



A simple method for the preparation of homogeneous and stable solid powder standards: Application to sulfide analysis by LA-ICP-MS

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ABSTRACT

A simple method for immobilizing powder samples was proposed to prepare calibration standards for the analyses of bulk elemental compositions of solid samples by LA-ICP-MS. Upon mixing with epoxy resin, the multielement doped powder was transformed into a stable and mechanically resistant target. Using this method, a sulfide standard, RPSS (resin preserved silver sulfide), was developed that contains 47 different elements, including PGE, chalcophile elements, siderophile elements, lithophile elements, and REE. The homogeneity of most elements in the original sulfide powder pressed pellet and RPSS was better than 10% (RSD, one sigma) at a microscale of larger than 24 μm . The mass fractions of most elements in the RPSS determined by LA-ICP-MS analyses, calibrated against the pressed pellet, agreed well with that of solution ICP-MS analyses. This result indicates no significant matrix effect between the RPSS target and the original powder pellet. The proposed method is convenient for quickly preparing homogenous and stable solid powder standards for LA-ICP-MS analysis. It is particularly suitable for the development of sulfide standards because it prevents them from oxidation when exposed to air; thus, the target can be preserved for long periods of time.

1. Introduction

Measurements of the bulk elemental compositions and spatial distributions of trace elements in sulfides are very hot topic in analytical geochemistry [1–6]. Elements in sulfides are not only economically valuable but also play an important role in geology and environmental geochemistry research [7–13]. For example, elements in magmatic or hydrothermal sulfides serve as sensitive geochemical tracers, which have been widely used to decipher magma genesis in the upper mantle and mantle evolution [14], to understand the magmatic-hydrothermal process in ore-genesis studies [2,6,11,13], and to indicate the thermodynamic conditions of mineral deposits in geological research [8,10].

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful tool for the in situ analysis of elements in sulfides with contextual information [5,11]. However, this useful technique is hampered by a lack of appropriate and well-characterized standard reference materials for the analysis of sulfides. These urgently desired sulfide reference materials should have good homogeneity on the microscale and be abundant in element types, matrix-matched with

natural samples, and suitable for long-period stable preservation. At present, there are three major methods for the preparation of sulfide reference materials: (1) synthesized minerals or compounds [15], (2) vitrified materials [16,17,18,19], and (3) pressed powder pellets [17]. Several sulfide standards have been developed by different geochemical laboratories for LA-ICP-MS analyses. For example, a cold-pressed pellet sulfide standard, MASS-1, was synthesized by precipitating a sulfate solution with an aqueous metal species [15]. A glass disk sulfide standard, STDGL2b2, was produced by fusing sulfides into a lithium borate glass [16]. Three pellets of noble metal sulfide standards, (Fe, Ni)_{1-x}S, etc., were synthesized by sintering Fe, Ni, and Cu metal powders and elemental sulfur under high pressure and temperature [20]. Among these major protocols for the preparation of reference materials, synthesized minerals or compounds require specific preparation conditions and cumbersome processes [15,19]. Materials vitrified by fusion tend to lose volatile elements [16,21], result in heterogeneous element distributions from phase separations, or be contaminated by fluxing agents [22,23]. Pressed powder pellets are a better choice because of their simplicity and convenience.

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As a widely used procedure for sample preparation, pressed powder pellets also have some defects, such as the use of binders [24–27] for their immobilization, which may introduce contamination from binding agents, and not using binders may result in a loss of the target stability with time after pressure relaxation. For example, a powdered soil sample was solidified as an immobilized target by mixing it with zinc oxide and 2-methoxy-4 (2-propynyl) phenol [28]. Recently, epoxy resin was employed to prepare stable targets for powder samples [29–31]. The silicate powder sample (500 mg) was shaped into a stable target by mixing it with a glue solution of methyl methacrylate resin (1 ml) with continuous stirring [32]. The introduction of a large amount of resin inevitably dilutes the sample powder, which is not conducive to the determination of the low-content elements. The remarkable difference in physicochemical properties between the powder sample and the resin makes its uniform distribution in the pellet very difficult. To overcome these problems, the sediment powder is formed as a cohesive target by impregnating it with spur low-viscosity epoxy resin [29,31].

The preparation method of the powder sample involving the use of resin has not yet been applied to sulfide powder. Most importantly, this method can effectively prevent the sulfide powder from oxidation when exposed to air, especially ultrafine particles, which are usually less than several microns in size, that are recognized as essential to produce representative and homogeneous sample aliquots [33–36]. However, due to the malleability of the sulfides, the pressed sulfide powder pellets are very tightly packed, and cannot be impregnated with low-viscosity epoxy resin.

In this study, a simple and novel method was proposed to prepare sulfide powder standards for LA-ICP-MS analyses. Upon mixing with epoxy resin, the multielement doped powder was transformed into a stable target. This ready-to-use target can be polished multiple times to ensure fresh sampling surfaces over long periods of time without suffering from oxidation or damage. Using this method, a sulfide standard, RPSS (resin preserved silver sulfide), containing 47 different elements, including PGE, chalcophile elements, siderophile elements, lithophile elements, and REE, was developed. The homogeneity and bulk elemental composition of the RPSS were tested by LA-ICP-MS and solution ICP-MS analyses, respectively. This standard RPSS can be used not only for the simultaneous analysis of multielements in natural sulfide but also for studies of elemental fractionation behaviors among different matrixes such as sulfide, silicate, and oxide during LA-ICP-MS analysis.

2. Material and methods

2.1. Sample preparation

A simple and fast method was developed to prepare the sulfide standard RPSS for LA-ICP-MS analysis (see Fig. 1). First, a multielement solution was prepared by mixing 3000 µg of Fe, Cu, Zn, and Pb with 1000 µg of other single element solution standards: PGE, Au, Ti, V, Cr, Mn, Co, Ni, Ga, Ge, As, Se, Y, Mo, Cd, In, Sn, Sb, Te, Re, Tl, Bi and REE (1000 µg/ml, produced by Central Iron & Steel Research Institute, China, commercially available); then, it was dried on a hot plate at 100 °C and diluted with 1 ml HNO₃ (2% in v/v). Second, the prepared multielement solution was doped into an aliquot of silver sulfide standard (6 g, powder, GBW04415, produced by the Institute of Mineral Resources, Chinese Academy of Geological Sciences). This multielement doped powder was then ground for 4 h with a grinding mill (Retsch MM400, Germany) to improve its homogeneity. Then, one aliquot of the multielement doped powder was directly pressed into a pellet for a contrast study (Fig. 1a). Another aliquot was fused to a pellet in a hermetic vessel heater at 1200 °C for 1.5 min following the procedure of Zhu et al. [17] (Fig. 1b). A third aliquot (0.5 g) was mixed with epoxy resin (1 ml, EpoThin™ 20-3440-032, Buehler, America) in a 5 ml round-bottomed plastic centrifuge tube. Before solidification, the powder-resin mixture was centrifuged for 10 min at 4000 rpm in a centrifuge (Xiangyi

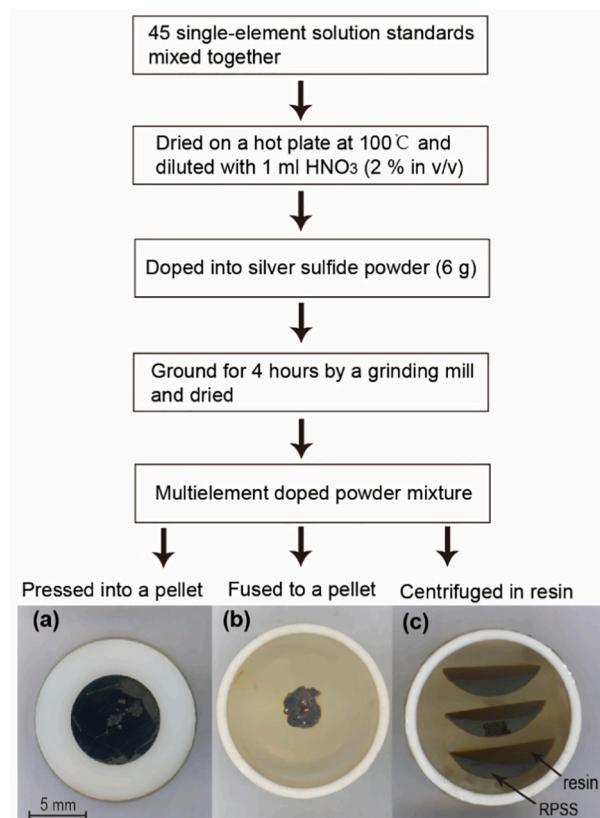


Fig. 1. Schematic diagram of sample preparation procedures and images of prepared samples in this study. (a) pressed pellet, (b) fused pellet, and (c) RPSS.

TDZ-5-WS, China). The powder was quickly deposited on the bottom of the centrifuge tube during centrifugation. Part of this prepared sulfide standard, referred to as resin preserved silver sulfide (RPSS), was cut and polished for solution ICP-MS and LA-ICP-MS analyses (Fig. 1c). Five batches of RPSS and three aliquots of powder pressed pellets were digested in HNO₃ by the traditional bomb method for solution ICP-MS analysis. The sample decomposition procedure was as follows: (1) Ten milligrams of sample was placed in an in-house PTFE-lined stainless-steel bomb [37], to which 2 ml of HNO₃ was added. (2) The sealed bomb was heated to 100 °C in an electric oven for 24 h. (3) After cooling, the bomb was opened and evaporated to dryness at 80 °C on a hotplate. (4) The residue was transferred to a polyethylene bottle and diluted to 20 g by the addition of 2% (v/v) HNO₃. A reagent blank solution was simultaneously prepared in the same way.

2.2. Instrumentation

The morphology of the fused pellets and RPSS was studied using scanning electron microscope (SEM) images at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (GPMR, CUG), Wuhan, China. The images were collected by a Zeiss Sigma 300 FESEM under the following analytical conditions: Magnification = 355–7380 X, working distance (WD) = 7.8–19 mm, and electronic high tension (EHT) = 10, 15 kV.

The bulk elemental compositions of the pressed pellet and RPSS were measured by an ICP-MS instrument (Agilent 7700, a quadrupole spectrometer with a single detector, Agilent Technologies, Tokyo, Japan) at GPMR, CUG. The solution was introduced into the spectrometer by a MicroFlow nebulizer (0.10 ml/min, PFA) and a double-path spray chamber. The instrument was tuned to obtain good signal intensities for Li, Y, Ce, and Tl while keeping the CeO⁺/Ce⁺ and Ce²⁺/Ce⁺ ratios below 1.2%. Instrument drift correction was performed by using indium as an

internal standard. The mass fraction of indium was independently measured beforehand by using the standard addition method since it was contained in the sample. The detailed instrument parameters are given in Table 1.

The homogeneities of the pressed pellet, fused pellet and five batches of RPSS were tested at GPMR, CUG, with an LA-ICP-MS instrument, which consists of an excimer 193 nm laser ablation system (Geolas 2005, MicroLas, Göttingen, Germany) and an Agilent 7500a ICP-MS (a quadrupole spectrometer with a single detector, Agilent Technologies, Japan). The instrument was optimized for maximum sensitivity for Ag⁺ while keeping the ThO⁺/Th⁺ ratio below 0.5% and the U⁺/Th⁺ ratio close to 1 using NIST SRM 610. All measurements were carried out using time-resolved analysis in fast, peak jumping mode. Each spot analysis consisted of 25 s of background and 40 s of sample acquisition. Helium was used as the carrier gas and argon as the make-up gas. NIST SRM 610 and the pressed pellet were used as external standards for calibration, usually bracketing five samples in a run. Silver was used as an internal standard for drift correction and ablation yield normalization. LA-ICP-MS data reduction was performed using custom software (ICPMSData-Cal) [38]. More details on the instrument parameters are given in Table 1.

3. Results & discussion

3.1. Sulfide powder pellets prepared by press

The grinding method has been commonly adopted for the preparation of single- or multielement doped powder standards [33–35,39]. Fig. 2 shows the effect of grinding time on the analytical precision of LA-ICP-MS of the pressed pellet. The analytical precision was expressed as the relative standard deviation (RSD, one sigma) of all ¹⁰⁷Ag-normalized ablation spectra. The results show that the obtained relative standard deviation (RSD, one sigma) was within 15–25% for most of the investigated elements after 30 min of grinding. This does not meet the requirement of our practical analysis. In contrast, the obtained relative standard deviation (RSD, one sigma) was decreased to less than 10% for

Table 1

Analytical parameters for solution nebulization and laser ablation ICP-MS in this study.

Laser ablation system parameters		
Laser type	193 nm ArF excimer laser/COMPexPro	
Laser pulse width	15 ns	
Fluence	7 J/cm ²	
Spot size	24, 32, 44, 60 μm	
Laser frequency	8 Hz	
Number of shots	400 per analysis	
Blank acquisition time	25 s	
ICP-MS operation parameters		
Sample introduction mode	Laser ablation	Solution nebulization
ICP-MS instrument	Agilent 7500a	Agilent 7700
Forward power (W)	1350	1350
Plasma gas flow (l/min)	16	15
Auxiliary gas flow (l/min)	1	1
Carrier gas flow (l/min)	He: 0.7	
Nebulizer gas (l/min)	Ar: 0.7	
Makeup gas flow (l/min)	Ar: 0.6	
Spray chamber	Scott double-pass type (2 °C)	
Sample uptake rate (ml/min)	0.15	
Dwell time per isotope (ms)	60	
Detector mode	Dual	Dual
Isotopes	³⁴ S, ⁴⁷ Ti, ⁵¹ V, ⁵³ Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶⁵ Cu, ⁶⁶ Zn, ⁶⁹ Ga, ⁷³ Ge, ⁷⁵ As, ⁷⁸ Se, ⁸⁹ Y, ⁹⁵ Mo, ¹⁰¹ Ru, ¹⁰³ Rh, ¹⁰⁵ Pd, ¹⁰⁷ Ag, ¹¹¹ Cd, ¹¹⁵ In, ¹¹⁸ Sn, ¹²¹ Sb, ¹²⁶ Te, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴¹ Pr, ¹⁴⁶ Nd, ¹⁵² Sm, ¹⁵³ Eu, ¹⁵⁷ Gd, ¹⁵⁹ Tb, ¹⁶³ Dy, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹ Tm, ¹⁷² Yb, ¹⁷⁵ Lu, ¹⁸⁵ Re, ¹⁸⁹ Os, ¹⁹³ Ir, ¹⁹⁵ Pt, ¹⁹⁷ Au, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi	

most of these elements after 240 min of grinding. This level of analytical precision is acceptable for LA-ICP-MS analysis. The result demonstrates that a sufficient grinding time is important for improving the homogeneity of elements in the sulfide powder. It is generally believed that the increased grinding time reduces the average size of the powder particles, which subsequently increases the homogeneity of the pressed pellet. However, this was not the case for this study. Compared to that of the original powder, the size of the ground sulfide powder particles after doping with a multiple-element standard significantly increased (see Fig. 3). This can be attributed to the good malleability of sulfides, which causes many small sulfide powder particles to merge into larger particles during grinding. Therefore, the improved analytical precision with an extended grinding time is due to the improved homogeneity distribution of elements in sulfide particles, which is not related to a change in the particle size.

Fig. 4a shows typical time-resolved signals of S, V, Fe, Co, Cu, Zn, Ru, Rh, Pd, Ag, In, Eu, Os, Ir, Pt, Au, and Pb during line scanning analysis of the pressed pellet. The line scanning ablation mode was used with a spot size of 32 μm, a line scanning speed of 16 μm/s, and a repetition rate of 8 Hz at a laser fluence of 7 J/cm². The excellent smooth and stable signals of S, V, Fe, Co, Cu, Zn, Ru, Rh, Pd, Ag, In, Eu, Os, Ir, Pt, Au, and Pb further suggest the homogeneous distribution of elements in the pressed pellet. Fig. 5a shows the analytical precision of the spot ablation analyses of the pressed pellet. The analytical precision is presented as a percentage as the relative standard deviation (RSD, one sigma) of all ¹⁰⁷Ag-normalized ablation spectra, which can numerically represent the homogeneity of each element based on the assumption that Ag is homogeneously distributed. The RSD values for most elements in the pressed pellet were below 10% at a spot size larger than 24 μm, a relatively small spot size for in situ LA-ICP-MS analysis. The results of the spot ablation analyses show that the pressed pellet is homogeneous under the high spatial resolution of the microscale. These results suggest that the obtained sulfide pressed powder pellets in this study are suitable for use as external standards for LA-ICP-MS analysis. The main problem with the sulfide pressed powder pellets is that they are easily damaged from oxidation and hydrolyze in air. Therefore, they can be used for only a short period and have to be kept in a special container.

3.2. Sulfide pellets prepared by powder fusion

Fig. 6a shows the SEM images of the sulfide pellets prepared by powder fusion. It can be seen from the image that there are some small silvery white nuggets in the sample. This phenomenon indicates that the sulfide powder had phase separation and formed nuggets during fusion. Fig. 5b shows the analytical precision of the spot ablation analyses of the fused pellet. Except for S, Mn, Co, Ni, Se, Pd, Cd, Te, Sm, Pt, Au, and Pb, the RSDs for the elements are higher than 20%, indicating their poor homogeneity. Therefore, sulfide pellet preparation by fusion results in heterogeneous distribution of some elements, which cannot meet the requirements for microanalysis of multi-elements.

3.3. Powder pellets prepared by centrifugation in resin

Fig. 6 (b and c) shows the SEM images of the sample surface and ablation crater in the RPSS. The surface of the RPSS shows clear smoothness and cohesion features. The ablation crater presents a round, regularly shaped wall and flat bottom without fractures around it. As seen in Fig. 6d, there are many melted ejecta (e.g., large droplets) around the laser crater. The observed large droplets are formed by molten material ejection, as a result of hydrodynamic sputtering. This observed melting phenomenon suggests that thermal processes are the dominant mechanisms of RPSS ablation in ns-LA. The morphology of the RPSS shows that the original powder was transformed into a uniform target. Since the target contains a certain amount of epoxy resin as the binder, it should retain the strength and stability of the resin to a certain extent [29–31]. In LA-ICP-MS, this kind of epoxy resin has been widely

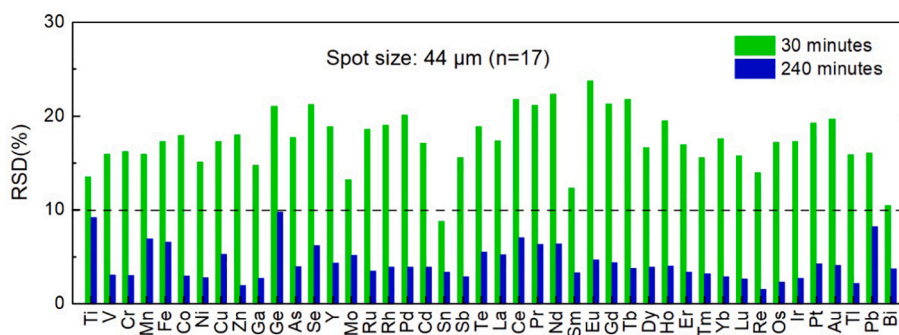


Fig. 2. Effect of grinding time on the analytical precision of LA-ICP-MS in the pressed pellets; analytical precision was expressed as the relative standard deviation (RSD, one sigma) of all ^{107}Ag -normalized ablation spectra.

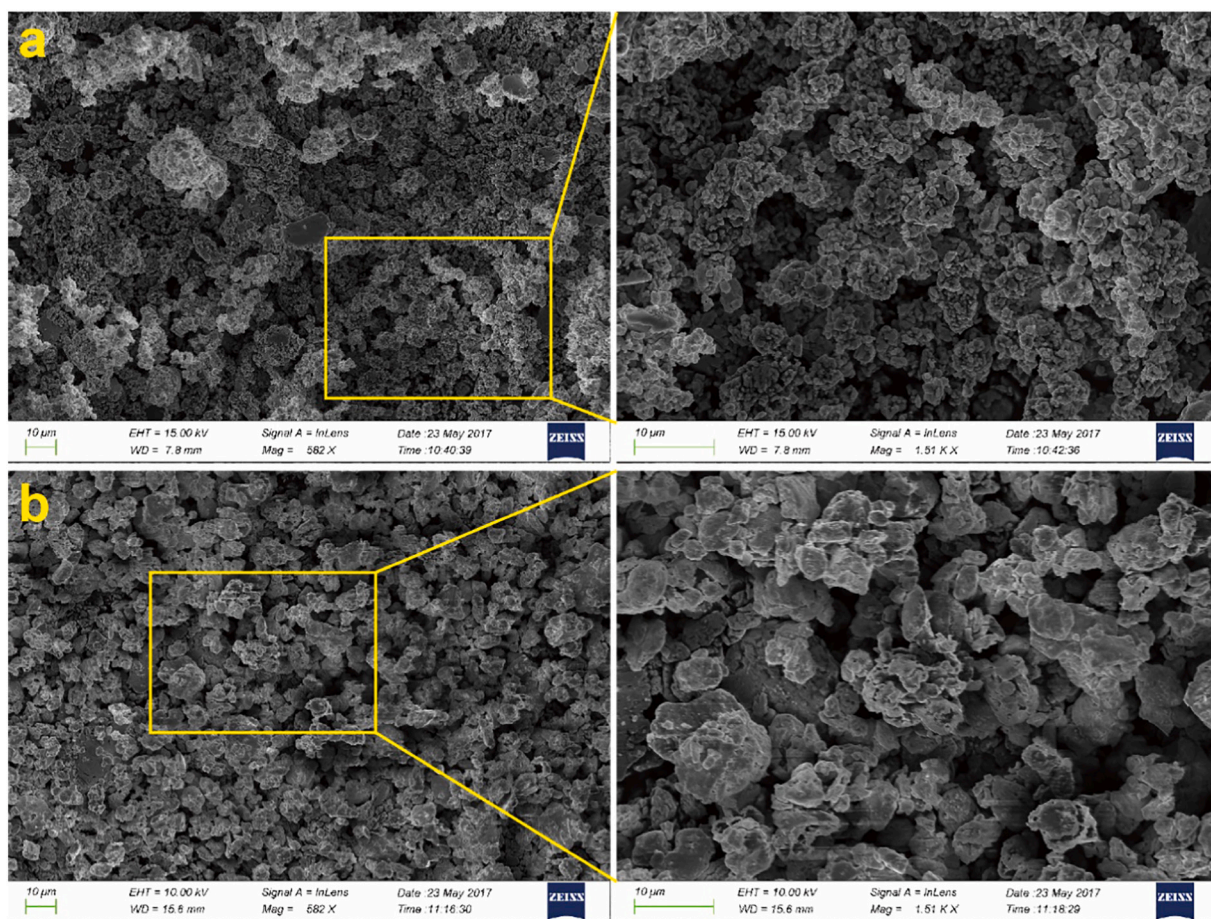


Fig. 3. (a) SEM images of the original powder GBW04415 and (b) the powder doped with multielement after grinding for 4 h.

used in the preparation of accessory mineral sample targets. The resin-preserved silver sulfide shows a good strength and mechanical resistance. For example, we found that it was difficult to cut it into pieces with a small steel blade. In the process of cutting, the target did not break into pieces. Therefore, we believe that this target is homogenous and mechanically resistant for microsampling-based solid sample analysis techniques, such as LA-ICP-MS. This target can be polished to expose new sample material for repeat use, which is not always possible for pressed powder pellets because they may suffer from damage from pressure relaxation or composition change due to oxidation in the air (see Fig. S1). Therefore, the stability of the RPSS over time is much better than that of the pressed pellet. The proposed resin preservation method is very simple and convenient for the consolidation and long-

term preservation of powder samples and is also suitable for the preparation of other powder samples, such as various accessory minerals and oxides.

The homogeneity of the elements in the RPSS was tested by line scanning and spot ablation LA-ICP-MS analyses. Fig. 4b shows typical time-resolved signals of some elements during the line scanning analysis of the RPSS (with resin blank). For the resin blank, nearly all the elements show no significant signal intensities increase as compared with the gas blank, which indicates that the contamination contribution from the resin to the powder is insignificant and negligible. The time-resolved signals of most elements in the RPSS remained smooth during scanning ablation, showing their homogeneous distributions. Fig. 5c shows the analytical precision of the spot ablation analyses of the RPSS. The RSD

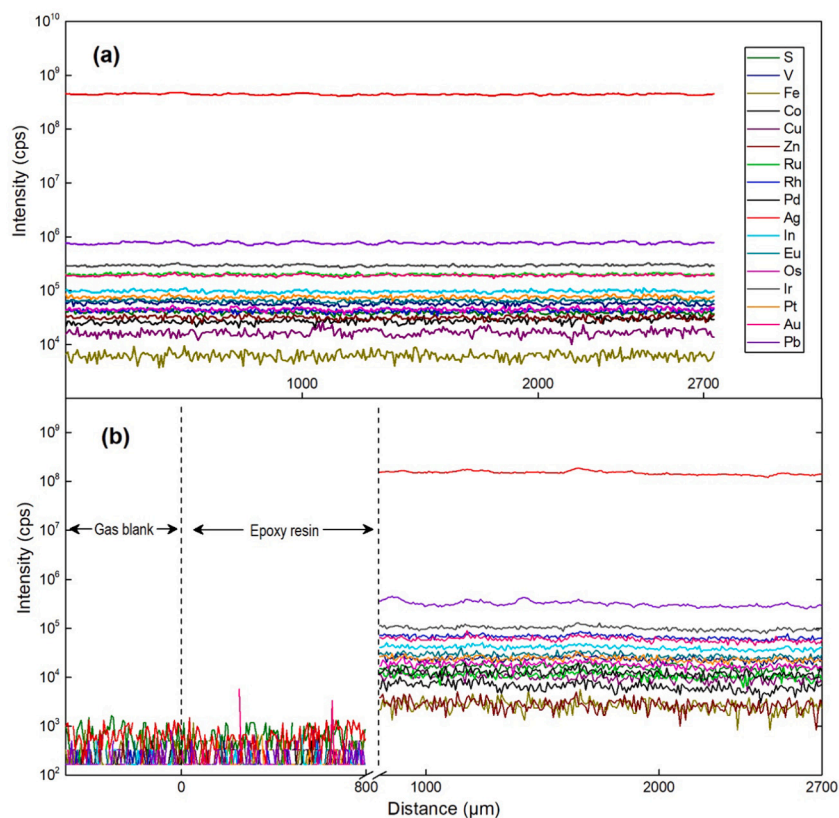


Fig. 4. Typical time-resolved signals of S, V, Fe, Co, Cu, Zn, Ru, Rh, Pd, Ag, In, Eu, Os, Ir, Pt, Au, and Pb during the line scanning LA-ICP-MS analyses of (a) the pressed pellet and (b) the RPSS with gas and resin blank.

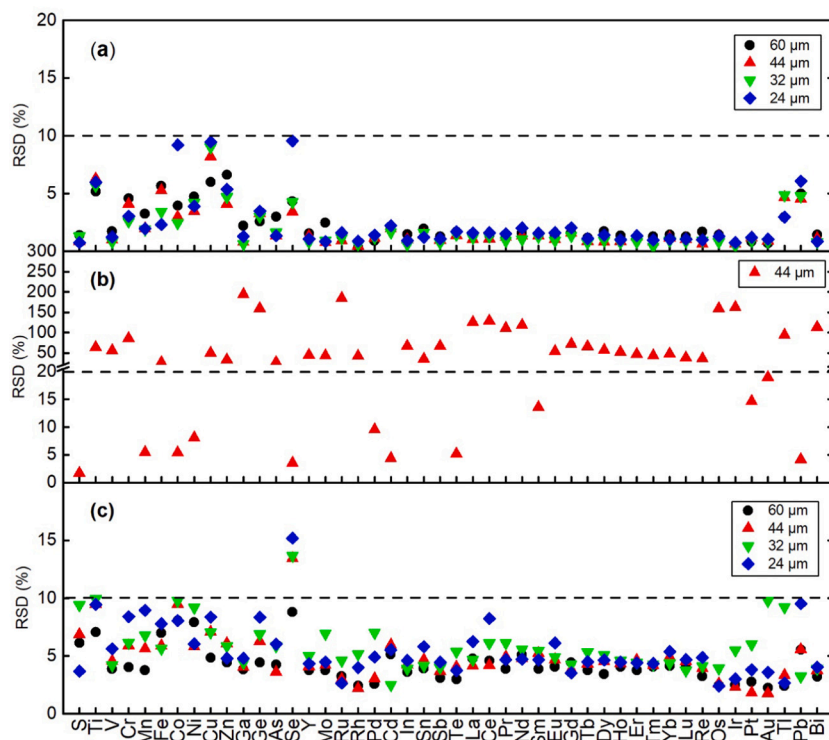


Fig. 5. Analytical precision of the spot ablation analyses of the (a) pressed pellet, (b) fused pellet, and (c) RPSS, which are presented as the relative standard deviation (RSD, one sigma) of all ^{107}Ag -normalized ablation spectra.

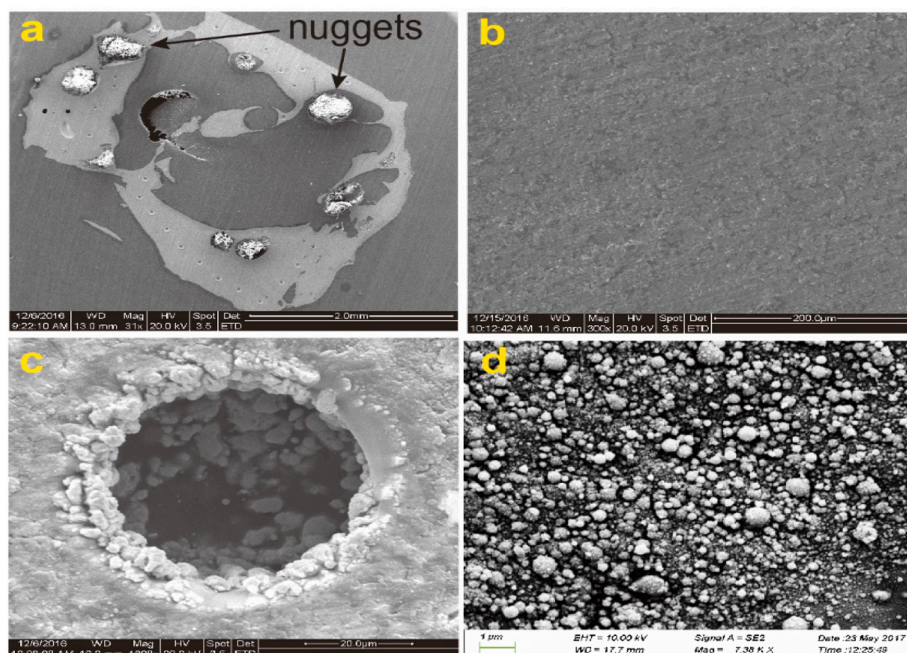


Fig. 6. SEM images of (a) the fused pellet and the (b) surface, (c) ablation crater, and (d) melted ejecta of the RPSS.

values for most elements in the RPSS are below 10% at a spot size larger than 24 μm , which shows that the RPSS is homogeneous under the high spatial resolution. It can be seen from Fig. 5 that the homogeneity of the fused pellet is very poor, while the homogeneity of the pressed pellet and RPSS is much better. However, it should be noted that the homogeneity of the RPSS is slightly worse than that of the pressed pellet. There are a few possible reasons for this. One is that centrifugation may cause settling of the denser particles to the bottom and leaving less dense particles near the top of the pellet (see Fig. S2), which could slightly reduce the vertical homogeneity of the pellet at a certain extent. The second is that the sample was diluted by resin, resulting in a lower mass fraction of elements. Therefore, the analytical sensitivity of the RPSS was lower under the same analytical conditions. For example, the average signal intensity of Ag in the powder pellet was $\sim 4.4 \times 10^8$ cps, while that in the RPSS was $\sim 1.5 \times 10^8$ cps. The third is that the resin in RPSS may cause matrix effects due to the changes of sample ablation efficiency, particle transport efficiency and aerosol ionization properties in ICP torch. Although the homogeneity of the powder sample becomes slightly degraded due to the addition of the resin, the homogeneity of the resin preserved sample (RPSS) is still very good (RSD below 10% under the high spatial resolution at the microscale) and can fully meet the requirements for microanalysis. In conclusion, the poor homogeneity of the fused pellet cannot meet the requirements of microanalysis, while the pressed pellet has good homogeneity but it cannot be reused for a long time. Only the resin preservation method can not only maintain the homogeneity of the original powder but also make the sample stable enough to be reused for a long time, which is an ideal method for the preparation of sulfide powder. After resin preservation, a cohesive, mechanically resistant, and homogenous target was readily obtained, which can be used as an ideal test target or calibration standard for microsampling-based analyses, such as LA-ICP-MS.

3.4. Bulk elemental composition of the RPSS

The mass fraction of each element in the RPSS and pressed pellet analyzed by solution ICP-MS are given in Table 2. As the mass fraction of S could not be accurately measured by ICP-MS after sample digestion by mineral acid, it was not reported in both samples. The mass fraction of Os in the pressed pellet and Rh, Pd, Os, Ir, Pt, and Au in the RPSS were

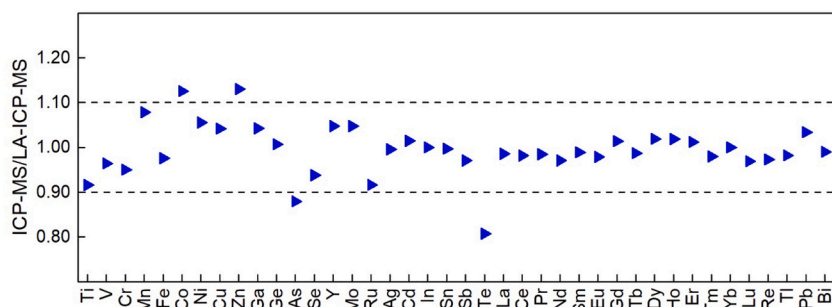
absent due to the lack of appropriate measurements (marked with “-”). The sample was silver sulfide, hydrochloric acid was not used in the digestion process to prevent the formation of a large amount of silver chloride precipitation in the solution. Thus, this digestion method without hydrochloric acid may not dissolve and stabilize some PGEs in solution, in particular Os, Pt, and Au, so the mass fractions of these elements cannot be accurately determined. The mass fraction of most elements in the RPSS measured by LA-ICP-MS analyses are within 10% of that of the solution ICP-MS analyses (Fig. 7). By statistical analysis of linear regression fitting between the results of LA-ICP-MS and ICP-MS (Fig. S3), it is evident that they have a good correlation with a goodness of fit R^2 of 0.9955, which shows that they can be accurately matched. Thus, the mass fractions of elements in RPSS from LA-ICP-MS measurements calibrated against the pressed pellet are accurate. In addition, as shown in Table 2, the mass fractions of elements in RPSS are about 75% of those in the powder pellet. This systematic bias might be caused by the presence of the resin in RPSS, which diluted the sample. The presence of resin may cause some matrix effect during LA-ICP-MS analysis, which cannot be corrected by internal standard normalization. For example, the obtained accuracy of Co, Zn, As, and Te was worse than 10%. In contrast, the accuracy for most of the other elements were better than 5%. Therefore, the proposed method for the preservation of powder samples with resin still keep the matrix of the prepared target matched to the original powder. The sulfide standard RPSS that we developed can be used as a potential calibration standard for the analysis of solid sulfide samples by LA-ICP-MS. When RPSS is used as a single point calibration standard, the analytical precision and accuracy can be evaluated by the data listed in Table 2. Because of the lack of appropriate measurements from solution ICP-MS, the mass fractions of Rh, Pd, Ir, Pt, and Au in the RPSS from the LA-ICP-MS analyses cannot be verified by comparison with that of the solution ICP-MS analyses. During the analysis of RPSS by LA-ICP-MS, the pressed pellet was used as an external standard for calibration. Different signal intensities of elements in pressed pellet and RPSS were obtained by changing the ablation spot size (32 μm , 44 μm and 60 μm). Through linear regression fitting, it was found that the signal intensities of PGE and Au had a good correlation with that of the internal standard indium (Fig. 8). The slope of the fitting line representing the elemental relative sensitivity (relative to the internal standard In) was consistent in powder pellet and RPSS, indicating

Table 2

Mass fractions of the pressed pellet and RPSS by solution ICP-MS analyses.

Element	Pressed pellet		RPSS				
	ICP-MS (n = 3)		ICP-MS (n = 5)		LA-ICP-MS (n = 260)		
	Mass fraction (µg/g)	RSD (%)	Mass fraction (µg/g)	RSD (%)	Mass fraction (µg/g)	Precision (1 s, %)	Accuracy (1 s, %)
Ti	113	1.73	80.6	2.89	88.0	11.1	9.18
V	89.6	1.51	67.0	3.38	69.5	6.84	3.73
Cr	148	1.77	115	5.64	121	5.44	5.22
Mn	55.1	2.01	41.4	1.85	38.4	3.84	7.25
Fe	453	10.3	360	8.94	369	8.44	2.50
Co	34.7	1.74	26.0	1.54	23.1	6.99	11.2
Ni	54.1	1.90	43.7	2.59	41.4	9.15	5.26
Cu	168	3.32	125	8.43	120	7.75	4.00
Zn	133	8.81	94.6	4.56	83.7	7.65	11.4
Ga	38.4	2.49	29.6	1.43	28.4	2.69	4.05
Ge	9.98	11.8	7.38	2.75	7.33	9.79	0.68
As	65.1	6.98	47.4	2.08	53.9	6.04	13.7
Se	95.6	8.31	67.5	3.22	72.0	12.5	6.67
Y	45.5	1.39	35.5	1.59	33.9	4.24	4.51
Mo	114	3.36	74.9	2.54	71.5	5.38	4.54
Ru	99.3	6.94	63.5	2.81	69.3	6.90	9.13
Rh	107	6.73	–	–	78.0	4.78	–
Pd	109	1.63	–	–	79.8	7.44	–
Ag	758,285	6.52	617,460	2.21	620,202	8.17	0.44
Cd	97.5	5.35	55.4	2.58	54.6	10.1	1.44
In	52.1	1.67	39.5	1.99	39.5	–	–
Sn	55.5	1.59	35.8	1.48	35.9	3.67	0.28
Sb	91.6	3.06	66.0	10.3	68.0	3.78	3.03
Te	90.6	5.20	65.8	2.68	81.5	6.67	23.9
La	36.1	1.59	27.3	1.29	27.7	4.15	1.47
Ce	35.0	1.60	26.3	1.25	26.8	4.10	1.90
Pr	34.4	1.82	25.9	1.25	26.3	4.26	1.54
Nd	35.2	1.60	26.4	1.29	27.2	5.19	3.03
Sm	35.1	1.62	26.5	1.22	26.8	4.85	1.13
Eu	35.7	1.61	27.2	1.27	27.8	3.83	2.21
Gd	37.6	2.00	29.2	1.38	28.8	4.00	1.37
Tb	40.1	1.59	30.2	1.37	30.6	3.33	1.32
Dy	41.6	1.63	32.3	1.49	31.7	3.90	1.86
Ho	43.2	1.67	33.4	1.50	32.8	3.23	1.80
Er	44.6	1.67	34.2	1.62	33.8	3.66	1.17
Tm	45.4	1.74	33.8	1.57	34.5	3.26	2.07
Yb	46.1	1.44	35.1	1.61	35.1	3.36	0.00
Lu	47.0	1.64	34.5	1.57	35.6	2.94	3.19
Re	38.4	4.76	28.9	1.13	29.7	4.10	2.77
Ir	105	6.45	–	–	74.8	3.82	–
Pt	101	6.59	–	–	68.2	6.12	–
Au	100	4.38	–	–	93.7	6.04	–
Tl	57.9	2.41	43.6	2.05	44.4	3.71	1.83
Pb	415	3.12	307	13.1	297	10.3	3.26
Bi	95.5	2.58	70.4	2.85	71.1	2.80	0.99

Mass fractions of Rh, Pd, Ir, Pt, Au in the RPSS were absent due to a lack of appropriate measurements (presented with “–”).

**Fig. 7.** Comparison of the bulk elemental compositions of the RPSS between LA-ICP-MS and solution ICP-MS analyses.

that the matrix effect between RPSS and pressed pellet for the determination of Rh, Pd, Ir, Pt, and Au can be corrected by using In as an internal standard. Therefore, the mass fractions of these elements in RPSS could be calibrated by using the powder pellet as external standard combined with In internal standard normalization. As a result, the

calibrated mass fractions of Rh, Pd, Ir, Pt, and Au in RPSS from the LA-ICP-MS analyses can be used as information values.

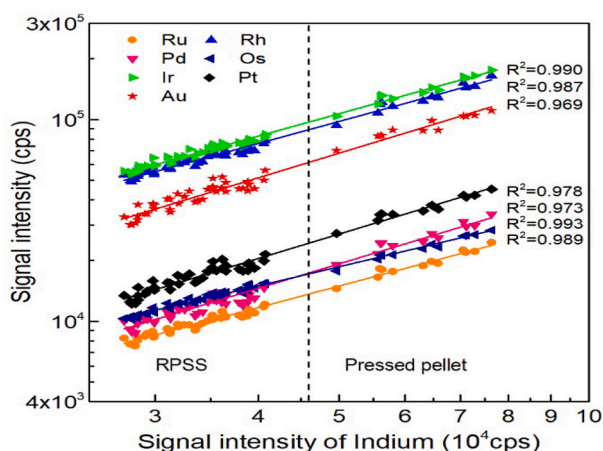


Fig. 8. Signal intensities of PGE and Au versus the internal standard indium between the pressed pellet and the RPSS by LA-ICP-MS analyses.

4. Conclusions

In this study, a simple and convenient method for the preparation of homogenous and stable solid powder samples that are suitable for bulk elemental composition analyses using LA-ICP-MS was proposed. Powder samples can be easily transformed into a stable and mechanically resistant target by mixing them with epoxy resin. The homogeneity of the resin-preserved target was obtained by grinding the original powder. This method for consolidating the powder target does not require long-time curing under critical conditions. The obtained target can be repolished to maintain fresh sample material for repeated use over long periods, which is not always possible with pressed powder pellets because of damage or oxidation upon exposure to air (see Fig. S1), especially with sulfide and ultrafine particles. Using the proposed method, other powder samples, such as various accessory minerals and oxides, can also be prepared for microsampling-based analytical techniques such as LA-ICP-MS.

A preliminary sulfide standard, RPSS, containing 47 different elements, including PGE, chalcophile elements, siderophile elements, lithophile elements, and REE, was developed by our method. The homogeneity of most elements in the RPSS was better than 10% (RSD, one sigma) at the microscale. The bulk elemental composition of the RPSS determined by LA-ICP-MS analyses, calibrated against the pellet pressed from the original powder, agrees well with that obtained with solution ICP-MS analyses. These results show that there is no significant matrix effect between the RPSS target and the original powder. The RPSS is a potentially suitable sulfide calibration standard for quantitative bulk elemental composition analysis by LA-ICP-MS. When RPSS is used as an external standard in LA-ICP-MS analysis, an advantage is presented over solution ICP-MS for difficult to digest elements e.g., PGEs and Au in a high Ag matrix. Furthermore, the preliminary standard RPSS can also be used for studies of element fractionation behaviors among different matrixes such as sulfide, silicate, and oxide during LA-ICP-MS analyses. Further studies will focus on the investigation of the RPSS target for isotope ratio analysis by using laser ablation multiple collector ICP-MS.

Author statement

Zhaochu Hu and Wenwu Yang conceived this study. Wenwu Yang, He Zhao, Wen Zhang, Tao Luo and Zhaochu Hu performed formal analysis and investigation. Wenwu Yang, Zhaochu Hu, Ming Li, Kang Chen and Shenghong Hu performed methodology. All authors contributed to the writing of the manuscript and have read and approved the final version.

Declaration of Competing Interest

There are no conflicts to declare.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- [1] N.J. Cook, C.L. Ciobanu, L.V. Danyushevsky, S. Gilbert, Minor and trace elements in bornite and associated Cu-(Fe)-sulfides: a LA-ICP-MS study Bornite mineral chemistry, *Geochim. Cosmochim. Acta* 75 (2011) 6473–6496.
- [2] D.A. Holwell, R.R. Keays, I. McDonald, M.R. Williams, Extreme enrichment of Se, Te, PGE and Au in Cu sulfide microdroplets: evidence from LA-ICP-MS analysis of sulfides in the Skaergaard Intrusion, east Greenland, *Contrib. Mineral. Petrol.* 170 (2015).
- [3] L.-M. Chen, X.-Y. Song, L.V. Danyushevsky, Y.-S. Wang, Y.-L. Tian, J.-F. Xiao, A laser ablation ICP-MS study of platinum-group and chalcophile elements in base metal sulfide minerals of the Jinchuan Ni-Cu sulfide deposit, NW China, *Ore Geol. Rev.* 65 (2015) 955–967.
- [4] N. Samalens, S.J. Barnes, E.W. Sawyer, A laser ablation inductively coupled plasma mass spectrometry study of the distribution of chalcophile elements among sulfide phases in sedimentary and magmatic rocks of the Duluth Complex, Minnesota, USA, *Ore Geol. Rev.* 90 (2017) 352–370.
- [5] B. Gourcerol, D.J. Kontak, P.C. Thurston, J.A. Petrus, Results of LA-ICP-MS sulfide mapping from Algoma-type BIF gold systems with implications for the nature of mineralizing fluids, metal sources, and deposit models, *Miner. Deposit.* 53 (2018) 871–894.
- [6] Y. Zhang, F. Chu, Z. Li, Y. Dong, H. Wang, X. Li, J. Long, Gold enrichment in hydrothermal sulfides from the Okinawa Trough: an *in situ* LA-ICP-MS study, *Ore Geol. Rev.* 116 (2020) 103255.
- [7] C.C. Wohlgeuth-Ueberwasser, F. Viljoen, S. Petersen, C. Vorster, Distribution and solubility limits of trace elements in hydrothermal black smoker sulfides: an *in situ* LA-ICP-MS study, *Geochim. Cosmochim. Acta* 159 (2015) 16–41.
- [8] H.L.J. Grant, M.D. Hannington, S. Petersen, M. Frische, S.H. Fuchs, Constraints on the behavior of trace elements in the actively-forming TAG deposit, Mid-Atlantic Ridge, based on LA-ICP-MS analyses of pyrite, *Chem. Geol.* 498 (2018) 45–71.
- [9] A. Soltani Dehnavi, C.R.M. McFarlane, D.R. Lentz, J.A. Walker, Assessment of pyrite composition by LA-ICP-MS techniques from massive sulfide deposits of the Bathurst Mining Camp, Canada: from textural and chemical evolution to its application as a vectoring tool for the exploration of VMS deposits, *Ore Geol. Rev.* 92 (2018) 656–671.
- [10] V. Maslennikov, S. Maslennikova, N. Aupova, A. Tseluyko, R. Large, L. Danyushevsky, U. Yatimov, High-tech elements in minerals of massive sulfide deposits: LA-ICP-MS data, in: S. Glagolev (Ed.), 14th International Congress for Applied Mineralogy (ICAM2019), 2019, pp. 107–110, https://doi.org/10.1007/978-3-030-22974-0_24.
- [11] A.T. Walker, K.A. Evans, C.L. Kirkland, A novel application of image analysis to interpret trace element distributions in magmatic sulphides, *Lithos* 362-363 (2020), 105451.
- [12] A. Oyebamiji, R. Hu, C. Zhao, T. Zafar, Origin of the Triassic Qinling Pb-Zn deposit in the western Yangtze block, SW China: insights from *in situ* trace elemental compositions of base metal sulphides, *J. Asian Earth Sci.* 192 (2020) 104292.
- [13] J.M. González-Jiménez, J.A. Proenza, M. Pastor-Oliete, E. Saunders, T. Aiglsperger, N. Pujol-Solà, J.C. Melgarejo, F. Gervilla, A. Garcia-Casco, Precious metals in magmatic Fe-Ni-Cu sulfides from the Potosí chromitite deposit, eastern Cuba, *Ore Geol. Rev.* 118 (2020), 103339.
- [14] Y. Du, X. Qin, C.G. Barnes, Y. Cao, Q. Dong, Y. Du, Sulphide melt evolution in upper mantle to upper crust magmas, Tongling, China, *Geosci. Front.* 5 (2014) 237–248.
- [15] S.A. Wilson, W.I. Ridley, A.E. Koenig, Development of sulfide calibration standards for the laser ablation inductively-coupled plasma mass spectrometry technique, *J. Anal. At. Spectrom.* 17 (2002) 406–409.
- [16] L. Danyushevsky, P. Robinson, S. Gilbert, M. Norman, R. Large, P. McGoldrick, M. Shelley, Routine quantitative multi-element analysis of sulphide minerals by laser ablation ICP-MS: standard development and consideration of matrix effects, *Geochem. Explor. Environ. Anal.* 11 (2011) 51–60.

- [17] L.Y. Zhu, Y.S. Liu, T.T. Ma, J. Lin, Z.C. Hu, C. Wang, *In situ* measurement of Os isotopic ratios in sulfides calibrated against ultra-fine particle standards using LA-MC-ICP-MS, *J. Anal. At. Spectrom.* 31 (2016) 1414–1422.
- [18] P. Onuk, F. Melcher, R. Mertz-Kraus, H.-E. Gäbler, S. Goldmann, Development of a matrix-matched sphalerite reference material (MUL-ZnS-1) for calibration of in situ trace element measurements by laser ablation-inductively coupled plasma-mass spectrometry, *Geostand. Geoanal. Res.* 41 (2017) 263–272.
- [19] L. Ding, G. Yang, F. Xia, C.E. Lenehan, G. Qian, A. McFadden, J. Brugger, X. Zhang, G. Chen, A. Pring, A LA-ICP-MS sulphide calibration standard based on a chalcogenide glass, *Mineral. Mag.* 75 (2018) 279–287.
- [20] C.C. Wohlgenuth-Ueberwasser, C. Ballhaus, J. Berndt, V. Stotter née Paliulionyte, T. Meisel, Synthesis of PGE sulfide standards for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *Contrib. Mineral. Petrol.* 154 (2007) 607–617.
- [21] C.X. Zhang, Z.C. Hu, W. Zhang, Y.S. Liu, K.Q. Zong, M. Li, H.H. Chen, S.H. Hu, Green and fast laser fusion technique for bulk silicate rock analysis by laser ablation-inductively coupled plasma mass spectrometry, *Anal. Chem.* 88 (2016) 10088–10094.
- [22] L.Y. Zhu, Y.S. Liu, Z.C. Hu, Q.H. Hu, X.R. Tong, K.Q. Zong, H.H. Chen, S. Gao, Simultaneous determination of major and trace elements in fused volcanic rock powders using a hermetic vessel heater and LA-ICP-MS, *Geostand. Geoanal. Res.* 37 (2013) 207–229.
- [23] J. Zhang, T. Zhou, Y. Tang, Y. Cui, J. Li, Determination of relative sensitivity factors of elements in high purity copper by doping-melting and doping-pressed methods using glow discharge mass spectrometry, *J. Anal. At. Spectrom.* 31 (2016) 2182–2191.
- [24] J. Mikolas, P. Musil, V. Stuchlikova, K. Novotny, V. Otruba, V. Kanicky, Infrared laser ablation study of pressed soil pellets with inductively coupled plasma atomic emission spectrometry, *Anal. Bioanal. Chem.* 374 (2002) 244–250.
- [25] C. O'Connor, M.R. Landon, B.L. Sharp, Absorption coefficient modified pressed powders for calibration of laser ablation inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 22 (2007) 273–282.
- [26] Y. Zhu, A. Hioki, K. Chiba, Quantitative analysis of the elements in powder samples by LA-ICP-MS with PMMA powder as the binder and Cs as the internal standard, *J. Anal. At. Spectrom.* 28 (2013) 301–306.
- [27] G. Bauer, A. Limbeck, Quantitative analysis of trace elements in environmental powders with laser ablation inductively coupled mass spectrometry using non-sample-corresponding reference materials for signal evaluation, *Spectrochim. Acta Pt. B* 113 (2015) 63–69.
- [28] M. Pakielna, M. Wojciechowski, B. Wagner, E. Bulska, A novel procedure of powdered samples immobilization and multi-point calibration of LA ICP MS, *J. Anal. At. Spectrom.* 26 (2011) 1539.
- [29] M.E. Shaheen, B.J. Fryer, A simple solution to expanding available reference materials for laser ablation inductively coupled plasma mass spectrometry analysis: applications to sedimentary materials, *Spectrochim. Acta Pt. B* 66 (2011) 627–636.
- [30] R. Hennekam, T. Jilbert, P.R.D. Mason, G.J. de Lange, G.-J. Reichart, High-resolution line-scan analysis of resin-embedded sediments using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), *Chem. Geol.* 403 (2015) 42–51.
- [31] M.E. Shaheen, J.E. Gagnon, B.J. Fryer, A. Polat, A simple and rapid method for preparing a diversity of powdered materials for analysis by laser ablation inductively coupled plasma mass spectrometry, *Int. J. Mass Spectrom.* 421 (2017) 104–115.
- [32] W. Klemm, G. Bombach, A simple method of target preparation for the bulk analysis of powder samples by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), *Fresen. J. Anal. Chem.* 370 (2001) 641–646.
- [33] L. Arroyo, T. Trejos, P.R. Gardinali, J.R. Almirall, Optimization and validation of a laser ablation inductively coupled plasma mass spectrometry method for the routine analysis of soils and sediments, *Spectrochim. Acta Pt. B* 64 (2009) 16–25.
- [34] P.K. Mukherjee, P.P. Khanna, N.K. Saini, Rapid determination of trace and ultra trace level elements in diverse silicate rocks in pressed powder pellet targets by LA-ICP-MS using a matrix-independent protocol, *Geostand. Geoanal. Res.* 38 (2014) 363–379.
- [35] G.O. Duodu, A. Goonetilleke, C. Allen, G.A. Ayoko, Determination of refractive and volatile elements in sediment using laser ablation inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 898 (2015) 19–27.
- [36] W. Zhang, Z.C. Hu, Y.S. Liu, W.W. Yang, H.H. Chen, S.H. Hu, H.Y. Xiao, Quantitative analysis of major and trace elements in NH_4HF_2 -modified silicate rock powders by laser ablation - inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 983 (2017) 149–159.
- [37] Z.C. Hu, S. Gao, Upper crustal abundances of trace elements: a revision and update, *Chem. Geol.* 253 (2008) 205–221.
- [38] Y.S. Liu, Z.C. Hu, S. Gao, D. Günther, J. Xu, C.G. Gao, H.H. Chen, In situ analysis of major and trace elements of anhydrous minerals by LA-ICP-MS without applying an internal standard, *Chem. Geol.* 257 (2008) 34–43.
- [39] D. Garbe-Schönberg, S. Müller, Nano-particulate pressed powder tablets for LA-ICP-MS, *J. Anal. At. Spectrom.* 29 (2014) 990–1000.