A Highly Efficient Method for the Accurate and Precise Determination of Zinc Isotopic Ratios in Zinc-rich Minerals Using MC-ICP-MS

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ABSTRACT: This study proposes a highly efficient method for the direct determination of Zn isotopes in Zn-rich minerals, without the use of column chromatography, via multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). Experiments (with or without column chromatography) were performed to evaluate the feasibility of directly obtaining non-deviated Zn isotopic ratios by MC-ICP-MS. For Zn isotopes determined without the use of column chromatography, the instrumental mass bias was corrected using the standard sample bracketing with Cu as the internal standard. The effects of acidity and concentration mismatch and the matrix effect were strictly assessed in a wet-plasma mode. The Long-term reproducibilities of $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$ better than $\pm 0.03\text{‰}$ ($n = 42$, 2 standard deviations (2s)) and $\pm 0.05\text{‰}$ ($n = 42$, 2s), respectively, were achieved by repeatedly measuring the NIST Standard Reference Materials (SRM) 682 solution doped with trace matrix elements over four months. Zn-rich minerals determined without employing column chromatography displayed little drift in $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$ values compared with minerals determined using column chromatography, with $\Delta^{66}\text{Zn}_{\text{without-with}}$ ($\Delta^{66}\text{Zn}_{\text{without-with}} = \delta^{66}\text{Zn}_{\text{without}} - \delta^{66}\text{Zn}_{\text{with}}$) ranging from -0.04 to $+0.01\text{‰}$ and $\Delta^{67}\text{Zn}_{\text{without-with}}$ ranging from -0.06 to $+0.01\text{‰}$. These results suggest that non-deviated Zn isotopic ratios in Zn-rich minerals can be achieved without column chromatography due to the low contents of undesired matrix elements.

INTRODUCTION

Zinc is a transition metal element with an atomic number of 30 and five stable isotopes, namely, ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn with relative abundances of 48.63%, 27.90%, 4.10%, 18.75%, and 0.62%, respectively.¹ Maréchal *et al.*² developed a pioneering high-precision method using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) to determine Zn isotope ratios, which has been increasingly adopted by the researchers due to its faster and more sensitive and precise measurements compared to thermal ionization mass spectrometry (TIMS). Zn is usually present in the form of Zn^{2+} and widely involved in various geological and biological processes. Zinc exists in different minerals or diverse

hydrothermal deposits and thus can be used as a tracer or an indicator of an ore-forming process. Significant isotopic variations for Zn have also been reported in microbially-mediated sulfide ores. Thus far, Zn isotope geochemistry has been successfully applied to studying the origin and evolution of the solar system,^{3,4} ore genesis,⁵⁻⁷ contamination sources,^{8,9} and life sciences.¹⁰⁻¹² In particular, because of the well-constrained formation conditions and high Zn abundance, the Zn isotopic compositions are useful to study ore deposits, especially for Zn-Pb deposits. For instance, sphalerite, a major sulfide mineral present in different types of lead-zinc deposits, and the zinc isotope composition of sphalerite is controlled by composition of the source-rock(s), temperature-related and kinetic fractionation during precipitation. Besides, the subsurface

cooling of hydrothermal fluids leads to precipitation of isotopically light sphalerite (Zn sulfide), and that this process is a primary cause of Zn isotope variation in hydrothermal fluids. Other studies have shown that by understanding how chemical processes that occur beneath the seafloor affect hydrothermal fluid $\delta^{66}\text{Zn}$, Zn isotopes may be used as a tracer for studying hydrothermal processes. Therefore, the Zn isotopes in sphalerite have been successfully applied to reveal the metal source, kinetic fractionation, and hydrothermal processes.^{5,6,13-15}

Over the past two decades, column chromatography and mass spectrometry have been essential for the precise and accurate determination of Zn isotope ratios. Zn undergoes a slight isotopic fractionation when exposed to anion exchange resins.² Therefore, a high Zn yield is a prerequisite for the precise and accurate determination of Zn isotopic ratios with column chromatography. In general, Zn solution is purified by AG MP-1 anion exchange chromatography. An established method has been used for the purification of Cu and Zn isotopes.² Sossi *et al.*¹⁶ developed an optimized separation methodology using AG1-X8 resin to separate Cu, Fe, and Zn from each other and from matrix elements in diverse rock samples. Their optimized method has minimized the preparation time, reagent consumption and total analytical blanks.

Previous studies have focused on the Fe and Cu isotope determination of ore minerals without using column chromatography. The good accuracy and precision have indicated that ore minerals with a simple matrix could be measured without employing column chromatography prior to mass spectrometry.¹⁷⁻²³ Some Fe-rich samples containing meteoritic iron, Fe-oxides, and carbonate minerals were dissolved in 6 M HCl and then purified using a two-step precipitation of Fe(III) hydroxide with NH_3 . Finally, the $\text{Fe}(\text{OH})_3$ precipitate was dissolved in 0.1% HCl solution for the determination of the Fe isotope.^{17,23} Zhang *et al.*²³ used the standard sample bracketing (SSB) technique with Ga as an internal standard to determine Cu isotopic ratios in twelve Cu-dominated minerals. They obtained $\Delta^{65}\text{Cu}_{\text{without-with}}$ ranging from -0.04 to $+0.02\text{‰}$, indicating that Cu isotope ratios in Cu-dominated minerals can be achieved without using column chromatography.

Herein, we conducted comparative studies for each of the six Zn-rich minerals (sphalerite, smithsonite, willemite, hemimorphite, troostite, and hydrozincite). For each mineral, we analyzed the sample with and without column chromatography. The matrix effects of ten elements (Ni, Ti, Ge, Ag, Cd, Fe, Pb, Sb, As, and Cu) were also evaluated. During the solution nebulization multi-collector inductively coupled plasma mass spectrometry (SN-MC-ICP-MS) analyses, the instrumental mass bias was corrected using the SSB technique with Cu as an internal standard. Our results indicate that the Zn isotope ratios obtained with column chromatography are consistent with the

results obtained without the use of column chromatography. Therefore, the non-deviated Zn isotope ratios can be acquired on Zn-rich minerals can be acquired without using column chromatography.

EXPERIMENTAL

Samples and reagents. All experiments were carried out in the State Key Laboratory of Continental Dynamics (SKLCD), Northwest University, China. Guaranteed reagent (GR) grade nitric acid, hydrochloric acid, and hydrofluoric acid were distilled separately twice in the sub-boiling distillation system (Minnetonka, MN, USA). The ultrapure water with a resistivity of 18.2 M cm^{-1} was obtained using a Milli-Q Element water purification system (Elix-Millipore, Billerica, MA, USA). Two milliliters of Bio-Rad AG MP-1M resin were packed in a Bio-Rad Poly-Prep column with a diameter of 8 mm and a length of 9 cm. All Polyfluoroalkoxy (PFA) vials were respectively cleaned in GR grade HNO_3 , high-pure HNO_3 , and deionized water prior to use.

The Zn-rich minerals, including sphalerite, smithsonite, willemite, hemimorphite, troostite, and hydrozincite, were analyzed under the microscope. Six sphalerites were collected from different types of Pb-Zn deposits, including skarn (KKZ61), sedimentary exhalative (SEDEX; Du2018-832 and Du2018-8321), volcanic-hosted massive sulfide (VHMS; DBK261), Mississippi valley (ZK2002-4), and hydrothermal vein (GBW07270) types. Zn reference materials NIST SRM 683 and NIST SRM 682 were used as in-house standards in the SKLCD. The Zn isotopic ratios of NIST SRM 683 and NIST SRM 682 are $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = +0.12 \pm 0.04\text{‰}$ ²⁴ and $\delta^{66}\text{Zn}_{\text{JMC-Lyon}} = -2.45 \pm 0.02\text{‰}$,²⁵ respectively, relative to the reference material JMC-Lyon. Alfa Cu (Stock #13867, Lot#012782G, $1000 \mu\text{g g}^{-1}$) purchased from the Johnson Matthey company (London UK) was used as an internal standard element to correct the instrumental mass bias.

Experimental design. Approximately 5 mg of each Zn-rich mineral sample was weighed into a 15 mL pre-cleaned PFA vial. Each of the Zn-rich minerals was dissolved in 4 mL of concentrated HF- HNO_3 (3:1, v/v) mixture. Subsequently, the capped beakers were placed on a hot plate at 120°C for two days to ensure full dissolution of the contents. All dissolved samples were evaporated to dryness and then re-dissolved in aqua regia. To ensure that the medium was completely converted to HCl medium for the following experiment, 6 M HCl was added two times.

To evaluate whether non-deviated Zn isotope ratios can be determined without column chromatography, the sample solution was divided into two parts for the two series of parallel experiments. For the first series of the experiment, three similar

aliquots containing 20 µg of Zn from each solution was taken for conducting the subsequent column chromatography. The Zn solutions collected from column chromatography were evaporated to dryness and re-dissolved in 2% HNO₃ (v/v) for mass spectrometry. The other parallel experiment measured the remaining Zn-rich sample solutions directly using MC-ICP-MS without column chromatography.

Chemical purification procedure. The chemical purification procedures followed those described by Chen *et al.*²⁶. The column was a 10 mL Bio-Rad Poly-Prep column with 2 mL of AG MP-1M (200 – 400 mesh) anion exchange resin. Before loading into the column, the resin was alternatively washed with 2 mL of 0.5 M HNO₃ and 2 mL of 6 M HCl six times. 10 mL of 6 M HCl was then added to the column for conditioning. Thereafter, 50 µL of the dissolved sample containing about 20 µg of Zn was loaded into the column, followed by loading 4 mL of 6 M HCl to elute most of the matrix elements (e.g., Na, Mg, Al, K, Ca, Ni, Ti, and Mn). The Co, Cu, Ga, and Fe were eluted using 6mL of 0.5 M HCl. Finally, Zn was collected in 10 mL of 0.5 M HNO₃. The collected Zn fractions were evaporated to dryness and dissolved in concentrated HNO₃. Subsequently, the dissolved solutions were re-evaporated to dryness. Before the Zn isotopic ratio analysis, the solutions were dissolved with 2% HNO₃ (v/v) to 1 µg g⁻¹. To verify the above procedures for Zn purification, every 1 mL of the eluate was continuously collected to measure the concentrations of matrix elements by an Agilent 7900 ICP-MS at the SKLCD, Northwest University.

SN-MC-ICP-MS analysis. High-precision Zn isotopic ratios were determined by MC-ICP-MS at the SKLCD on the Nu plasma 1700 MC-ICP-MS. During Zn isotope analysis, L4, L3, L2, Ax, H2, and H4 Faraday cups were used to collect ⁶²Ni, ⁶³Cu, ⁶⁴Zn, ⁶⁵Cu, ⁶⁶Zn, and ⁶⁷Zn, respectively. A “wet” plasma with a wet cone and a GE quartz nebulizer (100 µL min⁻¹) was used to determine Zn isotopic ratios. The SSB technique with Cu as an internal standard was selected to correct the instrumental mass bias. All Zn solutions were diluted with 2% (v/v) HNO₃ to achieve a Zn concentration of 1 µg g⁻¹ in the final solutions. The low mass resolution was used to resolve polyatomic interferences. Each measurement consisted of one block with 30 cycles, each of which had an integration time of 10 s. Samples were measured relative to NIST SRM 683 solution, and Zn isotopic ratios were reported in standard delta-notation in per mil relative to the JMC-Lyon by the following formulas:

$$\delta^{66}\text{Zn}(\text{‰}) = ((^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^{66}\text{Zn}/^{64}\text{Zn})_{\text{NIST SRM 683}} - 1) * 1000 + 0.12$$

$$\delta^{67}\text{Zn}(\text{‰}) = ((^{67}\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^{67}\text{Zn}/^{64}\text{Zn})_{\text{NIST SRM 683}} - 1) * 1000 + 0.18.$$

The specific operating parameters of Nu Plasma 1700 are displayed in Table 1.

RESULTS AND DISCUSSION

Before conducting the following experiments, the feasibility of the experiment was explored to ensure that the mass spectrometry process and design of experiments could be used. The matrix elements (such as Ni, Ti, Ge, Ag, Cd, Fe, Pb, Sb, As, and Cu) were doped into the NIST SRM 682 solution to obtain a trace-element of the six types of sphalerites and five types of Zn-rich minerals are reported in Table 2. In several sphalerite samples, the content of Fe is very high, and the value of Fe/Zn in DBK261 is 0.08. However, their Ca, As, Se and Cu contents are very low with the As/Zn, Se/Zn, and Cu/Zn ratios approximately 0. Among other Zn-rich minerals, willemite has the highest Mn/Zn ratio of 0.02, while troostite has the highest Fe/Zn ratio of 0.014. The contents of Mg, Al, Cu, Ti, and Ni are very low in all the minerals. The Zn isotope ratios of the six sphalerite samples and five Zn-rich minerals are presented in Table 3. The $\delta^{66}\text{Zn}$ of NIST SRM 682 solution without column chromatography was $-2.41 \pm 0.04\text{‰}$ (2s, n=3), which was identical with the reported reference value of $-2.45 \pm 0.02\text{‰}$ ²⁵. All pairs (with and without column) showed similar Zn isotopic ratios with $\Delta^{66}\text{Zn}_{\text{without-with}}$ ranging from -0.04 to 0.01‰ and $\Delta^{67}\text{Zn}_{\text{without-with}}$ ranging from -0.06 to 0.01‰ (Table 3).

Zn-rich mineral solution with a matrix element/Zn molar ratio of 0.001. This solution was divided into fifteen aliquots, three of which were directly measured by MC-ICP-MS, and the other twelve were analyzed after subjecting them to chemical separation. Subsequently, the Zn isotopic ratios with and without the column chromatography were determined. Direct measurements of the NIST SRM 682 solution doped with matrix elements without column chromatography yielded a mean $\delta^{66}\text{Zn}$ value of $-2.41 \pm 0.05\text{‰}$ (2s, n = 3), while measurements of the column-treated solution yielded a mean $\delta^{66}\text{Zn}$ value of $-2.42 \pm 0.05\text{‰}$ (2s, n = 12). These values agree well with the reported value of $-2.45 \pm 0.02\text{‰}$ for reference $\delta^{66}\text{Zn}$ ²⁵, suggesting that the purification process and mass spectrometry process were feasible.

Table 1. Nu Plasma 1700 MC-ICP-MS operating parameters for Zn isotope measurements

Instrumental parameters	Nu plasma 1700
RF power	1300 W
Cooling gas	13.0 L min ⁻¹
Auxiliary gas	0.8 L min ⁻¹
Nebulizer	39 Psi
Background of ⁶⁴ Zn	<3 mV
Sample cone and skimmer cone	Ni orifice
Resolution mode	Low resolution
Mass separation	0.5
Sample uptake	100 µL min ⁻¹

Table 2. Selected trace element compositions of Zn-rich minerals

Minerals	Ca/Zn	Fe/Zn	Ti/Zn	Ni/Zn	As/Zn	Se/Zn	Mg/Zn	Cd/Zn	Cu/Zn
Sphalerite (KKZ61)	0.003	0.021	0	0	0.001	0.002	0	0.011	0
Sphalerite (Du2018-832)	0.001	0.031	0	0	0.001	0.001	0	0.002	0.001
Sphalerite (Du2018-8321)	0.001	0.013	0	0	0.001	0.001	0	0.002	0.001
Sphalerite (DBK261)	0.003	0.08	0	0	0.003	0.006	0	0.005	0.001
Sphalerite (ZK2002-4)	0.001	-	-	0	0	0	0.017	0	0
Sphalerite (GBW07270)	0.005	0.031	0	0	0	0	0.018	0.002	0.002
Smithsonite	0.017	0.003	0	0	-	-	0	-	0
Willemite	0.001	0.007	0	0	-	-	0.002	-	0
Hemimorphite	0.003	0	0	0	-	-	0	-	0.002
Troostite	0.002	0.014	0	0	-	-	0	-	0
Hydrozincite	0.01	0	0	0	0	-	0.014	0	0

“-” denotes elements that could not be detected by Agilent 7900 ICP-MS due to their low signal intensities.

Table 3. Zinc isotope ratios of sphalerite samples and other types of Zn-rich minerals with/without column chromatography

Minerals	$\delta^{66}\text{Zn}_{\text{without}} (\text{‰})$	2s	n	$\delta^{66}\text{Zn}_{\text{with}} (\text{‰})$	2s	n	$\Delta^{66}\text{Zn}_{\text{without-with}} (\text{‰})$
Sphalerite (KKZ61)	0.21	0.02	3	0.23	0.06	3	-0.02
Sphalerite (Du2018-832)	-0.07	0.02	3	-0.04	0.04	3	-0.03
Sphalerite (Du2018-8321)	0.13	0.02	3	0.17	0.04	3	-0.04
Sphalerite (DBK261)	0.13	0.03	3	0.15	0.03	3	-0.02
Sphalerite (ZK2002-4)	0.20	0.03	3	0.22	0.03	3	-0.02
Sphalerite (GBW07270)	-0.05	0.01	3	-0.03	0.03	3	-0.02
Smithsonite	-0.27	0.01	3	-0.26	0.04	3	-0.01
Willemite	0.26	0.07	3	0.26	0.02	3	0.00
Hemimorphite	0.96	0.05	3	0.96	0.02	3	0.00
Troostite	0.09	0.05	3	0.11	0.01	3	-0.02
Hydrozincite	0.04	0.02	3	0.03	0.01	3	0.01
Minerals	$\delta^{67}\text{Zn}_{\text{without}} (\text{‰})$	2s	n	$\delta^{67}\text{Zn}_{\text{with}} (\text{‰})$	2s	n	$\Delta^{67}\text{Zn}_{\text{without-with}} (\text{‰})$
Sphalerite (KKZ61)	0.31	0.04	3	0.35	0.06	3	-0.04
Sphalerite (Du2018-832)	-0.09	0.02	3	-0.07	0.05	3	-0.02
Sphalerite (Du2018-8321)	0.21	0.04	3	0.27	0.09	3	-0.06
Sphalerite (DBK261)	0.21	0.06	3	0.23	0.06	3	-0.02
Sphalerite (ZK2002-4)	0.33	0.06	3	0.35	0.07	3	-0.02
Sphalerite (GBW07270)	-0.08	0.01	3	-0.05	0.07	3	-0.03
Smithsonite	-0.38	0.01	3	-0.38	0.06	3	0.00
Willemite	0.41	0.13	3	0.40	0.04	3	0.01
Hemimorphite	1.43	0.10	3	1.42	0.04	3	0.01
Troostite	0.13	0.05	3	0.15	0.04	3	-0.02
Hydrozincite	0.04	0.03	3	0.05	0.01	3	-0.01

Note: $\delta\text{Zn}_{\text{with}}$ and $\delta\text{Zn}_{\text{without}}$ denote Zn isotope ratios of minerals that were processed with column and without column, respectively; 2s refers to 2 standard deviations. Column “n” represents the total number of repeat analyses. $\Delta^{66}\text{Zn}_{\text{without-with}} = \delta^{66}\text{Zn}_{\text{without}} - \delta^{66}\text{Zn}_{\text{with}}$, $\Delta^{67}\text{Zn}_{\text{without-with}} = \delta^{67}\text{Zn}_{\text{without}} - \delta^{67}\text{Zn}_{\text{with}}$.

Effects of acidity and concentration mismatch. Previous studies have shown that the stable isotopic deviation of Zn can be caused by the concentration and acidity mismatches during mass spectrometry.²⁶⁻²⁸ In this study, we used 1.0 $\mu\text{g g}^{-1}$ of Alfa Zn

solution diluted with 2.0% (v/v) HNO_3 as the medium for the Zn isotopic analyses. The effects of acidity mismatch between the sample and the standard were tested using a series of 1.0 $\mu\text{g g}^{-1}$ Alfa Zn solutions diluted with 1.5 to 2.4% (v/v) HNO_3 . The SSB

Fig. 1 Effects of different acidities of Alfa Zn solution on $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$. Precisions are expressed as 2 standard deviations (2s), which are calculated based on four repeated measurements. Dotted line indicates the reference value. Grey area represents the 2s deviation range (0.05‰).

Fig. 2 Zn isotope ratio variations of Alfa Zn solution with different Zn concentrations from 0.5 to 2.0 $\mu\text{g g}^{-1}$. Errors are presented at the 2s level obtained by four repeated measurements. Dotted line indicates the reference value. Grey region expresses the 2s deviation range (0.05‰).

method with Cu as an internal standard was used to correct the instrument mass bias in the zinc isotope analysis. The lesser the effects of acidity mismatch on the test, the closer the values of $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ should be to 0. Fig. 1 shows that the differences in acidities between the sample and standard have a significant influence on the Zn isotopic compositions during mass spectrometry. When the difference in acidities between the sample and standard is within 10%, the obtained $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ values were within a deviation of 0.05‰. When the difference is $\geq 20\%$, the offset in $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ can be up to 0.10‰, which is significant. To eliminate the possible effects of the acidity mismatch, all dried samples were diluted using 2.0% (v/v) HNO_3 to ensure acceptable acidity differences ($<10\%$) before conducting mass spectrometry.

Fixing the Zn concentration of the bracketing standard at 1.0 $\mu\text{g g}^{-1}$, we measured a series of Alfa Zn solutions with different Zn concentrations ranging from 0.5 to 2.0 $\mu\text{g g}^{-1}$ to investigate the effects of the concentration mismatch between the sample and the standard. The lesser the effects of the concentration mismatch, the closer the values of $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ should be to 0.

Our results indicate that the differences in concentrations do not have a significant influence on the Zn isotopic compositions for the wet plasma method (Fig. 2). For a $C_{\text{sample}}/C_{\text{standard}}$ ratio ranging from 0.5 to 2.0, the $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ values of all samples agree well within the 0.05‰ deviation. To guarantee the precision and accuracy of Zn isotopic ratios, the $C_{\text{sample}}/C_{\text{standard}}$ ratio was kept at less than $\pm 20\%$ during mass spectrometry.

Effects of matrix elements. Natural sphalerite minerals usually comprise some trace elements, such as Ni, Ti, Ge, Ag, Cd, Fe, Pb, Sb, As, and Cu, which remain in the Zn solutions that are not subjected to column chromatography. The presence of these residual matrix elements can potentially affect the accuracy and precision of Zn isotopic analysis. In this study, we quantitatively assessed the potential effects of the ten matrix elements (Ni, Ti, Ge, Ag, Cd, Fe, Pb, Sb, As, and Cu) on Zn isotope measurements. These matrix elements of different concentrations were doped into 1.0 $\mu\text{g g}^{-1}$ Alfa Zn standard solutions and bracketed using the same pure Zn standard without any doping. The results of these analyses were plotted in Fig. 3. For most matrix elements with matrix element/Zn molar ratios up to 0.1, the $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ values were consistent with the true value within the 0.05‰ deviation, suggesting that the influence of these elements can be ignored during the measurements. When the molar ratio of Cu/Zn ranged from 0.25 to 3, Zn isotopic ratios showed no difference. Therefore, the addition of Cu in the sample would not affect the results of Zn isotope ratio measurements, it is feasible to use Cu as the internal standard.

However, small amounts of Ti and Ni residues in the Zn solutions will affect Zn isotopic ratios because $^{64}\text{Ti}^{+}$ and $^{48}\text{Ti}^{16}\text{O}^{+}$ can produce intense isobaric interferences on $^{64}\text{Zn}^{+}$. The matrix effects of Ti and Ni on Zn isotope ratios are also shown in Fig. 3. When the Ti/Zn ratio is less than 0.01, $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ values can be accurately obtained within the 0.05‰ deviation. When the Ni/Zn ratio is less than 0.005, $\delta^{66}\text{Zn}_{\text{Alfa Zn}}$ and $\delta^{67}\text{Zn}_{\text{Alfa Zn}}$ values with better accuracies can be obtained within the 0.05‰ deviation. Owing the low Ti and Ni contents in Zn-rich minerals (Ti or Ni/Zn <0.001), the Ti polyatomic and Ni interferences are negligible when the Zn isotope ratios are measured without column chromatography.

Quality control of the Zn isotope ratios of samples. The NIST SRM 682 solution doped with trace matrix elements was repeatedly measured at different periods by MC-ICP-MS for quality control. A total of 42 tests were conducted in December 2020, January 2021 and March 2021. Fig. 4 shows that the variations of Zn isotope ratios of NIST SRM 682 solutions were small within the four months, and the long-term precision of the $\delta^{66}\text{Zn}$ was $\pm 0.03\%$. The NIST SRM 682 solutions possessed a mean $\delta^{66}\text{Zn}$ of $-2.41 \pm 0.03\%$ (2s, $n = 42$) over the four months, which was consistent with the reference value within 2s deviation. The results confirm that our method was useful to determine the

Fig. 3 Zn isotope ratio variation of Alfa Zn solutions after doping with different proportions of matrix elements relative to Zn. Zn concentration of samples and bracketed standards (Alfa Zn) are the same ($1\mu\text{g g}^{-1}$). Errors(2s) were obtained by four repeated measurements. Dotted line represents the reference value. Grey region points out the 2s deviation range (0.05‰).

Zn isotope ratios in the Zn-rich solutions. The SSB with Cu as an internal standard was used to correct the quality deviation of the instrument for the accurate measurement of Zn isotope ratios in Zn-rich solution. Moreover, the total procedural Zn blanks were

lower than 20 ng, which was negligible compared with the 20 μg of Zn of the sample. Importantly, Zn-rich minerals analyzed without column chromatography yielded similar Zn isotope ratios compared with samples analyzed after column

Fig. 4 Long-term reproducibilities of $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$ measurements of NIST SRM 682 solution.

Fig. 5 Zinc three-isotope plot ($\delta^{67}\text{Zn}$ vs. $\delta^{66}\text{Zn}$) of all Zn-rich materials analyzed in this study.

Fig. 6 $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$ values for sphalerites and other types of Zn-rich minerals with and without column chromatography, respectively. Errors are presented at the 2s level and obtained through four repeated measurements.

Fig. 7 Deviations of $\Delta^{66}\text{Zn}_{\text{without-with}}$ and $\Delta^{67}\text{Zn}_{\text{without-with}}$ of sphalerites and other types of Zn-rich minerals, respectively.

chromatography, which indirectly supported the reliability of our method. The Zn three-isotope plots of all Zn-rich minerals are shown in Fig. 5. The $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$ fractionation line ($y = (1.48 \pm 0.01)x + (0.01 \pm 0.01)$, $R^2 = 0.999$) has a slope that is consistent with the kinetic (1.48) and equilibrium (1.49) fractionation within the error.²⁹ The trend of isotopic fractionation further confirms the efficiency of the direct determination of Zn isotopic ratios without column chromatography for Zn-rich minerals. This data demonstrates that the proposed high-performance method has an excellent stability, repeatability, accuracy, and precision.

Measurement of Zn isotopic ratios without column chromatography.

The Zn isotope ratios of sphalerite samples and other Zn-rich minerals obtained by routine column chromatography were served as reference values for comparison in the following section. To obtain accurate isotopic ratios of natural samples, matrix elements should be reduced or eliminated before mass spectrometry. This should be apply to most isotopic systems, otherwise, the matrix effects and isobaric interferences would lead to mass discrimination of elements, such as Mg,^{30,31} Ca,^{32,33} Zr,³⁴ Ba,³⁵ and V.³⁶ However, in the process of MC-ICP-MS analysis, matrix effects can be significantly reduced due to two factors: (a) the high zinc concentration in minerals with the highest zinc content and (b) SSB technique with Cu as the internal standard was used to correct the instrumental mass discrimination. For some stable systems in simple matrix samples, if the isobaric interference and matrix effect can be well suppressed, accurate isotopic data can be obtained without employing column chromatography. For example, Liu *et al.*³⁷ proposed that Ca isotope ratios can be measured without column

chemistry by TIMS using the ^{42}Ca - ^{43}Ca double-spike technique. Zhang *et al.*²³ suggested that the direct measurement of Cu isotope ratios without column chromatography was possible using the SSB technique with Ga as an internal standard. In the determination of Zn isotopes by MC-ICP-MS, the influence of matrix elements (such as Ni, Ti, Ge, Ag, Cd, Fe, Pb, Sb, As, and Cu) on the zinc isotope ratios is limited (see section 3.2). Therefore, we recommend using the SSB with Cu as an internal standard bracketing method so that MC-ICP-MS can directly measure the Zn isotopic ratios of Zn-rich materials without column chromatography. In Fig. 6 and Fig. 7, the eleven tested minerals show very small differences between the results obtained with and without the chemical separation. The $\Delta^{66}\text{Zn}_{\text{without-with}}$ ranges from -0.04 to +0.01‰ and the $\Delta^{67}\text{Zn}_{\text{without-with}}$ ranges from -0.06 to +0.01‰. Among all the minerals, nine samples possess $\Delta^{66}\text{Zn}_{\text{without-with}}$ values ranging from -0.02 to +0.01‰, and eight samples demonstrate $\Delta^{67}\text{Zn}_{\text{without-with}}$ values ranging from -0.02 to +0.01‰. Therefore, this method can guarantee the measuring accuracy of the Zn isotope ratio of Zn-rich minerals. In addition, if the analysis without column chromatography can meet the needs of the research within the range of the analytical error, this method can make the sample handling easier and eliminate the need for the sample separation time and save the cost of the reagents used. Our data show that, the direct determination of Zn isotopes of Zn-rich minerals by MC-ICP-MS does not require column chromatography.

CONCLUSIONS

We introduced a highly efficient technique to determine Zn isotopes directly in sphalerite samples and Zn-rich minerals (smithsonite, willemite, hemimorphite, troostite, and hydrozincite) by MC-ICP-MS without column separation. The results show that Zn isotopic ratios obtained without column chromatography are consistent with those obtained with column chromatography, and the $\Delta^{66}\text{Zn}_{\text{with-without}}$ and $\Delta^{67}\text{Zn}_{\text{with-without}}$ values range from -0.04 to +0.01‰ and from -0.06‰ to +0.01‰, respectively.

Because the acidity mismatch between the sample and the standard solution has a significant influence on the Zn isotope ratio, the acidity of the sample medium must be the same as that of the standard solution. However, when the concentration of the bracketing standard sample remains unchanged, differences in the sample concentrations can barely influence the measurements of the Zn isotopes. Due to low contents of matrix elements/Zn in Zn-rich minerals, the effects of matrix elements (Ge, Ag, Cd, Fe, Pb, Sb, and As) on the final Zn isotope ratio can be ignored. Moreover, the added internal standard Cu would not affect the measurements. Note the Ti/Zn molar ratio should be less than 0.01 and the Ni/Zn molar ratio should be less than 0.005 to guarantee the accuracy of the Zn isotope analysis. Repeated

analyses of the NIST SRM 682 solution have shown reveal that the external reproducibilities are better than $\pm 0.03\text{‰}$ (2s) and $\pm 0.05\text{‰}$ (2s) for $\delta^{66}\text{Zn}$ and $\delta^{67}\text{Zn}$, respectively. Therefore, this proposed high-performance method is advantageous to the economical and efficient determination of Zn isotopic ratios in Zn-rich minerals.

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Notes

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