MS analyses. The dark gray circle and red circle in each panel represent the determined average $\delta^{34}\text{S}_{\text{V-CDT}}$ value and its referenced value given by IR-MS, respectively.

nanoparticles, improving the mechanical strength of the pressed powder pellets and producing the finer ablation products.

Fig. 4 shows signal intensities of representative elements obtained from MASS-1 and 10th-01 using LA-ICP-MS. The single spot mode was used with a spot size of 120 μm , a repetition rate of 4 Hz at a laser energy density of 5 J cm^{-2} . The time-resolved ablation patterns of most elements during the analysis of MASS-

1 (Fig. 4a) shows a smooth and stable signal (Fe, Ru, Rh, Pd, Os, Ir, Pt and Pb), while that of Au presents some signal spikes, indicating an inhomogeneous distribution of Au in MASS-1. In 10th-01, the quality of controlled ablation resembles that of glass and produces very stable ion signals for all elements in ICP-MS (Fig. 4b).

In conclusion, the synthetic FeS_2 particles prepared by the hydrothermal method are nanometer scale with a typical grain

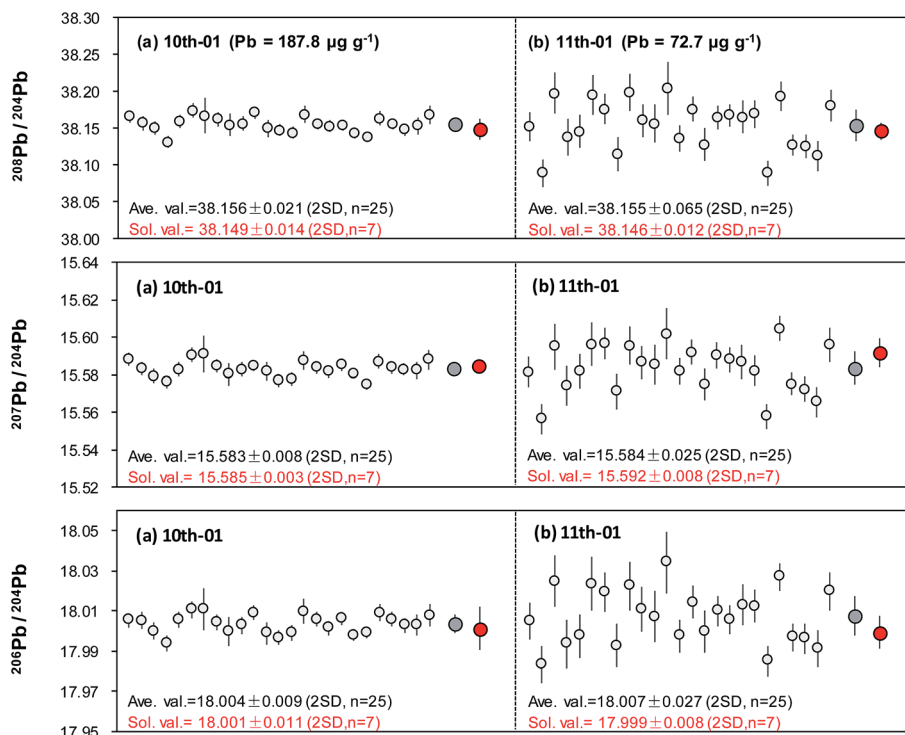


Fig. 7 Homogeneity test of Pb isotope compositions in 10th-01 and 11th-01 based on repeated LA-MC-ICP-MS analyses. The dark gray circle and red circle in each panel represent the determined average value and its referenced value given by solution-MC-ICP-MS, respectively.

Table 2 ICP-MS, MC-ICP-MS and IR-MS values of elements and S–Pb isotope compositions in four synthetic sulfide reference materials. The content of elements was determined by Q-ICP-MS. A part of PGEs (*) was determined by the isotope diluent method + Element XR. The RSD values (%) obtained using LA-ICP-MS are listed for showing the homogeneity of elements. IR-MS was used to determine the value of $\delta^{34}\text{S}_{\text{V-CDT}}$. Solution-MC-ICP-MS was used to determine the value of $^{208}\text{Pb}/^{204}\text{Pb}^a$

		10th-01		11th-01		11th-02		11th-03	
		SD		SD		SD		SD	
		Mean	(<i>n</i> = 3)	Mean	(<i>n</i> = 3)	Mean	(<i>n</i> = 3)	Mean	(<i>n</i> = 3)
Fe	% m m ⁻¹	25.8	0.2	24.2	0.2	31.1	0.1	33.0	0.6
Ni	μg g ⁻¹	39.6	0.3	52.2	0.5	19.2	0.2	17.2	0.2
Cu	μg g ⁻¹	35.7	0.2	36.2	0.2	19.1	0.3	19.8	0.4
Zn	μg g ⁻¹	4.9	0.1	5.9	0.1	4.5	0.0	4.6	0.2
Ru	μg g ⁻¹	35.1	0.0	15.3*	—	7.3*	—	4.2*	—
Rh	μg g ⁻¹	36.1	0.3	17.7	0.0	8.1	0.0	4.7	0.1
Pd	μg g ⁻¹	34.9	0.1	15.3*	—	7.6*	—	4.5*	—
In	μg g ⁻¹	0.9	0.0	0.9	0.0	0.9	0.0	0.4	0.0
Re	μg g ⁻¹	20.0	0.2	13.8	0.1	6.8	0.1	3.8	0.0
Os	μg g ⁻¹	81.1	7.8	51.3	3.9	27.3	2.8	14.9	1.3
Ir	μg g ⁻¹	35.8	0.1	13.4*	—	7.0*	—	3.9*	—
Pt	μg g ⁻¹	34.1	0.1	13.9*	—	6.8*	—	3.7*	—
Au	μg g ⁻¹	33.5	1.5	14.3*	—	7.2*	—	4.0*	—
Pb	μg g ⁻¹	187.8	0.2	72.7	0.0	41.4	0.1	23.2	0.1
		Mean	2SD (<i>n</i> = 5)	Mean	2SD (<i>n</i> = 6)	Mean	2SD (<i>n</i> = 6)	Mean	2SD (<i>n</i> = 6)
$\delta^{34}\text{S}_{\text{V-CDT}}$ (‰)		5.3	0.27	5.5	0.18	5.2	0.21	5	0.27
		Mean		2SD (<i>n</i> = 7)		Mean		2SD (<i>n</i> = 7)	
$^{208}\text{Pb}/^{204}\text{Pb}$		38.149		0.014		38.146		0.012	
$^{207}\text{Pb}/^{204}\text{Pb}$		15.585		0.003		15.592		0.008	
$^{206}\text{Pb}/^{204}\text{Pb}$		18.001		0.011		17.999		0.008	

^a *Determined by dilution method on Element XR. Please note that RSD was not calculated for Fe because it was the element used for normalization.

size of 500–600 nm, allowing us to produce pressed powder pellets without the addition of binder that have excellent cohesion suitable for laser ablation microanalysis.

3.2 Estimation of element and isotopic ratio homogeneity

The homogeneity of elements in four synthetic sulfide reference materials (10th-01, 11th-01, 11th-02 and 11th-03) were assessed by LA-ICP-MS spot analyses. The spot size of 60 μm was used with a repetition rate of 5 Hz and a laser energy density of 5 J cm⁻². The count rates of Fe were used to normalize these of the other elements. The relative standard deviation (RSD%) values of Fe-normalized count rates for Ru, Rh, Pd, Os, Ir, Pt, Re, Au and Pb were used to reflect sample homogeneity and are shown in Fig. 5. Four synthetic sulfide reference materials show RSD values of 1.5% to 5.5% for Ru, 1.7% to 2.0% for Rh, 1.8% to 3.8% for Pd, 1.6% to 4.4% for Os, 1.3% to 3.2% for Ir, 1.5% to 3.3% for Pt, 2.0% to 5.9% for Re, 2.5% to 3.2% for Au, 1.5% to 2.9% for Pb (Table S1, ESI†). The RSD values of most elements are better than 3%, except these of Os (4.4%), Ir (3.2%) and Re (5.9%) in 10th-01. We speculated the preparation of the tenth batch of samples (10th-01) may have a slight heterogeneity. In addition, the RSD of Ru (5.5%) and Pd (3.8%) in 11th-03 is slightly high, but it can satisfy natural geological sample analysis. Compared with

previous standards (Table S2, ESI†), our four synthetic sulfide reference materials are among the most homogeneous element compositions synthesized to date. In addition, the line scan analysis was completed and shown in Fig. S1 (ESI†). 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. There are straight and stable for the signal intensities of elements in the lines of ~1000–1200 mm. No obvious signal abnormalities were observed in four synthesis materials.

The homogeneity tests of S and Pb isotope compositions were assessed by LA-MC-ICP-MS spot analyses. For the S isotopic ratio analysis, the results of $\delta^{34}\text{S}_{\text{V-CDT}}$ in four synthetic sulfide reference materials are summarized in Fig. 6. Samples were determined with spot sizes of 90 μm spot size, a repetition rate of 2 Hz and a laser energy density of 5 J cm⁻². The natural pyrite reference material (PPP-1) was used as an external standard. Repeated analyses yield good external reproducibility for $\delta^{34}\text{S}_{\text{V-CDT}}$, such as 2SD of 0.22‰, 0.11‰, 0.19‰ and 0.23‰ for 10th-01, 11th-01, 11th-02 and 11th-03, respectively. The results indicate that these samples are homogeneous in S isotope ratios. In addition, *in situ* analytical results of $\delta^{34}\text{S}_{\text{V-CDT}}$ in four synthetic sulfide reference materials are consistent with the values obtained by IR-MS, confirming that these samples can be good candidates for in-house standards.

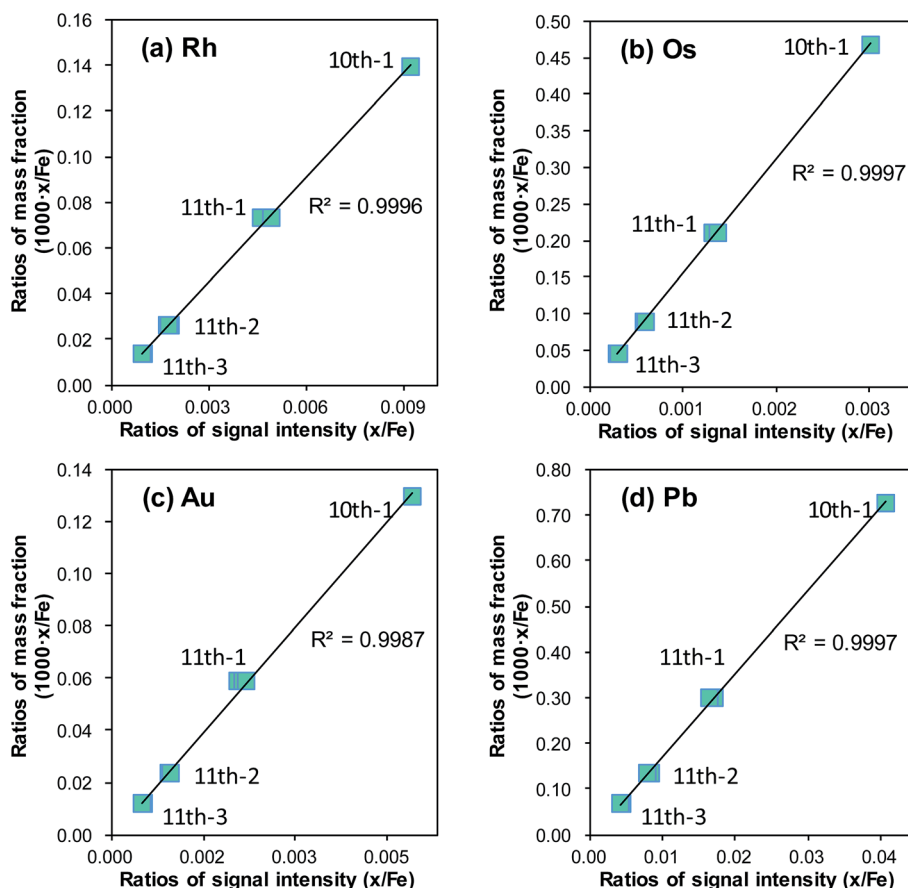


Fig. 8 Relationship between ablation signal ratios (Fe normalized) and mass fraction ratios (Fe normalized) for Rh, Os, Au and Pb in the four synthetic sulfide reference materials.

The Pb isotopic homogeneity of two synthetic sulfide reference materials, 10th-01 and 11th-01, was assessed at 120 μm with a repetition rate of 6 Hz and a laser energy density of 5 J cm^{-2} . 10th-01 has the highest mass fraction of Pb (187.8 $\mu\text{g g}^{-1}$) in the four synthetic sulfide reference materials and provided the total Pb signal intensities of ~ 2.2 V during LA-MC-ICP-MS analysis. The analytical results of 10th-01 are shown in Fig. 7a. Most of measurements fell within the $\pm 2\text{SD}$ range. The external reproducibilities (RSD, $k = 2$) were 0.06%, 0.05% and 0.05% for $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$, respectively. Fig. 7b shows *in situ* Pb isotope analytical results of 11th-01. The external reproducibilities of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ were 0.17%, 0.16% and 0.15%, respectively. Compared with 10th-01, the poor reproducibility of $^{208}\text{Pb}/^{204}\text{Pb}$ in 11th-01 was attributed to the lower mass fraction of Pb (72.2 $\mu\text{g g}^{-1}$), which resulted in a lower ^{204}Pb signal intensity. LA-MC-ICP-MS analyses of 10th-01 and 11th-01 suggested that they were homogeneous in terms of their Pb isotope compositions at the 120 μm scale.

3.3 Mass fractions of trace elements and S-Pb isotope compositions in synthetic sulfide reference materials

The principle of our synthetic sulfide reference materials is that trace elements during the FeS_2 growth process enter their

lattices in the form of isomorphism. The mass fraction of trace elements in synthetic sulfide reference materials depends on the element partition coefficients between the solution medium and FeS_2 particles. In this study, we added 0.5, 0.2, 0.1 and 0.05 mL of the multielement mixed standard solution to four synthetic sulfide reference materials (10th-01, 11th-01, 11th-02 and 11th-03) at the first step of sample synthesis, respectively. The mass fraction of trace elements in the four synthetic sulfide reference materials were determined by a solution method (Table 2). The results show that the mass fractions of Ru, Rh, Pd, Os, Ir, Pt, Au, Pb and Re appear in a certain proportion in the four synthetic sulfide reference materials. Using the sample 11th-03 (the lowest mass fraction) to normalize, the normalization values of these trace elements in 10th-01, 11th-01 and 11th-02 will decrease in proportion to 8.4 ± 1.1 , 3.5 ± 0.4 and 1.8 ± 0.1 , respectively. This proportional mode is similar to the predicted proportional mode obtained from the amount of added multielement mixed standard solutions (10.0, 4.0, 2.0). However, the mass fraction of each element in one sample is not the same, indicating the different partition coefficients. The lower mass fraction of Zn ($4.5\text{--}5.9 \mu\text{g g}^{-1}$) and In ($0.9\text{--}0.4 \mu\text{g g}^{-1}$) is attributed to the low partition coefficients between the solution medium and FeS_2 particles. The mass fractions of Cu and Ni show an irregular change in the four synthetic sulfide

Table 3 Measured and published mass fractions ($\mu\text{g g}^{-1}$) for two LA-ICP-MS sulfide reference materials

		Ni, $\mu\text{g g}^{-1}$	Cu, $\mu\text{g g}^{-1}$	Ru, $\mu\text{g g}^{-1}$	Rh, $\mu\text{g g}^{-1}$	Pd, $\mu\text{g g}^{-1}$	Re, $\mu\text{g g}^{-1}$	Os, $\mu\text{g g}^{-1}$	Ir, $\mu\text{g g}^{-1}$	Pt, $\mu\text{g g}^{-1}$	Au, $\mu\text{g g}^{-1}$	Pb, $\mu\text{g g}^{-1}$
MASS-1	This study ($n = 10$)	109	121 350	0.01	0.69	0.85	0.00	0.00	63.4	63.7	56.6	76.5
	SD	7	3444	0.01	0.03	0.05	0.00	0.01	1.4	1.3	2.2	1.9
	Wilson <i>et al.</i> (2002)	97 ^a	134 000						42 ^a		47	68 ^a
	SD	15	500									7
	Sylvester (2008) ^b	128	127 264							69	51	
	SD	10	13 331							6	10	
	Sen <i>et al.</i> (2010) ^c	91.5	125 000				0.50	0.03	63.5	61.8	48.4	
	SD	18.8	9000				0.02	0.01	4.6	4.0	2.0	
	Danyushevsky <i>et al.</i> (2011) Solution	94	132 202								54.2	69.1
	193 nm laser ^d	85.4	121 997								61.8	82.1
Yuan <i>et al.</i> (2012) ^e	SD	0.7	793								3.6	0.6
		91	122 400								47.0	76.0
	SD	4.0	3300								5.0	2.0
	Accepted values	247	367				15.2			13.4	17.3	60.0
STDGL3	This study ($n = 10$)	241	341	0.02	0.32	10.6	18.3	0.00	0.01	20.9	22.3	61.8
	SD	5	7	0.01	0.02	0.3	0.8	0.0	0.0	0.7	0.5	0.9
11th-02	This study	19.8	17.8	7.7	8.0	8.0	7.0	27.9	7.2	7.0	7.6	42.1
	SD ($n = 20$)	0.8	0.7	0.2	0.2	0.2	0.2	0.8	0.2	0.2	0.2	1.0
	Solution average	19.2	19.1	7.3 ^f	8.1 ^f	7.6 ^f	6.8	27.3	7.0 ^f	6.8 ^f	7.2 ^f	41.4
	SD ($n = 3$)	0.2	0.3	—	0.0	—	0.1	2.8	—	—	—	0.1

^a Values from the certificate of USGS. The value of Ir is information value. ^b Using NIST 610 as external standard and Fe as internal standard. ^c Using iron meteorite as external standard and Fe as internal standard. ^d Using STDGL2b2 as external standard and Fe as internal standard. ^e Using multiple glass reference materials as external standard and S as internal standard. ^f The values obtained by using dilution method on Element XR.

reference materials, which could be caused by contamination during the sample synthesis process or the impurity in the reagents. Fortunately, the distribution of Cu and Ni is homogeneous in the four synthetic sulfide reference materials (1.7% to 5.8%), which can satisfy the quantitative analysis of natural geological samples.

The S isotope ratios in the four synthetic sulfide reference materials were determined by an Isotope Ratio (IR)-MS. The $\delta^{34}\text{S}_{\text{V-CDT}}$ of the 10th-01, 11th-01, 11th-02 and 11th-03 are 5.3 ± 0.27 ($n = 5$), 5.5 ± 0.18 ($n = 6$), 5.2 ± 0.21 ($n = 6$) and 5.0 ± 0.27 ($n = 6$), respectively; these values are sufficiently homogenous in the individual sample for *in situ* S isotope analysis. However, the average value of $\delta^{34}\text{S}_{\text{V-CDT}}$ in the four synthetic samples is 5.25 ± 0.36 , showing a slightly higher precision compared to Ag_2S reference standards with a typical analytical precision of <0.25 (2SD, IAEA S-1, S-2 and S-3, ESI†). This outcome indicates that synthetic sulfide reference materials in different experimental batches may have slight heterogeneity of the S isotope composition. This heterogeneity could be caused by the heterogeneity of the S isotope composition in the initial sulfur powder.

10th-01 and 11th-01 were selected for the Pb isotope analysis due to their high mass fraction of Pb, that is, $187.8 \mu\text{g g}^{-1}$ and $72.7 \mu\text{g g}^{-1}$, respectively. The values of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ obtained using solution nebulization MC-ICP-MS are 38.149 ± 0.014 , 15.585 ± 0.003 , 18.001 ± 0.011 and 38.146 ± 0.012 , 15.592 ± 0.008 , 17.999 ± 0.008 , respectively. The consistent Pb isotope composition between 10th-01 and 11th-01 demonstrated no Pb isotope fractionation during the FeS_2 growth process and in different experimental batches.

The raw data described above for the element mass fractions and S-Pb isotope compositions in synthetic sulfide reference materials are provided in Table S3 (ESI†).

3.4 *In situ* analysis of PGEs and Au

To verify the availability of the synthetic sulfide reference materials, two sulfide reference materials, MASS-1 and STDGL3#35, were selected as unknown samples. Eleven trace elements, Ni, Cu, Ru, Rh, Pd, Re, Os, Ir, Pt, Au and Pb, were determined by LA-ICP-MS. Four synthetic sulfide reference materials, 10th-01, 11th-01, 11th-02 and 11th-03, were simultaneously measured as external standards. Fe was used as the internal standard element. The analysis strategy was to insert four synthetic sulfide reference materials before and after every 10 analysis points, of which 10th-01 was used to calibrate the signal drift of the instrument. Fig. 8 shows the fitting curves of Rh, Os, Au and Pb obtained from the ratios of the signal intensity (Fe normalized) and the ratios of the mass fraction (Fe normalized). These fitted curves show good values of the correlation coefficient (R^2), such as 0.9996, 0.9997, 0.9987 and 0.9997 for Rh, Os, Au and Pb, respectively, and can be used to quantify the unknown samples. Fitted curves of other elements were also obtained with similar correlation coefficients (Fig. S2, ESI†). The analytical results of MASS-1 and the reference values are listed in Table 3. Although MASS-1 has been produced for many years, only a few studies have reported the mass fraction of trace elements.^{13,22,48–50} The mass fraction of trace elements collected in the five studies showed a large difference (Table 3). The average values of mass fraction of Ni, Cu, Au and Pb in the five studies are 100 ± 28 , 128 ± 173 , 49.5 ± 5.5 and $71.0 \pm$

7.1, respectively, which are consistent with the measured values in this study within the uncertainty, such as 109 ± 7 , $121 \pm 350 \pm 3444$, 56.6 ± 2.2 and 76.5 ± 1.9 . The mass fractions of Ru, Rh and Pd in MASS-1 are low and lack reference values. The mass fractions of Re and Os were reported but very low (0.50 ± 0.02 and 0.03 ± 0.01 , respectively).⁵⁰ Ir and Pt have higher mass fractions and were reported by two studies. The measured mass fraction of Pt in this study is $63.7 \pm 1.3 \mu\text{g g}^{-1}$, which is consistent with the reported values of $69.0 \pm 6.0 \mu\text{g g}^{-1}$ and $61.8 \pm 4.0 \mu\text{g g}^{-1}$. The measured mass fraction of Ir is $63.4 \pm 1.4 \mu\text{g g}^{-1}$, which is consistent with the reported values of $63.5 \pm 4.6 \mu\text{g g}^{-1}$ from Sen *et al.*⁵⁰ but higher than the reported values of $42 \mu\text{g g}^{-1}$ from Wilson *et al.*²²

The analysis results of STDGL3#35 in this study shows that the measured mass fractions of Ni, Cu and Pb are consistent with the reference values. However, the measured mass fractions of Re, Pt and Au are higher than the reference values at approximately 20%, 56% and 29%, respectively. We cannot explain the reason for these deviations due to the few reported data of STDGL3#35. However, we can be sure that these deviations are not caused by the matrix effect because of the good analytical results of Ni, Cu and Pb in STDGL3#35.

In addition, 11th-02 was used as unknown sample and analyzed. 10th-01, 11th-01 and 11th-03 were measured as external standards. The measured mass fractions of Ni, Cu, Ru, Rh, Pd, Re, Os, Ir, Pt, Au and Pb are consistent with the values obtained using solution nebulization ICP-MS.

The raw data of the measured mass fractions for MASS-1, STDGL3#35 and 11th-02 are shown in Table S4 (ESI†).

4. Conclusions

In this study, four iron sulfide reference materials were synthesized by hydrothermal synthesis for *in situ* PGEs and S–Pb isotope compositions analyses. A new approach of sample synthesis was proposed in which elements enter synthetic sulfide lattice in the form of isomorphism during the crystal growth process. The synthetic nanosulfide powders have a typical grain size of 500–600 nm, allowing us to produce pressed powder pellets that have excellent cohesion suitable for laser ablation microanalysis without the addition of a binder. The analytical results obtained from LA-(MC)-ICP-MS showed the homogenous distributions of PGEs, Au and Pb (<3%) at spot sizes of 60 μm , S isotope compositions (0.11–0.23‰) at spot sizes of 90 μm and Pb isotope compositions (<0.06‰ for 10th-1 and <0.17‰ for 11th-1) at spot sizes of 120 μm . External calibration curves from four synthetic sulfide reference materials were used to quantify MASS-1 and STDGL3#35. The measured results of Ni, Cu, Ir, Pt, Au, and Pb in MASS-1 were consistent with the reference values within analytical uncertainty.

At present, the hydrothermal synthesis of different nanoparticle materials has been widely reported. The information reported in this study mainly suggests that hydrothermal synthesis can produce reference materials for *in situ* elements and isotope compositions analyses. It is noteworthy that when undertaking the hydrothermal synthesis of multielement reference materials, one should carefully understand the

partition coefficients of the elements in different materials, or combine this method with conventional multielement standard solution addition methods, such as mixing and mechanical milling.

Conflicts of interest

There are no conflicts to declare.

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