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New Quartz and Zircon Si Isotopic Reference Materials for Precise and Accurate SIMS Isotopic Microanalysis
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Journal Overview

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New Quartz and Zircon Si Isotopic Reference Materials for Precise and Accurate SIMS Isotopic Microanalysis

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Received: November 24, 2021; Revised: April 17, 2022; Accepted: April 23, 2022; Available online: April 25, 2022.

ABSTRACT: Here we report the Si isotope compositions of four potential reference materials, including one fused quartz glass (Glass-Qtz), one natural quartz (Qinghu-Qtz), and two natural zircons (Qinghu-Zir and Penglai-Zir), suitable for in-situ Si isotopic microanalysis. Repeated SIMS (Secondary Ion Mass Spectrometry) analyses demonstrate that these materials are more homogeneous in Si isotopes (with the spot-to-spot uncertainty of 0.090-0.102‰), compared with the widely used NIST RM 8546 (previously NBS-28) quartz standard (with the spot-to-spot uncertainty poorer than 0.16‰). Based on the solution-MC-ICP-MS determination, the recommended $\delta^{30}$Si values are $-0.10 \pm 0.04$‰ (2SD), $-0.03 \pm 0.05$‰ (2SD), $-0.45 \pm 0.06$‰ (2SD), and $-0.34 \pm 0.06$‰ (2SD), for Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir, respectively. Our results reveal no detectable matrix effect on SIMS Si isotopic microanalysis between the fused quartz glass (Glass-Qtz) and natural quartz (Qinghu-Qtz) standards. Therefore, we propose that this synthetic quartz glass may be used as an alternative, more homogenous standard for SIMS Si isotopic microanalysis of natural quartz samples.

INTRODUCTION

Silicon (Si) has three stable isotopes ($^{28}$Si, 92.23% abundance; $^{29}$Si, 4.68%; and $^{30}$Si, 3.09%), and variations in Si isotopic composition are typically expressed as $\delta^{30}$Si values, which is the permil deviation of $^{30}$Si/$^{28}$Si ratio relative to the NBS-28 quartz reference standard (N.B. NBS-28 is the historical name, and it is now referred to as NIST RM 8546; see section 2 for the mathematical definition). Following the pioneering works of Reynolds and Verhoogen1 and Allenby2 in the 1950s, and the development and application of MC-ICP-MS,3 Si isotopes have been widely used to address various problems in Earth sciences.4 More recently, the application of microbeam techniques such as SIMS and laser ablation (LA)-MC-ICP-MS to Si isotopic analysis has allowed for the investigation of Si isotopic variations at the micron scale, significantly improving our knowledge of metal-silicate differentiation of planetary bodies, the biogeochemical cycle of silicon, and plate tectonics in the Early Earth.5,6

Compared with bulk analytical methods such as Solution (S)-MC-ICP-MS (where samples are homogenized during dissolution and matrix elements are chemically removed prior to analysis), well-characterized, homogeneous (to the micron scale), matrix-matched reference materials (RMs) are prerequisites for high-precision isotopic microanalysis using SIMS and LA-MC-ICP-MS. Additionally, for SIMS analysis, the so-called "topography effect"7-9 introduces extra instrument mass fraction (IMF) due to the sample surface elevation and tilt. Thus, the surface of the analytical targets should be sufficiently flat. However, due to the hardness difference between the samples (usually mineral crystals) and the epoxy resin matrix, the sample grains such as quartz and zircon typically protrude from the epoxy resin after polishing. This
relief is especially evident in crystals with grain sizes smaller than 100 µm.

The NBS-28 quartz standard is not only the primary standard for Si isotopic compositions but is also commonly used as the standard for in situ Si and O isotope microanalysis. However, this quartz standard is provided as a powder with relatively small grain size (~100 µm). This small grain size means that the standard is difficult to adequately flatten during sample preparation. Hence, the "topography effect" is obvious during SIMS Si isotope analysis of NBS-28, hampering in situ precise Si isotopic microanalysis applications. For instance, the spot-to-spot precision of Si isotope analysis of NBS-28 using SIMS is about δ30Si ± 0.3 ‰ (2SD),9,10 significantly poorer than ~0.1 ‰ (2SD) for NIST glass 610.9 Even though the DTCA-X (dynamic transfer contrast aperture in the X direction) correction can be used to minimize the "topography effect", the spot-to-spot precision is still around 0.15 ‰ (2SD) which is generally worse than those of unknown samples (with larger grain sizes).9 Therefore, NBS-28 quartz has significant drawbacks as a suitable standard for high-precision SIMS Si isotope microanalysis due to its small grain size; a related issue is that NBS-28 is not a homogeneous “fused” sample, so there is the potential for Si isotopic heterogeneity between and within grains at the micron scale. Therefore, it is imperative to develop standards with sufficient grain size and homogenous isotopic compositions for SIMS Si isotopic microanalysis to allow for a precision better than δ30Si ± 0.1 ‰.

Herein, we present the results of a long-term study of Si isotopic measurements using SIMS and S-MC-ICP-MS techniques on four reference materials (previously developed for O-isotope microanalysis), including one fused quartz glass (Glass-Qtz), one natural quartz (Qinghu-Qtz), and two natural zircons (Qinghu-Zir and Penglai-Zir). Our analytical results demonstrate that these reference materials are homogeneous in Si isotopes at the micron scale and can be used for high-precision in situ Si microanalysis.

**SAMPLE DESCRIPTION AND PREPARATION**

Six samples were selected in this study, including two natural quartz samples (NBS-28 and Qinghu-Qtz), artificial quartz glass (Glass-Qtz), NIST-610 glass, and two zircon samples, Qinghu-Zir and Penglai-Zir. Silicon isotopic compositions are expressed as:

\[ \delta^{30}\text{Si} = \left( \frac{^{30}\text{Si} / ^{28}\text{Si}}{^{30}\text{Si} / ^{28}\text{Si}} \right)_{\text{sample}} / \left( \frac{^{30}\text{Si} / ^{28}\text{Si}}{^{30}\text{Si} / ^{28}\text{Si}} \right)_{\text{NBS-28}} - 1 \]

\[ \times 1000 \]

where the \((^{30}\text{Si} / ^{28}\text{Si})_{\text{NBS-28}} = 0.0341465 \pm 0.0000015 \) was used to calculate the “measured” δ30Si of each sample.

The NBS-28 quartz is distributed by the National Institute of Standards and Technology. It is commonly-utilized as the reference material for both Si and O isotope analysis, with O isotope analysis giving a bulk value of δ18Ovsmow = 9.57 ± 0.20 ‰ (2SD).9 Perhaps more importantly, it is the globally accepted primary standard for Si isotopic compositions. Therefore, NBS-28 δ30Si = 0.

The Qinghu-Qtz quartz, with dozens of grams in weight and ~ 500 µm in average grain size, was separated from the Qinghu monzonite pluton in the southwestern Nanling Range, South China.13 Previous analyses show that it is homogenous in oxygen isotopes, with δ18Ovsmow = 8.49 ± 0.20 ‰ (2SD).14

Glass-Qtz is a fused quartz glass that was produced in the Jingshi Company (Taicang, Jiangsu Province, China) by fusing high-purity quartz sand at 1700 °C.14 It was used as an in-house standard for oxygen isotope microanalysis at IGG-CAS,14 with δ18Ovsmow value of 1.68 ± 0.08 ‰ (2SD). The glass has a grain size of several centimeters, and there are dozens of grams available of the standard. It was crushed into shards of several hundreds of microns for SIMS analysis.

The NIST-certified reference material SRM 610 glass (NIST-610) was also analyzed in this study to monitor the external reproducibility of the instrument and to evaluate the IMF variation between different matrices. Literature values for this RM are δ18Ovsmow = 10.91 ± 0.18 ‰ (2SD)15 and δ30SiNBS-28 = 0.03 ± 0.11 ‰ (2SD).16

Qinghu-Zir and Penglai-Zir zircons are two Chinese National Certified Reference Materials, with reference numbers GBW04705 and GBW04482, respectively. The Qinghu-Zir zircon standard is picked from the Qinghu quartz monzonite. It has been used as a standard for zircon U-Pb dating.13 It is also homogenous in oxygen isotopic compositions, with δ18Ovsmow = 5.39 ± 0.22 ‰ (2SD).13 The Penglai-Zir zircon standard is picked from zircon megacrysts (ranging between several millimeters and over one centimeter in size) from the Early Pliocene alkaline basalts in northern Hainan Island, South China.17 It has been used as a standard for zircon O-Hδ isotope microanalysis, with δ18Ovsmow = 5.31 ± 0.10 ‰ (2SD) and 176Hf/177Hf = 0.282906 ± 0.0000010 (2SD).17

NIST-610 glass shards and NBS-28, Glass-Qtz, and Qinghu-Qtz quartz grains were embedded on the surface of one-inch epoxy resin Mount A. Qinghu-Zir, and Penglai-Zir zircons were cast in Mount B. In addition, a large piece (centimeter-sized) of NIST-610 was selected and prepared in Mount C. To minimize the position effect (X-Y effect),7 all analysis points were selected within a 12-mm diameter area. The sample mounts were polished with 3000 and 5000 mesh sandpaper successively prior to SIMS analysis. A polishing paste was avoided throughout sample mount preparation.
to reduce the "topography effect" influence. The polished mounts were cleaned several times using alcohol and deionized water. Afterward, the mounts were dried and gold-coated under vacuum, then placed in the vacuum chamber of the SIMS for ~ 24 hours before analysis to reduce the interference of hydrides.

**EXPERIMENTAL METHODS**

*In situ* Si isotope measurements using SIMS. *In situ* Si isotope measurements in this study were conducted on the Cameca IMS-1280 Large geometry Multi-Collector SIMS, located at the Institute of Geology and Geophysics, Chinese Academy of Sciences, in Beijing.

To overcome the low yield of silicon signal from quartz and zircon in SIMS analysis, a ~15 μm Cs+ primary beam with an intensity of 7 to 12 nA was tuned at the potential of +10 kV. A ~20 μm raster size was employed to avoid a deep crater. A high-density electron beam from a normal incidence electron gun (NEG) was tuned to obtain a maximum emission current of ~2.3 mA. During analysis, the entrance slit of 200 μm and field aperture of 5500 μm were used. Two Faraday cups located at the L'2 and H1 positions of the multi-collector system were used to measure the 28Si and 30Si signals simultaneously, connected to the pre-amplifiers with resistors of 1010 and 1012 Ω, respectively. Both detectors were equipped with a ~700 μm exit slit to obtain a broad flat top mass peak. Based on different NEG tunings, the typical secondary ion yield of 28Si was 5.4 to 7.1 × 107 cps/nA for quartz samples and 3.6 to 4.4 × 107 cps/nA for the zircon samples, respectively.

With a data integration time of 120 s, the total analytical time of each analysis was ~4.5 min, which included a pre-sputtering of 30 s to ensure a stable secondary ion intensity. Before data acquisition, the secondary ion beam centering procedure, including the dynamic transfer field aperture (DTFA-X and DTFA-Y) and the DTCA-X, was applied automatically to minimize the influence of the "topography effect". Drift correction against time and DTCA-X correction9 were performed when necessary. Our previous study9 showed that using the linear relationship between the measured δ30Si value and the DTCA-X parameters in the same session to correct the obtained Si-isotope data can effectively improve the accuracy and precision of *in situ* Si isotope analysis. Specific principles and detailed correction methods can be found in Liu et al.9 Our measured Si isotopic compositions were normalized to the value from the S-MC-ICP-MS analysis to compare the results from different analytical sessions.

During *in situ* silicon isotope analysis using SIMS, the apparent mass resolution (MRP) M/ΔM was ~1470 (~10 % peak height) with ΔM of about 0.020 a.m.u., due to the exit slit setting of 700 μm. Thus, the 30SiH+ hydride peak was challenging to separate from the 30Si− signal effectively. As shown in Fig.1, the lower intensity peak on the right side of the 30Si− was 29SiH+, while the lowest intensity was 29SiH−. The magnetic field was locked at the left quarter of the flat top of the 30Si− signal. Under this condition, the 29SiH+ intensity was dropped by more than two orders of magnitude. Thus, the influence of its tailing on 30Si− was about ten ppm, which can be ignored during the measurement of 30Si−.

**Bulk analysis of Si isotopes using S-MC-ICP-MS.** Two multi-collector mass spectrometer laboratories, one in the School of Earth and Environmental Sciences, University of St Andrews (UA), and one in the Chinese Academy of Sciences’ Key Laboratory of Crust-Mantle Materials and Environments at the University of Science and Technology of China (USTC), were involved in the Si isotope characterization of the geo standards via S-MC-ICP-MS. The two quartz samples, Qinghu-Qtz and Glass-Qtz were measured in both laboratories. The two zircon samples, Qinghu-Zir and Penglai-Zir, were determined at UA. A brief description of the methods is given below.

At St Andrews, all samples were dissolved prior to Si isotope purification using the NaOH alkali fusion method, first described by Georg et al.3 Briefly, the mineral separates were powdered to a smaller grain size, and then between 2 and 10mg of sample powder was weighed into a high-purity (>99%) silver crucible. The NaOH flux (semi-conductor grade, Merck) was then added to the crucible in pellet form — usually, a minimum of 100mg and a maximum of 200mg of flux was utilized. The crucible containing the sample powder and flux was then placed in a muffle furnace, preheated to 720°C, and left for around 15 minutes for the fusion to take place. Following the fusion, the crucibles were removed from the furnace and quenched in MQ-e water (in 30ml PFA vials) and left overnight. Subsequently the fusion cake was transferred to pre-cleaned storage bottles, diluted with enough MQ-e water to result in a solution of between 10 and 25ppm Si, and acidified with...
enough conc. high purity HNO\textsubscript{3} to both neutralize the NaOH and reduce the pH of the solution to ~ 2.

The sample Si was purified for S-MC-ICP-MS analysis using the single-stage cation exchange procedure first described in Georg et al.\textsuperscript{3} and further discussed in Savage and Moynier (2013).\textsuperscript{18} Here, enough sample solution containing 20µg of Si was loaded into a BioRad Polyprep column containing 1.8 mL of precleaned AG50W-X12, 200–400 mesh cation exchange resin, Bio-Rad, USA. The Si, at low pH, is in the neutral H\textsubscript{4}SiO\textsubscript{4} or anionic H\textsubscript{3}SiO\textsubscript{4} forms and so can be eluted immediately using 5ml of MQ-e water (whereas matrix cations are retained on the resin). Once the Si was eluted, it was acidified to 0.22M HNO\textsubscript{3} before MC-ICPMS analysis. Silicon yield from the columns is always >99% and total procedural blanks are ≤ 50ng of Si, which is negligible compared to the 20µg of Si in sample.

Si isotopes were measured on a Thermo-Fischer Neptune-Plus MC-ICP-MS instrument. Samples were introduced into the instrument via an ESI PFA 75µl min\textsuperscript{-1} Microflow nebulizer, into the Thermo SIS spray chamber. The instrument was fitted with nickel “Jet” sampler and H-skimmer cones and operated at medium mass resolution (M/∆M ≈ 7500) to resolve the large molecular interferences on the \textsuperscript{30}Si and \textsuperscript{30}Si isotope beams. Sample isotope ratios were measured using the “sample-standard bracketing” procedure, using NBS-28 as the bracketing standard. Isotope beams were measured in the L3 (\textsuperscript{28}Si), C (\textsuperscript{28}Si), and H3 (\textsuperscript{28}Si) Faraday collectors and with 25 cycles of ~8 sec integrations, bracketed by on-peak blank measurements. The blank corrections, isotope ratios, and δ\textsuperscript{30}Si and δ\textsuperscript{28}Si values were calculated offline.

At USTC, the sample powder mixed with high purity NaOH powder was heated in a silver crucible at 720°C for 10 min to produce a water-soluble metastable silicate. The crucible was kept at the temperature of 80°C for 12 h on a hotplate. Nitric acid was added to the sample solution to attain a solution acidity of 1% HNO\textsubscript{3} (v/v) for column chemistry. A cation exchange resin (2 mL of AG50W-X12, 200–400 mesh, Bio-Rad, USA) was used to purify Si. The sample solution, containing ~30 µg of Si, went through the column after the resin was sequentially cleaned with 3 mol L\textsuperscript{-1} HNO\textsubscript{3}, 6 mol L\textsuperscript{-1} HNO\textsubscript{3}, and 6 mol L\textsuperscript{-1} HCl and then conditioned with water. Silicon was collected right after the column was loaded and was further eluted with 6 mL of water. The yield of Si was >99%, and the total procedural blank was ~20 ng, which is negligible relative to the ~30 µg of Si loaded into the column.

Silicon isotope ratios were analyzed with an MC-ICP-MS instrument (Neptune Plus from Thermo-Fisher Scientific). During analysis, nickel cones (H skimmer and Jet sampler, Thermo-Fisher Scientific) were used. Three stable isotopes of Si (\textsuperscript{28}Si, \textsuperscript{29}Si, and \textsuperscript{30}Si) were collected using FCs on L3, C, and H3, respectively, at a medium resolution (>5500). The mass bias of the instrument during isotope measurements was corrected using the sample-standard bracketing method.

**RESULTS**

**External reproducibility of SIMS Si-isotope microanalysis.** A large piece of NIST-610 glass on Mount C was determined to check the “best” external reproducibility of SIMS Si-isotope analysis using the current instrument settings. In the analytical period from February to March 2021, four repeated experiments were carried out on NIST-610 glass. After rejecting six discrete points with a deviation larger than 2 SD, the remaining 90 Si-isotopic measurements were included in the statistics (listed in Table S1 and plotted in Fig. 2). After normalizing to the reference value (~0.03 ‰), the overall external error of the 90 spot measurements is 0.072‰ (all uncertainties throughout the text are quoted at the 2 SD level unless otherwise indicated). These data show improved external reproducibility compared with those reported in the previous study (~0.11 ‰).\textsuperscript{3}

**Si-isotopic homogeneity at micron scales.** In situ silicon isotopic compositions of samples on Mount A and B (including NIST-610, NBS-28, Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir) were determined over several analytical sessions, resulting in over 1100 data (Table S2). The samples on Mount A were determined concurrently over ten sessions (NIST-610 was only determined in five sessions), and the zircon samples on Mount B were measured separately. To study the homogeneity of each sample, the data was organized primarily by sample. The internal error of each Si isotope spot measurement (Table S2) includes the SIMS counting statistic error and propagation of the “best” external error of the NIST-610 glass standard (0.072 ‰, see Section 4.1). The IMF
Table 1. Summary of SIMS $\delta^{29}$Si homogeneity check of the six samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Primary beam (nA)</th>
<th>Sessions</th>
<th>n</th>
<th>2SD (%) over all</th>
<th>2SD (%) range in each session</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-Qtz</td>
<td>7.3-10.9</td>
<td>10</td>
<td>234</td>
<td>0.090</td>
<td>0.06-0.13</td>
</tr>
<tr>
<td>Qinghu-Zir</td>
<td>7.4-10.9</td>
<td>10</td>
<td>207</td>
<td>0.102</td>
<td>0.06-0.14</td>
</tr>
<tr>
<td>NBS-28</td>
<td>7.4-10.1</td>
<td>10</td>
<td>181</td>
<td>0.160</td>
<td>0.11-0.31</td>
</tr>
<tr>
<td>NIST-610</td>
<td>9.4-10.7</td>
<td>5</td>
<td>85</td>
<td>0.112</td>
<td>0.07-0.12</td>
</tr>
<tr>
<td>Qinghu-Zir</td>
<td>6.0-13.1</td>
<td>7</td>
<td>260</td>
<td>0.094</td>
<td>0.07-0.13</td>
</tr>
<tr>
<td>Penglai-Zir</td>
<td>8.1-15.7</td>
<td>5</td>
<td>148</td>
<td>0.096</td>
<td>0.08-0.10</td>
</tr>
</tbody>
</table>

Table 2. Solution MC-ICP-MS data summary of Glass-Qtz, Qinghu-Qtz, NBS-28, NIST-610, Qinghu-Zir, and Penglai-Zir. The data in Table S2 were used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\delta^{29}$Si</th>
<th>2SD</th>
<th>2SE</th>
<th>$\delta^{30}$Si</th>
<th>2SD</th>
<th>2SE</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-Qtz</td>
<td>-0.09</td>
<td>0.02</td>
<td>0.01</td>
<td>-0.06</td>
<td>0.02</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td>USTC_1*</td>
<td>-0.12</td>
<td>0.01</td>
<td>0.01</td>
<td>-0.06</td>
<td>0.05</td>
<td>0.03</td>
<td>3</td>
</tr>
<tr>
<td>USTC_2</td>
<td>-0.05</td>
<td>0.01</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.07</td>
<td>0.04</td>
<td>3</td>
</tr>
<tr>
<td>USTC_3</td>
<td>-0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>-0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>6</td>
</tr>
<tr>
<td>USTC_4</td>
<td>-0.09</td>
<td>0.06</td>
<td>0.03</td>
<td>-0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>5</td>
</tr>
<tr>
<td>UA**</td>
<td>-0.09</td>
<td>0.04</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>23</td>
</tr>
<tr>
<td>Grand Average</td>
<td>-0.10</td>
<td>0.04</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.04</td>
<td>0.04</td>
<td>23</td>
</tr>
</tbody>
</table>

* Represents the data from the University of Science and Technology of China.
** Represents the data from School of Earth and Environmental Sciences, University of St Andrews.

corrected results were normalized to their reference values (or S-MC-ICP-MS determined value). The results are summarized in Table 1 and shown in Fig. 3.

A total of 234 SIMS Si-isotope measurements were performed for Glass-Qtz quartz within ten sessions. The overall external reproducibility of 0.09 % was achieved, with a rejection of seven measurements beyond the 2 SD error range. Similarly, 207 Si-isotope measurements were collected for the Qinghu-Zir sample within ten analytical sessions. After six analyses were rejected, the reproducibility of the remaining analysis was 0.10 %. Within the ten sessions, a total of 181 spot analyses were conducted on NBS-28 quartz. With seven outlined, the external reproducibility was 0.16 %, similar to those reported in the previous works.9,10 Within five sessions, 81 out of 85 analyses on NIST 610 glass gave external reproducibility of 0.11 %.

In situ silicon isotopic compositions of the Qinghu-Zir zircon were measured in seven sessions. A total of 260 (4 rejected for the significant deviation and abnormal internal precision) data sets yielded an external reproducibility of 0.094 %. A total of 148 (3 rejected) SIMS Si-isotopic analyses were conducted on the Penglai-Zir zircon in five sessions, with an external reproducibility of 0.096 %.

Si-isotope results using the S-MC-ICP-MS method. All Si-isotope data determined by S-MC-ICP-MS are listed in Table 2 and Table S3. To monitor the accuracy and reproducibility of Si isotope data, some external standards, including Diatomite, BHVO-2, AGV-2 and BCR-2, were analyzed in both UA and USTC. The $\delta^{29}$Si and $\delta^{30}$Si values of these standards agree well with literature data within error (Table S3) and demonstrate that the analytical methods used by two laboratories can achieve good levels of precision and reproducibility.

Both USTC and UA laboratories gave consistent Si isotopic results for the Glass-Qtz and Qinghu-Qtz quartz samples. For Glass-Qtz quartz, the $\delta^{29}$Si and $\delta^{30}$Si value obtained at USTC were $-0.11 \pm 0.04 \%$ and $-0.05 \pm 0.04 \%$ (n = 18), identical within errors with those obtained at UA ($\delta^{29}$Si = $-0.09 \pm 0.06 \%$, and $\delta^{30}$Si = $-0.04 \pm 0.03 \%$, n = 5). The grand mean of the data sets gives $\delta^{29}$Si and $\delta^{30}$Si of $-0.10 \pm 0.04 \%$ and $-0.05 \pm 0.04 \%$ (n = 23). Similarly, the $\delta^{29}$Si and $\delta^{30}$Si values for the Qinghu-Qtz quartz obtained from the two laboratories are identical within errors, with a grand mean of $-0.03 \pm 0.05 \%$ and $-0.01 \pm 0.06 \%$ (n =20), respectively.

**DISCUSSION**

New reference materials of Si isotope microanalysis. The NIST-610 glass standard has previously been shown to be homogeneous with respect to both chemical and isotopic compositions9,20. The NIST-610 glass shard we used on mount C is larger than 10 mm for SIMS Si isotopic microanalysis, effectively eliminating the “topography effect” of SIMS measurement. Our SIMS Si isotopic results of NIST-610 give the internal and external (spot-to-spot)
The δ^{30}Si values were calculated for each sample, and a mean value of δ^{30}Si was determined for each session. The results are summarized in Table 3.

Table 3. The IMF determination between the natural quartz samples and the synthetic samples in ten sessions.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Mean value of δ^{30}Si</th>
<th>Calculated IMF</th>
<th>ΔIMF</th>
<th>2SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-Qtz</td>
<td>-0.30 ± 0.12</td>
<td>-0.20</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.18 ± 0.08</td>
<td>-0.18</td>
<td>0.02</td>
<td>0.13</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.22 ± 0.10</td>
<td>-0.19</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>Glass-Qtz</td>
<td>-0.15 ± 0.07</td>
<td>-0.05</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.09 ± 0.04</td>
<td>-0.09</td>
<td>-0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.08 ± 0.05</td>
<td>-0.05</td>
<td>0.01</td>
<td>0.12</td>
</tr>
<tr>
<td>Glass-Qtz</td>
<td>-0.01 ± 0.05</td>
<td>0.09</td>
<td>0.00</td>
<td>0.08</td>
</tr>
<tr>
<td>NBS28</td>
<td>0.07 ± 0.04</td>
<td>0.07</td>
<td>-0.01</td>
<td>0.15</td>
</tr>
<tr>
<td>Qinghu</td>
<td>0.02 ± 0.05</td>
<td>0.05</td>
<td>-0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>Glass-Qtz</td>
<td>-0.70 ± 0.60</td>
<td>-0.60</td>
<td>0.00</td>
<td>0.13</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.59 ± 0.59</td>
<td>-0.59</td>
<td>0.02</td>
<td>0.14</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.48 ± 0.48</td>
<td>-0.48</td>
<td>-0.03</td>
<td>0.16</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.09 ± 0.08</td>
<td>-0.09</td>
<td>-0.08</td>
<td>0.19</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.05 ± 0.02</td>
<td>-0.02</td>
<td>-0.01</td>
<td>0.10</td>
</tr>
<tr>
<td>Glass-Qtz</td>
<td>-0.76 ± 0.66</td>
<td>-0.66</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.68 ± 0.68</td>
<td>-0.68</td>
<td>-0.03</td>
<td>0.18</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.66 ± 0.63</td>
<td>-0.63</td>
<td>-0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>Glass-Qtz</td>
<td>-0.13 ± 0.03</td>
<td>-0.03</td>
<td>0.00</td>
<td>0.06</td>
</tr>
<tr>
<td>NBS28</td>
<td>-0.02 ± 0.05</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.15</td>
</tr>
<tr>
<td>Qinghu</td>
<td>-0.07 ± 0.04</td>
<td>-0.04</td>
<td>-0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>NBS28</td>
<td>0.02 ± 0.12</td>
<td>0.12</td>
<td>0.00</td>
<td>0.08</td>
</tr>
<tr>
<td>Qinghu</td>
<td>0.14 ± 0.14</td>
<td>0.14</td>
<td>0.02</td>
<td>0.15</td>
</tr>
<tr>
<td>NBS28</td>
<td>0.09 ± 0.12</td>
<td>0.12</td>
<td>0.00</td>
<td>0.08</td>
</tr>
<tr>
<td>Qinghu</td>
<td>7.84 ± 7.87</td>
<td>7.87</td>
<td>7.75</td>
<td>0.12</td>
</tr>
<tr>
<td>NBS28</td>
<td>0.20 ± 0.20</td>
<td>0.20</td>
<td>-0.02</td>
<td>0.11</td>
</tr>
<tr>
<td>Qinghu</td>
<td>0.18 ± 0.21</td>
<td>0.21</td>
<td>0.00</td>
<td>0.11</td>
</tr>
<tr>
<td>NBS28</td>
<td>7.94 ± 7.97</td>
<td>7.97</td>
<td>7.75</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Figure 3 summarizes the results of the δ^{30}Si microanalysis for different quartz samples using SIMS analysis, including two quartz crystals, one fused glass O-isotope standard, the NIST-610 glass, and two zircon age and O-Hf isotope standards. All analyses of six standards show Gaussian distributions, suggesting they are homogeneous in Si isotopes. The Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and NIST-610 standards have the external precision of 0.090 ‰, 0.102 ‰, 0.094 ‰, and 0.112 ‰, respectively, suggesting that all of them are suitable for the Si isotope microanalysis. Among them, the Glass-Qtz quartz has the best level of homogeneity of Si isotopes. Based on S-MC-ICP-MS analyses, the δ^{30}Si value of Glass-Qtz is −0.10 ± 0.04 ‰ (2SD), −0.03 ± 0.05 ‰ (2SD), −0.45 ± 0.06 ‰ (2SD), and −0.34 ± 0.06 ‰ (2SD) are recommended for Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Glass-Zir, respectively. Considering that these quartz standards are homogeneous in Si isotopes at the micron level, the calculated Si-isotope fractionation between quartz and zircon: δ^{30}Si(qtz) – δ^{30}Si(zir) = δ^{30}Si(qtz-zir) = 0.42 ± 0.06 ‰, which corresponds to ~671 °C based on the first-principles calculation of equilibrium fractionation of Si isotopes in quartz and zircon system. This Si-isotope thermometry result agrees with the O-isotope equilibrium temperature of 656 ± 62 °C in quartz and zircon, further supporting the reliability of our Si isotope results.

Compared with the NIST-610 glass standard, quartz, and zircon standards described above, our NBS-28 quartz analyses provide a much poorer external precision of about 0.16 ‰ for Si isotopes at the micron scale, similar to those reported in previous works. Therefore, we posit that NBS-28 is not an ideal standard for high-precision Si isotopic microanalysis; although it is likely homogeneous in Si isotopes at the milligram level typically processed for S-MC-ICPMS measurements, we suggest that a suite of well-characterized standards (such as those described above) that are homogeneous at the micron level vs. NBS-28 in terms of its Si isotope composition are more ideal for SIMS δ^{30}Si and δ^{30}Si measurements.

Glass-Qtz as an alternative standard for precise SIMS quartz Si isotopic microanalysis. Our SIMS analytical results demonstrate that the Glass-Qtz quartz has excellent homogeneous Si-isotopic compositions. However, it is noteworthy that the structure of synthetic uncrystallized quartz glass is different from that of natural crystallized quartz crystals. Therefore, when assessing the use of a synthetic quartz standard (such as Glass-Qtz quartz) for bracketing natural SIMS quartz Si-isotope analysis, we must consider the potential for a matrix effect between the two. As described in experimental section, all quartz standards Glass-Qtz, Qinghu-Qtz, NBS-28, and NIST-610 were concurrently measured using SIMS. These analytical results can be used to investigate the feasibility of using Glass-Qtz quartz glass as an alternative standard for precise SIMS quartz Si isotopic microanalysis. Reference values of NBS-28 (δ^{30}Si = 0 ‰) and NIST-610 glass (−0.03 ‰), and our newly obtained δ^{30}Si values for Qinghu-Qtz (−0.03 ‰) and Glass-Qtz (−0.10 ‰) are used as recommended values. The difference between the calculated IMF and the reference value (IMF_{ref} = IMF_{calc}) was defined as ΔIMF hereafter.

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SIMS Si-isotope analysis.

On the contrary, the NIST-610 glass has a ΔIMF value ranging from 7.53 to 7.75 ‰, which is neither close to zero nor constant. Although NIST-610 glass is considerably homogenous in Si isotopes on the micron scale, it is not suitable as an RM for SIMS Si isotope microanalysis.

CONCLUSIONS

In this study, we improve the external reproducibility of SIMS Si-isotope microanalysis from 0.11 ‰ (2SD)9 to 0.07 ‰ (2SD) for large shards of NIST 610 glass. Four standards previously utilized for SIMS O-isotope microanalysis, including Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir, are herein proved to be homogeneous in their Si-isotopic compositions at the micron scale, and their Si-isotopes have been precisely determined by S-MC-ICP-MS. Thus, they can be used as standards for both O- and Si-isotope microanalysis, allowing the SIMS isotope data to be recast relative to VSMOW and NBS-28. We also demonstrate that there is no detectable matrix effect of SIMS Si isotope microanalysis between the synthetic quartz (Glass-Qtz) and natural quartz standards at the 0.1‰ precision level. Therefore, the synthetic Glass-Qtz quartz glass can be used as an alternative RM for precise SIMS quartz Si isotope analysis.

ASSOCIATED CONTENT

The supporting information (Tables S1-S4) is available at www.at-spectrosc.com/as/home

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ACKNOWLEDGMENTS

We thank Hong-Xia Ma for her excellent sample preparation work. We also thank two anonymous reviewers for their helpful comments, which greatly improved this manuscript. This work was financially supported by the National Key R&D Program of China (2018YFA0702600) and National Science Foundation of China (41890831).

REFERENCES


Continuous Online Leaching System Coupled with Inductively Coupled Plasma Mass Spectrometry for Assessment of Cr, As, Cd, Sb, and Pb in Soils

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Received: August 20, 2021; Revised: October 29 2021; Accepted: November 01, 2021; Available online: November 08, 2021.

DOI: 10.46770/AS.2021.827

ABSTRACT: Incidental ingestion of soil containing Cr, As, Cd, Sb, and Pb has been attracting global attention as it can significantly impact human health. Many bioaccessibility methods have been developed to simulate the amount of contaminants extracted by gastrointestinal fluids following incidental ingestion. Although the continuous online leaching method (COLM) offers various advantages over conventional batch bioaccessibility methods, such as reduced analysis time, elemental source apportionment, and isotopic analysis, it has not yet been applied to soil and directly compared to validated, published methods. This study uses the COLM with simulated gastrointestinal fluids from the United States Environmental Protection Agency (US EPA), United States Pharmacopeia (USP), and unified bioaccessibility method (UBM) to measure the bioaccessibility of Cr, As, Cd, Sb, and Pb in NIST 2710, NIST 2710a, NIST 2711a, and BGS 102. When the US EPA gastrointestinal fluid was used, no significant difference was observed between the COLM bioaccessible + residual, aqua regia extraction, or certificate concentrations for all the elements and soils studied. Furthermore, COLM bioaccessibility was within the acceptable range of control limits and bioavailability (animal) studies for most reference materials. In addition, no statistically significant difference was observed between either the US EPA batch method or the stomach phase of the UBM batch method and the stomach stage of the COLM, indicating that the COLM could be incorporated into current bioaccessibility analyses to improve soil contamination characterization in the future.

INTRODUCTION

Cr, As, Cd, Sb, and Pb can be toxic, carcinogenic, or have other neurological or adverse health effects, and therefore, their presence in soil can adversely affect humans, other animals, and the natural environment. Cd, for instance, can cause nephrotoxicity in humans. Cr and Sb have been observed to have adverse health effects in rats. Pb can cause neurotoxicity in children. As is a known carcinogen. In addition, Sb and Cr have been recognized as risk drivers in human health risk assessment. Various methods have been validated to determine As, Pb, and Cd in soils. Some soil types are naturally rich in one or more of these elements, while others can be contaminated with these elements through human activities. Therefore, the United Nations Sustainable Development Goals aim to reduce illness and death resulting from hazardous soil pollution and contamination (Target 3.9), provide access to safe green and public spaces (Target 11.7), reduce the release of chemicals into soil and their adverse impacts on the human health and environment (Target 12.4), and restore degraded land and soil to achieve a land degradation-neutral world (Target 15.3). Over 1300 active contaminated Superfund sites have been identified by the United States Environmental Protection Agency (US EPA). The Federal Contaminated Sites Action Plan has identified 4982 active contaminated sites in Canada. Across Europe, 340,000
contaminated sites will likely require remediation according to the European Environment Agency. To facilitate the remediation of these sites and assessment of other sites, agencies often perform a human health risk assessment.

Although humans can be exposed to Cr, As, Cd, Sb, and Pb in soils through dermal absorption or inhalation, the most significant exposure occurs through incidental ingestion.\(^5\) One of modeling this ingestion is by using bioaccessibility methods. Bioaccessibility is the amount made available for absorption into the circulatory system by the gastrointestinal fluids, whereas bioavailability is the amount actually absorbed into the bloodstream (Fig. S1). Bioavailability methods are time-consuming and expensive. In addition, animal subjects (such as pigs, mice, or monkeys)\(^7-9\) need to be fed contaminated soils to evaluate the uptake and excretion of Cr, As, Cd, Sb, and Pb, which is conducted by analyzing their urine, feces, blood, and sometimes tissues. By contrast, bioaccessibility methods use artificial gastrointestinal fluids to assess the solubility of elements, which theoretically estimates the maximum possible bioavailable concentration. The relevance of such methods is established through a strong correlation between bioaccessibility and bioavailability, \(i.e.,\) their validation, according to specific criteria.\(^10,11\)

The US EPA employs a method in which samples are agitated for 1 h in simulated gastric fluids at 37 °C.\(^12\) This method is widely used and has been validated for Pb\(^13\) and As.\(^14,15\) It has also been used to predict the relative bioavailability from bioaccessibility measurements. Many studies have also utilized a method based on the United States Pharmacopeia (USP)\(^16\) that incorporates artificial saliva, gastric, and intestinal fluids.\(^17-19\) In addition, the Bioaccessibility Research Group of Europe has developed a method called the unified bioaccessibility method (UBM), in which samples are mixed for 1 h with simulated saliva and gastric fluids, and then subjected to an additional 4 h of mixing in duodenal and bile fluids.\(^20\) This method has also been adopted by the International Organization of Standardization (ISO) and validated to assess the oral bioavailability of Pb, As, and Cd in an interlaboratory trial.\(^21\)

The methods discussed above use certified reference materials (CRMs) for quality control and validation studies. Some commonly used CRMs for these purposes are produced by the National Institute of Standards and Technology (NIST), specifically NIST 2710, NIST 2710a, and NIST 2711a. Additionally, the British Geological Survey (BGS) produced BGS 102, a reference material that has been extensively studied for use with the UBM.\(^21-24\) The published bioavailability results and historic use of these CRMs with validated methods are important for assessing non-validated methods.

All these methods employ inductively coupled plasma mass spectrometry (ICPMS) for elemental analysis because of its high sensitivity, low detection limits, and a large linear dynamic range.\(^25\) Although ICPMS can be sensitive to matrix effects and spectroscopic interferences,\(^26\) flow injection (FI) can reduce these matrix effects,\(^27\) and inert (He) or reactive (H\(_2\)) gases can react with possible interfering ions in a collision reaction cell or a collision reaction interface (CRI). While these approaches can facilitate analyte detection, they can also lower the sensitivity.\(^28\)

A significant drawback of the aforementioned bioaccessibility methods is that they require a long extraction time prior to ICPMS analysis, which can be avoided by using the continuous online leaching method (COLM). To use the COLM, the sample is placed in a mini-column. Each gastrointestinal fluid is then sequentially pumped through the mini-column and directly to the nebulizer of the instrument. The gastrointestinal fluids and mini-column are then submerged in a water bath maintained at 37 °C to simulate the average human body temperature. Fig. 1 illustrates the COLM setup with an ICPMS detector and a low-pressure manifold. Since the gastrointestinal fluid is directly sent to the ICPMS instrument, the sample-handling is greatly reduced, which in turn reduces any potential contamination. Additionally, the extracts produce transient time-resolved peaks that provide real-time information on the leaching kinetics of elements and allow for the analysis of multiple gastrointestinal fluids in under 30 min.\(^17\) These temporal profiles can allow the identification of different sources of elements, as differential leaching can be observed in real time.\(^17\) In addition, it allows isotopic source apportionment, which can help

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**Fig. 1** Schematic representation of the continuous online leaching method (COLM) using a low-pressure manifold.
identify the source of the contaminants (for instance, from Pb added to gasoline).\textsuperscript{29,30} The COLM has been used for seafood,\textsuperscript{18} wheat,\textsuperscript{31} bread,\textsuperscript{32} and rice,\textsuperscript{33} however, it has not yet been used for soils, or directly compared to other validated bioaccessibility methods.

Unlike food samples, soils contain refractory components. This study aims to verify whether the COLM can be successfully applied to soils. It also directly compares the COLM with other soil bioaccessibility methods, including the validated US EPA method, USP method, and validated UBM, in order to justify its continued and wide-spread application.

**EXPERIMENTAL**

**Certified reference materials.** Four CRMs, representing soils typically used as controls in bioaccessibility studies, were selected for the study as they have available bioavailability results for comparison: NIST 2710, NIST 2710a, NIST 2711a, and BGS 102. The details of these CRMs can be found in Table S1. They were mixed prior to weighing (0.5–1.0 g, depending on the method). When not in use, the CRMs were stored in the dark at room temperature.

**Reagents.** All methods used doubly deionized water (DDW) purified to a resistivity of 18.2 MΩ cm using either an Arium Pro UV/DI (Sartorius Stedim Biotech, Göttingen, Germany) or Milli-Q Direct 8 (Millipore Sigma, Burlington, MA, USA) water purification system. The acids were of American Chemical Society (ACS) reagent grade. Analytical-grade HCl and HNO\textsubscript{3} were used for the UBM. A DST-1000 sub-boiling distillation system (Savillex, Minnetonka, MN, USA) was used for the purification of acids for the aqua regia extraction.

The USP bioaccessibility fluids were prepared in accordance with previous studies\textsuperscript{37,34} and analyzed using the COLM. Enzymes were omitted from the stock solutions and added only on the day of analysis. For saliva stock, 0.896 g of KCl (ACS grade; Sigma-Aldrich), 0.200 g of KSCN (ACS grade; Sigma-Aldrich), 0.888 g of Na\textsubscript{2}H\textsubscript{2}PO\textsubscript{4} (ACS grade; Sigma-Aldrich), 0.570 g of NaHPO\textsubscript{4} (ACS grade; Sigma-Aldrich), 0.298 g of NaCl (ACS grade; BioShop, Burlington, ON, Canada), 0.072 g of NaOH (ACS grade; BioShop), 0.200 g of urea (ACS grade; Sigma-Aldrich), 0.015 g of uric acid (ACS grade; Sigma-Aldrich), and 0.050 g of mucin (ACS grade; Sigma-Aldrich) were mixed and diluted to 1 L with DDW. The pH was maintained at 6.5 by adding 0.2 mol L\textsuperscript{-1} NaOH.

To prepare the gastric stock solution, 2.00 g of NaCl and 7.0 mL of HCl (ACS grade; Fisher Scientific, Ottawa, ON, Canada) were combined and diluted to 1 L with DDW and the pH was maintained at 1.2 using HCl. To prepare the intestinal stock, 6.80 g of KH\textsubscript{2}PO\textsubscript{4} (ACS grade; Fisher Scientific, NJ, USA) and 77 mL of 0.2 mol L\textsuperscript{-1} NaOH were mixed and diluted to 1 L with DDW after adjusting to pH 6.8 using NaOH. On the day of analysis, enzymes were added by combining 250 mL of the stock with 0.0729 g of α-amylase (USP grade; Sigma-Aldrich) for saliva, 0.800 g of pepsin (USP grade; Sigma-Aldrich) for gastric juice, and 2.50 g of pancreatin (a mixture of amylase, lipase, and protease) (USP grade; Sigma-Aldrich) for intestinal fluid.

**US EPA batch method.** Following the standard operating procedure,\textsuperscript{12} three 1-g aliquots of soil were weighed into 125-mL high-density polyethylene (HDPE) bottles. A simulated gastric fluid was prepared by mixing 30.03 g of glycine (Reagent Plus Grade; Sigma-Aldrich, Oakville, ON, Canada) in up to 1 L of DDW at 37 °C and then adding HCl (ACS reagent grade; Fisher Scientific, Saint-Laurent, QC, Canada) to obtain a pH of 1.50 ± 0.05. Then, 100 mL of gastric fluid was added to each HDPE bottle and set to rotate end-over-end in an Innova 4230 refrigerated incubator shaker (Eppendorf (previously New Brunswick Scientific), Enfield, CT, USA) at 37 °C for 1 h at 60 rpm. The sample extracts were filtered through a 0.45-µm nylon syringe filter (National Scientific, Claremont, CA, USA) and diluted 100-fold with DDW.

**Continuous online leaching method (COLM).** To overcome the back-pressure experienced with densely packed samples\textsuperscript{18} when 1-g soil aliquots were used, a Spectra SYSTEM P4000 HPLC pump (Thermo Fisher Scientific, Waltham, MA, USA) was used with high-pressure metal mini-columns (emptied guard columns). These mini-columns were 6-cm long with a 1-cm outer diameter and 0.6-cm inner diameter. Two ~0.6-cm-diameter disks of Whatman filter paper (Cytiva, Marlborough, MA, USA) were placed at each end of the mini-column filled with 1 g of soil. During the analysis, the prepared mini-columns were submerged in a 37 °C water bath (VWR, Mississauga, ON, Canada) and the artificial gastrointestinal fluids (also maintained at 37 °C) were pumped through them. Elution took 5–15 min, depending on the gastrointestinal fluid and sample. Eluents from the mini-column were combined with an In internal standard using a Y-connector and nebulized into the ICPMS instrument. External calibration was performed using matrix-matched standards (prepared in each gastrointestinal fluid) and an FI manifold with a 100-µL injection loop. As this method was used with US EPA and USP gastrointestinal fluids, each was denoted as COLM-G (for the glycine-HCl fluid of the US EPA) and COLM-USP, respectively.

**Unified bioaccessibility method (UBM).** The UBM fluids were prepared in accordance with ISO 17924:2018\textsuperscript{20} and following a previously reported method.\textsuperscript{24} First, 1 L of inorganic and organic components of each gastrointestinal fluid was prepared according to the ISO protocol and then combined in a 2-L HDPE bottle at 37 °C. For the batch method, 0.6-g aliquots of soil were combined with 9.0 mL of saliva in a polycarbonate centrifuge tube and hand shaken for 10 s. Then, 13.5 mL of gastric fluid was added, and the pH was adjusted to 1.2 ± 0.5. This resulting fluid was then mixed end-over-end in a custom-built water bath for 1 h at 37 °C. The samples were then centrifuged at 4500 × g for 15 min, decanted,
and acidified with 9.0 mL of 0.1 M HNO₃ for storage prior to analysis. This made up the “stomach” phase. For the “stomach + intestinal” phase, the same steps were followed as above; however, after rotation for 1 h, the pH was maintained between 1.2 and 1.5. Then, 27 mL of the duodenal fluid and 9 mL of the bile fluid were added, and the pH was adjusted to 6.3 ± 0.5 by adding 37% (v/v) HCl or 1 M NaOH dropwise. The samples were then mixed for another 4 h in a water bath at 37 °C. Finally, the pH was recorded, the samples were centrifuged at 4500 × g for 15 min, decanted, and acidified with 9.0 mL of 0.1 M HNO₃ for storage. All samples were diluted 10-fold prior to the ICPMS analysis.

For the COLM-UBM, a mini-column was prepared following a method described in previous studies. Low-pressure polytetrafluoroethylene (PTFE) tubing, a peristaltic pump, and a FI manifold were used. To reduce the back-pressure, 0.6 g soil was used. Each mini-column had an inner diameter of 7 mm, an outer diameter of 8 mm, and a length of 5 cm. Glass wool (Acros Organics, Fair Lawn, NJ, USA) was cleaned overnight in 10% (v/v) HNO₃, soaked in artificial saliva to matrix-match, dried in air, and then stored in an airtight bag. The mini-columns were prepared by rolling 0.6 g of soil in glass wool and inserting it into the tubing. A glass wool plug was inserted at each end to secure the sample in place. Three blank mini-columns were prepared by inserting glass wool without any samples. Saliva, gastric juice, duodenal fluid, and bile fluid were sequentially pumped through the mini-columns while continuously monitoring the eluted elements by ICPMS.

**Aqua regia extraction.** Residual soil CRM from each mini-column was placed in a PTFE digestion vessel (Savillex) and dried. Additionally, 1 g of fresh CRM (matching that of the residual) was weighed into a separate digestion vessel to determine the total extractable concentration of each element. Then, 5 mL of aqua regia (3:1 v/v HCl: HNO₃) was made fresh daily and added to each digestion vessel. Aqua regia was also added to one blank vessel without soil. These vessels were sealed and extracted on a hotplate at ~180 °C for 2 h. The samples were then transferred to Falcon tubes, filtered through a 0.45-µm hydrophilic polyvinylidene fluoride filter (Foxx Life Sciences, Salem, NH, USA), and diluted 1000-fold with DDW.

**Instrumentation.** Samples, excluding those extracted with the UBMs, were analyzed using a Varian 820MS quadrupole-based ICPMS instrument equipped with a Pt sampler cone with a 0.9-mm diameter opening and a CRI Ni skimmer cone with a 0.4-mm diameter opening. The samples were introduced into a PTFE concentric nebulizer and a Peltier-cooled Scott-type double-pass spray chamber maintained at 3 °C. Torch alignment was conducted each day using 5 µg L⁻¹ of a tuning solution containing Be, Mg, Co, In, Ce, Pb, and Ba in 1% HNO₃. Batch bioaccessibility, total concentrations, and residual data were acquired in the steady-state mode with five points per peak, 20 scans per replicate, and five replicates per sample, whereas the COLM data were acquired in the time-resolved mode with three points per peak, one scan per replicate, and a dwell time of 80 ms. Other operating conditions are summarized in Table S2. The samples were analyzed with a 5 µg L⁻¹ In internal standard added online using a Y-connector and matrix-matched external calibration.

Samples extracted using the UBMs were analyzed with an Agilent 7500 quadrupole-based ICPMS instrument equipped with Ni cones and an octupole collision reaction system using He and H₂ gases for interference reduction. The samples were introduced using a Searay glass concentric nebulizer (AMETEK UK, Leicester, UK) and a quartz Scott-type spray chamber. Torch alignment and tuning were conducted daily using aqueous multi-element solutions. Batch UBMs were analyzed in the steady-state mode and COLM-UBM data were acquired in the time-resolved mode with 50-ns measurements and a sample-uptake rate of 1 mL min⁻¹. The samples were analyzed by adding 5 µg L⁻¹ of In internal standard to the nebulizer using a T-connector and matrix-matched external calibrations. For the UBM batch method, 25 µg L⁻¹ of multi-element standard solution and a major elemental solution were analyzed at the beginning and end of the analysis daily and after every 20 samples.

**Data processing.** All data were imported into Microsoft Excel (Microsoft, Redmond, WA, USA) for further processing. For the data acquired in the steady-state mode, the samples were internally standard-corrected, converted from count-per-second (c/s) to mg L⁻¹ using external calibration, blank subtracted, and converted to mg kg⁻¹ using the dilution factors and original sample masses. For all the data acquired in the time-resolved mode, elution profiles were internal standard corrected by dividing the analyte signal by the In signal point by point, baseline-corrected by taking an average of the baseline on either side of the peak and subtracting from the points along the peak. The peak areas were computed using the following modified trapezoidal equations:

\[
T_n = \Delta X \left[ \sum_{i=0}^{n} f(x_i) - \frac{f(x_0)}{2} - \frac{f(x_n)}{2} \right]
\]

Where \( \Delta X = (b - a)/n \), \( T_n \) is the peak area, \( f(x_0) \) is the signal at the onset of the peak, \( f(x_n) \) is the signal at point \( n \) along the peak, \( f(x_i) \) is the signal at the end of the peak, \( a \) is the first time point of the trapezoid, \( b \) is the last time point of the trapezoid, and \( n \) is the number of equally spaced trapezoids under the peak. A peak area was obtained for each extraction, which was then converted to mg kg⁻¹ using external calibration and sample masses.

The percent bioaccessibility was calculated by dividing the total bioaccessible concentration with the total concentration extracted by aqua regia. To compare the data sets, an F test for variance was first performed to compute the appropriate Student’s t-tests. Next, analysis of variance (ANOVA) was conducted using the XLSTAT add-on in Microsoft Excel.
RESULTS AND DISCUSSION

Reproducibility with the COLM versus batch methods. All analyte concentrations were above the detection limits (Table S3) that were calculated using three times the standard deviation of the blank signal. The ranges of percent relative standard deviations (%RSDs) across all elements (Table S4) were 1–130% for the US EPA batch method, 4–170% for the COLM-G, 1–110% for the UBM, 9–64% for the COLM-UBM, and 74–170% for the COLM-USP. Mean %RSDs for each method were 27% for the US EPA batch method, 66% for the COLM-G, 30% for the COLM-USP, 26% for the UBM, and 29% for the COLM-UBM. Thus, it appears that the %RSDs with the COLM using a low-pressure system (COLM-UBM) are generally smaller than those observed with the COLM using a high-pressure system (COLM-G and COLM-USP), even when the same CRM was used. In fact, with the low-pressure system, the average %RSD for the COLM-UBM is similar to that with the UBM, whereas the range of RSDs is narrower with the COLM-UBM than that obtained with the UBM. In contrast, both the range of RSDs and the mean %RSD were greater than those obtained using the batch method when a high-pressure system was used for the COLM. Given the inherent heterogeneity of soils, better reproducibility was expected with 1-g aliquots for COLM-G and COLM-USP than with 0.5-g aliquots with COLM-USM; however, the inverse result was observed. The generally high RSDs with the COLM when using a high-pressure system are thus completely unexpected. We will investigate this topic in a future work.

Stomach-equivalent extractions. A comparison of the bioaccessible concentrations of the stomach-equivalent phases obtained by different methods is shown in Table 1. BGS 102 was the only CRM analyzed by all three methods, as it has been specifically developed for bioaccessibility and was used in the validation of the UBM for As, Pb, and Cd bioaccessibility. The stomach-equivalent phase represents the bioaccessible amount in both saliva and gastric fluids. Because the NIST CRMs were previously used for validation of the USEPA method for As and Pb, they were also used for direct comparison with the COLM-G. For the US EPA method (where no saliva is used), the gastric phase is assumed to also extract what would have been extracted by saliva. With ANOVA, no statistically significant difference was observed between the batch, COLM-G, COLM-USP, and COLM-UBM methods for Cr, As, Cd, and Pb (Table 2). However, for Sb, a significant difference was observed. Further investigation into the model parameters (Table 3) indicated significant differences between the methods with different extraction fluids. However, no difference was observed between the US EPA batch and the COLM-G for Sb. Thus, the differences in the method conditions between the US EPA batch and COLM-UBM, COLM-USP, and UBM batches likely explain the different results for Sb. Additionally, none of these methods is validated for Sb determination, and the certificate of BGS 102 provides no guidance concentration for Sb (Table S1). In any case, additional

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Table 1. Bioaccessible concentrations in mg kg⁻¹ (mean ± standard Deviation, n=3) of Cr, As, Cd, Sb, and Pb in the stomach-equivalent phase of all bioaccessibility methods

<table>
<thead>
<tr>
<th>CRM</th>
<th>Method</th>
<th>Cr</th>
<th>As</th>
<th>Cd</th>
<th>Sb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 2710</td>
<td>USEPA batch</td>
<td>0.019 ± 0.024</td>
<td>195.8 ± 2.0</td>
<td>19.69 ± 0.50</td>
<td>3.81 ± 0.26</td>
<td>4362 ± 54</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>0.019 ± 0.013</td>
<td>195 ± 27</td>
<td>19.9 ± 7.0</td>
<td>3.91 ± 0.55</td>
<td>4500 ± 2200</td>
</tr>
<tr>
<td>NIST 2710a</td>
<td>USEPA batch</td>
<td>0.26 ± 0.22</td>
<td>309 ± 41</td>
<td>7.48 ± 0.98</td>
<td>9.9 ± 1.1</td>
<td>3165 ± 540</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>0.27 ± 0.46</td>
<td>318 ± 540</td>
<td>7.5 ± 6.7</td>
<td>10 ± 14</td>
<td>3400 ± 3400</td>
</tr>
<tr>
<td>NIST 2711a</td>
<td>USEPA batch</td>
<td>0.072 ± 0.039</td>
<td>33.00 ± 0.35</td>
<td>57.5 ± 1.6</td>
<td>3.94 ± 0.46</td>
<td>1204 ± 23</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>0.072 ± 0.017</td>
<td>33.8 ± 6.0</td>
<td>47.5 ± 4.2</td>
<td>3.89 ± 0.16</td>
<td>1213 ± 301</td>
</tr>
<tr>
<td></td>
<td>USEPA batch</td>
<td>3.58 ± 0.28</td>
<td>1.51 ± 0.61</td>
<td>0.319 ± 0.058</td>
<td>0.91 ± 0.14</td>
<td>35 ± 36</td>
</tr>
<tr>
<td></td>
<td>COLM-UBM</td>
<td>3.6 ± 3.9</td>
<td>1.50 ± 0.22</td>
<td>0.32 ± 0.27</td>
<td>0.92 ± 0.29</td>
<td>35 ± 14</td>
</tr>
<tr>
<td></td>
<td>COLM-USP</td>
<td>29 ± 40</td>
<td>4.5 ± 6.1</td>
<td>0.14 ± 0.18</td>
<td>0.13 ± 0.18</td>
<td>11.3 ± 8.7</td>
</tr>
<tr>
<td>BGS 102</td>
<td>UBM batch</td>
<td>35.66 ± 0.65</td>
<td>3.90 ± 0.22</td>
<td>0.2177 ± 0.0073</td>
<td>0.0325 ± 0.0062</td>
<td>17.2 ± 2.6</td>
</tr>
<tr>
<td></td>
<td>COLM-UBM</td>
<td>34.652 ± 0.033</td>
<td>4.2955 ± 0.0037</td>
<td>0.21787 ± 0.00021</td>
<td>0.032435 ± 0.000035</td>
<td>11.535 ± 0.039</td>
</tr>
</tbody>
</table>

Table 2. Analysis of variance (ANOVA) and type III sum of squares (SS) between the results from the USEPA batch method, COLM-G, COLM-USP, COLM-UBM, and UBM batch method for Cr, As, Cd, Sb, and Pb, including the number of observations (n), degrees of freedom (DF), coefficient of determination (R²), mean squares (MS), F statistic (F), and P-value (P) associated with the F statistic. The P-values in bold indicate a significant (P≤ 0.05) difference in the methods at the 95% confidence interval

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>As</th>
<th>Cd</th>
<th>Sb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
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<tr>
<td>DF</td>
<td>9</td>
<td>9</td>
<td>9</td>
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<td>9</td>
</tr>
<tr>
<td>R²</td>
<td>0.486</td>
<td>0.23</td>
<td>0.251</td>
<td>0.901</td>
<td>0.348</td>
</tr>
<tr>
<td>DF</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>SS</td>
<td>3018</td>
<td>27</td>
<td>0.073</td>
<td>2.46</td>
<td>1884</td>
</tr>
<tr>
<td>MS</td>
<td>755</td>
<td>7</td>
<td>0.018</td>
<td>0.615</td>
<td>471</td>
</tr>
<tr>
<td>F</td>
<td>2.125</td>
<td>0.672</td>
<td>0.754</td>
<td>20.484</td>
<td>1.2</td>
</tr>
<tr>
<td>P</td>
<td>0.16</td>
<td>0.628</td>
<td>0.58</td>
<td>0.0002</td>
<td>0.375</td>
</tr>
</tbody>
</table>
Table 3. Model parameters for the ANOVA between the results from the COLM-G, COLM-USP, COLM-UBM, UBM batch method and US EPA batch method for Sb, including the Student’s t (t) and P-value (P) associated with the Student’s t-test. The P-values in bold indicate a significant (P<0.05) difference between the US EPA batch method and the other methods at the 95% confidence Interval

<table>
<thead>
<tr>
<th>Method</th>
<th>Value</th>
<th>Standard error</th>
<th>T</th>
<th>P</th>
<th>Lower bound (95%)</th>
<th>Upper bound (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COLM-G</td>
<td>0.007</td>
<td>0.142</td>
<td>0.052</td>
<td>0.96</td>
<td>-0.313</td>
<td>0.328</td>
</tr>
<tr>
<td>COLM-UBM</td>
<td>-0.877</td>
<td>0.142</td>
<td>-6.199</td>
<td>&lt;0.0001</td>
<td>-1.197</td>
<td>-0.557</td>
</tr>
<tr>
<td>COLM-USP</td>
<td>-0.779</td>
<td>0.142</td>
<td>-5.507</td>
<td>&lt;0.0001</td>
<td>-1.1</td>
<td>-0.459</td>
</tr>
<tr>
<td>UBM batch</td>
<td>-0.877</td>
<td>0.158</td>
<td>-5.544</td>
<td>&lt;0.0001</td>
<td>-1.235</td>
<td>-0.519</td>
</tr>
<tr>
<td>US EPA batch</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Comparison between the COLM-UBM and conventional UBM batch extraction phases, and stomach-phase COLM-UBM and certificate bioaccessibility concentrations in mg kg⁻¹ (mean ± standard deviation, n=3) of Cr, As, Cd, Sb, and Pb in BGS 102 using Student’s t-test at 95% confidence interval

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>As</th>
<th>Cd</th>
<th>Sb</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>COLM-UBM</td>
<td>34.652 ± 0.033</td>
<td>4.2955 ± 0.0037</td>
<td>0.21787 ± 0.00021</td>
<td>0.032435 ± 0.000035</td>
<td>11.535 ± 0.039</td>
</tr>
<tr>
<td>UBM batch</td>
<td>35.66 ± 0.65</td>
<td>3.90 ± 0.22</td>
<td>0.2177 ± 0.0073</td>
<td>0.0325 ± 0.0061</td>
<td>17.2 ± 2.6</td>
</tr>
<tr>
<td>Certificate bioaccessibility</td>
<td>5.6 ± 2.4</td>
<td>13 ± 6</td>
<td>1.782</td>
<td>0.772</td>
<td>2.262</td>
</tr>
<tr>
<td>COLM-UBM</td>
<td>56.66 ± 0.091</td>
<td>6.1631 ± 0.0053</td>
<td>0.29223 ± 0.00031</td>
<td>0.050498 ± 0.000051</td>
<td>37.34 ± 0.12</td>
</tr>
<tr>
<td>UBM batch</td>
<td>2.7 ± 1.2</td>
<td>2.63 ± 0.14</td>
<td>0.061 ± 0.065</td>
<td>0.0839 ± 0.0040</td>
<td>0.42 ± 0.20</td>
</tr>
<tr>
<td>US EPA batch</td>
<td>0.005 ± 0.053</td>
<td>14.521 ± 0.039</td>
<td>10.336</td>
<td>4.303</td>
<td>4.303</td>
</tr>
</tbody>
</table>

Fig. 2 Percent bioaccessibilities (± standard deviation) of Cr, As, Cd, and Pb in BGS 102 extracted using the COLM-UBM, UBM batch bioaccessibility method (n = 3), certificate values, and bioavailability values for As and Pb. No certificate or bioavailability value has been reported for Cr and Cd (indicated as “N/A”).

This result can be explained based on the lower solubility of elements at a higher pH of 6.3 of the duodenal and bile fluids. For the sum of the saliva and stomach phases during the COLM, no statistically significant difference was observed at the 95% confidence interval between either the stomach phase of the UBM or certificate bioaccessibility values (Table 4). However, the combined stomach and intestinal fluid evidently differed between the two methods because the sample was exposed to the duodenal and bile phases separately and sequentially with COLM-UBM, which further increased the amount of the analyte released and provided a more conservative estimate of the risk. Although multiple samples can be extracted simultaneously with the UBM, all four gastrointestinal fluids can be extracted in less than 1 h with the COLM-UBM, while it takes over 5 h with the UBM.

Fig. 3 shows that the COLM-G and US EPA batch bioaccessible concentrations of Cr, As, Cd, Sb, and Pb in the
Fig. 3 Comparison of the concentrations (in mg kg$^{-1}$ ± standard deviation, n = 3) of Cr, As, Cd, Sb, and Pb in NIST 2710, NIST 2710a, NIST 2711a, and BGS 102 using COLM-G, aqua regia extraction, and certificate values.

CRMs are similar despite the COLM-G requiring a fraction of the time needed for the US EPA batch method. The values determined by the two methods did not show any statistically significant difference for any element (Table S6). The matrix spike recovery during the analysis of BGS 102 using the US EPA batch method was 96.6%.

Table 5 compares the percent bioaccessibility for Pb and As obtained using the US EPA batch method and COLM-G based on the available control limits\textsuperscript{12} and bioavailability studies\textsuperscript{40,41} for each CRM (as control limits and bioavailability results for Cr, Cd, and Sb are unavailable). For both methods, the percent bioaccessibility for Pb agreed with both the control limits and...
Table 5. Percent bioaccessibilities (mean ± standard deviation) of As and Pb with the US EPA batch method and COLM-G compared to control limits and bioavailability (animal) studies for NIST 2710, NIST 2710a, NIST 2711a, and BGS 102

<table>
<thead>
<tr>
<th>CRM</th>
<th>Method</th>
<th>As</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIST 2710</td>
<td>USEPA batch</td>
<td>41.5 ± 3.5</td>
<td>87.9 ± 2.2</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>31.9 ± 4.4</td>
<td>81 ± 40</td>
</tr>
<tr>
<td></td>
<td>Control limits</td>
<td>17-60</td>
<td>63-88</td>
</tr>
<tr>
<td></td>
<td>Bioavailability</td>
<td>37-50</td>
<td>73-79</td>
</tr>
<tr>
<td>NIST 2710a</td>
<td>USEPA batch</td>
<td>24.3 ± 3.9</td>
<td>60 ± 13</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>18 ± 31</td>
<td>61 ± 62</td>
</tr>
<tr>
<td></td>
<td>Control limits</td>
<td>24.4-52.5</td>
<td>56-69</td>
</tr>
<tr>
<td></td>
<td>Bioavailability</td>
<td>39-45</td>
<td>39-84</td>
</tr>
<tr>
<td>NIST 2711a</td>
<td>USEPA Batch</td>
<td>37.2 ± 6.2</td>
<td>85.5 ± 8.8</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>31.6 ± 5.6</td>
<td>60 ± 15</td>
</tr>
<tr>
<td></td>
<td>Control Limits</td>
<td>N/A</td>
<td>70-89</td>
</tr>
<tr>
<td></td>
<td>Bioavailability</td>
<td>N/A</td>
<td>83-89</td>
</tr>
<tr>
<td>BGS 102</td>
<td>USEPA Batch</td>
<td>1.82 ± 0.90</td>
<td>37 ± 50</td>
</tr>
<tr>
<td></td>
<td>COLM-G</td>
<td>1.48 ± 0.22</td>
<td>86 ± 34</td>
</tr>
<tr>
<td></td>
<td>Control limits</td>
<td>3.0-7.5</td>
<td>8.8-24</td>
</tr>
<tr>
<td></td>
<td>Bioavailability</td>
<td>1.72-12.56</td>
<td>10.7-19.4</td>
</tr>
</tbody>
</table>

a Derived (see “Control limits for NIST 2710” in Supplemental material); b Control limits for BGS 102 using the UBM for informational comparison only; c N/A = No control values, concentrations reportedly too low. 12

bioaccessibility ranges for most CRMs. In BGS 102, the higher Pb bioaccessibility (using either method) and lower As bioaccessibility than the reported ranges were likely because the control limits were determined with the UBM, which uses different gastrointestinal fluids.

**Verification of the mass balance for the COLM.** Fig. 3 compares the sum of bioaccessible plus residual concentrations using the COLM-G to the concentrations obtained by the US EPA batch method, aqua regia extraction, and certificate values. The values determined by the COLM-G sum and aqua regia extraction, COLM-G sum and certificate values, and aqua regia extraction and certificate values according to Student’s t-test at the 95% confidence interval were not statistically significant for any of the elements.

A similar comparison was performed using COLM-USP on BGS 102 (Fig. 4). Again, the individual Student’s t-tests between the COLM-USP sum and the aqua regia extraction concentrations, or the COLM-USP sum and the certificate values did not show any statistically significant difference at the 95% confidence interval. Additionally, most elements were extracted into the gastric phase, with only Pb having a significant portion in the intestinal phase. As previously reported for soil,37 all elements showed almost no extraction into the saliva phase.

Generally, the COLM could be incorporated into both the US EPA and UBM methods without any discrepancy in bioaccessibility, as demonstrated by ANOVA and Student’s t-test. The COLM could also provide valuable information about real-world samples through source apportionment17 and isotope ratio analysis.20

**CONCLUSIONS**

The COLM was used to measure the bioaccessibility of Cr, As, Cd, Sb, and Pb in NIST 2710, NIST SRM 2710a, NIST SRM 2711a, and BGS 102 using gastrointestinal fluids obtained using the US EPA, USP, and UBM methods. With COLM-G, the bioaccessible + residual, total aqua regia extraction, and certificate concentrations were not statistically significantly at the 95% confidence interval. Pb bioaccessibility was within the control limits and bioavailability ranges, whereas As was at the lower end of the bioavailability ranges. Mass balance was additionally verified by using the COLM-USP on BGS 102. Most of the elements extracted in the gastric phase; very little extraction was observed in saliva. ANOVA did not yield any statistically significant difference between the COLM and the UBM stomach and US EPA methods. The COLM-UBM agreed with the certificate bioaccessibility values for BGS 102.

Overall, this investigation confirms that the COLM can be incorporated into existing bioaccessibility protocols, particularly for As and Pb. Although conventional batch methods can be used to simultaneously perform multiple extractions, further refinement of the COLM could allow for a more robust bioaccessibility analysis. We plan to focus on eliminating the cause of degradation in RSD when using a high-pressure system for the COLM in our future work. Additional elements that affect human health, such as Hg, Sn, and Cu, can also be investigated using the COLM. The COLM would be particularly advantageous for Hg, as it provides fewer opportunities to Hg for adsorption to vessel walls and loss through volatilization. The development of a data processing Excel add-in would further streamline the COLM analysis, allowing for automatic peak integration and conversion from count-per-second measurements to concentrations. Additionally, the kinetic leaching information obtained through the COLM can
be used for source apportionment, which is not possible with batch bioaccessibility methods. We will analyze soils with known contaminant sources (such as Pb from gasoline) in our future work to identify different sources of elements and isotopic source apportionment, as it would allow for a more comprehensive soil analysis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information (Table S1-S6, Fig S1, and Control limits for NIST 2710) is available at www.at-spectrosc.com/as/home

AUTHOR INFORMATION

Diane Beauchemin received her Ph.D. in 1984 from Université de Montréal. She is a professor (Full) and Undergraduate Chair at Queen’s University. Her research efforts are focused on inductively coupled plasma mass spectrometry (ICPMS) and ICP optical emission spectrometry (OES) along with applications of ICPMS/OES to geochemical exploration, risk assessment of food safety, characterization of nanoparticles, and forensic analysis. She has been working as member of editorial board for Atomic Spectroscopy. Diane Beauchemin won the Alan Date Memorial Award (1988) from VG Elemental, the Distinguished Service Award (2001) from Spectroscopy Society of Canada, the Maxxam Date Memorial Award (1988) from VG Elemental, the Distinguished Service Award (2017) and Clara Benson Award (2019) from Canadian Society for Spectroscopy, and the Gerhard Herzberg Award (2018) from the Canadian Society for Analytical Sciences and Spectroscopy. She is author or co-author of over 100 articles published in peer-reviewed scientific journals.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada for funding (RGPIN 39487-2018 to DB and RGPIN 2018-04885 to IK). AK also thanks David Patch for training, Queen’s University School of Graduate Studies for graduate awards, and Mitacs Globalink for funding (FR38334).

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At. Spectrosc. 2022, 43(2), 107–116.


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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Received: October 21, 2021; Revised: December 01, 2021; Accepted: December 02, 2021; Available online: December 05, 2021.

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 ± 0.03‰ (n = 42, 2 standard deviations (2σ)) and ± 0.05‰ (n = 42, 2σ), 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 \( \Delta\delta^{66}\text{Zn}_{\text{with-with}} \) \( \equiv \) \( \delta^{66}\text{Zn}_{\text{with-with}} - \delta^{66}\text{Zn}_{\text{with}} \) ranging from -0.04 to +0.01‰ and \( \Delta\delta^{67}\text{Zn}_{\text{with-with}} \) ranging from -0.06 to +0.01‰. 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, \( ^{64}\text{Zn} \), \( ^{66}\text{Zn} \), \( ^{67}\text{Zn} \), \( ^{68}\text{Zn} \), and \( ^{69}\text{Zn} \) 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 $\delta^{66}$Zn, Zn isotopes may be used as a tracer for studying hydrothermal processes. Therefore, the Zn isotopes in sphalerites 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 Fe(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 $\Delta^{66}$Cu$_{\text{without}}$ with ranging from −0.04 to +0.02‰, 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 Ga 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 Polyfluroalkoxy (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 $\delta^{66}$ZnMC-Lyon = $+0.12 \pm 0.04$‰ 24 and $\delta^{66}$ZnMC-Lyon = $-2.45 \pm 0.02$‰, 25 respectively, relative to the reference material JMC-Lyon. Alfa Cu (Stock #13867, Lot#012782G, 1000 µg 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
aliquote 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. 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 preconditioning. 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 6 mL 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 isotopes analysis, L4, L3, L2, Ax, H2, and H4 Faraday cups were used to collect ⁶⁵Ni, ⁶³Cu, ⁶⁴Zn, ⁶²Cu, ⁶⁰Zn, 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:

\[
\delta^{66}\text{Zn}(\%o) = (\delta^{66}\text{Zn}_{\text{sample}}/\delta^{66}\text{Zn}_{\text{NIST SRM683}} - 1) \times 1000 + 0.12
\]

\[
\delta^{67}\text{Zn}(\%o) = (\delta^{67}\text{Zn}_{\text{sample}}/\delta^{67}\text{Zn}_{\text{NIST SRM683}} - 1) \times 1000 + 0.18
\]

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, willenite 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 δ⁶⁶Zn of NIST SRM 682 solution without column chromatography was -2.41 ± 0.04‰ (2s, n=3), which was identical with the reported reference value of -2.45 ± 0.02‰. All pairs (with and without column) showed similar Zn isotopic ratios with Δ⁶⁶Zn without ranging from -0.04 to 0.01‰ and Δ⁶⁶Zn without 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 δ⁶⁶Zn value of -2.41 ± 0.05‰ (2s, n = 3), while measurements of the column-treated solution yielded a mean δ⁶⁶Zn value of -2.42 ± 0.05‰ (2s, n = 12). These values agree well with the reported value of -2.45 ± 0.02‰ for reference δ⁶⁶Zn, 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.

<table>
<thead>
<tr>
<th>Instrumental parameters</th>
<th>Nu plasma 1700</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1300 W</td>
</tr>
<tr>
<td>Cooling gas</td>
<td>13.0 L min⁻¹</td>
</tr>
<tr>
<td>Auxiliary gas</td>
<td>0.8 L min⁻¹</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>39 Psi</td>
</tr>
<tr>
<td>Background of ⁶⁶Zn</td>
<td>&lt;3 mV</td>
</tr>
<tr>
<td>Sample cone and skimmer cone</td>
<td>Ni orifice</td>
</tr>
<tr>
<td>Resolution mode</td>
<td>Low resolution</td>
</tr>
<tr>
<td>Mass separation</td>
<td>0.5</td>
</tr>
<tr>
<td>Sample uptake</td>
<td>100 µL min⁻¹</td>
</tr>
</tbody>
</table>
caused by the concentration and acidity mismatches during mass studies have shown that the stable isotopic deviation of Zn can be 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. In this study, we used 1.0 μg g⁻¹ of Alfa Zn solution diluted with 2.0% (v/v) HNO₃ 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 μg g⁻¹ Alfa Zn solutions diluted with 1.5 to 2.4% (v/v) HNO₃.

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

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

“-” 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

<table>
<thead>
<tr>
<th>Minerals</th>
<th>δ⁶⁷Zn_without (%)</th>
<th>2s</th>
<th>n</th>
<th>δ⁶⁷Zn_with (%)</th>
<th>2s</th>
<th>n</th>
<th>Δ⁶⁷Zn_without-with (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphalerite (KKZ61)</td>
<td>0.21</td>
<td>0.02</td>
<td>3</td>
<td>0.23</td>
<td>0.06</td>
<td>3</td>
<td>-0.02</td>
</tr>
<tr>
<td>Sphalerite (Du2018-832)</td>
<td>-0.07</td>
<td>0.02</td>
<td>3</td>
<td>-0.04</td>
<td>0.04</td>
<td>3</td>
<td>-0.03</td>
</tr>
<tr>
<td>Sphalerite (Du2018-8321)</td>
<td>0.13</td>
<td>0.02</td>
<td>3</td>
<td>0.17</td>
<td>0.04</td>
<td>3</td>
<td>-0.04</td>
</tr>
<tr>
<td>Sphalerite (DBK261)</td>
<td>0.13</td>
<td>0.03</td>
<td>3</td>
<td>0.15</td>
<td>0.03</td>
<td>3</td>
<td>-0.02</td>
</tr>
<tr>
<td>Sphalerite (ZK2002-4)</td>
<td>0.20</td>
<td>0.03</td>
<td>3</td>
<td>0.22</td>
<td>0.03</td>
<td>3</td>
<td>-0.02</td>
</tr>
<tr>
<td>Sphalerite (GBW07270)</td>
<td>-0.05</td>
<td>0.01</td>
<td>3</td>
<td>-0.03</td>
<td>0.03</td>
<td>3</td>
<td>-0.02</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>-0.27</td>
<td>0.01</td>
<td>3</td>
<td>-0.26</td>
<td>0.04</td>
<td>3</td>
<td>-0.01</td>
</tr>
<tr>
<td>Willemite</td>
<td>0.26</td>
<td>0.07</td>
<td>3</td>
<td>0.26</td>
<td>0.02</td>
<td>3</td>
<td>0.00</td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>0.96</td>
<td>0.05</td>
<td>3</td>
<td>0.96</td>
<td>0.02</td>
<td>3</td>
<td>0.00</td>
</tr>
<tr>
<td>Troostite</td>
<td>0.09</td>
<td>0.05</td>
<td>3</td>
<td>0.11</td>
<td>0.01</td>
<td>3</td>
<td>-0.02</td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>0.04</td>
<td>0.02</td>
<td>3</td>
<td>0.03</td>
<td>0.01</td>
<td>3</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Note: δZn_without and δZn_with 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. Δ⁶⁷Zn_without-with = δ⁶⁷Zn_without - δ⁷⁷Zn_with, Δ⁶⁷Zn_without-with = δ⁶⁷Zn_without - δ⁷⁷Zn_with.
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 $\delta^{64}$Zn and $\delta^{66}$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 $\delta^{64}$Zn and $\delta^{66}$Zn values were within a deviation of 0.05‰. When the difference is ≥ 20%, the offset in $\delta^{66}$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 μg g$^{-1}$, we measured a series of Alfa Zn solutions with different Zn concentrations ranging from 0.5 to 2.0 μg 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 $\delta^{64}$Zn and $\delta^{66}$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 $C_{\text{sample}}/C_{\text{standard}}$ ranging from 0.5 to 2.0, the $\delta^{64}$Zn and $\delta^{66}$Zn values of all samples agreed 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 ± 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 were of different concentrations were doped into 1.0 μg 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 $\delta^{64}$Zn and $\delta^{66}$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 $^{64}$Ni$^+$ and $^{48}$Ti$^{18}$O$^+$ can produce intense isobaric interferences on $^{64}$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, the $\delta^{64}$Zn and $\delta^{66}$Zn values can be accurately obtained within the 0.05‰ deviation. When the Ni/Zn ratio is less than 0.005, $\delta^{64}$Zn and $\delta^{66}$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 and 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 $\delta^{66}$Zn was ± 0.03‰. The NIST SRM 682 solutions possessed a mean $\delta^{66}$Zn of -2.41 ± 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 μg 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 $\delta^{66}$Zn and $\delta^{67}$Zn measurements of NIST SRM 682 solution.

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

Fig. 6 $\delta^{66}$Zn and $\delta^{67}$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 $\Delta^{66}$Zn and $\Delta^{67}$Zn of sphalerites and other types of Zn-rich minerals, respectively.

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. 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. proposed that Ca isotope ratios can be measured without column 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 $\delta^{66}$Zn and $\delta^{67}$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. 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.
chemistry by TIMS using the $^{48}$Ca–$^{49}$Ca double-spikes 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 minerals 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 $\Delta^{66}$Zn without values range from -0.04 to +0.01‰ and the $\Delta^{67}$Zn without values range from -0.06 to +0.01‰. Among all the minerals, nine samples possess $\Delta^{66}$Zn without values ranging from -0.02 to +0.01‰, and eight samples demonstrate $\Delta^{67}$Zn without 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 isotope ratios obtained without column chromatography are consistent with those obtained with column chromatography, and the $\Delta^{66}$Zn without and $\Delta^{67}$Zn 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 $\pm 0.03‰$ (2s) and $\pm 0.05‰$ (2s) for $\delta^{66}$Zn and $\delta^{67}$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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ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (42173033, 41825007, 42073051, and 41803040) and the MOST Research Foundation from the State Key Laboratory of Continental Dynamics (207010021).

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Depth Profiling at a Steel-aluminum Interface Using Slow-flow Direct Current Glow Discharge Mass Spectrometry


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Received: June 16, 2021; Revised: November 16, 2021; Accepted: November 17, 2021; Available online: Dec 03, 2021.

DOI: 10.46770/AS.2021.607

ABSTRACT: Direct current glow discharge mass spectrometry (dc-GDMS), which relies on sector field mass analyzers, is not commonly used for depth profiling applications because of its slow data acquisition. Nevertheless, dc-GDMS has good reproducibility and low limits of detection, which are analytical features that are encouraging for investigating the potential of dc-GDMS for depth profiling applications. In this work, the diffusion of traces of chromium and nickel was profiled at the interface of a steel-aluminum bilayer using a new sensitive dc-GDMS instrument. The depth profile of the non-treated sample was compared with that of a heat-treated specimen at 400°C for 30 min. Scanning electron micrographs, energy dispersive X-ray spectroscopy (EDS), and electron probe microanalysis (EPMA) were used to study the diffusion process. The results of the study show that both chromium and nickel are enriched at the steel-aluminum interface, with higher concentrations of both elements for the heat-treated specimen. Two peaks for both chromium and nickel were clearly present at the interface, with a high concentration of chromium in the aluminum layer. This observation is likely a consequence of elemental diffusion from the interface towards the aluminum layer. The presence of the third layer, steel beneath the aluminum layer, might also have contributed to this observation.

INTRODUCTION

The manufacturing of advanced materials with desirable mechanical properties is important for solving some of today’s challenges, such as excessive carbon dioxide emissions. Steel and aluminum-based alloys are among the most common metals used worldwide for automotive, aviation, and marine applications. While steel offers the advantages of high strength and low cost, aluminum alloys are lightweight and are corrosion resistant. One way to reduce carbon dioxide emissions is by using lightweight materials in automotive components. Therefore, joining steel to aluminum in these structures can improve mechanical properties while reducing fuel consumption. Thus, research is underway to understand how the manufacturing of metal composites can be improved. The manufacturing process used during the joining process has a major influence on the strength of the final joint and the performance of the final processed material. During the bonding process it is possible to form intermetallic layers with mechanical properties different from those of the base materials. For instance, the intermetallic layer thickness, and type of phases present, can influence the strength of the final joint. The chemical composition of the base materials has been found to influence the formation of intermetallic phases along the joint interface. However, the exact mechanism of phase formation and the influence of each element are not well understood. Hence, there is a need to develop profiling techniques that monitor the changes in the concentration of alloying elements near the interface to understand elemental diffusion.
Several analytical techniques are available for the depth profiling of materials, including but not limited to secondary ion mass spectrometry (SIMS), laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), glow discharge optical emission spectroscopy (GDOES), and glow discharge mass spectrometry (GDMS). In this study, we focus on GDMS-related depth profiling and present the features and limitations of various types of GDMS instruments. A popular instrument for depth profiling is a GDMS instrument with a pulsed-radio frequency source coupled to a time-of-flight (TOF) mass analyzer. Some of the particularly useful features of this instrument include acquisition of full spectra at a high speed, time-gated detection, separation of various glow discharge regions, reduction of interference and good signal to noise ratio, direct analysis of non-conductive materials, and the possibility of analysis of thermosensitive samples. Furthermore, the use of the pulsed mode increases the instantaneous power while reducing the heat generation during the sputtering process, thereby increasing the signal intensity. This instrument type was successfully used for the profiling of ion implants in silicon substrates and for the profiling of layered materials (Nb/Al, Nb/Al1-x-Cox, and Si/Co) of various thicknesses. Furthermore, applications of this instrument type in solar cell research for the profiling of silicon thin films and cadmium telluride (CdTe) solar cells have been investigated. Another notable feature of this instrument is the ability to generate molecular ions, which allows for the characterization of polymer-based composite materials. Plasma profiling time-of-flight mass spectrometry (PP-TOFMS) is one of these instrument types introduced by the HORIBA Jobin-Yvon (France) company in 2014. This instrument allows the characterization of flat-shaped samples in either continuous or pulsed radiofrequency (RF) mode. Likewise, the Lumas 30 (Lumex Ltd., Russia) instrument introduced in 2007 uses hollow cathode geometry for sample characterization in pulsed direct current mode using a TOF analyzer. In 2014, Bodnar et al. reported the depth profiling measurement of fluorine in a fluorine-doped potassium titanyl phosphate crystal material. Another recent study from the same group reported depth profiling of a conductive metal coating on a silicon substrate as well as semiconductive and multi-layer nonconductive coatings on glass substrates.

TOF instruments have a limit of detection in μg/g, which is two to three orders of magnitude lower than sector-field instruments. Hence, the sector-field instruments are more suitable when detecting low levels of impurities is important, for instance in solar cell research. Sector-field instruments, such as the Element GD (Thermo Electron now Thermo Fischer Scientific, Germany, 2005) and VG 9000 (VG Elemental, UK, production discontinued), are currently the most common GDMS instruments in research institutes, universities and contract laboratories. These instruments are often referred to as “fast-flow” and “slow-flow” instruments respectively, which are named after the discharge gas flow rates. It is worth mentioning some notable research works that use these instruments.

Using fast-flow GDMS, Su et al. demonstrated the depth profiling of major and trace elements in nickel-based superalloys. Di Sabatino et al. estimated the limits of detection of impurities in silicon used for solar cells using matrix-specific relative sensitivity factors (RSFs). The profiling of impurities in solar cell silicon at the ng/g level was carried out as well. Likewise, other notable study from the same group is measurement of copper diffusion in silicon substrate.

For quality control of the final silicon wafers, the impurity content of processed ingots is routinely assessed. In such studies, the distribution of dopants is investigated in entire silicon ingots, which can be of several meters in height. As the depth profiling of such large ingots is not possible, the ingots are systematically sampled at various locations of the ingot where bulk analysis of each slice is performed. The bulk measurements of dopants of several samples obtained from different locations were combined, resembling a depth profile.

Notable work has been carried out using the VG 9000 for the characterization of coated and layered materials, such as platinum-aluminide coatings on a nickel base and hafnium-doped aluminide coatings. As VG 9000 production was discontinued in 2005, there is a need to understand the depth-profiling capabilities of similar slow-flow instruments that are currently available, such as the Astrum GDMS (Nu Instrument, UK) and the AutoConcept GD 90 (Mass Spectrometry Instruments, UK). Despite their introduction in 2010 and 2008 respectively, there is limited information available in the literature demonstrating the depth-profiling capabilities of these two instruments. In this work, nickel and chromium present in the steel-aluminum bilayer were profiled using an Astrum GDMS instrument. This work aims to improve the understanding of the diffusion of trace elements that are involved in the formation of intermetallic layers.

**QUANTIFICATION OF IMPURITIES**

For this work, the determination of the concentration of chromium and nickel present in the bilayer material was performed using a certified aluminum reference material. At present, it is not possible to correct for differences in the sputtering rates of the steel and aluminum matrices. Therefore, a compromise was made by assuming that a steel layer was present on the top of the aluminum layer. RSFs were applied to the depth profiles using several certified aluminum reference materials to calibrate the data. Eq. 1 was used to determine the concentration of impurity elements.

\[
C_{X/Al} = \frac{I_X}{I_{Al}} \times \frac{A_{Al}}{A_X} \times \text{RSF}_{X/Al}
\]

(1)
where \( CX/Al \) is the mass fraction of impurity element/isotope \( X' \) present in the aluminum matrix, \( I_{X'} \) and \( I_{Al} \) are the intensities of the impurity analyte and aluminum, respectively, \( A_{X'} \) and \( A_{Al} \) are the natural isotope abundances of the impurity analyte and aluminum, respectively, and \( RSF_{X'/Al} \) represents the relative sensitivity factor of a specific analyte, \( X' \) present in an aluminum matrix. RSFs are estimated mathematically as the inverse of the slope of the calibration curve \( IBR_{X'/Al} \) versus mass fraction \( CX/Al \) (Eq. 2). The ion beam ratio \( IBR_{X'/Al} \) was generated by measuring the materials.

\[
RSF_{X'/Al} = \frac{CX/Al}{IBR_{X'/Al}}
\]  

(MATERIALS AND METHODS)

**Sample preparation.** The steel-aluminum joints were prepared by a cold roll bonding procedure using 99.8 wt% AA1080 grade aluminum and 355 MC E grade steel (with matrix composition of 0.07 wt% C, 0.01 wt% Si, 0.62 wt% Mn, 0.05 wt% Al, 0.03 wt% Cr and 0.03 wt% Ni) as base materials. The sample materials were cut to the desired dimensions of 120 mm \( \times \) 15 mm. The initial thicknesses of the aluminum and steel before rolling were 0.4 mm and 1 mm, respectively. Prior to this, the steel sample was rolled at room temperature from 3 mm to 1 mm, followed by annealing at 750 °C for 4 h in a furnace under an argon atmosphere to soften the steel and prevent oxidation. The total thickness reduction of the rolled composite material was in the range of 60%–65%. It should be noted that the steel layer was grinded. A detailed procedure for the sample production can be found in literature³.

The sample materials were cleaned with acetone and the surface was prepared by manual brushing with a 0.3 mm steel-wire brush followed by blowing clean with compressed air. The purpose of the brushing step was to generate a rough surface to promote bonding. The specimens were stacked together in the sequence steel-aluminum-steel and fastened with aluminum rivets at each end to prevent lateral movement during rolling. To further promote bonding, the stacked material was preheated in a furnace for 10 min at 185°C until the desired rolling temperature of 150°C was reached. After preheating, the samples were removed from the furnace and rolled using a high rolling mill with a roll diameter of 205 mm and a rolling speed of approximately 10 rpm. After rolling, the material was immediately submerged in water.

The rolled steel-aluminum-steel composite material was cut by SiC cutoff blade to produce samples with dimensions of 30 mm \( \times \) 25 mm to fit the GDMS flat sample holder. One set of samples was heated at 400 °C for 30 min. The composite material was manually grinded to reduce the thickness of the steel layer using a series of silicon carbide papers to obtain a mirror finish. Finally, the specimen was cleaned with ethanol and dried in air.

**GDMS method.** Before analyzing the samples, the instrument (Astrum, Nu Instruments, UK) was tuned and calibrated for different masses with tantalum: \(^{12}\text{C}, \(^{36}\text{Ar}^{+}, \(^{36}\text{Ar}^{+}, \(^{40}\text{Ar}^{+}, \(^{181}\text{Ta}^{+}, \(^{181}\text{Ta}^{+}\text{Ar}^{+}\) at discharge conditions of 2 mA and 1 kV. The \(^{181}\text{Ta}^{+}\text{Ar}^{+}\) signal intensity of 1.4 \( \times \) 10³ A was observed with a magnet scan at a resolution power of approximately 4000 (M/ΔM, 10% of peak height approach). The glow discharge cell of the instrument was cryogenically cooled, and 99.9999% argon was used as the discharge gas. For GDMS, the size of the orifice of the tantalum front plate used in the flat sample holder determines the lateral resolution. For this study, an orifice with a diameter of 10 mm was used, which contributed to the lateral size of crater profiles of approximately 10 mm. It is important to mention that for GDMS-related depth profiling, the edge of the crater is also analyzed. For \(^{58}\text{Fe}^{+} \text{and}^{27}\text{Al}^{+}\) an integration time of 160 ms was used. These elements were detected using a Faraday cup. For \(^{52}\text{Cr}^{+} \text{and}^{60}\text{Ni}^{+}\) an integration time of 80 ms was used. These elements were detected using an electron multiplier. The most abundant isotope of nickel, \(^{58}\text{Ni}^{+}\), suffers from monoatomic interference due to \(^{58}\text{Fe}^{+}\). Therefore, \(^{60}\text{Ni}^{+}\) was chosen as the isotope for this study. The measurements were performed at a resolution power of approximately 4000 (M/ΔM, 10% of the peak height approach). For depth profiling study, the composite and base materials were subjected to glow discharge setting of 5 mA, 0.75 kV in a constant current mode. The current and voltage readback values were largely stable during the analysis period. The GDMS craters were measured mechanically using a profilometer (MarSurf M 400, Mahr GmbH, Göttingen, Germany) immediately after the sputtering event.

**Other complimentary techniques.** After GDMS analysis, the composite materials were cut in half and immobilized on a substrate using epoxy resin. The samples were prepared by standard metallographic procedures, involving grinding on silicon carbide discs, and polishing on cloth with diamond paste until a deformation-free mirror finish was obtained. The craters were further investigated using an optical microscope (Zeiss Axiosvert, Carl Zeiss AG, Jena, Germany). Scanning electron microscope (SEM) images were taken using a Zeiss Supra 55-VP (Jena, Germany) and energy-dispersive X-ray spectroscopy (EDS) standardless analysis using an EDAX Octane PRO-A detector (Ametek, USA). Elemental analysis was carried out using JEOL JXA-8500F electron probe microanalyzer (EPMA) with an electron beam size of 1 μm. For quantitative wavelength-dispersive X-ray spectroscopy (WDS) in EPMA, a pure standard of 100 % aluminum and one steel standard SRM663 were used. The composition of the steel standard was 95.01 wt% iron, 0.24 wt% aluminum, 1.31 wt% chromium and 0.32 wt% nickel.
RESULTS AND DISCUSSION

Crater shape. The prerequisite for depth profiling applications is uniform sputtering of the sample. Therefore, after completion of the sputtering event, it is advisable to check the crater shape. Ideally, the crater bottom should be flat with a minimum edge effect and a crater wall that is perpendicular to the crater bottom. The evolution of the crater profile with changes in the glow discharge condition can be found in the literature.31 The crater shape can also vary from one matrix specimen to another. Therefore, as a first step we determined the discharge conditions that lead to the optimum crater shapes for the base materials. Figs. S1A and S1B represent the crater shape for aluminum and steel base materials, respectively, after sputtering for 1.5 h. The sputtering rate was 129.4 nm/min and 79 nm/min for aluminum and steel, respectively, at discharge condition of 5 mA and 0.75 kV. The argon flow of 0.69 ml/min and 0.48 ml/min were used for obtaining the discharge condition for aluminum and steel base materials, respectively.

It is important to mention that the shape of the steel crater profile is not ideal. However, as the idea was to profile the steel-aluminum joint, a compromise had to be made. Furthermore, any change in the glow discharge condition during the sputtering process (with the aim of obtaining the optimum crater) would influence the signal stability. Additionally, the specimen analysis brought other challenges such as matrix-specific calibration, the lack of direct access to aluminum (stacked between two steel layers), and the slow sputtering rate of Astrum GDMS instrument. Hence, the steel layer was manually grinded, where the composite material was assumed to be steel on top of the aluminum rather than the steel-aluminum bilayer. Therefore, only one side of the composite material was characterized.

For simplicity, the heat-treated composite material is referred to as the “treated” sample while the non-heat-treated material is referred to as the “untreated” sample. The crater shapes of the untreated and treated samples are presented in Fig. 1, where the untreated sample was sputtered to a greater depth compared to the treated sample. The total sputtering time for untreated and treated samples were 16 h 20 min and 8 h 30 min corresponding to sputtering rates of 143.9 nm/min and 111.3 nm/min, respectively. The differences in sputtering depth and time are related to inconsistency in the steel layer thickness in the samples. The untreated sample (Fig. 2) had a thicker steel layer compared to the treated sample (Fig. 3). The optical microscopy images shown in Figs. 2 and 3 were taken after cutting the sample at the crater, followed by investigation of the lateral sections of the samples. Furthermore, the redisposition of steel and aluminum layers outside the crater was clearer for the untreated sample compared with the treated sample.

RSFs determination. In this work, the reported concentration of impurities is based on the RSFs determined using certified aluminum reference materials. Using Eq. 2, these values are determined as the inverse of the slopes obtained from the linear plots presented in Fig. 4 for chromium and nickel. The RSFs were calculated at discharge conditions of 5 mA, 0.75 kV. The RSFs values for $^{52}$Cr and $^{60}$Ni in aluminum were found to be 0.91 and 1.25, respectively.

Fig. 1 The crater profile of untreated (A) and treated (B) samples after sputtering for 16 h 20 min and 8.5 h at glow discharge condition of 5 mA, 0.75 kV using argon flow rates of 0.85 ml/min and 0.83 ml/min respectively.

Fig. 2 The lateral view of the untreated sample cut at the crater after GDMS sputtering. Optical microscopy images of the crater at low resolution (top) with a shaded area around which a high-resolution image is taken (bottom).

Fig. 3 The lateral view of the treated sample cut at the crater after GDMS sputtering. Optical microscopy images of the crater at low resolution (top) with a shaded area around which a high-resolution image is taken (bottom).
Depth profiling. The GDMS bulk measurements of the aluminum and steel base materials are presented in Table S1. The same discharge conditions were used (5 mA, 0.75 kV) for the base materials as for the composite materials to enable direct comparison between them. As observed from the depth profile (Fig. 5), the initial concentrations of chromium and nickel in steel were comparable to the bulk concentrations in the steel base material (Table S1). This observation was consistent for both untreated and treated samples. Likewise, the bulk concentration of nickel in the aluminum base material was consistent with its concentration in the aluminum layer for both untreated and treated samples. However, the concentration of chromium in the aluminum layer was more than two orders of magnitude higher than the bulk concentration in the aluminum base material. The values were surprisingly high and therefore were verified by using the complementary technique of EPMA. The EPMA results confirmed a higher chromium concentration in the aluminum layer (Table S2) compared to the bulk concentration in the aluminum base material (Table S1). These EPMA experiments were performed for both treated and untreated samples. The average chromium concentration of 830 µg/g for the treated sample measured by EPMA is comparable to the approximate concentration of 900 µg/g measured from the GDMS depth profile in the aluminum layer. A plausible explanation for the higher chromium content in the aluminum layer is the high diffusion coefficient of chromium in aluminum compared to chromium in steel.\(^{32,33}\) Furthermore, it is worth repeating that aluminum is stacked between two steel layers, which may potentially increase the chromium diffusion to aluminum. It is important to stress that the concentrations of both chromium and nickel are slightly higher in the treated sample than in the untreated one, which can be explained through heat treatment of 400°C for 30 min. As the untreated sample was also subjected to preheating before the rolling process, and diffusion can occur as a result of exposure to elevated temperatures during the rolling process. Therefore, this is probably why chromium concentration in untreated sample is also high both in depth profile (Fig. 5) and EPMA bulk measurement (Table S2) similar to the treated sample.

Depth resolution. Depth resolution is often used to estimate the ability of analytical techniques to measure local changes of analytes as a function of depth. In general, for GDMS studies, the depth (typically expressed in terms of µm or nm) between 16 % and 84 % of analyte concentration is taken as the depth resolution.\(^{34}\) The lower the depth resolution, the sharper the transition of changes in the depth profile. In the present study, untreated and treated samples exhibited depth resolutions of about 29 µm and 13 µm, respectively (Fig. 5). For GDMS depth profiling, an edge effect is non-homogenous sputtering of the crater center as compared to the crater edge that contributes to a reduced depth resolution. For the samples investigated in this study, non-homogenous sputtering was greater for the untreated sample than for the treated sample (Fig. 1), contributing to a reduced depth resolution of the untreated sample profile. In addition to the edge effect, the diffusion length of the analytes and the layer thickness also affect the depth resolution. Wang et al. demonstrated that a sample with a film thickness in the range of 4–5 µm resulted in a depth resolution in the range of 0.5–0.7 µm.\(^{35}\) A slow-flow instrument (AutoConcept GD 90) was used in that study, which is similar to the Astrum GDMS in terms of operating parameters and sputtering rates.\(^{35}\) Therefore, poor depth resolution is potentially linked to the thickness of the steel layer for the samples used in the present study, which is approximately 80 and 30 µm for the treated and untreated samples, respectively (Figs. 2 and 3).

Intermetallic Layer. Enrichment of both the impurity elements of chromium and nickel with two distinct transitions for each element was observed at the interface for both the untreated and treated samples. This can be attributed to the free surface energy at the interface, which leads to the segregation of the impurity elements. The same sample treated at a slightly higher
temperature (450°C for 2 h) has been shown to result in the formation of two distinct phases within the intermetallic layer (IML): Fe₄Al₁₃ adjacent to the aluminum layer and Fe₂Al₅ adjacent to the steel layer. However, such results were not obtained for the samples used in this study. Since Fe₄Al₁₃ is reported to form prior to Fe₂Al₅ at the interface, only one phase might be present after the heat treatment at 400°C for 30 min, as shown in Fig. 6. However, the IML formed was too thin to generate EPMA results because of the 1 µm electron beam cross-section. In this case, the two peaks (Fig. 5) might correspond to differences in impurity concentrations of nickel and chromium, where the smaller peak is a buildup in the steel material, while the largest peak is the intermetallic layer. Furthermore, the results clearly show that even a small amount of chromium and nickel in the steel base material accumulates at the interface, thereby influencing the IML formation and growth. Previous studies have demonstrated the enrichment of impurities at the interface where steel base materials with higher chromium

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**Fig. 5** Depth profile of iron and aluminum (A), chromium (B) and nickel (C) of untreated (left) and treated (right) steel-aluminum composite material after subjecting to discharge condition of 5 mA, 0.75 kV using argon flow rates of 0.85 ml/min and 0.83 ml/min, respectively.
and nickel contents were used.\textsuperscript{5,37}

Interestingly, the results from SEM and EDS indicate that chromium-iron precipitates were found in the aluminum layer for both treated and untreated samples, indicating diffusion of both chromium and iron into the aluminum layer (Fig. S2 & Table S3). Previous studies have indicated that diffusion of chromium towards aluminum potentially prevents further migration of iron to the aluminum layer.\textsuperscript{36}

**CONCLUSIONS**

This study presents the first results of depth profile analysis of a steel-aluminum bilayer using the Astrum GDMS instrument. The slow sputtering rate of the Astrum GDMS posed challenges for metallographic sample preparation, where grinding of the steel layer was required and could not be reproduced. The composite material was treated as a steel layer on top of aluminum, to allow the use of RSFs from a certified aluminum reference material to calibrate the data. The results of the study indicated an enrichment of both chromium and nickel at the steel-aluminum interface, which was higher in the heat-treated sample than in the untreated one. There are valuable findings in this study on the development of thin intermetallic layers caused by the short heat-treatment time, and on the diffusion behavior of chromium. The observation of higher chromium content in the aluminum layer has not been reported in the literature as far as the authors’ knowledge. These results increase our knowledge of the mechanisms that govern the formation and growth of intermetallic phases and the influence of alloying elements. This is helpful for optimizing the manufacturing of steel-aluminum joints with regard to the material composition in the joints and the optimal post-joining heat treatment.

**ASSOCIATED CONTENT**

**Supporting Information.** The Supporting Information (Figs. S1-2, Tables S1-3) is available at www.at-spectrosc.com/as/home

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENT**

The authors are thankful to senior engineer Morten Peder Raanes at the Department of Materials Science and Engineering at NTNU for EPMA analysis. Likewise, the engineers Elin Harboe Albertsen, Anita Storsve and Pei Na Kui from the same department are thanked for continuous support in the laboratory.

**REFERENCES**

Zircon ZS - a Homogenous Natural Reference Material for U–Pb Age and O–Hf Isotope Microanalyses

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Received: January 17, 2022; Revised: April 01, 2022; Accepted: April 01, 2022; Available online: April 06, 2022.
DOI: 10.46770/AS.2022.033

ABSTRACT: A well-formed natural zircon crystal ~10 g in weight from Sri Lanka was introduced as a reference material for the geochemical microanalysis of U–Pb–O–Hf isotopes. For the U–Pb system, a total of 96 secondary ion mass spectrometry (SIMS) and 174 laser-ablation inductively coupled plasma mass spectrometry analyses showed that zircon ZS was homogeneous within a ~20 μm area level. According to chemical abrasion isotope dilution thermal ionization mass spectrometry, the U–Pb system is concordant within the uncertainties, yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 560.6 ± 1.3 Ma (2 standard deviation (SD), n = 18) and a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 561.1 ± 3.5 Ma (2SD, n = 18). The U and Th concentrations were 570 ± 40 μg g$^{-1}$ (1SD) and 132 ± 28 μg g$^{-1}$ (1SD), respectively. The homogeneity of the O isotopes was confirmed by 261 SIMS analyses, and that of Hf isotopes was determined by 100 laser-ablation multi-collector inductively coupled plasma mass spectrometry (MC–ICP–MS) analyses. A weighted mean δ$^{18}$O value of 13.69‰ ± 0.11‰ (2SD, n = 12) obtained by laser fluorination isotope ratio mass spectrometry (IRMS) and a weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ value of 0.281668 ± 0.000010 (2SD, n = 7) by solution MC–ICP–MS are recommended as the best reference values for zircon ZS.

INTRODUCTION

Zircon (ZrSiO$_4$) is commonly found in various types of intermediate-acid igneous rocks, metamorphic rocks, and sedimentary rocks. The in-situ U–Pb age, Hf–O isotopes, and geochemical composition of zircon can be obtained through the use of microbeam analysis techniques such as secondary ion mass spectrometry (SIMS) and laser-ablation inductively coupled plasma mass spectrometry (LA–ICP–MS), which have a broad range of applications in isotope geochronology and geochemical tracer research. The matrix effect is one of the main concerns that need to be considered during SIMS and LA–ICP–MS microanalyses. Matrix-matched reference materials are key to overcoming the matrix effect and obtaining accurate results. More than 20 zircon age standards have been reported, with several zircons such as SA01, SA02, and SA02 serving as good standards. However, qualified zircon reference materials are still rare because they need to meet the following criteria: (1) uniformity in radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, and $^{207}\text{Pb}/^{235}\text{U}$; (2) isotopic concordance; (3) a negligible concentration of initial Pb; and (4) sufficient radiogenic Pb concentration. The first SIMS zircon standard SL3, which has a high U content, can introduce matrix effects during the SIMS calibration procedure. The low radiogenic Pb makes it difficult for the widely used zircon standard...
cathodoluminescence (CL) presented in the reflection grains.

were polished to obtain flat surfaces and expose the interior of the Tanz, selected polished portion of small fragments that were obtained after crushing. The selected polished zircon fragments that were embedded in epoxy are presented in the reflection (c–e), back-scattered electron (BSE) (f–h), and cathodoluminescence (CL) images (i–k).

9150017,18 to monitor 207Pb/206Pb fractionations in SIMS tests. An ideal zircon reference material should possess a relatively high U and radiogenic Pb content while having negligible metamictization damage. Zircon standard M257 meets the above criteria, but its supply is limited.19 Here, we report a zircon reference material with moderate Pb content. The results show that this ~10 g zircon ZS crystal is homogenous with respect to U–Pb ages and Hf–O isotopes, making it a suitable reference material for microanalysis.

**EXPERIMENTAL**

**Samples.** A zircon crystal (named as ZS) purchased from mineral dealers was collected from Sri Lanka. However, the exact provenance and petrological characteristics of the crystal were unknown. The brown, semitransparent mega-crystal had the most extended dimension of approximately 3 cm and a total weight of ~10 g (Fig. 1a). This crystal was crushed into small shards (Fig. 1b), and cleaned twice with distilled water and ethanol. The small fragments contained a small number of cracks, but no visible inclusions were observed in the reflection (Figs. 1c–1e), back-scattered electron (BSE) (Figs. 1f–1h), or cathodoluminescence (CL) images (Figs. 1i–1k).

**Instruments and operating conditions.** The samples were separated into four groups. Approximately 200 fragments (150–300 μm) were selected from each group and randomly distributed into four epoxy mounts with zircon reference materials GBW04409 (Penglai),20 GBW04705 (Qinghu),21,22 91500,17,18 Tanz,11 TEMORA 2,23 and Plesovice24 for analysis. The mounts were polished to obtain flat surfaces and expose the interior of the grains.

**Raman spectra.** Raman spectra of the samples were obtained using a LabRam micro-Raman spectrometer (Horiba Jobin Yvon, Paris, France) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China. A He–Ne laser (532 nm) was used for excitation. A charge-coupled device detector with a 50× magnification working-distance objective were used. The spectral resolution of the instrument was ~2 cm⁻¹. Further description can be found in Ling et al. 25

**U–Pb Age**

**SIMS.** U, Th, and Pb isotope analyses were conducted using a CAMECA IMS-1280HR SIMS at the IGGCAS in Beijing. Four analytical sessions were performed on each of the four mounts. A description of the instruments used for analyses and the analytical procedure can be found in Li et al. (2009), and only a brief summary is provided here.26 The primary O⁻ ion beam spot was approximately 20 μm × 30 μm in size and had a 6–9 nA intensity. A single electron multiplier was used in the ion-counting mode to measure the secondary ion beam intensities using the peak jumping mode, with each measurement consisting of seven cycles. In the analyses, the zircon standard was interspersed with unknown grains. Pb/U calibration and the concentrations of U and Th were calibrated relative to the zircon standard Tanz during sessions 1 and 4, zircon standard TEMORA 2 during session 2, and zircon standard 91500 during session 3. A second standard, GBW04705 (Qinghu), was also analyzed with zircon grains as an unknown. Long-term uncertainty for the 206Pb/238U measurements of the standard zircons was propagated to the unknowns (1 relative standard deviation (RSD) = 1.5%).27, 28 By using the measured non-radiogenic 204Pb signals and an average of the present-day crustal composition, the measured compositions were corrected.29

**LA–ICP–MS.** Forty grains of zircon ZS were analyzed during the first session to determine U–Pb dating with a Thermo iCAP RQ ICP–MS coupled with a Resonetics Resolution S-155 193 nm laser ablation system at the State Key Laboratory of Continental Dynamics (Northwest University. Xi’an, China). The analyses were performed at a pulse rate of 6 Hz, beam energy of 4 J/cm², and spot diameter of 30 μm. Zircon standard 91500 was used to calibrate the mass discrimination and elemental fractionation. GBW04705 (Qinghu) was used as the secondary standard. Background and analytical signal integration, time-drift correction, and quantitative calibration were performed for the U–Pb isotopes using Isoliët v4.0 software.30

The second and third zircon dating analytical sessions were performed using an ArF excimer laser system (GeoLas Pro, 193 nm wavelength) coupled with a quadrupole ICP–MS (Agilent 7700e) at the University of Science and Technology of China (USTC). A total of 26 and 59 grains were subjected to analyses in the second and third sessions, respectively. All analyses were performed at a laser energy of 10 J/cm², beam diameter of 32 μm,
and repetition rate of 10 Hz. The sample signal and background were measured at approximately 60 and 30 s, respectively. Additional details on the analytical techniques used in the U–Pb analyses in this study are available in Hou et al. \(^3^1\) The zircon standard 91500 and zircon standard SA01 were used as external standards. U/Pb ratios were processed using the macro program LaDating@Zrn written in Excel spreadsheet software. Common Pb was corrected using the method described by Andersen. \(^3^2\)

The fourth LA–ICP–MS U–Pb analysis session was conducted at Wuhan Sample Solution Analytical Technology Co., Ltd., Wuhan, China. Fifty spots were analyzed on 20 different zircon ZS grains using a GeoLas HD 193 nm laser coupled with an Agilent 7900 ICP–MS instrument. The analytical conditions included an ablation pit of 32 µm diameter and a repetition rate of 5 Hz. Elemental fractionation and instrumental mass discrimination were corrected by normalization to the reference zircon GJ-1, \(^3^3\) which was analyzed during the analytical session under the same conditions as the samples. For further details on the analytical protocols and data processing methods used for the U–Pb analyses, see Liu et al. \(^3^4\)

**Chemical abrasion isotope dilution thermal ionization mass spectrometry (CA–ID–TIMS).** Approximately 100 small zircon ZS shards (100–150 µm) were selected under a binocular microscope for CA–ID–TIMS analysis at IGGCAS and the British Geological Survey (BGS, UK). The methods used in both laboratories were similar and are discussed in the following paragraphs.

CA–ID–TIMS (IGGCAS). The CA–ID–TIMS procedures implemented at IGGCAS were similar to those reported by Chu et al. \(^3^5\) and Wang et al. \(^3^6\); therefore, only a brief description is provided here. The small zircon ZS fractions were pretreated using a chemical abrasion procedure. The fragments were placed in a quartz dish, annealed at 900 °C for 60 h in a muffle furnace, and then cleaned twice with HNO₃ and Milli-Q water at room temperature. The shards were loaded into Teflon microcapsules containing HF and placed in an oven at 200 °C for 12 h for leaching. The leached zircon grains were washed in two cycles of Milli-Q water, 6 mol L⁻¹ HCl, and HNO₃, left on a hotplate (120 °C) for 1 h, and then immersed for 1 h in an ultrasonic bath. Sixty thoroughly rinsed grains were transferred under a microscope using a pipet (set to approximately 3 µL), and the grains were loaded into 13 small 300 µL Savillex PFA caps and spiked with an in-house mixed ²⁰⁶Pb–²⁰⁷Pb–²³⁵U–²³⁸U isotopic tracer solution (IGG-1) \((Xu \text{ et al., in resubmission}). Dissolution was achieved using ~100 µL of concentrated hydrofluoric acid (HF) in Teflon microcapsules in a Parr pressure vessel placed in a 220 °C oven for 48 h. The dissolved zircon solution was successively dried to salts at 80 °C on a hotplate and redissolved in Teflon microcapsules in a Parr pressure vessel with ~150 µL of 6 mol L⁻¹ HCl at 180 °C for 12 h. After redrying and redissolving in ~50 µL of 3 mol L⁻¹ HCl, Pb and U were chemically purified from the solutions through 50 µL microcolumns of anion exchange resin and were finally dried with the addition of 10 µL of 0.05 mol L⁻¹ phosphoric acid (H₃PO₄). Purified Pb and U were loaded onto single predegassed zone-refined Re filaments with 3 µL of silica acid gel emitter solution. The Pb and U isotopic ratios were successively measured on a Thermo Triton Plus thermal ionization mass spectrometer (TIMS) in peak-jumping mode using a secondary electron multiplier (SEM) at IGGCAS. The Pb isotopes were measured as mono-atomic ions (Pb⁺) and uranium was measured as oxide ions (UO₂²⁺). The SEM dead times for Pb and U were set to 15 and 16 ns, respectively. The Pb isotope fractionation effect was corrected by an external method using NBS981 Pb as a reference standard (Pb fractionation coefficient: 0.16 ± 0.08%, 2σ). The U isotope fractionation effect was corrected by an external method using U500 as the reference standard (U fractionation coefficient: 0.058 ± 0.028%, 2σ). The total common Pb in each zircon analysis was attributed to laboratory Pb.

CA–ID–TIMS (BGS). Seven zircon shards were analyzed for U and Pb isotopes using the CA–ID–TIMS method at the BGS. The methods were similar to those of Yang et al. \(^3^7\). After annealing, the zircon shards were chemically abraded in HF and HNO₃ in an oven set at 210 °C for 12 h. The zircon ZS samples were spiked with mixed ²⁰⁶Pb–²⁰⁷Pb–²³⁵U–²³⁸U (ET2535) EARTHTIME isotopic tracer solutions. U and Pb isotopic measurements were performed using a Thermo Fisher Scientific Triton thermal ionization mass spectrometer.

Both laboratories used the Tripoli and ET_Redux applications to conduct data reduction, date calculations, and uncertainty propagation. Corrections to the ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages for the initial ²³⁰Th disequilibrium were determined assuming a Th/U ratio of 2.8. The decay constants were obtained from Jaffey et al. \(^3^8\). A ²³⁸U/²³⁵U isotopic composition of 137.818 ± 0.045 was used.

**Oxygen Isotope Measurements.** The homogeneity of the zircon oxygen isotopes was checked using a CAMECA IMS-1280 SIMS in IGGCAS. The primary beam Cs⁺ ions were accelerated at 10 kV and focused using a Gaussian mode with an intensity of 1.0–2.0 nA. The analytical spot size was approximately 20 µm in diameter, with a 10 µm beam diameter and 10 µm raster area. The signals of ¹⁶O and ¹⁸O were collected simultaneously using two Faraday cups in the multi-collection mode. The charge effect was compensated by a normal electron gun.

**Isotope ratio mass spectrometry (IRMS).** The oxygen isotopes of the zircon ZS crystals were acquired using a laser-based fluorination oxygen-extraction line at the Stable Isotope Laboratory. The Chinese national reference material GBW04409 (Penglai) was used as a quality monitor. A detailed description of the instrumentation and analytical procedures can be found in
**RESULTS AND DISCUSSION**

**Hf isotope homogeneity and determination.** A total of 100 in-situ Lu–Hf isotope measurements were carried out in two sessions on two mounts on a Neptune Plus MC–ICP–MS (Thermo Fisher Scientific, Germany) coupled with a Geolas Pro 193 nm excimer laser ablation system (Coherent, USA) at IGCCAS. The analytical spot was 44 μm in diameter. Laser had a frequency of 4 Hz and a beam energy density of 6 J/cm², and the ablation time was 26 s. Zircon standards GBW04409 (Penglai), Mud Tank, GBW04705 (Qinghu), and ZS. Representative Raman spectra obtained from the analyzed samples are shown in Fig. 2. The spectra of all zircon samples are similar to those of crystalline zircons that have experienced few alpha decay events. All samples exhibited characteristic peaks at approximately ~356, ~439, and ~1008 cm⁻¹, which are reference peaks from those of synthetic zircon. These peaks were interpreted to represent the internal vibrations of the SiO₄ tetrahedra. The most intense peaks observed for GBW04409 (Penglai), 91500, ZS, TEMORA 2, GBW04705 (Qinghu), and Plesovice zircons were visible at 1008, 1006, 1004, 1004, and 1001 cm⁻¹, respectively. The slight shift from the standard 1008 cm⁻¹ was attributed to radiogenic damage. The approximate radiation dose that has been absorbed by a zircon material can be evaluated based on the U–Th concentration and age. The degree of lattice damage can be described as “displacements-per-atom (dpa)”. The Dₐᵥ value demonstrates that zircon ZS experiences no disturbance during the oxygen isotope test and would not cause a “high-U matrix effect” during SIMS age dating.

**U–Pb Age of zircon ZS.** The isotopic U–Pb ratios and ages of the zircon ZS shards obtained using SIMS are listed in Table S1. A summary of the zircon U–Pb measurements is presented in Table 1 and displayed in Fig. 3. The uncertainties of the individual zircon analyses are reported at the 1σ level in the data tables. The four SIMS analytical sessions included 12, 12, 16, and 56 analyses in sessions 1, 2, 3, and 4, respectively. Each point shows a concordant U–Pb age within the uncertainties. The Concordia U–Pb ages determined from each session were 559 ± 5 Ma (2SE, n = 12, Fig. 3a), 559 ± 5 Ma (2SE, n = 12, Fig. 3b), 560 ± 5 Ma (2SE, n = 16, Fig. 3c), and 561 ± 3 Ma (2SE, n = 56, Fig. 3d), respectively. The average ages of 206Pb/238U and 207Pb/206Pb were 560 ± 2 Ma (2SE, n = 96, Figs. 3i and 3j) and 562 ± 4 Ma (2SE, n = 95, with one spot with a relatively high common Pb discarded (Figs. 3k and 3l), respectively. The data for individual LA–ICP–MS U–Pb analyses are listed in Table S2. The internal error determined during LA–ICP–MS zircon U–Pb dating was approximately 1%. The respective LA–ICP–MS Concordia ages calculated from the four sessions were as follows: 564 ± 4 Ma (2SE, n = 40, Fig. 3e), 557 ± 5 Ma (2SE, n = 26, Fig. 3d), 563 ± 3 Ma (2SE, n = 59, Fig. 3g), and 554 ± 2 Ma (2SE, n = 49, with one spot with a small inclusion being discarded, Fig. 3h). The

**Trace element concentration.** The trace elements in the zircon ZS samples were determined using LA–ICP–MS at Wuhan Sample Solution Analytical Technology Co., Ltd. For more details regarding the experimental and data reduction procedures, see Hu et al. and Liu et al. An Agilent 7900 ICP–MS equipped with a GeoLas HD 193 nm laser ablation system was used. External calibration was performed relative to NIST610 standard glass. ARM-1 glass and SA01 zircon were used for quality control monitoring.

**Structural study using Raman spectroscopy.** We measured the Raman spectra of six well-characterized zircon standards: 91500, TEMORA 2, Plesovice, GBW04705 (Qinghu), GBW04409 (Penglai), and ZS. Representative Raman spectra obtained from the analyzed samples are shown in Fig. 2. The spectra of all zircon samples are similar to those of crystalline zircons that have experienced few alpha decay events. All samples exhibited characteristic peaks at approximately ~356, ~439, and ~1008 cm⁻¹, which are reference peaks from those of synthetic zircon. These peaks were interpreted to represent the internal vibrations of the SiO₄ tetrahedra. The most intense peaks observed for GBW04409 (Penglai), 91500, ZS, TEMORA 2, GBW04705 (Qinghu), and Plesovice zircons were visible at 1008, 1006, 1004, 1004, and 1001 cm⁻¹, respectively. The slight shift from the standard 1008 cm⁻¹ was attributed to radiogenic damage. The approximate radiation dose that has been absorbed by a zircon material can be evaluated based on the U–Th concentration and age. The degree of lattice damage can be described as “displacements-per-atom (dpa)”. The Dₐᵥ value demonstrates that zircon ZS experiences no disturbance during the oxygen isotope test and would not cause a “high-U matrix effect” during SIMS age dating.
Table 1 Summary of the U–Pb dating methods for zircon ZS from different laboratories

<table>
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<tr>
<th>Analytical Methods</th>
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<th>U–Pb age</th>
<th>U–Pb age</th>
<th>Weighted Mean</th>
<th>ISD, Ma</th>
<th>RSD, %</th>
<th>Weighted Mean</th>
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</table>

IGGCAS: Institute of Geology and Geophysics, Chinese Academy of Sciences, China; NWU: State Key Laboratory of Continental Dynamics (Northwest University); USTC: Chinese Academy of Sciences (CAS) Center for Excellence in Comparative Planetology at the University of Science and Technology of China; WHSS: Wuhan Sample Solution Analytical Technology Co. Ltd., China; BGS: British Geological Survey, UK.

Fig. 3 The U–Pb ages of zircon ZS. (a–d) The Concordia diagrams show SIMS U–Pb dating results and (e–h) the LA–ICP–MS U–Pb dating results. The average (i) (k) and histograms (j) (l) show the $^{206}$Pb/$^{238}$U age and the $^{207}$Pb/$^{206}$Pb age results obtained during SIMS. The average (m) (o) and histograms (n) (p) show the $^{206}$Pb/$^{238}$U age and the $^{207}$Pb/$^{206}$Pb age results obtained during LA–ICP–MS. All error symbols are given at 2σ.

Systematic uncertainties of LA–ICP–MS zircon U–Pb dating should be considered. Then, systematic uncertainties of 2% (2σ) for the $^{206}$Pb/$^{238}$U and 0.55% (2σ) for the $^{207}$Pb/$^{206}$Pb measurements were propagated to the samples. The average age...
### Table 2. U–Pb TIMS Zircon Data

<table>
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<tr>
<th>Sample</th>
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<th>207Pb/204Pb</th>
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a Total mass of common Pb. All common Pb assumed to be laboratory blank. Blank isotopic composition at IGG: 206Pb/204Pb = 17.78 ± 0.50, 207Pb/204Pb = 15.31 ± 0.34, 208Pb/204Pb = 38.51 ± 0.57.

b Th contents calculated from radiogenic 230Th and 234Th-corrected 206Pb/204Pb date of the sample, assuming concordance between U–Pb and Th–Pb systems.

c Measured ratio corrected for fractionation and spike contribution only.

d Error correlation between 207Pb/206Pb and 208Pb/235U.

### Table 3. Summary of the oxygen isotopes for zircon ZS

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<td>GBW04409 Penglai</td>
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<td>13.69</td>
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Fig. 4 Concordia diagram of the zircon ZS grains obtained using CA–ID–TIMS. (a) The green symbols represent the IGGCAS results, and (a) the blue symbols represent the BGS results.

Fig. 5 Mean value and frequency distributions of $\delta^{18}$O values of the zircon ZS: (a), (b), (c), (d), and (e) are the $\delta^{18}$O SIMS values obtained for zircon ZS during sessions 1, 2, 3, 4, and 5, respectively. (f) shows the $\delta^{18}$O RIMS values for zircon ZS.
of $^{206}\text{Pb}^{238}\text{U}$ was 558 ± 2 Ma (2SE, $n = 174$; Figs. 3m and 3n). The average age of $^{207}\text{Pb}^{206}\text{Pb}$ was determined to be 564 ± 7 Ma (2SE, $n = 174$; Figs. 3o and 3p). Both SIMS and LA–ICP–MS data indicated that zircon ZS has a uniform U–Pb age.

Twenty C-A–ID–TIMS analyses were performed on the zircon ZS. The complete TIMS U–Pb isotopic ratios are listed in Table 2 and the U–Pb results are presented in Fig. 4. All errors that were observed during the TIMS analyses are quoted in the text, tables, and error ellipses in the Concordia diagram and given at 2σ. Thirteen analyses were conducted at IGCCAS, and two of these analyses with significantly higher uncertainty for the $^{206}\text{Pb}^{238}\text{U}$ age of the zircon ZS and the $^{206}\text{Pb}^{207}\text{Pb}$ results are presented in Fig. 4. All errors that were obtained for the GBW04409 zircon were 0.14‰, 0.23‰, 0.33‰, and 0.41‰, respectively, indicating that the instrument conditions. The analytical precision 2SD of the five sessions obtained for the GBW04409 zircon was approximately 0.1% (2 RSE). Seven analyses carried out at BGS yielded a weighted mean $^{206}\text{Pb}^{238}\text{U}$ age of 560.7 ± 0.4 Ma (2SE, $n = 7$) and a weighted mean $^{207}\text{Pb}^{206}\text{Pb}$ age of 561.1 ± 0.7 Ma (2SE, $n = 7$). By combining all the above analyses, the recommended $^{206}\text{Pb}^{238}\text{U}$ age of the zircon ZS and the $^{207}\text{Pb}^{206}\text{Pb}$ age were obtained as 560.6 ± 1.3 Ma (2SD, $n = 18$) and 561.1 ± 3.5 Ma (2SD, $n = 18$), respectively.

**Oxygen Isotopes Using SIMS and IRMS.** Oxygen isotopic measurements were performed in five sessions to evaluate micron-level homogeneity. The raw data from the five sessions are shown in Table S3, and a summary of the SIMS data is listed in Table 3. The GBW04409 zircon (Penglai) was analyzed to monitor the instrument conditions. The analytical precision 2SD of the five measurements during five sessions was 0.3‰–0.5‰. SIMS oxygen analysis can achieve excellent repeatability (2SD < 0.3‰), but only under ideal measurement conditions. The results indicate that the intra- or intergrain variations observed in the oxygen isotopes are sufficiently small to show the homogeneity of the zircon ZS. The oxygen isotope compositions obtained using IRMS are summarized in Table 3. The recommended value for zircon ZS was 13.69 ± 0.11‰ (2SD, $n = 12$; Fig. 5f) based on 12 analyses. The $\delta^{18}O$ value determined by SIMS was consistent with that determined by IRMS within uncertainty.

**MC–ICP–MS Hf isotope data.** The complete isotopic ratios of Lu–Hf are listed in Table S4. A summary of these analyses is provided in Table 4. The mean Lu–Hf isotopic results for SA01, Mud tank, GBW04409 (Penglai), and SA02 zircon reference materials under the same conditions were determined to be 0.282282 ± 0.000047 (2SD), 0.282502 ± 0.000042 (2SD), 0.282928 ± 0.000049 (2SD), and 0.282294 ± 0.000061 (2SD), respectively, which are consistent with the recommended results within uncertainties. Sixty individual Hf isotope analyses during session 1 obtained $^{176}\text{Hf}^{177}\text{Hf}$ values ranging from 0.281620 to 0.281753. Forty zircon ZS shards analyzed in session 2 showed $^{176}\text{Hf}^{177}\text{Hf}$ values ranging from 0.281618 to 0.281732. The 100 Lu–Hf isotope measurements formed a Gaussian distribution with a grand mean of 0.281676 ± 0.000050 (2SD, $n = 100$; Figs. 6a and 6b). Seven aliquots of zircon ZS were obtained by solving the MC–ICP–MS measurements, and the yield of $^{176}\text{Hf}^{177}\text{Hf}$ values ranged between 0.281663 and 0.281675. All seven $^{176}\text{Hf}^{177}\text{Hf}$ datasets had a weighted mean of 0.281668 ± 0.000010 (2SD, $n = 7$; Fig. 6c), which was identical to the mean of the LA–MC–ICP–MS results within uncertainties.

According to the laser ablation and solution measurements conducted in this study, the zircon ZS mega crystal has relatively homogeneous Hf isotopic compositions. The mean value of $^{176}\text{Hf}^{177}\text{Hf} = 0.281668 ± 0.000010$ (2SD) determined by solution MC–ICP–MS measurements is the best recommended value for zircon ZS.

![Fig. 6](image-url)
Table 5 Trace element composition of zircon ZS

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**CONCLUSIONS**

Raman spectroscopy, SIMS, IRMS, ICP–MS, and TIMS were used to evaluate a 10 g natural zircon ZS crystal. The Raman results showed that zircon ZS was well crystallized without metamict. The analytical results via SIMS and LA–ICP–MS suggest that the samples are homogeneous in terms of U–Pb–O–Hf isotope composition at the ~20 µm scale, indicating that the crystal is a qualified reference material for SIMS U–Pb–O isotopic analysis and for LA–ICP–MS Hf isotope measurement. As determined by CA–ID–TIMS, the recommended ²⁰⁶Pb/²³⁸U values and ²⁰⁶Pb/²⁰⁶Pb age for zircon ZS are 560.6 ± 1.3 Ma (2SD) and 561.1 ± 3.5 Ma (2SD), respectively. The weighted mean δ¹⁸O value of 13.69 ± 0.11‰ (2SD) determined by laser fluorination IRMS and the mean ¹⁷⁶Hf/¹⁷⁷Hf value of 0.281668 ± 0.000010 (2SD) determined by solution MC–ICP–MS are the best reference values for zircon ZS.

All zircon materials are available from the corresponding author if required.

**ASSOCIATED CONTENT**

The supporting information (Tables S1-S5) is available at www.at-spectrosc.com/as/home

**AUTHOR INFORMATION**

Qiu-Li Li is a full professor of Geochemistry at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). He received his B.S. degree in Geology from Northwest University (NWU, Xi’an city) in 1998, and completed Ph.D in Geochemistry from University of Science and Technology of China. He worked as postdoctoral research fellow at the IGGCAS (2003-2007), associate professor from 2008 to 2012 and full professor since 2013 at the IGGCAS. From 2017, he started to work as director of ion probe laboratory at the IGGCAS. From 2022, he acts as chairman of Microbeam Analysis
Professional Committee of Chinese society for mineralogy petrology and geochemistry. His research focused on micro area iso trope geochemistry. Based on the ion probe platform, he has developed a variety of in-situ U-Th-Pb dating methods for many accessory minerals, which provides effective dating means for solving geological chronological problems such as ultra-alkaline rocks, carbonates, clastic sedimentary rocks, medium and low temperature metamorphic rocks, low-temperature deposits and extraterrestrial samples; Through the analysis of small beam spots of zirconium containing minerals, he accurately determined that the Chang'e-5 basalt was formed 2 billion years ago. He has been working as member of editorial board for Atomic Spectroscopy. Qiu-Li Li published more than 50 SCI papers of the first or corresponding author in journals such as Nature, Nature Communications and EPSL, and other more than 180 cooperative papers.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully thank the National Key Research and Development Plan (2018YFA0702600) and the National Natural Science Foundation of China (41773044, 41773047, and 42173037) for financially supporting this work. We thank Anton Azaro for providing the zircon materials. We also appreciate technical assistance from Hongxia Ma, Lanzhen Guo, Hongwei Li, Zheng Liu, Lu Chen, and Wenquan Fan. Lastly, the authors gratefully acknowledge the detailed reviews from the editors and the reviewers.

REFERENCES

Cadmium Isotope Analysis of Environmental Reference Materials via Microwave Digestion–Resin Purification–Double-Spike MC-ICP-MS

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Received: November 13, 2021; Revised: January 27, 2022; Accepted: January 27, 2022; Available online: February 07, 2022.

DOI: 10.46770/AS.2021.1109

ABSTRACT: Cadmium isotope fractionation is a promising indicator for tracing the source, transport, and transformation of Cd in the environment; therefore, a high-precision method for the Cd isotope analysis of environmental samples is urgently required. In this study, eight environmental reference materials (NIST 2711a, GSS-1, GSS-4, GSS-5, GSD-11, GSD-12, GSD-30, and BCR-679) with different matrices were digested under microwave irradiation and purified via anion exchange. Thereafter, their Cd isotope ratios were analyzed using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) with double-spike correction. The samples digested under microwave irradiation exhibited high Cd recovery (> 96%). One step of anion-exchange-based purification can remove most interfering elements without any detectable loss of Cd. If the purified solution contained Zn/Cd > 0.04, Zr/Cd > 0.01, Mo/Cd > 0.2, Pd/Cd > 4 × 10^{-5}, In/Cd > 0.02, or Sn/Cd > 0.1, a secondary step using the same purification procedure would be necessary. The measured δ^{114/110}Cd values of reference materials (from −0.558 to 0.550‰) were in adequate agreement with those of previous studies, suggesting that this method can be used to analyze the Cd isotope ratios in soil, sediment, and plant samples. In addition, the large variation in the Cd isotope ratios of these reference materials implies that the Cd isotope ratio is promising for identifying pollution sources and the biogeochemical cycle of Cd.

INTRODUCTION

Cadmium (Cd) is a heavy metal physiologically toxic to plants, animals, and humans. Cd in the environment is derived from both natural and anthropogenic sources.1 The major natural sources of Cd include volcanic eruptions and rock weathering.2 With industrialization, large amounts of Cd have been released into the environment via anthropogenic activities, such as the production of Ni-Cd batteries, waste incineration, coal combustion, and fertilizer application.3 Soil suffers from severe Cd pollution because it is the main contaminant sink.4 When entering the soil, Cd can be adsorbed or immobilized by different soil components, internalized by plant roots, and eventually translocated to different plant tissues.5, 6 The complexities of the pollution sources and biogeochemical cycles of Cd in soil significantly restrict the solution to environmental Cd pollution.
Cd has eight stable isotopes with mass numbers in the range of 106–116. Cd isotope fractionation has been shown to occur during the evaporation/condensation and biological cycling of Cd. Recent studies have reported a significantly large degree of Cd isotope fractionation among the products and waste produced during coal combustion, metal smelting/refining, and metal coating, which implies that isotope fractionation can be used to identify Cd pollution sources. Researchers have identified the main Cd sources and their contribution to Cd pollution by determining the Cd isotope ratios of various sources and contaminated receptors (e.g., soil and sediments). Cd isotope fractionation also occurs during its adsorption-desorption between the solid and liquid phases and translocation to different plant tissues (e.g., roots, shoots, and grains). These observations have demonstrated that Cd isotope analysis is a promising tool for tracing the sources of Cd in contaminated sites and can also be used as an indicator for probing the behavior of Cd in the environment.

In early research, Cd isotope analysis was typically accomplished using thermal ionization mass spectroscopy. With improvements in mass spectroscopy, the use of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for metal isotope analysis became practical. Since MC-ICP-MS can easily overcome the first ionization potential of Cd via plasma ionization, it is currently the dominant technique for Cd isotope analysis. To accurately determine Cd isotope ratios, possible interfering substances must be removed from samples, which requires the samples to be completely digested, purified, and recovered. For environmental sample digestion, the most widely used protocol is to sequentially add sample and mineral acids (e.g., HNO₃ and HCl) to high-pressure bombs or perfluoroalkoxy (PFA) vials. Digestion is then performed using an oven or a hot plate for tens of hours.

Although these methods can completely digest samples, they are time-consuming and exhibit poor organic matter removal performance due to the incomplete oxidation of carbon. Unfortunately, most environmental samples, such as agricultural soils and plants, contain large amounts of organic matter that can significantly affect the analytical accuracy of Cd isotope ratios. Due to the increasing use of Cd isotope fractionation in environmental research, establishing an effective and efficient digestion method for environmental samples has become necessary. In addition, most soil samples contain interfering elements (e.g., Zn, Zr, Mo, In, and Sn) in amounts that are 1–2 orders of magnitude higher than that of Cd. Thus, it also becomes necessary to evaluate whether current purification processes can effectively remove the matrix and interfering elements in a single operation, and if not, whether the content of interfering elements in the Cd sample solution can meet the requirements for Cd isotope analysis. Furthermore, if the Cd sample solution does not meet the test requirements, the performance of the secondary purification procedure needs to be evaluated.

Therefore, eight environmental reference materials, including soil, sediments, and plants, were tested to evaluate the use of microwave digestion and anion-exchange-based chemical purification procedures using double-spike MC-ICP-MS for Cd isotope analysis. In addition, the effects of isobaric (Pd, In, and Sn) and polyatomic (Zn, Zr, and Mo) interferences on Cd isotope analysis were evaluated and discussed.

**EXPERIMENTAL**

**Reagents, standard solutions, and samples.** TraceMetal grade HNO₃ and hydrochloric acid (HCl) were procured from Thermo Fisher Scientific (Waltham, MA). Analytical-grade HF and hydrogen peroxide (H₂O₂) were procured from Beijing Chemicals (Beijing, China). HNO₃ and HCl were distilled twice using a Savillex DST-1000 sub-boiling acid system. The ¹¹¹Cd–¹¹³Cd double-spike solution used in this study was prepared using the enriched ¹¹¹Cd (purity of 96.00%) and ¹¹³Cd isotopes (purity of 94.90%) from Isotopes for Science, Medicine, and Industry (San Francisco, CA). Briefly, the enriched ¹¹¹Cd and ¹¹³Cd isotopes were individually dissolved in 2 mol L⁻¹ HNO₃, and suitable volumes of the individual isotope solutions were weighed and mixed to obtain a double-spike solution with a ¹¹¹Cd-to-¹¹³Cd ratio of 1, which could then provide high precision for the double-spike method. Finally, after the double-spike solution was stabilized for 12 h, it was diluted to 10 µg g⁻¹. An AG-MP-1M ion-exchange resin (100–200 dry mesh size, Bio-Rad Laboratories AB, Solna, Sweden) was used for sample purification. Milli-Q water (18.2 MΩ cm⁻¹) was used in all experimental procedures.

Four mono-elemental Cd solutions were used to validate the method: (1) an NIST SRM3108 Cd solution, a common reference material for Cd isotope studies (Lot 130116); (2) AAS-Cd, a commercial ICP standard solution (Lot 1797541); (3) Thermo-Cd, a commercial ICP standard solution (Lot 9158147) (Alfa Aesar, Thermo Fisher Scientific, Leicestershire, United Kingdom); and (4) GSB-Cd, a mono-elemental Cd standard solution (GSB 04-1721-2004) (Iron and Steel Research Institute, Beijing, China). Other mono-elemental (Mg, Ca, Mn, Cu, Zn, Zr, Mo, Pb, Sn, and Pb) standard solutions used in this study were also procured from the Iron and Steel Research Institute (Beijing, China).

Eight environmental reference materials with certified Cd concentrations and isotopic compositions were used to evaluate treatment processes, including four soil reference materials (NIST 2711a, GSS-1, GSS-4, and GSS-5), three stream sediment reference materials (GSD-11, GSD-12, and GSD-30), and one plant reference material (BCR-679).

**Sample digestion.** Samples were digested using microwaves. For
mass spectrometry (ICP). The concentration was measured using inductively coupled plasma (ICP) for chemical purification. The residue was transferred into a pre-cleaned centrifuge tube, and 2% (w/w) HNO₃ and Milli-Q water were used to remove matrix elements and purify Cd. The chemical purification procedure used herein was modified from the procedures reported by Wen et al. and Wei et al. The steps in the purification procedure are listed in Table 2. Briefly, a micro-column was filled with 3 mL pre-cleaned resin (10% (w/w) HNO₃ and Milli-Q water), and the resin column was then sequentially cleaned with Milli-Q water (10 mL) and 2% (w/w) HNO₃ (10 mL). The sample in 2 M HCl (2 mL) was loaded onto a column equilibrated with 2 M HCl (10 mL). Thereafter, matrix elements were eluted by 2 M HCl (10 mL), 0.3 M HCl (30 mL), 0.06 M HCl (20 mL), and 0.012 M HCl (6 mL). The Cd fraction was then collected with 0.0012 M HCl (20 mL) in a 25 mL PFA beaker, after which it was evaporated to dryness on a hot plate at 145 °C. During heating, 0.2 mL of concentrated HNO₃ was added into the beaker to remove possible organic matter from the resin. The residue remaining in the beaker after evaporation was then dissolved in 2 mL of 2% HNO₃ (w/w). To evaluate the extent of purification, 0.5 mL of this solution was then taken and the concentration of Cd and interfering elements measured. The entire procedural blank of Cd was below 0.1 mg, which was negligible.

To assess the purification procedure, an artificial mixed solution (Cd: Mg: Ca: Mn: Cu: Zn: Zr: Mo: Pd: In: Sn: Pb = 1: 200: 300: 100: 100: 40: 40: 10: 2.5: 1: 2.5: 5) was purified using the same procedure. The composition and proportion of the artificial mixed solution were designed to simulate the soil composition.

The concentrations of Mg, Ca, Cu, Mn, and Pb in the eluent were measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES), and the concentrations of Zn, Sn, In, Pd, Zr, Mo, and Cd were measured using ICP-MS.

**Measurement using MC-ICP-MS.** Cd isotope ratios were measured using MC-ICP-MS (Neptune Plus, Thermo Fisher Scientific, Bremen, Germany) at Jianghan University (Wuhan, China). Instrumental parameters are presented in Table 3. The ion currents of ¹¹⁰Cd, ¹¹¹Cd, ¹¹²Cd, and ¹¹⁴Cd were collected using L2, L1, C, and H1 Faraday cups, respectively. To investigate and correct the isobaric interference of ¹⁰⁹Pd on ¹¹⁰Cd, ¹¹¹In on ¹¹²Cd, and ¹¹⁴Sn on ¹¹⁴Cd, the ion currents of ¹⁰⁹Pd, ¹¹¹In, and ¹¹⁴Sn were simultaneously collected using L4, H2, and H4 Faraday cups, respectively. For MC-ICP-MS measurements, an Aridus II membrane desolvation system was used for sample introduction. Parameters (gas flow, torch position, lens settings, and zoom optics) were optimized to obtain a ¹¹⁴Cd (100 μg kg⁻¹) signal over 13 V. Before each measurement, the sample introduction system was rinsed with 5% HNO₃ (w/v) for 1 min and 2% HNO₃ (w/v) for 2 min.

**Data correction.** MC-ICP-MS data were corrected in three steps. First, the instrumental mass bias was corrected using the generalized power law:

\[
 f = \frac{\ln(R / r)}{\ln(m_2 / m_1)}
\]
where \( f \) is the mass fractionation factor of the instrument; \( R \) and \( r \) correspond to the measured and true Cd isotope ratios, respectively; and \( m_1 \) and \( m_2 \) are the masses of the two Cd isotopes. Before each sample measurement sequence, a pure NIST 3108 solution was tested, and the isotope ratio of \(^{114}\text{Cd} \) to \(^{106}\text{Cd} \) was used to calculate the mass fractionation factor \( f \). The \( f \) cannot be ignored, otherwise, it will produce percent-level bias in the measured isotopic composition from the true isotopic composition of sample.\(^{38}\)

Second, the isobaric interferences of \(^{109}\text{Pd} \) on \(^{109}\text{Cd} \), \(^{115}\text{In} \) on \(^{115}\text{Cd} \), and \(^{114}\text{Sn} \) on \(^{114}\text{Cd} \) were corrected as follows: (1) using the ion current of \(^{109}\text{Pd} \) to calculate the ion current of \(^{109}\text{Cd} \); (2) using the ion current of \(^{115}\text{In} \) to calculate the ion current of \(^{115}\text{Cd} \), and then using the ion current of \(^{115}\text{In} \) (corrected ion current of \(^{115}\text{Sn} \)) to calculate the ion current of \(^{115}\text{In} \); and (3) using the ion current of \(^{118}\text{Sn} \) to calculate the ion current of \(^{114}\text{Sn} \). Thereafter, the measured ion currents of \(^{109}\text{Cd} \), \(^{113}\text{Cd} \), and \(^{114}\text{Cd} \) were corrected using the calculated ion currents of \(^{109}\text{Pd} \), \(^{115}\text{In} \), and \(^{114}\text{Sn} \), respectively, to obtain the true ion currents of \(^{109}\text{Cd} \), \(^{113}\text{Cd} \), and \(^{114}\text{Cd} \). The interferences of \(^{109}\text{Pd} \), \(^{115}\text{In} \), and \(^{114}\text{Sn} \) were calculated as follows:\(^{25}\):

\[
^{109}\text{Pd}_{\text{corr}} = \frac{^{109}\text{Pd}_{\text{meas}} \times \left(^{110}\text{Pd} / ^{109}\text{Pd}\right)_{\text{aff}} \times \left(110 / 105\right)}{\left(^{110}\text{Pd} / ^{109}\text{Pd}\right)_{\text{aff}}}
\]

(2)

\[
^{115}\text{In}_{\text{corr}} = \frac{^{115}\text{In}_{\text{meas}} - ^{115}\text{Sn}_{\text{meas}}}{\left(^{115}\text{In} / ^{115}\text{Sn}\right)_{\text{aff}}} \times \left(^{113}\text{In} \times ^{115}\text{In}_{\text{aff}} / 113\right)
\]

(3)

\[
^{115}\text{Sn}_{\text{corr}} = \frac{^{118}\text{Sn}_{\text{meas}} \times \left(^{115}\text{Sn} / ^{118}\text{Sn}\right)_{\text{aff}} \times \left(115 / 118\right)}{\left(^{115}\text{Sn} / ^{118}\text{Sn}\right)_{\text{aff}}}
\]

(4)

\[
^{114}\text{Sn}_{\text{corr}} = \frac{^{118}\text{Sn}_{\text{meas}} \times \left(^{114}\text{Sn} / ^{118}\text{Sn}\right)_{\text{aff}} \times \left(114 / 118\right)}{\left(^{114}\text{Sn} / ^{118}\text{Sn}\right)_{\text{aff}}}
\]

(5)

where \( m \) and \( n \) correspond to the measured signal and the corresponding isotope natural abundance ratio, respectively; and \( f \) is the mass fractionation factor of the instrument. Considering similar mass number of Pd, In, and Sn to that of Cd, the same \( f \) was used here.\(^{25}\)

Third, the three measured isotope ratios, \(^{111}\text{Cd} \)-to-\(^{110}\text{Cd} \), \(^{113}\text{Cd} \)-to-\(^{110}\text{Cd} \), and \(^{114}\text{Cd} \)-to-\(^{110}\text{Cd} \), were inserted into three simultaneous nonlinear equations that can be iteratively solved to obtain the true isotopic composition of the sample after infinitely excluding the double-spike composition based on a mathematical algorithm.\(^{29, 30}\)

Cd isotopic compositions were reported in \( \delta \)-notation relative to the NIST SRM3108 Cd solution, which is defined as follows:

\[
\delta = \frac{\left(^{114}\text{Cd} / ^{110}\text{Cd}\right)_{\text{sample}} - 1}{\left(^{114}\text{Cd} / ^{110}\text{Cd}\right)_{\text{SRM3108}}} \times 1000
\]

(6)

## RESULTS AND DISCUSSION

**Efficiency of the microwave digestion procedure.** The reference and measured Cd concentrations of the eight reference materials are listed in Table 4. According to these results, microwave digestion completely digested the samples and did not cause a significant loss of Cd, which is indicated by the Cd recoveries of 99.5%, 98.7%, 98.0%, 99.7%, 99.1%, 96.4%, 98.9%, and 101% for NIST 2711a, GSS-1, GSS-4, GSS-5, GSD-11, GSD-12, GSD-30, and BCR-679, respectively. Compared to the time required for hot plate digestion or high-pressure bombs, significantly lesser resources were consumed.

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**Table 4** Cd concentration and isotopic compositions of the environmental reference materials used in this study and references

<table>
<thead>
<tr>
<th>Reference materials</th>
<th>Zn or Sn/Cd (Before purification)</th>
<th>Zn or Sn/Cd (After purification)</th>
<th>Reference value (mg kg(^{-1}))</th>
<th>Measured value (mg kg(^{-1})) in this study</th>
<th>( \delta^{114}\text{Cd} ) (‰) in references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil NIST 2711a</td>
<td>Zn/Cd &gt; 7</td>
<td>Zn/Cd &lt; 0.01</td>
<td>54.1 ± 0.5</td>
<td>53.8 ± 0.6</td>
<td>0.550 ± 0.046</td>
</tr>
<tr>
<td>Soil GSS-1</td>
<td>Zn/Cd &gt; 158</td>
<td>Zn/Cd &lt; 0.01</td>
<td>4.3 ± 0.4</td>
<td>4.23 ± 0.08</td>
<td>0.099 ± 0.054</td>
</tr>
<tr>
<td>Soil GSS-4</td>
<td>Zn/Cd &gt; 600</td>
<td>Zn/Cd &lt; 0.01</td>
<td>0.35 ± 0.06</td>
<td>0.34 ± 0.01</td>
<td>−0.303 ± 0.044</td>
</tr>
<tr>
<td>Soil GSS-5</td>
<td>Zn/Cd &gt; 1000</td>
<td>Zn/Cd &lt; 0.2</td>
<td>0.45 ± 0.06</td>
<td>0.45 ± 0.01</td>
<td>−0.558 ± 0.046</td>
</tr>
<tr>
<td>Sediment GSD-11</td>
<td>Zn/Cd &gt; 160</td>
<td>Zn/Cd &lt; 0.05</td>
<td>2.3 ± 0.2</td>
<td>2.28 ± 0.05</td>
<td>−0.320 ± 0.067</td>
</tr>
<tr>
<td>Sediment GSD-12</td>
<td>Zn/Cd &gt; 120</td>
<td>Zn/Cd &lt; 0.04</td>
<td>4.0 ± 0.4</td>
<td>3.86 ± 0.01</td>
<td>−0.041 ± 0.030</td>
</tr>
<tr>
<td>Sediment GSD-30</td>
<td>Zn/Cd &gt; 21</td>
<td>Zn/Cd &lt; 0.7</td>
<td>4.3 ± 0.3</td>
<td>4.25 ± 0.04</td>
<td>0.289 ± 0.042</td>
</tr>
<tr>
<td>Plant BCR-679</td>
<td>Zn/Cd &gt; 48</td>
<td>Zn/Cd &lt; 0.0</td>
<td>1.66 ± 0.07</td>
<td>1.68 ± 0.06</td>
<td>0.203 ± 0.012</td>
</tr>
</tbody>
</table>
time (~3 h) was required for microwave digestion, including sample weighing, reagent addition, digestion, and cooling. Although microwave digestion consumed a large volume of acid mixtures (10 mL), and the acid mixtures must be evaporated after digestion (approximately 2 h), the overall time requirement was still significantly lower than that of other digestion methods. In addition, microwave digestion effectively destroyed the organic matrix in the samples, as supported by the changes in the color of the digestion solution (transparent or pale yellow) and the subsequent chemical purification performance. Microwave digestion simultaneously digested 40 samples (including blanks), and the digestion performance was highly parallel. Therefore, microwave irradiation can be efficiently used to digest environmental samples for the subsequent Cd isotope analysis.

Performance of the chemical purification procedure. Cd isotope analysis is marred by a variety of interferences that must be removed, including the matrix effect, isobaric interference, and polyatomic interference. First, interference removal was attempted using an anion-exchange-based resin purification procedure with an artificial mixed standard solution. As shown in Fig. 1, the matrix elements (Mg, Ca, Mn, and Cu) were almost completely leached from the column in the first stage (2 M HCl), and the interfering elements (Zn, Zr, and Mo), which can form polyatomic molecules, were completely leached out of the column before the fourth stage (0.012 M HCl). Pd was immobilized on the column and was not detected in any eluents, while In was eluted out of the column in the second stage (0.3 M HCl). Most Sn was eluted out of the column in the third (0.06 M HCl) and fourth stages (0.012 M HCl), and a small fraction of Sn was observed together with Cd in the last stage (0.0012 M HCl). Elution curves were in adequate agreement with those of other studies. However, previous studies have indicated that Cd isotopes are not significantly fractionated when the recovery after chemical purification is higher than 95%. The recovery of Cd in the procedure used in this study, monitored using a mixed standard solution, was >98%, which guarantees data quality. The above results suggest that this chemical purification procedure can efficiently separate the matrix and interference elements from Cd without causing any loss of Cd.

To further verify the performance of the purification procedure, the digestion solutions of the eight environmental reference materials were purified after evaporation and re-dissolution. The Cd recoveries for all eight samples after purification exceeded 98%, as determined using ICP-MS analysis. In addition, interference elements, including Zr, Mo, Pd, and In, were not detected after purification, but small amounts of Zn and Sn remained in some analyte solutions (Table 4). This may be related to the matrix composition of the sample and the relative content of the interference elements in the sample. For example, the matrices of NIST 2711a, GSD-12, GSD-30, and BCR-679 are relatively simple (Table 4), and the concentration ratios of Zn to Cd and Sn to Cd in the analyte solution after purification were extremely low. However, for GSS-1, GSS-4, GSS-5, and GSD-11, the concentration ratios of Zn to Cd and Sn to Cd after purification were higher.

These results demonstrate that the above procedure can effectively purify the samples. However, in some samples with high concentrations of interference elements, the interference elements were not completely removed. Thus, it is necessary to evaluate whether the concentration of the interference elements in the analyte solution after purification can cause bias during MC-ICP-MS measurements, and whether secondary chemical purification is required for subsequent MC-ICP-MS analysis.

Evaluation of polyatomic and isobaric interferences. During instrumental detection, the non-target elements in analyte solutions can cause spectral interference during Cd isotope measurements, including polyatomic and isobaric interferences. Polyatomic interferences include 94Zr16O+, 94Mo16O+, 70Zn40Ar+ on 100Cd, 96Mo16O+ on 110Cd, 97Mo16O+ on 111Cd, and 98Mo16O+ on 114Cd. Isobaric interferences include 100Pd on 100Cd, 113In on 113Cd, and 114Sn on 114Cd. Therefore, the thresholds for these interferences must be evaluated. Cd isotopes were measured in a series of NIST SRM3108 solutions (100 μg L−1) doped with different concentrations of Zn, Zr, Mo, Pd, In, and Sn. As shown in Fig. 2, Zn/Cd > 0.04, Zr/Cd > 0.01, and Mo/Cd > 0.2 in the analyte solution result in significant Cd isotopic deviation. Isobaric interferences can theoretically be corrected using mathematical calculations, but their correction is difficult when the concentration ratios of these elements to Cd exceed a certain range. In this study, isotopic deviations could not be corrected when the ratios of Pd to Cd > 4 × 10−5, In to Cd > 0.02, and Sn to Cd > 0.1 (Fig. 3). These
observations differ from those of some previous studies. The threshold ratios of polyatomic interference elements as reported elsewhere ranged from 0.01 to 0.1 for Zn, 0.001 to 0.005 for Zr, and 0.1 to 1 for Mo. In this study, the results for Zn, Zr, and Mo adhered to those ranges. In addition, the threshold ratios of isobaric interference elements varied among the studies. Insufficient information is available about the threshold ratio of Pd because of the low levels in environmental and geological samples. However, our results for Pd were similar to those reported by Liu et al. For In, previously reported threshold ratios ranged from 10^{-3} to 0.02.25,28 Our result for In was similar to that reported by Peng et al. For Sn, different levels (0.02 to 0.5) of Sn-to-Cd ratios were reported by different laboratories,26-28 and our result for Sn fell within that range. However, the interference trends of In and Sn in this study were different from those reported previously. For In, the test range far exceeded that reported by Liu et al.,25 and δ^{114}/^{110}Cd values decreased when the ratio of In to Cd increased from 0.02 to 0.05 and increased when the ratio of In to Cd exceeded 0.05. This may be due to the fact that a high In signal, produced from high In content, can disrupt the data correction of Cd. For Sn, δ^{114}/^{110}Cd values decreased when the ratio of Sn to Cd increased, but the decrease was small. As mentioned earlier, the threshold ratios of Sn were different among different studies.26-28 In addition, Liu et al.25 reported that the interference of Sn can be corrected. Therefore, the threshold ratios of interference may be related to different instruments and experimental conditions that may produce different mass discrimination,26,28 as well as the difference in the trend of interference.

As mentioned above, when the concentration ratio of any interfering element to Cd after the first purification exceeds its corresponding threshold, a second chemical purification procedure is required. According to the interfering elements in the solution after the first purification, the reference materials GSS-4, GSS-5, GSD-11, and GSD-12 needed to be purified for a second time. After the secondary chemical purification procedure, the concentrations of the interfering elements in the purified solution decreased to their corresponding threshold without a loss of Cd, and the Cd isotopic ratios were consistent with those reported in previous studies (Table 4).

Another point that should be emphasized is the selection of laboratory equipment. A heating plate with an anti-rust coating was initially used in this laboratory, and no abnormalities were observed during the initial period of use. However, over time, rusting occurred around the plate, leading to a significant increase in the Zn concentration in the analyte solution. Therefore, a graphite-coated heating plate was used to avoid Zn contamination.

Precision, accuracy, and Cd isotope ratios of environmental reference materials. To evaluate the precision and accuracy of this method, three types of samples were measured: (1) four pure Cd solutions; (2) a synthetic solution containing matrix elements in three pure Cd solutions (NIST SRM3108, Thermo-Cd, and GSB-Cd); and (3) eight environmental reference materials.

The long-term precision of NIST 3108 was ±0.05‰ (2SD, n = 28). The δ^{114}/^{110}Cd value of AAS-Cd in this study (−0.699 ± 0.048‰, 2SD, n = 21) was in adequate agreement with that reported by Liu et al.25 The average δ^{114}/^{110}Cd values for Thermo-
Cd and GSB-Cd (two commercial mono-elemental standard solutions) were $-1.208 \pm 0.049$ (2SD, $n = 20$) and $4.441 \pm 0.053\%$ (2SD, $n = 22$), respectively (Fig. 4). To verify that the purification process did not change the true Cd isotope ratios of the samples, synthetic solutions (with double-spike) were purified and analyzed. Their $\delta^{114/110}{\text{Cd}}$ values were $-0.028 \pm 0.056$ (NIST SRM3108, 2SD, $n = 3$), $-1.218 \pm 0.043$ (Thermo-Cd, 2SD, $n = 3$), and $4.437 \pm 0.063\%$ (GSB-Cd, 2SD, $n = 3$), which is in adequate agreement with those of pure solutions. These results demonstrate that the chemical purification procedure did not change the true Cd isotope ratios of the samples. In addition, the Cd isotope ratios of the eight environmental reference materials were measured. Samples were digested under microwave irradiation, a double-spike solution was added before purification, and the ratios were then measured using MC-ICP-MS. $\delta^{114/110}{\text{Cd}}$ values of the eight environmental reference materials varied from $-0.558$ to $0.550\%$, with Cd concentrations from $0.45$ to $54.1 \text{mg kg}^{-1}$, which was in adequate agreement with that reported in previous studies (Table 4).

CONCLUSIONS

In this study, microwave digestion was conducted to prepare environmental samples for high-precision Cd isotope analysis. Compared with the digestion efficiency of traditional digestion methods (hot plate or high-pressure bombs), that achieved herein was significantly higher. Typically, the chemical purification procedure using an anion exchange resin effectively removed matrix elements without the loss of Cd. However, a secondary purification step was required for the analyte solutions with high concentrations of interference elements (Zn/Cd $> 0.04$, Zr/Cd $> 0.01$, Mo/Cd $> 0.2$, Pd/Cd $> 4 \times 10^{-5}$, In/Cd $> 0.02$, or Sn/Cd $> 0.1$). The $\delta^{114/110}{\text{Cd}}$ values of the eight environmental reference materials with different matrices varied from $-0.558$ to $0.550\%$, with Cd concentrations from $0.45$ to $54.1 \text{mg kg}^{-1}$, which was in adequate agreement with that reported in previous studies. The developed microwave digestion–resin purification–double-spike MC-ICP-MS method is useful for the Cd isotope analysis of environmental matrices and can improve the understanding of the source, transportation, and transformation of Cd in the environment.
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ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of Shandong (ZR2020ZD20), National Natural Science Foundation of China (21976193, and 21777178), and National Key R&D Program of China (2018YFC1800400). Y. Yin acknowledges the supports from National Young Top-Notch Talents (W03070030) and Youth Innovation Promotion Association of the Chinese Academy of Sciences (Y202011).

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Coal Proximate Analysis Based on Synergistic Use of LIBS and NIRS

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Received: April 13, 2022; Revised: April 28, 2022; Accepted: April 28, 2022; Available online: April 28, 2022.
DOI: 10.46770/AS.2022.099

ABSTRACT: Rapid and accurate analysis of the coal properties is essential for its clean and efficient utilization. However, the complexity of the physical-chemical characteristics of coal complicates accurate quantification of its properties using rapid spectroscopic technologies. Herein, a synergistic method is proposed to achieve optimum results for coal proximate analysis using spectra obtained via laser-induced breakdown spectroscopy (LIBS) and near-infrared reflectance spectroscopy (NIRS). Firstly, the ash content was analyzed by LIBS, and the moisture content was analyzed by NIRS. The calorific value and volatile content were then analyzed using the fusion data obtained from LIBS and NIRS, combined with the ash and moisture results. Finally, the fixed carbon content was calculated by subtracting the mass percentage fractions of ash, moisture, and volatile matter from 100%. The results indicated that the proposed method achieved good quantitative performance for coal proximate analysis. The root mean square errors of prediction for ash, moisture, calorific value, volatile matter, and fixed carbon were 0.743%, 0.304%, 0.187 MJ/kg, 0.662% and 0.972%, respectively. Thus, we believe that the proposed method based on the synergy of LIBS and NIRS opens avenues for efficient prospective analysis of coal properties.

INTRODUCTION

Coal is the primary source of energy worldwide. According to the BP Statistical review of World Energy 2021, the global coal consumption in 2020 is 151.42 EJ.1 Such a large volume of coal consumption contributes to high carbon emissions. However, to achieve the goals stated in the Paris Agreement, carbon emissions must be reduced.2 The clean and efficient utilization of coal, assisted by intelligent burner operation, is vital for reducing carbon emissions, and therefore, online measurements of multiple coal properties are essential. Currently, some rapid analysis techniques for coal properties, such as prompt gamma neutron activation analysis (PGNAA)3 and X-ray fluorescence (XRF)4 analysis, have been put into practice. However, PGNAA machine is bulky and needs to be strictly regulated because its neutron source has potential health and environmental hazards.5 XRF is not capable of detecting light elements, such as C and H.6 These disadvantages limit the wider application of PGNAA and XRF in coal property analysis.

Laser-induced breakdown spectroscopy (LIBS) is a promising technique for coal analysis7–9 and demonstrates advantages such as effortless sample preparation, real-time detection, and capability to detect all elements. Gaft et al.10 first applied LIBS to online analysis of ash content and the results were in good agreement with those from an existing online PGNAA machine. Ctvrtnickova11,12 used LIBS to measure ash in coal, and they established calibration curves for the elements contained in ash, demonstrating excellent correlation between element...
concentration and spectral intensity. Zhang et al.\textsuperscript{13} used principal component analysis (PCA) to extract the principal components from LIBS data as the inputs for a support vector regression (SVR) model to analyze coal properties. Yuan et al.\textsuperscript{14} proposed a non-linearized multivariate dominant factor based partial square least (PLS) model to correlate LIBS data with coal properties. Hou et al.\textsuperscript{15} proposed a hybrid quantification model to analyze coal properties, which integrated spectrum standardization, the dominant factor PLS, and a database system to improve sample-to-sample reproducibility. Song et al.\textsuperscript{16} used an ensemble variable selection method to filter LIBS data for a PLS model and proposed a synergistic regression to describe the linear and nonlinear relationship between LIBS data and coal properties.\textsuperscript{17} Yan et al.\textsuperscript{18–20} employed a kernel extreme learning machine combined with different variable selection methods to filter LIBS data to optimize the measurement of coal properties. Tao et al.\textsuperscript{21} used characteristic lines in LIBS to analyze coal properties based on an artificial neural network (ANN) optimized by a genetic algorithm, and reported that the analysis result is better than that obtained from a neutron activation coal online analyzer. Zhang et al.\textsuperscript{22} used the wavelet threshold de-noising method to identify available variables in LIBS to optimize the analysis of coal properties based on SVR. Lu et al.\textsuperscript{23} proposed the PLS method combined with ash classification to determine coal properties and discovered that the method improved the accuracy of analysis. Zhang et al.\textsuperscript{24} compared the performance of the PLS method, SVR and ANN in LIBS analysis of coal properties and discovered that the ANN demonstrates the best prediction performance. Although several efforts have been made to improve coal analysis using LIBS, matrix effects and the relatively high measurement uncertainty still limit its wide application.\textsuperscript{25,26}

Near-infrared reflectance spectroscopy (NIRS) is another available technique for coal analysis; it detects organic functional groups in substances according to molecular vibrations.\textsuperscript{27} NIRS has previously been used to analyze the coal properties and demonstrates several advantages, such as no sample preparation requirements, fast response, and simple operation. Bona et al.\textsuperscript{28–30} used near-infrared spectroscopy to analyze coal properties based on PLS method coupled with cluster analysis. The results indicated that the parameters related to organic matter exhibited a low prediction error. Kim et al.\textsuperscript{31} selected several near-infrared spectral bands to predict the properties of coal on a conveyor belt, and the prediction error met the requirement of ASTM/ISO standards. Begum et al.\textsuperscript{32,33} chose five maximum absorption bands distributed in the visible-near-infrared region to analyze coal properties and compared the performance of PLS, random forest, and extreme gradient boosting regression methods. Wang et al.\textsuperscript{34} proposed a deep synergy adaptive-moving window partial least square-genetic algorithm to correlate NIRS data with coal properties. Dong et al.\textsuperscript{35} proposed a deep belief network combined with a derivative function and regularization two-layer extreme learning machine (DF-RTELM) model to determine coal properties based on visible-infrared spectral data and discovered that the model outperformed other models such as convolutional neural network extreme learn machine and PLS-based models. However, the performance of NIRS is impaired by its lack of the sensitivity and absence of direct correlation with inorganic components. Coal property analyses using LIBS and NIRS were partially summarized in Table 1.

\begin{table}[h]
\centering
\caption{Summary of coal property analysis by LIBS and NIRS}
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Calibration} & \textbf{Method} & \textbf{Results} \\
\hline
PCA-SVR\textsuperscript{15} & Ash content: $R^2 = 0.96$, RMSEP = 1.82\%, ARE = 5.48\%; Volatile matter: $R^2 = 0.95$, RMSEP = 1.22\%, AAE = 4.42\%; Calorific value: $R^2 = 0.91$, RMSEP = 0.95 MJ/kg, ARE = 3.68\%; Moisture content: $R^2 = 0.97$, RMSEP = 0.87\%, AEE = 26.2\%; Ash content: $R^2 = 0.93$, RMSEP = 3.49\%, AEE = 12\%; Calorific value: $R^2 = 0.97$, RMSEP = 1.33 MJ/kg, ARE = 2.71\% \\
\hline
Non-linearized & & \\
\textbf{multivariate} & & \\
\textbf{dominant} & & \\
\textbf{factor} & & \\
\hline
PLS\textsuperscript{15} & Ash content: AAE = 1.661\%, mRSD = 1.649\%; Volatile matter: AAE = 0.664\%, mRSD = 0.317\% \\
\hline
Standardized & & \\
\textbf{spectra} & & \\
\textbf{combined} & & \\
\textbf{with} & & \\
\textbf{Dominant} & & \\
\textbf{factor} & & \\
\textbf{based} & & \\
\textbf{PLS}\textsuperscript{16} & & \\
\hline
PLS\textsuperscript{36} & Volatile matter: $R^2 = 0.9301$, RMSEP = 0.8534\%; Ash content: $R^2 = 0.96$, RMSEP = 1.7618\%; Calorific value: $R^2 = 0.9034$, RMSEP = 0.8436 MJ/kg \\
\hline
Synergic regression\textsuperscript{17} & Heat value: $R^2 = 0.959$, RMSEP = 0.3733 MJ/kg, MAE = 0.299 MJ/kg; \\
\hline
PESOs-KELM\textsuperscript{20} & Volatile content: $R^2 = 0.93$, RMSEP = 0.7909, MAE = 0.9009; Ash content: $R^2 = 0.938$, RMSEP = 1.112 MJ/kg, MAE = 0.8355% \\
\hline
V-WSP-PSEOSKELM\textsuperscript{20} & Ash content: $R^2 = 0.9926$, RMSEP = 2.0485\%; Volatile matter: $R^2 = 0.9945$, RMSEP = 1.0874\%; Calorific value: $R^2 = 0.9872$, RMSEP = 0.6999 MJ/kg \\
\hline
WTD-SVR\textsuperscript{22} & Ash content: $R^2 = 0.97$, RMSEP = 0.8534\%; Ash content: $R^2 = 0.99$, RMSEP = 0.55\%, AEE = 2.99\%; RMSEP = 0.69\% \\
\hline
SVM-PLS\textsuperscript{37} & Ash content: $R^2 = 0.972$, RMSEP = 0.9065\%; Volatile matter: $R^2 = 0.9999$, RMSEP = 0.4903 MJ/kg \\
\hline
ANN\textsuperscript{20} & Calorific value: $R^2 = 0.99$, RMSEP = 0.47 MJ/kg, AAE = 1.82 MJ/kg; Moisture content: RMSEP = 0.1984; Ash: RMSEP = 3.50\%; Fixed carbon: RMSEP = 3.12\% \\
\hline
PLS\textsuperscript{20} & Moisture content: $R^2 = 0.322$, Ash: $R^2 = 0.523$; Volatile matter: $R^2 = 3.70\%$, Fixed carbon: $R^2 = 5.13\%$. Heating value: RMSEP = 557.04 kcal/kg \\
\hline
MLR\textsuperscript{5} & Moisture content: RMSEP = 1.02\%, Volatile matter: RMSEP = 1.20\%; Ash: RMSEP = 1.74\%, Fixed carbon: RMSEP = 1.97\% \\
\hline
MLR\textsuperscript{5} & Calorific value: $R^2 = 0.92$, RMSEP = 1.64 MJ/kg \\
\hline
DASA-MWPLS-GA\textsuperscript{36} & Volatile matter: RMSEP = 0.50\%, Heat value: RMSEP = 0.946 MJ/kg, AAE = 0.49\% \\
\hline
DNISDF-RTELM\textsuperscript{20} & Moisture content: $R^2 = 0.96$, RMSEP = 1.67\%; Ash content: $R^2 = 0.95$, RMSEP = 3.38\%; Volatile matter: $R^2 = 0.97$, RMSEP = 3.54\%; Fixed carbon: $R^2 = 0.99$, RMSEP = 3.54\% \\
\hline
\end{tabular}
\end{table}

*\textsuperscript{1}R\textsuperscript{2} denotes determination coefficient, RMSEP denotes Root Mean Square Error of Prediction, ARE denotes Average Relative Error, MAE and AAE denote Mean/Average Absolute Error, ASD denotes Average Standard Deviation, mRSD and ARSD denote Mean/Average Relative Standard Deviation.
Evidently, the combination of LIBS and NIRS should achieve much better results than either of them individually because LIBS provides elemental information, while NIRS provides molecular information, and the properties of coal are related to both its elemental and molecular composition. Garcia et al.\textsuperscript{37} used the integration of LIBS with NIRS to reveal the relationship between the heavy metals content and mineralogical concentration in perlite. Sánchez-Esteva et al.\textsuperscript{38} used a combination of LIBS and visible near-infrared spectroscopy to improve soil phosphorus determination based on the PLS method. Oliveira et al.\textsuperscript{39} discovered that the fusion of LIBS and NIRS data demonstrates better predictive accuracy than individual LIBS and NIRS data for determination of micro- and macro elements in vegetable samples. Bricklemyer et al.\textsuperscript{40} revealed that the combination of visible NIRS and LIBS data provides the best prediction of total carbon in soil. In a previous work,\textsuperscript{41} we have proven that the combination of LIBS and NIRS improves the analysis of multiple coal property indices. The results of that study obtained the RMSEP for calorific value, volatile matter, ash content, and moisture content as 0.192 MJ/kg, 0.672%, 0.774%, and 0.308%, respectively.

As can be inferred the above literature review, a modelling method directly correlates spectral data with coal properties; therefore, it may suffer from low accuracy when determining coal properties with complex characteristics. In contrast, methods that are more dependent on the physical correlation between the spectra and coal properties should yield a more accurate and robust analytical performance. In the present study, we developed a step-by-step method to utilize the spectral information synergistically.

**METHOD**

Coal properties with different characteristics were determined using various information. Ash is the residue obtained from burning coal, primarily composed of the oxides of elements such as Si, Al, Fe, Ca, Mg and K\textsuperscript{42}, which contribute to high spectral emissions in LIBS. Moisture, in regards to coal proximate analysis, refers to the free water content in coal,\textsuperscript{43} and NIRS is sensitive to moisture.\textsuperscript{44} The calorific value is the total energy released from the complete combustion of a unit mass of coal under specified conditions.\textsuperscript{45} The evaporation of moisture absorbs some of the heat released during combustion. The minerals in ash are decomposed by endothermic reactions, which also absorbs some amount of heat.\textsuperscript{46} Volatile matter is a gaseous mixture of thermal decomposition products formed when coal is heated at high temperature under air-free conditions.\textsuperscript{45} Volatile matter components originate from the decomposition of organic matter as well as from minerals,\textsuperscript{47} such as the water of hydration and sulfur compounds. Moreover, the metal cations in ash reduce the total volatile yield because they promote re-deposition of the primary volatile material.\textsuperscript{48} Thus, calorific value and volatile matter are not only related to both the elemental and organic molecular compositions, but are also dependent on ash content and moisture content to a certain extent. Accordingly, we proposed a step-by-step method to synergistically utilize the spectral information to improve the analysis of these properties of coal, as shown in Fig.1. First, the ash content was analyzed using LIBS and moisture content was analyzed using NIRS. Then, the ash and moisture results were combined with the fusion data obtained from LIBS and NIRS to deduce the calorific value and volatile matter content. Finally, the fixed carbon content was calculated according to its formula definition by subtracting the previously determined percentage mass fractions of ash, moisture, and volatile matter from 100%. The novelty of this work is to propose a step-by-step method to synergistically utilize the spectral information to determine coal properties with different characteristics.

Owing to high dimensionality and collinearity present in LIBS and NIRS data, quantitative analysis models of ash and moisture content were established based on PLS\textsuperscript{49} method. The relationship between calorific value, volatile matter, moisture content, and ash content is complex. The contribution of moisture to the calorific value and volatile content is affected by the form of water and other factors.\textsuperscript{50} In reference to the heat of metal oxides formation, ash contributes positively to the calorific value, while the presence of oxidized metals results in the absorption of energy.\textsuperscript{46} Ash is mainly composed of oxidized metals, so it contributes negatively to calorific value. For volatile matter, inorganic constituents not only promote the conversion of heavier hydrocarbon species to light gases, but also promote the polymerization of tars to form non-volatile species.\textsuperscript{51} Meanwhile, LIBS data, NIRS data and the ash and moisture content all have significant differences in terms of order of magnitude. Therefore, three approaches were proposed to establish quantitative analysis models for calorific value and volatile matter.

![Fig. 1](https://www.at-spectrosc.com/ea/article/pdf/2022099)

**Fig. 1** Step-by-step method for utilization of the spectral information to improve coal property analysis.
volatile matter. The three approaches are described as follows:

1. The generalized spectral variables (GS) approach initially uses decimal scaling to normalize the LIBS and NIRS data and the ash and moisture results. Then, LIBS and NIRS data and the ash and moisture results are connected end-to-end to form GS. Finally, the GS are used to determine the calorific value and volatile matter based on the PLS method.

2. The multiple linear regression coupled with PLS (MLR-PLS) technique directly uses the ash and moisture results to preliminarily deduce the calorific value and volatile matter based on a multiple linear regression (MLR) method. Then, the residuals between the preliminary analysis value from the MLR and the certified value are corrected using the LIBS and NIRS data based on PLS method. The result represents the sum of the preliminary analysis value and corrected residuals.

3. Non-linear multivariate regression coupled with PLS (non-linear MR-PLS) methodology directly used the determined ash and moisture results and their quadratic term to preliminarily determine the calorific value and volatile matter based on the MLR method, which is called non-linear multivariate regression. Then, the residuals between the preliminary analysis value obtained from the non-linear multivariate regression and the certified value are corrected using the LIBS and NIRS data based on PLS. The result is the sum of the preliminary analysis value and the corrected residuals.

These quantitative analysis models were evaluated according to \( R^2 \), RMSEP, AAE and mRSD. The mRSD denotes the mean value of the relative standard deviation (RSD) of all samples in the validation set, and the RSD value is calculated based on 4 repeated measurements. In the PLS regression model, the input variables were selected according to the PLS regression coefficient method described in the literature.

### EXPERIMENTAL

**Coal samples.** The coal samples used in this study were 60 coal samples collected from different coal-fired power plants located in China. The coal samples were ground and sieved to particle sizes of less than 0.2 mm. The certified calorific value, volatile matter, ash content, moisture content, and fixed carbon content were analyzed by standard off-line methods on an air-dried basis. Table 2 lists the statistical results of the certified values of coal samples. Among the chosen samples, 12 coal samples were randomly selected for the validation set. The remaining 48 coal samples were assigned to the calibration set.

**LIBS spectra collection.** In present work, the LIBS and the NIRS setup are independent instruments and LIBS and NIRS spectra were collected independently. A detailed description of the LIBS experimental setup is provided in the literature. Briefly, the excitation source was a 1064 nm Q-switch Nd:YAG pulse laser (Quantel Brilliant Easy, USA). The laser pulse duration was 5 ns, and the repetition frequency was 2 Hz. The laser energy was optimized to 55 mJ per pulse. The laser was focused using a lens with a focal length of 50 mm to ablate the sample and generate plasma. The focal point was located 2 mm below the sample surface. Plasma emission was coupled to an optical fiber and then transmitted to a four-channel spectrometer (Avantes, Netherlands). The spectrometer covered a wavelength range of 178 to 827 nm, with a nominal resolution of 0.08-0.1 nm and fixed gate-width of 1.05 ms. The delay time of the spectrometer acquisition signal was set as 1 μs. During the experiment, approximate 3 g of powdered coal from each sample was pressed into a 25 mm diameter pellet using a tablet machine (Pike Technologies Crushir). The sample pellets were exposed to ambient air and placed on an automatic three-dimensional mobile platform. For each sample, 320 spectra were collected from 16 locations on the pellet’s surface.

**NIRS spectra collection.** NIRS spectra were collected using an MPA Type Fourier transform NIR spectrometer (Bruker, Germany). The instrument was controlled using the software package OPUS7.5 from Bruker and NIRS spectra were collected in diffuse reflectance mode. The background spectrum was collected using air as the blank sample to correct the coal spectra. Each powdered coal sample was held in a diffuse reflectance sample cup and, the surface was flattened using a spatula. Each spectrum was recorded by co-adding 64 scans over the range of 12,500 to 4000 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\) and 4 NIRS spectra were collected from each coal sample.

### RESULTS AND DISCUSSION

Typical LIBS and NIRS spectrum of coal collected in this study is presented in Fig. 2. LIBS spectra were preprocessed using the channel normalization method to reduce the fluctuation of spectral...
Table 3 Statistical results of the certified value of coal properties

<table>
<thead>
<tr>
<th>Empirical equation</th>
<th>Coal origin</th>
<th>GCV (MJ/kg)</th>
<th>GCV range</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCV = -0.11M + 0.33VM + 0.35FC - 0.003A *</td>
<td>India</td>
<td>12.75-28.37</td>
<td></td>
</tr>
<tr>
<td>GCV = -37.77 + 0.64VM - 0.089M + 0.387A **</td>
<td>United States</td>
<td>4.82-34.85</td>
<td></td>
</tr>
<tr>
<td>GCV = 35.91 - 0.47M + 0.028VM + 0.364A *</td>
<td>Afghanistan</td>
<td>3.66-32.65</td>
<td></td>
</tr>
<tr>
<td>GCV = -0.266M + 0.293VM + 0.371FC - 0.004A *</td>
<td>United States</td>
<td>4.82-34.85</td>
<td></td>
</tr>
<tr>
<td>GCV = -0.053M + 0.296VM + 0.353FC - 0.002A *</td>
<td>China</td>
<td>12.71-26.53</td>
<td></td>
</tr>
<tr>
<td>GCV = 76.56 - 1.30(VM+A) + 7.03×10^{-3}(VM+A)^2 **</td>
<td>Turkish</td>
<td>15.63-30.37</td>
<td></td>
</tr>
</tbody>
</table>

* Received basis; ** Dry basis; Where GCV, M, VM, FC and A denote the gross calorific value, moisture content, volatile matter, fixed carbon, and ash content, respectively.

Fig. 2 Typical spectrum of coal: (a) LIBS, (b) NIRS.

Fig. 3 Ash content analyzed using LIBS.

Fig. 4 Moisture content analyzed using NIRS.

Correlation between coal properties. The empirical equation correlating the calorific value with proximate analysis was first proposed by Goutal in early 20th century. Subsequently, several empirical equations that consider ash and moisture as important components for calculating the calorific value of coal on a dry basis or received basis, have been developed, as listed in Table 3. It can be observed from the reported empirical equation that ash and moisture contribute negatively to the calorific value.

Volatile matter is related to the decomposition of organic substances and associated mineral matter. To quantify the correlation between the calorific value, volatile matter, and determined ash and moisture results, a distance correlation (DC) analysis was conducted. The DC method can disclose both linear and nonlinear relationships between the independent variable (X) and dependent variable (Y). As presented in Table 4, the distance correlation coefficient for the calorific value with ash or moisture data.
Table 4 Results of distance correlation analysis

<table>
<thead>
<tr>
<th></th>
<th>Ash content</th>
<th>Moisture content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorific value</td>
<td>Correlation</td>
<td>0.797</td>
</tr>
<tr>
<td></td>
<td>Sig.</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>Correlation</td>
<td>0.905</td>
</tr>
<tr>
<td></td>
<td>Sig.</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

exceeds 0.523. The distance correlation coefficient is greater than 0.880 for the volatile matter, ash, and moisture. Besides, significance test was conducted according to the correlation coefficient and t test at the 95% confidence level. Therefore, calorific value and volatile matter strongly correlate with the ash and moisture content. The ash and moisture results were considered for the determination of calorific value and volatile matter.

Calorific value and volatile content. As discussed above, calorific value and volatile matter have complex characteristics, which are related to both elemental and molecular composition and correlate with ash content and moisture content. Thus, the calorific value and volatile matter were analyzed by the combination of NIRS and LIBS data with ash and moisture results using GS, MLR-PLS and non-linear MR-PLS approaches. For comparison, the conventional approach based on PLS with only the LIBS and NIRS data was also used to determine the calorific value and volatile matter. The X loading weights for the calibration models based on the GS approach are presented in Fig. 5 for calorific value and volatile matter. The loading weight of ash and moisture data is greater than that of most variables, which indicates that the ash and moisture data play an important role in the determination of calorific value and volatile matter.

The analysis results of the calorific value and volatile matter obtained from different approaches are shown in Figs. 6 and 7. The results obtained from the GS, MLR_PLS and non-linear MR_PLS approaches are better than those from conventional approach. Moreover, the non-linear MR_PLS approach exhibits the best performance. When compared with the conventional approach, for the non-linear MR_PLS, the RMSEP, AAE and mRSD decrease from 0.536 MJ/kg to 0.187 MJ/kg, 0.449 MJ/kg to 0.154 MJ/kg and 0.937% to 0.262%, respectively, for the calorific value, and from 1.125% to 0.662%, 0.940% to 0.506% and 3.192% to 1.045%, respectively, for volatile matter. In the non-linear MR_PLS method, non-linear multivariate regression manages the linear and non-linear relationships between the calorific value, volatile matter, ash, and moisture. Furthermore, the residuals between the preliminary analysis value obtained from the non-linear multivariate regression and the certified value are corrected by LIBS and NIRS data, which provides abundant elemental and molecular information related to the calorific value and volatile content.

Fixed carbon content. The fixed carbon content was indirectly determined by subtracting the resultant summation of ash, moisture and volatile content from 100%. To obtain all proximate analysis indices, the fixed carbon content was calculated using its definition formula with the results of ash and moisture and the result of volatile matter predicted by the non-linear MR_PLS method. The calculation results for fixed carbon content are shown in Fig. 8.

CONCLUSIONS

A step-by-step method to synergistically utilize spectral information was proposed to improve the analysis of various properties of coal with different characteristics. The ash content was determined using LIBS, and the moisture content was determined using NIRS. The RMSEP value of ash and moisture content are 0.743% and 0.304%, respectively. Subsequently, the ash and moisture results were combined with the fusion data of LIBS and NIRS to determine calorific value and volatile matter, and this approach outperformed the conventional approach that
Fig. 6 Analysis results for calorific value obtained from different approaches: (a) conventional approach, (b) GS, (c) MLR_PLS, and (d) non-linear MR_PLS.

Fig. 7 Analysis results for volatile matter obtained from different approaches: (a) conventional approaches, (b) GS, (c) MLR_PLS, and (d) non-linear MR_PLS.
used only the fusion data of LIBS and NIRS. The non-linear MR_PLS approach exhibited the best performance. Compared with the conventional approach, for the non-linear MR_PLS method, the RMSEP, AAE and mRSD for calorific value decreased from 0.536 to 0.187 MJ/kg, 0.449 to 0.154 MJ/kg and 0.937% to 0.262%, respectively, and the corresponding values for volatile matter decreased from 1.125% to 0.662%, 0.940% to 0.506%, and 3.192% to 1.045%, respectively. Following the analysis of ash, moisture, and volatile matter content, the fixed carbon content was determined using its definition formula. These results demonstrate that the proposed method can improve the accuracy and precision of coal analysis.

AUTHOR INFORMATION

Shunchun Yao received his Bachelor's in 2006 from the Soochow University, China, and PhD in 2011 from the school of Electric power, South China University of Technology (SCUT). He is a research professor of power engineering and engineering thermos-physics at the school of electric power, SCUT. His major research interests are laser-induced breakdown spectroscopy (LIBS), tunable diode laser absorption spectroscopy (TDLAS), and their application to intelligent sensing and on-line monitoring for clean and efficient utilization of energy. He has been working as associate director in Guangdong Province Engineering Research Center of High Efficient and Low Pollution Energy Conversion and LIBS young scientist of Chinese Society for Optical Engineering. Shunchun Yao is author or co-author of over 90 articles published in peer-reviewed scientific journals, with an h-index of 20 (Scopus). His work is supported by Guangdong Natural Science Funds for Distinguished Young Scholar.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Fund of China (51676073), Guangdong Natural Science Funds for Distinguished Young Scholar (2021B1515020071), The Fok Ying-Tong Education Foundation for Young Teachers in the Higher Education Institutions of China (171047), Foundation of State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering (2022-K72), Technological Innovation and Entrepreneurship Team Project of Foshan (1920001000052), Natural Science Foundation of Guangdong, China (2022A151501074), the Guangdong Province Key Laboratory of Efficient and Clean Energy Utilization (2013A061401005).

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http://doi.org/10.1016/0016-2361(91)90054-E

https://doi.org/10.1214/009053607000000505

http://doi.org/10.1080/03610910701418028
High-precision Fe Isotope Analysis on MC-ICPMS Using a $^{57}\text{Fe}$-$^{58}\text{Fe}$ Double Spike Technique

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Received: March 11, 2022; Revised: April 15, 2022; Accepted: April 15, 2022; Available online: April 16, 2022.

DOI: 10.46770/AS.2022.062

ABSTRACT: Herein we report procedures based on multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) for high-precision Fe isotopic analysis using a $^{57}\text{Fe}$-$^{58}\text{Fe}$ double spike technique. Iron purification was achieved using AG1-X8 in HCl media following previously or newly established procedures. In the new procedure, smaller columns with 4 mm diameter were used, containing 0.4 mL AG1-X8, thus greatly reducing the operation time and the amount of acid and resin consumed compared to the previously established method using 1 mL resin. Potential trace Ni interference on $^{58}\text{Fe}$ was suppressed by increasing the total Fe ion intensity to $\geq 120$ V. Measurements of GSB Fe solutions doped with mono-elements demonstrated that a mass bias correction by the $^{57}\text{Fe}$-$^{58}\text{Fe}$ double spike was robust if Ca/Fe $\leq 1.0$, Al/Fe $\leq 1.0$, Cu/Fe $\leq 1.0$, Co/Fe $\leq 0.1$, Ni/Fe $\leq 10^{-4}$, and Cr/Fe $\leq 10^{-4}$. Monitoring of pure Fe standard solutions, viz. IRMM-014 and NIST3126a, and geological reference materials, viz. JP-1, BHVO-2, W-2a, GSP-2, and COQ-1, over nine months yielded $\delta^{56}\text{Fe}$ (relative to IRMM-014) values of 0.003 ± 0.013‰ (2 SD, N = 20), 0.368 ± 0.011‰ (2 SD, N = 30), 0.019 ± 0.018‰ (2 SD, N = 15), 0.109 ± 0.017‰ (2 SD, N = 30), 0.049 ± 0.018‰ (2 SD, N = 17), 0.155 ± 0.018‰ (2 SD, N = 14), and -0.066 ± 0.022‰ (2 SD, N = 20), respectively, consistent with the recommended values within quoted errors. Based on repeated analyses of the standards, the long-term precision of our double spike method is better than 0.02‰ for $\delta^{56}\text{Fe}$ on average, proving its ability to distinguish small isotope fractionation among high-temperature samples.

INTRODUCTION

Iron (Fe) has long been of great interest to geochemists because of its abundance, role in biological activities, and sensitivity to redox changes.1-3 It has four stable isotopes, $^{54}\text{Fe}$, $^{56}\text{Fe}$, $^{57}\text{Fe}$, and $^{58}\text{Fe}$, with relative abundances of 5.84, 91.76, 2.12, and 0.28%, respectively. The mass difference among them (up to 6.9% between $^{54}\text{Fe}$ and $^{58}\text{Fe}$) intrinsically drives isotope fractionation, which is a potential tool for tracing a variety of geological, biological, and environmental processes, such as partial melting,4 magma differentiation,6-11 mantle metasomatism,12-14 and redox exchange between the deep Earth and surficial spheres,15-17 redox change of paleo-oceans,18,19 and microbe and human metabolism.20-22

Compared with low-temperature archives, Fe isotope fractionation among the high-temperature geological samples is relatively restricted. For example, the majority of the pristine mantle peridotites, island arc basalts and boninites, mid-ocean ridge basalts, and ocean island basalts display a limited $\delta^{56}\text{Fe}$ variation of 0.10 ± 0.15‰.1 Hence, high-precision isotopic analyses are necessary to resolve and decode Fe isotope fractionation in high-temperature systems. However, there are analytical challenges in obtaining high-precision and accurate Fe isotopic data, arising mainly from isobaric interferences and the correction of instrumental mass bias. Polyatomic ion interferences (e.g., $^{40}\text{Ar}^{16}\text{O}$ on $^{56}\text{Fe}^+$) are routinely discriminated by (pseudo-) high mass resolution on new generations of MC-ICPMS (e.g., Nu Plasma 1700, Nu Plasma, and Neptune plus).23-26 Instrumental
mass bias can be corrected using standard sample bracketing (SSB), element doping, and double spike techniques. The SSB method is used widely and assumes mass bias during sample measurements to be the same as that of bracketing standard measurements. Validation of this assumption requires a well-controlled laboratory environment (e.g., temperature, humidity, and air exhaust rate), instrument stability, and a highly matched matrix (1 and the references therein). The element doping method assumes that the isotopes of the doped element exhibit an isotope fractionation behavior similar to those isotopes of the element of interest and helps to overcome mass bias fluctuations. Nevertheless, the doped element and the element of interest (e.g., Ni and Fe) could exhibit different isotope fractionation behaviors during measurements. In an optimized case, a long-term precision (2 SD) for $^{56}{\text{Fe}}/^{54}{\text{Fe}}$ better than 0.03% can be routinely achieved, provided that each sample is measured nine times by MC-ICPMS.

Theoretically, the double spike technique can be used to accurately correct instrumental mass bias and yield high-precision isotopic data. Millet et al. reported a procedure to measure Fe isotope ratios using a $^{57}{\text{Fe}}/^{56}{\text{Fe}}$ double spike and demonstrated that the external reproducibility could be as good as 0.02% for $^{56}{\text{Fe}}$. Nevertheless, isobaric interferences (e.g., trace $^{58}{\text{Ni}}$ on $^{54}{\text{Fe}}$ and polyatomic interferences) may hinder accurate analyses. In particular, $^{58}{\text{Ni}}$ is an abundant isotope (~68.08% 34), whereas $^{56}{\text{Fe}}$ is a trace isotope (~0.28% 35). The improper correction of trace $^{58}{\text{Ni}}$ interference using $^{60}{\text{Ni}}$ routinely monitored on a Faraday cup may cause significant uncertainty in the deduced $^{56}{\text{Fe}}/^{54}{\text{Fe}}$ using the double spike method (namely, the trace Ni correction problem). Finlayson et al. illustrated that the precision of $\delta^{56}{\text{Fe}}$ can be improved three-fold from ±0.145 to ±0.052‰ when $^{60}{\text{Ni}}$ is monitored on an ion counter instead of a Faraday cup, allowing improved correction of $^{58}{\text{Ni}}$ interference.

In this study, we developed an improved purification procedure to efficiently separate Fe from the sample matrix and present high-precision Fe isotope ratio measurements utilizing a $^{57}{\text{Fe}}/^{56}{\text{Fe}}$ double spike. The on-peak-zero fluctuations (partially contributed by tails of polyatomic ions) and trace Ni correction problems were suppressed by increasing the signal-to-noise ratio. The robustness of this method was demonstrated by repeated measurements of solutions (GSB Fe, IRMM-014, and NIST3126a) and geological standards (JP-1, BHVO-2, W-2a, GSP-2, and COQ-1), indicating a 2 SD reproducibility and accuracy for $\delta^{56}{\text{Fe}}$ better than 0.020‰. Fe isotopic analyses of such high precision can help distinguish limited Fe isotope fractionation during high-temperature processes.

THEORETICAL OPTIMIZATION

Iron isotopic analyses using a $^{57}{\text{Fe}}/^{56}{\text{Fe}}$ double spike on MC-ICPMS have been previously attempted in Zhu et al. In this early study, $\delta^{56}{\text{Fe}}$ was measured at low signals (i.e., a $^{56}{\text{Fe}}$ signal within 15 ± 5 V), yielding a long-term precision of 0.10‰ for single time measurements and showing no superiority in precision or accuracy compared to that of the SSB method using element doping. The merits of the double spike technique in accurate mass bias correction may have been counteracted by the trace Ni correction problem stemming from the introduction of the trace isotope $^{58}{\text{Fe}}$ into data deduction. The trace Ni correction problem was previously overcome by monitoring $^{60}{\text{Ni}}$ on an ion counter. Herein, we evaluate the trace Ni correction problem via Monte Carlo calculations for measurements using Faraday cups only. Theoretical runs were simulated for a spiked standard with $\delta^{56}{\text{Fe}} = 0$, an optimized $^{57}{\text{Fe}}/^{56}{\text{Fe}}$ double spike proportion (referred to as β hereafter) of 0.457 and a mass bias (referred to as β hereafter) of -1.5. Internal errors from counting statistics and Johnson noise of the measured ratios during data acquisition were calculated based on equations listed by Lehn et al. using an integration time of 4.194 s; 10$^4$Ω resistors were adopted for all Faraday cups, except that a 10$^6$Ω resistor was used for $^{56}{\text{Fe}}$ when its signal was > 40 V. To account for the trace Ni correction problem, trace Ni ($^{60}{\text{Ni}}/^{56}{\text{Fe}} = 10^{-5}$) was introduced. Despite being theoretically negligible, it could cause a problem during measurements. The non-linear behavior of Faraday cups connected with the 10$^4$Ω resistors has been previously observed for signals below 1 mV on the Nu instrument, and the hardware manual for Neptune plus suggests that 10$^4$Ω resistors may not accurately measure signals < 0.1 mV. A limit (e.g., 0.1 mV, 0.2 mV, and 0.3 mV) was set, and for a signal below this limit (i.e., $^{60}{\text{Ni}}$ in this study), the relative error from Johnson noise ($\sigma_{\text{Ni}}$) contributed by this signal was calculated by dividing the value of the limit with that of the signal, i.e., [limit]/[signal]. Compared to the theoretical value of 0.02 mV for 4.194 s of integration on 10$^4$Ω resistors, this assumption experimentally enlarged the Johnson noise of the trace $^{60}{\text{Ni}}$ signal to examine the non-linear and inaccurate behavior during data acquisition. Measured ratios were randomly obtained for 40 cycles by setting normally distributed errors around theoretical values, and then the mean $\delta^{56}{\text{Fe}}$ and two standard errors (2 SE) were deduced using equations listed in He et al. The calculation was performed and repeated 1000 times for the sum of the signals ranging from 2 to 200 V with an increment of 2 V. The results are illustrated in Fig. 1 and show considerable extra errors from the correction of trace Ni interference being propagated to the deduced mean $\delta^{56}{\text{Fe}}$, particularly at a low sum of signals. For example, for a sum of signals of 10 V, the internal error for $\delta^{56}{\text{Fe}}$ is 0.099‰, 0.162‰, and 0.235‰ when the trace signal limit is set to 0.1 mV, 0.2 mV, and 0.3 mV, respectively, compared to the case (~0.064‰) without Ni correction. Internal errors for $\delta^{56}{\text{Fe}}$ with or without the trace Ni correction problem converge at a high sum of signals, and the trace Ni correction problem can be suppressed by an increased signal-to-noise ratio or with a sum of signals >120 V.
Experimental Methods

Reference materials and the $^{56}\text{Fe-}^{58}\text{Fe}$ double spike. Three pure Fe standard solutions (GSB Fe, IRMM-014, and NIST3126a) were used to monitor the reproducibility of isotopic analyses using mass spectrometry. GSB Fe, an in-house standard prepared by mixing mono-element solutions from the China Iron and Steel Research Institute (CISRI), has a δ$^{56}\text{Fe}$ of 0.729 ± 0.005‰ (2 SE) relative to IRMM-014. GSB Fe that passed through the column was used as a bracketing standard and doped with mono-element solutions from CISRI for the doping experiments. Five well-characterized rock standards from the United States Geological Survey (USGS) and the Geological Survey of Japan (GSJ) were processed and analyzed to evaluate the reproducibility and accuracy of the procedure. A $^{57}\text{Fe-}^{58}\text{Fe}$ double spike was adopted and prepared using single spikes from the Oak Ridge National Laboratory (USA), according to the optimized proportion calculated by Rudge et al. The double spike composition was previously calibrated, with $^{56}\text{Fe}/^{58}\text{Fe} = 0.026621 ± 0.000005$, $^{57}\text{Fe}/^{58}\text{Fe} = 3.8452 ± 0.0005$, and $^{58}\text{Fe}/^{58}\text{Fe} = 3.9807 ± 0.0005$.

Sample digestion and chemical purification. Sample powders containing ≥ 250 μg of Fe were dissolved in a mixture of concentrated HF-HNO$_3$ (2:1, v/v). After the optical check, precipitate-free solutions were evaporated to dryness at 160 °C and refluxed in aqua regia (HCl:HNO$_3$ = 3:1, v/v) and trans aqua regia (HNO$_3$:HCl = 1:2, v/v) to remove fluorides and completely oxidize Fe$^{2+}$. The resultant solutions were dried at 90 °C and refluxed with concentrated HCl. The final samples were dissolved in 0.5 mL of 6 N HCl prior to column chromatography. Fe was purified using AG1-X8 resin (200-400 mesh chloride form, Bio-Rad, Hercules, CA, USA) (Table 1). The resin was pre-cleaned by sequentially rinsing with 6 N HCl, 1 N HNO$_3$, 0.4 N HCl, and Milli-Q H$_2$O. At the beginning of this study, the previously established procedure was adopted using 10 mL columns from Bio-Rad, USA, having a diameter of ca. 8 mm, filled with 1 mL AG1-X8 resin. Most of the matrix elements were eluted with 8 mL 6 N HCl, and Fe was collected using 9 mL of 0.4 N HCl. The recovery of Fe was estimated to be -99.95 ± 0.13% (2 SD, n = 5) after a single pass. Chromatography was routinely repeated a second time to completely remove interference elements, such as Cr and Ni.

To reduce the amount of acid and resin consumption and increase efficiency, smaller columns from Booming Technology Limited, China (http://www.boomingtect.com), having a diameter of 4 mm, packed with 0.4 mL AG1-X8 resin, were also tested. The elution behavior of the new column was evaluated using BHVO-2, and the results are shown in Fig. 2. Most major (e.g., K, Ca, Na, Mg, Al, Ti, and Mn) and trace (e.g., Cr and Ni) matrix elements could be quantitatively (> 99.9%) washed out in the first 4 mL of 6 N HCl, except for Cu and Co, which could be efficiently eluted without losing Fe by using more 6 N HCl. Since most high-temperature samples (except for Cu- and Co-bearing minerals or
Deduced fluctuation in mass bias (as filled symbols expressed as by two representative sessions on April 11, 2021 and September 04, 2021. As demonstrated by BHVO-2 after a single pass, the elute the matrices for efficiency. Iron was then collected by 4 mL yield of Fe was approximately 99.67 ± 1.02% (2 SD, n = 4), and levels (all major isobaric element/Fe ratios were reduced to insignificant Fe processed. Using β relative to the first measurement of each session) is noted. Considered negligible (< 2‰) compared to the ≥10 μg of sample Fe processed.

Thermo Fisher Neptune Plus MC-ICPMS at the Isotope Geochemistry Lab at the China University of Geosciences, Beijing (CUGB). The samples were introduced into the plasma through a PFA self-aspiration micro-nebulizer with an uptake rate of 50 μL/min and a Scott double-pass quartz glass spray chamber, which used a Cetac ASX-110 autosampler. Iron isotopes were measured at the lower mass shoulders in high-resolution modes, with\( ^{55}\text{Cr} (^{54}\text{Cr} + ^{56}\text{Fe}), ^{56}\text{Fe}, ^{56}\text{Fe} + ^{58}\text{Ni}, \) and \( ^{60}\text{Ni} \) statically collected by Faraday cups, L3, L1, C, H1, H2, and H4, respectively. \( ^{56}\text{Cr} \) and \( ^{60}\text{Ni} \) were monitored to correct the isobaric interferences of \( ^{56}\text{Cr} \) and \( ^{58}\text{Ni} \) using experiential ratios previously obtained for 100 ppb GSB Cr and Ni solutions (\( ^{56}\text{Cr} / ^{56}\text{Fe} = 0.2571 \) and \( ^{60}\text{Ni} / ^{56}\text{Ni} = 0.408761) \). The sample and standard solutions were spiked in optimized q ~0.46 prior to either the column chemistry or isotopic analyses, with bulk concentrations of 8–12 ppm to obtain a total Fe signal >120 V. To account for the >70 V \( ^{56}\text{Fe} \) signal, a 10\( \Omega \) resistor amplifier was used for the central Faraday cup, and 10\( \Omega \) resistors were used for the other cups. Each analysis consisted of an idle time of 3 s and 40 cycles of 4.194 s integration time. Each analysis sequence consisted of a blank of 0.15 N HNO\(_3\) for the on-peak-zero correction and several blocks of sample and standard solutions, which were routinely repeated four times. GSB Fe was used as the bracketing standard for every five samples. The data were deduced offline using an Excel macro program. A burst of residual argide-based interferences was not observed, as indicated by the absence of a jump in the deduced \( ^{56}\text{Fe} \) of bracketing GSB Fe in each session (Fig. 3). Nevertheless, a monotone drift in the deduced \( ^{56}\text{Fe} \) value of bracketing GSB Fe was observed when the high-resolution split was aged. In this case, the split was replaced before the validated measurements. The Fe isotopic compositions were reported in δ notation, (δ\( ^{56}\text{Fe} \)‰) = (\( ^{56}\text{Fe} / ^{54}\text{Fe} \))\(_{\text{Sample}}\) / (\( ^{56}\text{Fe} / ^{54}\text{Fe} \))\(_{\text{Standard}}\) - 1) × 1000, relative to IRMM-014 unless specified otherwise, and were converted by the following equation:\( \delta^{56}\text{Fe}_{\text{IRMM-014}} = \delta^{56}\text{Fe}_{\text{GSB}} + \delta^{56}\text{Fe}_{\text{IRMM-014}} \) (GSB Fe) + \( \delta^{56}\text{Fe}_{\text{GSB}} \times \delta^{56}\text{Fe}_{\text{IRMM-014}} \) (GSB Fe) / 1000. The isotopic data were reported as the mean values of four repeated analyses, and the uncertainties were given as two standard errors of the mean (2 SE), with an error of \( \delta^{56}\text{Fe}_{\text{IRMM-014}} \) (GSB Fe) being considered ((2 SE)\(_{\text{IRMM-014}}\) = (2 SE)\(_{\text{GSB}}\)Fe + 0.005\(^{\circ}\)).

**RESULTS AND DISCUSSION**

Internal and external errors arising from data acquisition. As shown in Section 2, the internal errors (2 SE) during the data collection by MC-ICPMS are predicted in Fig. 1 after Lehn et al. while considering the trace Ni correction problem. Most of the

<table>
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<th>Table 2. Comparison of different purification processes</th>
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Fig. 3 Mass bias correction by the \( ^{56}\text{Fe} -^{56}\text{Fe} \) double spike method illustrated by two representative sessions on April 11, 2021 and September 04, 2021. Deduced \( ^{56}\text{Fe} \) (open symbols) show no drifting with time, despite a fluctuation in mass bias (as filled symbols expressed as δ values calculated using β relative to the first measurement of each session) is noted.
Fig. 4 Results for pure Fe solution standards (a) IRMM-014 and (b) NIST3126a measured over nine months. The horizontal solid lines and gray bars represent the mean values and two standard deviations, respectively, calculated for the results of multiple analyses (large black diamonds) consisting of four single-time measurements (gray small diamonds) each. Recommended values (RV) for IRMM-014 and NIST3126a are from He et al.23 and Zhu et al.31, respectively. For raw data, refer to Table S1.

Fig. 5 Measured δ56Fe for a suite of solutions with known isotope compositions that were prepared by mixing IRMM-014 and GSB Fe. Measurements in this study were done using Fe solutions ≥ 8 ppm to maintain a sum of signals ≥ 120 V, while a few measurements were performed at a lower sum of signals (~87 V), either of which yielded internal errors of δ56Fe mostly below the expected values with a limit for the trace signal of ~0.3 mV (Fig. 1). As exemplified by bracketing GSB standards, internal errors of δ56Fe were 0.018 ± 0.009‰ (2 SD, n = 209) and 0.029 ± 0.013‰ (2 SD, n = 44) for measurements having the sum of signals within 145.5 ± 30.6 V and 86.9 ± 5.2 V, respectively. To monitor the external precision for single-time measurements on MC-ICPMS, IRMM-014 and NIST3126a solutions were measured against GSB Fe via different analytical sessions over nine months, and ~0.030‰ for δ56Fe (2 SD) (Fig. 4) was obtained. The long-term precision could be further improved via multiple analyses by a factor of \(\sqrt{n}\), where n is the number of measurements on each sample.23,23 Herein, we routinely measured each sample four times using MC-ICPMS, and the external precision was expected to be approximately 0.015‰, confirmed by the results of IRMM-014 and NIST3126a. The long-term mean δ56Fe of IRMM-014 relative to GSB Fe was -0.726 ± 0.013‰ (2 SD, N = 20), whereas that of NIST3126a relative to IRMM-014 was 0.368 ± 0.011‰ (2 SD, N = 30) (Fig. 4), agreeing well with the long-term values previously obtained by the SSB and Ni-doping methods in the same lab (-0.729 ± 0.005‰ (2 SE)23, 0.365 ± 0.005‰ (2 SE)31). To further validate the accuracy and ability of this method to distinguish minor Fe isotope fractionation, a suite of Fe solutions with known isotopic compositions was prepared by mixing IRMM-014 with GSB Fe. Measurements of these solutions yielded a shift of -0.007 ± 0.013‰ (2 SD, N = 6) between the measured and expected δ56Fe (Fig. 5). These results demonstrate that by increasing the signal-to-noise ratios, the trace Ni correction problem could be suppressed, and δ56Fe could be routinely measured using MC-ICPMS with an external precision and accuracy better than 0.02‰, provided that each sample was measured four times.

Evaluation of isobaric interference and matrix effect. The presence of matrix elements in the sample solutions may have caused bias during Fe isotopic analyses on MC-ICPMS owing to isobaric interference and matrix effects.23,25,30 Herein, we evaluated the effect of Cu, Co, Ca, Al, Cr, and Ni on Fe isotopic analyses using a 57Fe-58Fe double spike by measuring the GSB Fe doped with mono-element solutions (Fig. 6). Cu and Co could not be completely removed by chromatography using either a previously established method or the one described herein.23 The matrix effect of Cu and Co with [Cu or Co]/Fe ratios up to 1:1 was previously demonstrated to be negligible for the SSB method.23 Thus, it was not surprising to find no bias in the deduced δ56Fe values for Cu (Fig. 6a). Nevertheless, the doped solution with Co/Fe = 1:1 yielded a biased high δ56Fe of up to 0.074 ± 0.018‰ (2 SE), although this effect was negligible when Co/Fe ≤ 0.1 (Fig. 6b). Herein, we attributed the bias caused by doped Co to 59Co+ as an isobaric interference on 54Ni, indicated by a higher 54Ni/56Fe

Fig. 6 Doping experiments to evaluate the matrix effect on $\delta^{56}$Fe determination. The horizontal solid lines and gray bars represent the expected value banded by the long-term reproducibility (0 ± 0.02‰). For raw data, refer to Table S2.

of ~0.000410 for the Co/Fe = 1:1 solution, compared to that of the bracketing GSB Fe (~0.000024). Over-correction of $^{58}$Ni$^+$, caused by $^{59}$Co$^+$H$^+$ with a productivity of 5 ppm, could explain the observed erroneously high $\delta^{56}$Fe$_{GSB}$ when Co/Fe = 1. The matrix effect of Co was not expected to cause any significant bias on the deduced $\delta^{56}$Fe for most high-temperature samples wherein it is at trace levels. However, special caution was suggested to sufficiently remove Co from Co-abundant samples (e.g., Co-rich crust) when Fe isotopic analyses were conducted using the double spike method. Calcium and Al possibly generated polyatomic ion interferences ($^{40}$Ca$^{14}$O$^+$ and $^{27}$Al$^{2+}$, $^{56}$Fe$^{+}$, $^{40}$Ca$^{16}$O$^{+}$ and $^{57}$Fe$^{+}$) which could not be resolved by double spike data deduction. Millet et al. observed using a Nu Plasma MC-ICPMS that the presence of 20% Ca and ≥5% Al could lead to an erroneously low deduced $\delta^{56}$Fe. Herein, we observed no bias in the deduced $\delta^{56}$Fe values for the doping experiments with Ca and Al (Fig. 6c and 6d). This indicates that either the productivity of polyatomic ion interferences was low or that these interferences were discriminated by the high mass resolution mode on our instruments. However, even in the highest mass resolution mode, isobaric $^{56}$Cr$^+$ and $^{58}$Ni$^+$ could not be resolved from Fe, which was routinely monitored by $^{53}$Cr$^+$ and $^{60}$Ni$^+$ and corrected using...
samples in this study.


Notes:

Table 3. Average iron isotopic compositions of geological RMs measured during Jan. 2021 and Sept. 2021

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Notes: #: 2 SE is the mean of internal errors (95% CI) on δ56Fe for individual measurements. $ denotes the usage of old batch of standards (i.e., W-2 and GSP-1) in the literature.

empirical ratios 54Cr/56Cr ~ 0.2571 and 60Ni/58Ni ~ 0.4088.24 Doping experiments validated this empirical correction method when both Cr/Fe and Ni/Fe were < 1 × 10^-8 (Fig. 6e and 6f). It is noted that Cr and Ni can be effectively removed by our purification procedure, e.g., eluted Fe from BHVO-2 having Cr/Fe < 1.8 × 10^-8 and Ni/Fe < 1.7 × 10^-7, after single chromatographic run, while this was routinely duplicated. Therefore, the isobaric interference of 54Cr+ and 58Ni+ was negligible for the purified samples in this study.

Whole procedure precision and accuracy. Five well-characterized geological reference materials (JP-1, BHVO-2, W-2a, GSP-2, and COQ-1) were repeatedly measured over nine months, and the corresponding results are reported in Table S3 and summarized in Table 3. Two types of column procedures were used independently, and the sample loading varied from 10 μg to 1000 μg during this study. As shown in Fig. 7, no systematic bias was observed when either the sample loading or chromatography was adopted (Table S3). Runs with spiking prior to chromatography and isotopic analyses also yielded consistently deduced δ56Fe values, indicating insignificant artifacts from the chromatography. Accordingly, all the raw data were considered equally. JP-1, BHVO-2, W-2a, GSP-2, and COQ-1 yielded average δ56Fe values of 0.019 ± 0.018‰ (2SD, N = 15), 0.109 ± 0.017‰ (2SD, N = 30), 0.049 ± 0.018‰ (2SD, N = 17), 0.155 ± 0.018‰ (2SD, N = 14), and -0.066 ± 0.022‰ (2SD, N = 20), respectively, in agreement with the results previously reported within the quoted uncertainties20,30,31 (Table 3). These results demonstrated an external 2 SD precision and accuracy, on average, of better than 0.02‰ for δ56Fe.

Merits and pitfalls of the double spike versus those of other techniques. To date, high-precision Fe isotopic analyses can be routinely achieved by either SSB,23,25 SSB with element doping,30 or SSB with double spiking (30, and this study). SSB plus double spiking is the only technique that can routinely measure Fe isotopic data with a long-term 2 SD precision of ±0.02‰ (30, and this study), while the best precision reported for SSB with or without element doping is approximately ±0.03‰.23,25,31 Multiple analyses are generally required for both SSB (with or without element doping) (nine times in the cases of SSB,23,25 and double spike techniques (four times in the current case), indicating an improvement in precision at the cost of efficiency. Since the double spike technique can accurately correct the mass bias without drift in the deduced δ56Fe, bracketing standards are measured for every five samples in the current study, instead of every sample, as in the case of SSB,23,25 or every two or three samples in case of SSB with element doping.30 Accordingly, the procedures reported herein also double or triple the measurement efficiency compared to that for SSB with or without element doping. Millet et al.30 reported a precision of ±0.02‰ for single-time measurement that consists of three blocks, each of which contains 120 s background measurements, peak centering, and 40 × 5 s long integrations. In addition, to account for the occasional burst of argide interferences, each measurement on unknown samples was bracketing by standard measurements.30 Therefore, the overall measurement efficiency of this study is comparable to that reported by Millet et al.30

When compared with SSB and SSB with element doping techniques, special care should be taken about isobaric interferences30 and the trace isotope, 56Fe, which is introduced into the data deduction of the double spike technique (30 and this study). Incomplete discrimination of Fe from argide interferences, which may burst during measurements, can cause substantial artifacts.30 Improper correction of trace isobaric Ni or significant Co contamination may cause problems in the precision and accuracy of Fe isotope analyses (30, and this study). In addition, the double spike data deduction assumes that Fe isotope fractionation in natural samples follows a certain fractionation law (e.g., the
Fig. 7 Iron isotopic compositions of five geological reference materials (JP-1, BHVO-2, W-2a, GSP-2 and COQ-1). RV from He et al., calculated using data compiled from 10 independent laboratories, are shown for a comparison. For raw data, refer to Table S3.

exponential fractionation law), meaning that any information about either equilibrium versus kinetic isotope fractionation or mass-independent fractionation will be overlooked. Lastly, this study adopted measurements of high ion intensities to suppress isobaric interferences, with the $^{56}$Fe signal usually >70 V. Damage to the Faraday cups was not observed during this study, but its relevant risk cannot be ruled out.

**CONCLUSION**

Herein, we report an improved procedure for Fe purification and high-precision isotopic analyses using MC-ICPMS with a $^{57}$Fe-$^{58}$Fe double spike. In our new column procedure, less resin and acid were consumed compared to previously reported methods, thus providing a direct, efficient, and rapid method for Fe purification. The trace Ni correction problem was suppressed by increasing the total Fe signal to ≥ 120 V to maintain a high signal-to-noise ratio. Based on the monitoring of pure Fe standard solutions (IRMM-014 and NIST3126a) and geological reference materials (JP-1, BHVO-2, W-2a, GSP-2, and COQ-1) over nine months, $\delta^{56}$Fe could be routinely measured with a long-term precision of better than 0.02‰, provided the measurements were performed in quadruplicate. High-precision iron isotopic analyses will promote a better understanding of minor but important isotope fractionation among high-temperature geological samples.
ASSOCIATED CONTENT
The supporting information (Tables S1-S3) is available at www.at-spectrosc.com/as/home

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ACKNOWLEDGMENTS

The efficient editorial efforts by Prof. Wei Guo and constructive comments from two anonymous reviewers are greatly appreciated. We thank Dr. Shitou Wu and Dr. Hao Wang for their helps in ICPMS measurements on eluates. This work is supported by the National Key R&D Program of China (2019YFA0708403), the National Natural Science Foundation of China (42122019), the Fundamental Research Funds for the Central Universities (3-7-5-2019-07), the 111 Project of the Ministry of Science and Technology, China (BP0719021) and State Key Lab of Geological Processes and Mineral Resources.

REFERENCES

Review of In-situ Online LIBS Detection in the Atmospheric Environment

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Received: June 21, 2021; Revised: August 24, 2021; Accepted: August 25, 2021; Available online: September 11, 2021.

DOI: 10.46770/AS.2021.609

ABSTRACT: The aim of this review is to provide a brief introduction to recent research advances in in-situ online detection of atmospheric pollutants based on laser-induced breakdown spectroscopy (LIBS) under atmospheric environments. Atmospheric pollution has drawn much public attention, and there is increasing demand for rapid and accurate evaluation of atmospheric environments. LIBS has the advantages of in-situ online detection, simultaneous multi-element analysis, and noncontact measurement, making it a highly competitive analytical technique in the field of environmental monitoring. In terms of the different target samples, some typical research cases, including atmospheric particulate matter, atmospheric pollution sources, halogens in VOCs, atmospheric sulfur, and stable isotope abundance, are presented to illustrate the current development and problems of LIBS detection in this field.

INTRODUCTION

In recent decades, there has been ever-increasing demand for the rapid detection of atmospheric pollutants, including volatile organic compounds (VOCs), heavy metals, NOx, and other hazardous substances, as the global atmospheric environment has worsened owing to natural changes and anthropogenic activities in many countries, and thus there has been ever-increasing demand for the rapid detection of these atmospheric pollutants.1 The presence of these atmospheric pollutants has caused serious atmospheric environmental problems such as haze, increased size of the ozone hole, and photochemical smog, and it has become a serious threat to the global ecological environment and human health,2,3 a problem that is gaining the attention of world governments. To solve these environmental problems or reduce their negative effects on the environment and human health, it is essential to first determine the composition of the atmosphere in a targeted area and then take specific measures after that. However, the types and concentrations of the components in the atmosphere vary from hour to hour with air flow. Hence, detection must be accomplished in a very short time to ensure the validity of further analysis and the timeliness of the measurement results, which is a great challenge for current detection methods.

Laser-induced breakdown spectroscopy (LIBS) is a well-known atomic emission spectroscopy (AES) technique. In LIBS measurements, the target sample is ablated to a high-temperature plasma by a high-intensity pulse laser, and then the atomic, ionic, and molecular spectra containing the compositional information emitted from the plasma are qualitatively and quantitatively analyzed to determine all the components and their concentrations in the sample.4 LIBS has attracted significant attention since it was first reported at the X Colloquium Spectroscopicum Internationale by Brech and Cross in 1962.5 Shortly thereafter, Runge et al. established a calibration curve for quantitative analysis of target elements based on the intensity of the characteristic line and the plasma radiation mechanism,6 demonstrating that LIBS could be a useful tool for spectrochemical analysis. Over the past several decades, much scientific work covering a wide range of subjects has been carried out by research groups worldwide,7 and the basic theory of LIBS has gradually matured. Now, it has a wide variety of applications in many fields, such as in material sorting,8-12 coal analysis,13-16 food testing,17-19 medical testing,20-22 environmental monitoring,23-26 ocean exploration,27-30 and space exploration.31-33
Unlike current chemical analytical methods, LIBS is a novel optical analytical method with many distinguishing features, such as rapid and precise response, high sensitivity, small sample loss, and simultaneous multi-element analysis, and it is pollution-free.34,35 These unique advantages make the LIBS technique an effective method for compositional analysis. Moreover, detection based on the LIBS technique requires no sample preparation, and it can be performed on gaseous, liquid, and solid samples under atmospheric pressure,36-38 which gives LIBS detection a great advantage over the current analytical techniques in terms of environmental detection. The elemental information of the sample can be determined according to the obtained emission spectra in a short time, providing real-time detection. Therefore, it is appropriate and promising to apply the LIBS technique to the in-situ online detection of atmospheric environmental pollutants. However, compared with its application for the detection of liquid and solid samples, there are few publications on the detection of gaseous samples, especially in-situ detection under atmospheric pressure, because the low density of gas samples makes it difficult to observe the characteristic lines of the target element in the emission spectra. With the development of laser techniques and the theory of light-matter interaction, some novel LIBS techniques, such as femtosecond LIBS and dual-pulse LIBS,39-42 have been applied to improve the intensity and stability of the spectral signal. More and more studies are currently being carried out to improve the performance of the LIBS detection of gas, and the LIBS technique is playing an increasingly important role in the detection of atmospheric environmental pollution.

Research advances in LIBS applications in the field of environmental monitoring have been widely reported in many other reviews.43-46 This paper mainly introduces the development of atmospheric environment detection based on the LIBS technique in recent years. To adequately demonstrate the scientific research development of LIBS detection in an atmospheric environment, several typical cases are discussed to illustrate the current development and future trends in this field.

EXPERIMENTAL

A diagram of a typical LIBS system used for gas detection is shown in Fig. 1. The pulse laser is the core device of this system, and it plays a key role in the ablation of the target sample. As shown in Fig. 1, a nanosecond Nd:YAG laser system is used as the excitation laser, which is operated at a fundamental wavelength of 1064 nm. Three dielectric lenses and a plano-convex lens are used to focus the laser pulse onto the target sample. An air pump is used to control the flow direction of the gas sample and ensure that the focus point is filled with the gas sample. The emission spectra emitted from the plasma are recorded using a spectrometer. Moreover, because bremsstrahlung caused by the collision of electrons in the plasma interferes with the atomic and molecular emission, which contains the compositional information of the target sample, a digital delay is set between the spectrometer and laser system to control the integral delay time of each LIBS measurement and avoid the effect of background noise.

CASE STUDIES

Some studies have been conducted on the detection of atmospheric environments based on LIBS detection, most of which can be found in other reviews.47,48 In this review, some typical cases carried out in the last few years are carefully analyzed to illustrate the current development and problems in this field.

Atmospheric particulate matter analysis. Air quality is closely related to health. However, air quality has steadily declined because of the use of fossil fuels, and thus the air in many cities has reached a serious level of pollution. The main pollutant in most cities is floating particulates, which is the main reason for the formation of haze in the air. A variety of heavy metal elements exist in these atmospheric particulates, such as lead, mercury, chromium, arsenic, and cadmium.49 Once these heavy metal element particulates enter the human body through breathing, they do great harm to bodily health and can lead to diseases of the respiratory system, cardiovascular system, reproductve system, etc.50 More seriously, these heavy metal pollutants are mostly nondegradable, and they could exist in the bodies of animals and plants for a long time, traveling up the food chain and causing more serious damage to the human body. Hence, the detection of heavy metal elements in atmospheric particulates based on the LIBS technique is worth studying.

It is difficult to directly perform LIBS measurements of particulate matter (PM) without any pretreatment because of the low density of PM samples in air. Many different preconcentration methods have been used to increase the hit efficiency of the laser pulse. The filter-based technique is a simple but useful tool to focus PM onto a membrane or substrate. Kwak et al. developed a LIBS experimental system with a particle collection substrate stage that could automatically move in a specific time interval.51 The detection results of the PM in every time interval were
averaged to obtain time-resolved compositional information about the PM. Zhang et al. carried out research on the qualitative and quantitative detection of heavy metal elements in PM samples. The PM was collected using an air pump and focused onto a quartz fiber filter (QFF) membrane. The LIBS signal was greatly improved after this preconcentration. The recorded spectra showed clear spectral lines of Na, Al, Si, Cu, Mg, and Fe in the emission spectra. In addition, the authors established a calibration curve of Pb using the internal standard method. However, the filter-based technique required a lot of time to extract the PM from the air, and thus the LIBS measurement could not be performed in real time or accomplished in a short time. Chances are that some pollutants that only existed for a short time were not observed in the spectra after the preconcentration process. In addition, the detection accuracy of the LIBS technique is greatly influenced by the matrix effect caused by the use of a substrate or filter membrane. To solve these problems, some new methods have been proposed to rapidly extract PM. Diwakar et al. designed an electrostatic aerosol collection system to collect particles for LIBS measurements. The aerosol particles were charged using a corona needle to which a 5-kV positive potential was applied and then collected by the flat tip of a microneedle electrode. The particle capture efficiency was as high as 99% over a wide range of particle sizes, 30–600 nm, using this aerosol collection system. The elements Cd, Cr, Cu, Mn, Na, and Ti were simultaneously measured using LIBS, and a calibration curve was constructed by plotting the peak-to-base (P/B) ratio as a function of mass deposited on the collection needle tip. The limits of detection (LODs) of these elements were calculated to be 5.03, 0.035, 0.138, 0.155, 0.018 and 0.44 ng, respectively, at a flow rate of 1.5 L min\(^{-1}\) with sampling times of 5 min. Similarly, Park et al. developed an aerosol-focusing LIBS system with sheath air focusing to determine the elemental composition of fine and ultrafine metal aerosol particles. Maeng et al. established a novel LIBS system with timed ablation and applied it to the determination of the elemental composition of individual airborne particles. Saari et al. studied the identification of fungal spores and bacteria particles in biological aerosols using an electrodynamic balance-assisted LIB electrodynamic balance (EDB) chamber. The above works demonstrate that preconcentration methods can improve the detection efficiency of the LIBS technique. However, even combined with these methods, the LIBS technique cannot realize the in-situ detection of PM.

Some researchers have attempted to improve conventional LIBS systems to enhance the detection capability of particles in specific environments. Xiong et al. studied the in-situ detection of TiO\(_2\) nanoparticle aerosols based on low-intensity phase-selective LIBS (PS-LIBS). In novel, low-intensity LIBS measurements, the laser fluence as the excitation source is between the breakdown thresholds of the gas and particle phases. Hence, only the solid phase nanoparticles would break down, forming plasmas, without any surrounding gas-phase breakdown. PS-LIBS emissions were also enhanced with secondary resonant excitation by matching the excitation laser wavelength with an atomic transition line in the formed plasma. The enhancement factor of this method can be up to 220 times with advantageously selected lines. Heikilä et al. studied single-particle elemental analysis of airborne aerosols by combining EDB trapping with the LIBS technique. A corona-based aerosol charger, double-ring EDB trap were imposed in the LIBS setup to increase the detection efficiency and reduce the LOD.

**Atmospheric pollution sources.** Clean air is a prerequisite not only for human life, but also for all life on the planet. However, a large number of emission sources of various environmental pollutants have seriously damaged the atmospheric environment and cause both local pollution and wide-area pollution. It is essential to understand the pollution source and the properties of the pollutants before taking measures. Studying the rapid online detection of these atmospheric pollutants is meaningful for determining emission sources and helpful for choosing the corresponding degradation methods according to the sources of pollution.

Coal is the major fuel used for producing electricity in many countries, and the emission of coal ash produced during the combustion of coal in the plant causes severe haze and acid rain. Zhu et al. therefore carried out a study on the quantitative analysis of Fe and the detection of multiple elements in coal ash via the LIBS technique. Taking Al as the reference element, a calibration curve of Fe concentration was established by plotting the relative intensity of Fe lines versus the Fe concentration in the coal ash based on the internal standard method. Then, the Fe concentration of unknown coal ash could be determined according to the calibration curve, and thus the sorting of coal ash could be rapidly realized. In addition, X-ray fluorescence spectrometry (XRF) was used to test the accuracy of the quantitative analysis based on LIBS measurements. Yin et al. studied the quantitative analysis of Pb in coal ash and the rapid detection of various metal elements, nonmetal oxides, and salts based on the LIBS technique, which is of great importance in coal utilization.

As a result of constant media attention and efforts made by government departments, many scientists have joined the study of wide-area pollution, and much research has been carried out. However, local pollution, which impacts people’s daily lives, has seldom been stressed. The online detection of local air pollution is an important part of environmental protection and is beneficial to the health of people who work or live indoors.

Mosquito-repelling incense is often used to reduce biting in summer, where a large amount of smoke is emitted from the burning incense. It is noted that most brands of incense include Mn for the purpose of repelling mosquitoes. Although Mn is an essential trace element in the human body, excessive intake of Mn can cause neurological disorders in the brain and irreversible damage to the central nervous system. Qu et al. studied the
online real-time detection of smoke by using a mosquito-repelling incense as a representative example of local air pollution. Metal elements, including Mg, Fe, Ca, and Ti, as well as some toxic elements, such as Sr, Cr, and Cd, were simultaneously observed in the spectra. Furthermore, there was also a characteristic spectral line of F I (685.6 nm) in the spectra, which proved the existence of meperfluthrin (C_{17}H_{16}C_{12}F_{4}O_{3}) in the mosquito-repelling smoke. Moreover, the real-time detection of the ambient air via the LIBS technique and its effect on human breathing were also discussed to enlarge the scope of the developed LIBS system in the local environment.

Incense is widely used by people who practice Buddhism and Taoism in some developing countries or regions. Large quantities of inferior incense containing a variety of poisonous substances are extensively produced and sold by manufacturers because of its low cost. Hence, incense smoke causes local air pollution in indoor environments, especially in temples. Long-term exposure to these poisonous substances from burning incense can seriously damage the skin, respiratory system, and nervous system. Yim et al. studied the online and offline detection of incense smoke via LIBS. Mass spectrometry was also used to determine and analyze the elemental composition of incense smoke using a home-built single-particle aerosol mass spectrometer (SPAMS). Through measurements based on the combination of LIBS and SPAMS, the authors not only obtained elemental information but also identified the particle size and chemical composition of a single particle with extremely high temporal and spatial resolution.

There are many smokers worldwide, and it is generally known that cigarette smoking is harmful to one’s health owing to the toxic ingredients in cigarettes. Moreover, cigarette smoking, which contains nicotine, tar, Pb, As, and other noxious ingredients, also has pernicious effects on nonsmokers. Many studies have demonstrated that second-hand smoke can cause a wide range of diseases, such as lung cancer and heart attacks. Nonsmokers exposed to second-hand smoke have shown increased risk of heart disease by 25%–30% and lung cancer risk by 20%–30%. Hence, it is important to accurately evaluate the local pollution caused by cigarette smoke in public areas. Zhang et al. carried out research on the in-situ detection of cigarette smoke in public areas. By using a strong pulse Nd:YAG laser (260 mJ/pulse) as the excitation source, LIBS was applied to the sidestream smoke of a burning cigarette. The characteristic lines of most metal elements, including Mg, Ca, Sr, Na, and K, were observed in the obtained spectra, as shown in Fig. 2. Moreover, the matrix effect of the smoking detection was also discussed by comparing the LIBS spectra of cigarette smoke and cigarette ash.

Pollutants in the air, especially over a wide area, mostly originate from a variety of different sources. For example, the haze that occurs frequently in cities is a mixture of construction
dust, vehicle exhaust, factory emissions, and power plant fumes. Therefore, studies on the classification and source tracing of atmospheric pollutants are necessary for detection in complex environments. The classification of samples is mainly dependent on the analysis of characteristic lines in the spectra, which could reflect the compositional information of the different pollutants. However, it is common that air pollution is caused by two or more atmospheric pollutant sources, and it is difficult to distinguish them by simple elemental analysis based on the LIBS technique. However, by combining LIBS with machine learning algorithms, it is possible to determine the pollutant sources based on their characteristics. Typically, the spectral data of characteristic lines are extracted from the spectra and used as a sample set to establish a suitable classification model. Currently, the most common algorithms used in LIBS analysis are principal component analysis (PCA),82-85 linear discriminant analysis (LDA),86-88 support vector machine (SVM),89-91 random forest (RF),92-94 and artificial neural networks (ANN).95-98 For the classification of pollutants, these methods work equally well. Lu et al. applied PCA, SVM, and back-propagation artificial neural networks (BP-ANN) for real-time in-situ detection and classification of some typical pollutants. Classification models were established according to the principal components extracted from the characteristic lines. The test experiments showed that the recognition rates of the models based on the SVM and BP-ANN algorithms were 90.00% and 93.33%, respectively. The combination of these algorithms and LIBS significantly improved the recognition accuracy of the classification established based on LIBS analysis.

**Isotopic detection.** Nuclides of the same element with the same proton number but different neutron numbers are called isotopes, and many elements have more than two types of isotopes in nature. It is noted that stable isotopes obtained from different sources are likely to have different isotope ratios.100 Based on this principle, there have been many studies on contamination tracing via the isotopic technique.101-105 Currently, the detection of stable isotopes is based on mass spectrometry. However, mass spectrometry generally requires complicated sample pretreatment procedures, and the measurement must be performed in a vacuum environment. Moreover, it is difficult to accurately distinguish the peaks of different elements or fragments in the mass spectrum if there are more than two possibilities for the identification results. The LIBS technique is promising as a supplement or alternative for the detection and analysis of mass spectrometry owing to its merits mentioned above.

Yin and Zhang et al. carried out research on the quantitative detection of three principal Pb isotopes (Pb, Pb, and Pb) in smoke from a burning cigarette and incense based on the combination of LIBS and SPAMS.76 The concentration of Pb and the abundance ratio of isotopes were analyzed according to the obtained LIBS spectrum and mass spectrum, as shown in Fig. 3. Such studies have successfully proved that the assistance of LIBS measurements could greatly improve the identification accuracy of the peaks in the mass spectrum. However, measurements based on the combination of these two methods require too much time, and the drawbacks, such as complicated sample pretreatment and rigorous experimental conditions, still restrict the application of these techniques in the field of isotopic detection.

In recent years, isotopic analysis based on the LIBS technique, termed laser ablation molecular isotope spectrometry (LAMIS), has drawn significant attention.106,107 In LAMIS, both the atomic lines and molecular emission bands are recorded using a spectrometer. The characteristic atomic lines provide elemental information, whereas the molecular bands can be used for compositional analysis. Here, we take the carbon-nitrogen free radical emission band as an example to illustrate the formation of diatomic molecules in plasma and isotopic analysis based on the LAMIS technique. The temperature in the outer layer of the plasma is lower than the temperature in the center, and the molecular fragments can be directly released from the sample and combined with the molecular fragments in ambient atmosphere.108-110 The formation of CN radicals can be explained by the reaction of carbon in the sample with nitrogen in the air, as shown in Fig. 4. Carbon isotopes have two principal mass numbers, C and C, and the variation in the mass number of carbon atoms leads to a change of the reduced mass of the CN molecule. Then, the emission band of CN shifts a certain distance because of the isotopic effect. Hence, there is a wavelength
Fig. 4 The formation mechanism of CN radical. In the outer layer of plasma, the carbon in the sample combined with the nitrogen in the air.

difference between the emission bands of $^{12}$CN and $^{13}$CN, and it is easy to distinguish the carbon isotopes using the LAMIS technique. Furthermore, the intensities of the molecular bands emitted from different molecules have a significant linear correlation with the abundance of each isotope, which is the foundation of the quantitative analysis of isotopes.

Zhang et al. carried out research on the online detection of carbon isotopes and studies the atmospheric carbon cycle by LIBS. The carbon element in the PM generated from burning coal, wood, and paper samples was determined first. Then, isotopic shifts of the CN molecular emission bands in the LIBS spectrum of gaseous CO$_2$ were experimentally measured, as shown in Fig. 5. Theoretical calculations based on density functional theory were performed to obtain the energy differences of the isotopic shifts of the CN molecular band, as well as those of many other molecules formed by different types of isotopes. Recent research has shown that LIBS is a useful tool for the stable isotope analysis of several elements.

However, only a few types of molecular bands have been reported, and most of the free radicals have never been observed in LIBS measurements. Moreover, the isotopic effect on the molecular band was highly related to the mass number of the element. The larger the mass number, the smaller the isotopic shift of the emission band. Hence, it is difficult to accomplish the isotopic analysis of the heavy metal element in atmospheric pollutants merely by LIBS. Other techniques, such as mass spectrometry, must be applied in combination with LIBS.

Detection of halogens in VOCs. VOCs are the major atmospheric pollutants. VOCs are the precursors to the formation of ozone and secondary organic aerosols, such as fine PM, which can cause serious atmospheric environmental problems. In addition, some specific VOCs that contain bromine and chlorine atoms have long been regarded as culprits in the destruction of the ozone layer. Therefore, the rapid direct detection of VOCs in the atmospheric environment is of great significance for environmental protection.

Most of the current studies on the LIBS technique have focused on the qualitative and quantitative analysis of metal elements in target samples. In contrast, there are few studies on the LIBS analysis of nonmetallic elements, such as F, Cl, Br, I, and S. Compared with metallic elements, the LIBS detection of nonmetallic elements, especially halogens and sulfur, presents particular difficulty for LIBS analysis because of the high ionization energy of such elements and the relative weakness of their spectral lines, which is unfavorable for the appearance of the characteristic emission lines in the measurements. Furthermore, most of the spectral lines of such elements lie in the vacuum ultraviolet (VUV) (110–190 nm) spectral range, and the requirement for the collection of emission spectra is so robust that it hinders the development of LIBS applications in environmental detection.
To address this challenging issue, there has been significant effort to enhance the ability of LIBS to detect nonmetallic elements in the last several years. The experimental environment has a significant effect on the signal strength and quality of the spectral lines of halogens. Asimellis et al. performed LIBS detection under a controlled inert gas ambient atmosphere so that F and Cl could be detected in the upper visible and near-infrared (NIR) wavelengths (650–850 nm).118 The signal-to-noise (S/N) ratio of the spectral line was further enhanced under optimal He pressure in the range of 60 mbar. Zhang et al. detected iodine in buffer gases of N₂ and air using nanosecond and picosecond breakdowns of CH₃I at reduced pressure.119 The results showed that the use of buffer gases reduced the quenching rate of excited iodine in air. It was demonstrated that the interference of the continuum emission from the plasma decreased as the pressure decreased. However, it is extremely difficult to use buffer gases or create a low-pressure environment in open air. These methods are far from being recognized as realistically suitable for the detection of halogen traces in the atmosphere. These experiments can only be applied to the detection of halogens in solid or liquid samples.

In addition to optimizing the environmental parameters, determining the concentration of some nonmetallic elements by analyzing the related molecular emission in the LIBS spectra is also an effective solution in some specific cases. A recent review summarized advances in halogen detection by molecular emission.120 Gaft et al. studied the elemental analysis of halogens in minerals,121–122 including fluorine, chlorine, bromine, and iodine, using molecular emission. The authors developed corresponding detection methods for these halogens by combining them with alkali-earths and other elements to form molecules whose spectra could be easily identified, and then the analytical methods were successfully applied to real conditions. Thus, the molecular spectra enabled detection under ambient conditions with much higher sensitivity than that of F I and Cl I atomic lines. Similarly, Llamas et al. studied fluorine quantification in calcium-free samples through the analysis of CaF molecular bands.116 Tang et al. investigated the determination of fluorine in copper ore using LIBS assisted by the SrF molecular emission band.123 To improve the sensitivity of detection, Nagli et al. proposed combining LIBS with molecular laser-induced fluorescence (MLIF).124 Comparing the ordinary LIBS method with LIBS-MLIF demonstrated that the combination of LIBS and MLIF significantly improved the detection sensitivity by approximately 10 times.

The LIBS detection of nonmetallic elements assisted by the above methods is realized at the cost of speed and generalizability. Furthermore, in terms of atmospheric VOCs, it is unfeasible to apply such complicated treatments in an open environment. To realize the direct detection of halogens in air, Zhang et al. designed a novel LIBS experimental system coupled with SPAMS, as shown in Fig. 6.125 Taking Halon 2402, Freon R11, and iodomethane gas as target samples, the online direct detection of F, Cl, Br, and I elements was carried out under atmospheric pressure using an extremely strong pulse laser of 200 mJ as the excitation source in the LIBS system. The LIBS and SPAMS spectra of the Halon 2402 gas sample were captured, as shown in Fig. 7.

The atomic lines (Br I) and ionic lines (Br II) of bromine were simultaneously observed in the LIBS spectrum. The different isotopes of bromine and chlorine could be clearly distinguished at the same time based on the SPAMS analysis. It was thus demonstrated that the LIBS-SPAMS technique can provide elemental and isotopic information of halogen atoms in atmospheric VOCs. Furthermore, this method enables remote LIBS detection to meet the actual needs of halogen detection in most cases, especially in the atmosphere.

**Detection of atmospheric sulfur.** The LIBS detection of sulfur has the same problem as halogen detection because the strong sulfur lines in the NIST database lie within the VUV or NIR spectral range,126 which poses great difficulty in terms of capturing the emission spectra in open air. Because the spectral emission in the VUV band rapidly decays in air, studies on the detection of sulfur are carried out in a vacuum environment. Ytsma et al. used the LIBS spectra of standard geological samples to quantify sulfur and other main elements under a variety of atmospheric conditions,127 including vacuum, Mars, and Earth atmospheres. The authors established a quantification model based on multivariate analysis; however, the experimental results showed that there was poor linearity between the actual and predicted concentrations, and thus the method was impractical for determining the sulfur concentration. Kubitz et al. studied the detection of sulfur in lunar analogs at concentrations ranging from 0.5 to 4.0 at% by conducting LIBS experiments in a high-vacuum environment.128 Zhang et al. proposed a new analytical method for sulfur determination in sulfur-bearing powder samples.
Fig. 7 The characteristic peaks of bromine in the LIBS-SPAMS spectra of Halon 2402. (a) The atomic lines (Br I) and ionic lines (Br II) of bromine in the LIBS spectrum, and (b) the mass peaks of bromine at m/z 79 and 81 in the SPAMS spectrum.

Fig. 8 The ionic lines of sulfur in the LIBS spectrum of a DMS gas sample at a laser energy of 1000 mJ/pulse.

using resonance Raman scattering combined with the LIBS technique. Compared to the calibration curve achieved by sulfur atomic emission, the linear coefficient ($R^2$) and detection limit were significantly better.

However, this method is not suitable for LIBS detection of atmospheric sulfur because it is difficult to create a vacuum environment for detection in air. Sulfur is widely distributed in coal, petroleum, and other fossil fuels, and massive sulfide pollutants are emitted into the atmosphere during the combustion of these fuels and derivatives in factories. The detection of these atmospheric pollutants in air is of great significance for environmental protection. To apply the LIBS technique to the in-situ detection of atmospheric sulfur, Zhang et al. established a novel LIBS experimental apparatus specializing in the detection of gas samples and applied it to the online direct detection of sulfur in the gas phase under atmospheric pressure. The characteristic ionic lines of sulfur were also clearly observed in the LIBS spectrum of a dimethyl sulfide (DMS) gas sample, as shown in Fig. 8. In addition, a quantitative calibration model of sulfur was established by fitting the intensity of the line and concentration of sulfur compounds, and the LOD of sulfur by LIBS was calculated to be 46 mg/L. The experimental results also demonstrated the potential of LIBS detection of sulfur based on the analysis of sulfur ionic lines in the visible range.

However, compared to the other techniques that have been applied to the detection of sulfur, the LOD in LIBS measurements is relatively high and insufficient for the actual environmental quality control. The high LOD severely limits the application of LIBS in the in-situ detection of atmospheric sulfur. Hence, it is essential and meaningful to focus subsequent studies of this subject on the enhancement of the LIBS signal and decreasing the LOD of sulfur.

CONCLUSIONS

LIBS is a novel optical analytical method that has attracted
significant attention in recent years. Because of its unique advantages in terms of rapid and precise response, noncontact measurement, and simultaneous multi-element analysis, the LIBS technique has been expected to play an important role in the field of environment detection or even replace conventional analytical methods under some circumstances since its inception. However, compared with the detection of solids, liquids, and aerosols, progress in atmospheric detection by LIBS was disappointingly slow in the early years. As some advanced laser techniques, including femtosecond pulse lasers, have become available, and the fundamental theory of light-matter interaction has been improved, development in this field has significantly increased in the last few decades.

In this review, a brief introduction to the in-situ online detection of the atmospheric environmental pollutants using the LIBS technique is presented, and we have highlighted recent advances in the research on the LIBS detection of atmospheric particulate matter, atmospheric pollution sources, and stable isotope abundance.

Over the past 30 years, the experimental instruments, methods, and analytical algorithms have been greatly improved, and LIBS detection now stands at its highest level of functionality. Our current research on the in-situ online detection of atmospheric environmental pollutants is focused on using LIBS to detect pollutants with extremely low concentrations and the analysis of the molecular structure of the organic matter.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by National Key R&D Program of China (2017YFC0212700), National Natural Science Foundation of China (U1932149), Natural Science Foundation of Jiangsu Province (BK20191395), Key Research and Development Program of Anhui Province (202104j07020009), and Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX21_0989).

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Electron Probe Microanalysis in Geosciences: Analytical Procedures and Recent Advances

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Received: October 07, 2021; Revised: December 31, 2021; Accepted: January 03, 2022; Available online: January 09, 2022.

DOI: 10.46770/AS.2021.912

ABSTRACT: Electron probe microanalysis (EPMA) is an in-situ and non-destructive analytical technique with high spatial resolution and an increasingly important analysis tool in materials science and geosciences. This study summarizes the principles and functions of EPMA, and the problems and difficulties, along with the recent advances in quantitative analysis of EPMA. A routine EPMA procedure includes preparing samples, setting analytical conditions, acquiring data, and evaluating results. Caution is required in all steps to obtain high-quality analytical results. The problems and difficulties commonly encountered in EPMA are discussed and the corresponding measures and solutions required to resolve them are proposed. Specific analytical methods are suggested to make accurate analysis of some specific minerals. We also summarized the challenges and solutions in light element analysis, trace element analysis, EPMA U-Th-Pb total dating, combined analysis with wavelength- and energy-dispersive X-ray spectroscopy, submicron spatial resolution analysis at low accelerating voltages, iron oxidation state analysis, and standard reference materials.

INTRODUCTION

Electron probe microanalysis (EPMA) is a modern technique based on the physical mechanism of electron-stimulated X-ray emission and X-ray wavelength-dispersive spectroscopy (WDS), which Raymond Castaing developed as part of his Doctor of Philosophy dissertation in Paris back to 1951.1 It is one of the most useful microanalytical methods for precise, non-destructive, and quantitative elemental analyses of solid materials, including...
metal alloys, glasses, ceramics, and minerals, at micrometer scale. The EPMA instrument can also be used for elemental line scan and mapping along with image acquisition, such as backscattered electron image (BSEI), secondary electron image (SEI) and cathodoluminescence (CL) image. Therefore, EPMA is a widely used technique with a significant impact on research in materials science and geosciences.3

Previous studies2,8 provided some overviews on the principles, functions, analytical procedures, and instrumental and methodological developments of EPMA in geosciences. As the most commonly applied analytical technique in geosciences, we focused on recent advances in quantitative EPMA in geoscience in this study and emphasized on the following: 1) precautions that need to be considered when preparing samples and setting experimental conditions and evaluation of data quality and 2) challenges and solutions in EPMA, such as the analyses of light and trace elements, U-Th-Pb dating, combined WDS and energy dispersive spectrometer (EDS) analysis, a higher spatial resolution, iron oxidation state analysis, and standard reference materials, aiming to further extend its applications in geosciences.

PRINCIPLES AND FUNCTIONS

There are several major EPMA instrument manufacturers, such as JEOL (Japan), Shimadzu (Japan), and CAMECA (France). An EPMA instrument comprises several components, including electron gun, electron lenses, sample stage, EDS, WDS, BSE detector (Fig. 1a). From the area on the sample surface bombarded by the electron beam, various signals, such as backscattered electrons, secondary electrons, characteristic X-rays, CL, transmitted electrons, and Auger electrons (Fig. 1b), are generated, detected, and processed in the EPMA to produce information on images (such as BSEI and SEI), chemical compositions, and structures.6 When the incident electron energy is greater than critical excitation energy of the element, the electron in the inner electron layer of the orbit is removed, creating an electron vacancy. Subsequently, the outer electrons of the excited state in the high-energy shell are transferred to the inner low-energy shell electron layer (Fig. 1c), and the characteristic X-rays with specific energy are emitted. The X-rays emitted are known as continuous X-rays when the incident electrons are decelerated under the nuclear Coulomb field without removing an electron.

The main functions of EPMA include imaging, quantitative analysis, qualitative analysis, line scan, and elemental mapping.6 The types of images include BSEI and SEI, the former is a function of the mean atomic number of the materials and is mainly used to demonstrate the compositional differences, whereas the later (SEI) is used to display the sample surface morphologies. Qualitative analysis involves identifying and semi-quantifying most elements (theoretically from Be to U) in the analyzed area or line. Line scan and mapping are essential in acquiring concentration variation of the element of interest within a line segment and a selected area in the sample, respectively. Furthermore, mapping provides an intuitive image of the element distribution within the area of interest. Accurate quantitative analysis of elements is the most essential EPMA application in geosciences, which is discussed in the subsequent section.

QUANTITATIVE ANALYSIS

Quantitative analysis by EPMA can be accomplished through both EDS and WDS. Although EDS is comparatively faster, it has a less energy resolution and a worse ability to detect elements present in low concentrations when compared to WDS.2 Therefore, we focused on WDS in this study. According to Moseley’s law,9 wavelength (λ) of the elemental characteristic X-rays is related to its atomic number \(Z\),7 as shown in equation (1):

\[
\lambda = \frac{B}{(Z-C)^2}
\]

where B and C are constants. Therefore, the wavelength of a characteristic X-ray emitted from a sample can be used to identify the elements present in the sample.

A WDS spectrometer utilizes a diffracting crystal to diffract the characteristic X-rays generated from the electron beam and sample interaction, which are subsequently detected by a gas flow or sealed proportional X-ray counter. The X-ray source in the sample, the diffracting crystal, and the proportional counter defines a circle known as Rowland circle with a constant
Table 1. Diffracting crystals for the common elements

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Crystal</th>
<th>2d(nm)</th>
<th>Analysis elements</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LIF</td>
<td>0.4027</td>
<td>K–Rb</td>
</tr>
<tr>
<td></td>
<td>LIFL</td>
<td></td>
<td>K–Br</td>
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<tr>
<td></td>
<td>LIFH</td>
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<td>Ca–Ga</td>
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<tr>
<td></td>
<td>PET</td>
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</tr>
<tr>
<td></td>
<td>PETL</td>
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<td>Al–Cr</td>
</tr>
<tr>
<td></td>
<td>PETH</td>
<td></td>
<td>Si–Ti</td>
</tr>
<tr>
<td></td>
<td>TAP</td>
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<td>O–P</td>
</tr>
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<td></td>
<td>TAPL</td>
<td></td>
<td>O–Si</td>
</tr>
<tr>
<td></td>
<td>TAPH</td>
<td></td>
<td>F–Al</td>
</tr>
<tr>
<td>Shimadzu</td>
<td>LiF</td>
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<td>Ca–Ge</td>
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<td>PET</td>
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<td>ADP</td>
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<td>F–P</td>
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<tr>
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<td>Extend LTAP</td>
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<td>LLiF</td>
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</tr>
<tr>
<td></td>
<td>LiF</td>
<td></td>
<td>Te–Am</td>
</tr>
</tbody>
</table>

Table 1. Diffracting crystals for the common elements

The diffracting crystals diffract the characteristic X-rays when they satisfy Bragg’s law (Fig. 2b; equation 2):

\[ n\lambda = 2d \sin \theta \]  

where \( n, \lambda, d, \) and \( \theta \) correspond to diffraction order (an integer), wavelength (Å) of the X-rays, interplanar spacing (nm) of the diffracting crystal, and diffraction angle of the X-rays, respectively. The characteristic X-ray wavelength depends on the element present in the sample, while the X-ray intensity is related to the concentration of the element. With the movement of the diffracting crystals and the proportional counter in a Rowlan circle, the X-ray diffraction angle is adjusted within a specific range to diffract the characteristic X-rays with certain wavelengths onto the X-ray counter. In addition, a diffracting crystal can only diffract one characteristic X-ray line at a time. A diffracting crystal with an appropriate interplanar spacing need to be selected for a specific characteristic X-ray line. Common diffracting crystals used by major instrument manufacturers are listed in Tables 1 and 2.

Quantitative analysis is based on a positive correlation between concentration of element and intensity of the corresponding characteristic X-ray. Given the concentration of a specific element in a standard, \( C_{\text{std}} \), the concentration of the same element in an unknown sample, \( C_{\text{unk}} \), can be calculated using the formula presented in equation (3):

\[ C_{\text{unk}} = \frac{I_{\text{unk}}}{I_{\text{std}}} \times \frac{ZAF_{\text{unk}}}{ZAF_{\text{std}}} = k \times C_{\text{std}} \times \frac{ZAF_{\text{unk}}}{ZAF_{\text{std}}} \]  

where \( I_{\text{unk}} \) is the net intensity of the characteristic X-rays from the unknown sample, \( I_{\text{std}} \) is the net intensity of the same characteristic X-rays from the standard, and \( ZAF_{\text{unk}} \) and \( ZAF_{\text{std}} \) are the matrix correction factors of the unknown sample and standard, respectively. The \( k \) refers to the ratio of the unknown intensity to the standard intensity, known as k-ratio.

**SAMPLE PREPARATION**

Polishing. Sample preparation for EPMA includes cutting, embedding, grinding, and polishing. A flat and well-polished sample surface is required for EPMA. The quality of polishing of a sample directly affects the accuracy of the analytical results. An irregular geometry of the sample surface could strengthen or reduce the collection of X-rays. Moreover, a poorly polished sample surface makes it hard to focus, leading to the loss of the characteristic X-ray intensity (Fig. 3) because the location where an electron beam bombards the sample may be out-of-focus during analysis. The surface irregularities such as scratches or
Fig. 3 The loss of characteristic X-ray intensity when the analytical position is out-of-focus (shift from Rowland Circle) in Z direction (a) and X direction (b) during analysis (after JEOL\textsuperscript{10}).

![Image](https://example.com/image1.png)

Table 2. Diffracting crystals for the light elements

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Crystal</th>
<th>2d(\text{nm})</th>
<th>Analysis elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>STE</td>
<td>10</td>
<td>B-O</td>
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</tr>
<tr>
<td>LDE1</td>
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<td>C-F</td>
<td></td>
</tr>
<tr>
<td>LDE2</td>
<td>10</td>
<td>B-O</td>
<td></td>
</tr>
<tr>
<td>LDEB</td>
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<td>Bc-B</td>
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<td>C-F</td>
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<tr>
<td>LDE6L</td>
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<td>B-C</td>
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<tr>
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<td>B-C</td>
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<tr>
<td>JEOL</td>
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<td></td>
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<td>LSA120</td>
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<td>LAS200</td>
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<td>Shimadzu</td>
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<tr>
<td></td>
<td>(L)PC0</td>
<td>4.5</td>
<td>N-Na</td>
</tr>
<tr>
<td></td>
<td>(L)PC1</td>
<td>6</td>
<td>C-F</td>
</tr>
<tr>
<td></td>
<td>(L)PC2</td>
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</tr>
<tr>
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<tr>
<td></td>
<td>L Boron</td>
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<td></td>
<td>L Nitrogen</td>
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<td>N</td>
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<tr>
<td>CAMECA</td>
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</tbody>
</table>

Table 2. Diffracting crystals for the light elements

- **Manufacturer**: STE, JEOL, Shimadzu, CAMECA
- **Crystal**
- **2d(\text{nm})**
- **Analysis elements**

- **STE**
  - **Crystal**: STE
  - **2d(\text{nm})**: 10
  - **Analysis elements**: B-O

- **JEOL**
  - **Crystal**: PbST, LSA55, LSA70, LSA80, LSA120, LAS200, LSA300
  - **2d(\text{nm})**: 10.02, 5.5, 7.7, 8, 12, 20, 30
  - **Analysis elements**: B-N, C-F, C-O, B-N, B-C, Be-B, Be

- **Shimadzu**
  - **Crystal**: (L)PC0, (L)PC1, (L)PC2, (L)PC3, L Boron, L Nitrogen
  - **2d(\text{nm})**: 4.5, 6, 10, 20, 14.5, 6
  - **Analysis elements**: N-Na, C-F, B-O, Be-B, B, N

- **CAMECA**
  - **Crystal**: (L)PC0, (L)PC1, (L)PC2, (L)PC3, L Boron, L Nitrogen
  - **2d(\text{nm})**: 4.5, 6, 10, 20, 14.5, 6
  - **Analysis elements**: N-Na, C-F, B-O, Be-B, B, N

X-ray by the samples. Fig. 4 shows the additional absorption of the characteristic X-ray by the sample around the pit on the sample surface owing to the extended trajectory of the characteristic X-ray. The additional absorption affects the detected intensity of the characteristic X-ray and absorption correction, generating spurious results. Furthermore, poorly polished sample surfaces have more severe effects on the analysis of light elements.\textsuperscript{8} Thus, the surfaces of the samples must be flat and unscratched to avoid surface morphology effects.

**Coating.** For electron microanalysis, a thin conductive film needs to be coated on the surface of non-conductive samples to prevent the charging effect on the sample surface and sample heating,\textsuperscript{11} which could affect detection of characteristic X-ray and image observation. The elemental composition of the coating material should be different from the element to be analyzed in the samples to minimize effect of coating on the analytical results. Carbon and some metals and alloys, for example, Au and Au-Pd alloy, are commonly used for the sample surface coating. Gold has an atomic number of 79 and produces a complicated family of X-ray lines when interacting with an electron beam, thus strongly interfering with and absorbing the X-rays generated in the sample. Gold also affects the landing energy of the incident electron beam. Thus, gold coating is unsuitable for EPMA, although gold is often used to coat samples for SEM imaging. In contrast, carbon is a light element with an atomic number of 6 and is almost transparent to characteristic X-rays from the sample. Its effect on the X-rays from the sample is minimal and can be ignored during analysis. Therefore, carbon coating is used for EPMA. However, the effect of the carbon coating must be considered in the analysis of light elements or carbon-containing samples.

The thickness of the carbon coating affects the X-ray intensity. Kerrick et al.\textsuperscript{12} reported that the characteristic X-ray intensities of F, Si, Fe, Na, and Sr decreased with an increase in the thickness of the carbon film, especially for light elements (Fig. 5). Differences in the thickness of the carbon coating between the samples and standards lead to errors in the analytical results, especially for lower-energy X-rays.\textsuperscript{13,14} However, the loss of characteristic X-ray caused by the carbon film remains the same for the unknown sample and standard with similar carbon film thickness. Thus, it is essential to have the same thickness of the carbon coating on both the standards and samples for the quantitative analysis. Nevertheless, it is challenging to maintain the same thickness of the carbon coating for all thin sections loaded in the coating device even during the same evaporation process. Zhang and Yang\textsuperscript{13} proposed a suitable method to minimize the difference in carbon film thickness during coating.

Unknown samples and standards are often coated at different times, which makes it difficult to coat them with the same carbon film thickness. Therefore, a mathematical model was proposed to
Analytical Procedures and Experimental Conditions

A peak search is required for the element of interest before the quantitative analysis, especially for the minor and trace elements, because the peak of the minor and trace elements cannot be searched in the sample during the analysis. These conditions include accelerating voltage, beam current, beam diameter, counting time, diffracting crystal, characteristic X-ray line, background, analysis sequence of elements, and standards.

Accelerating voltage. It is desirable to select an accelerating voltage higher than two times the critical excitation energy to improve the excitation efficiency of characteristic X-rays and obtain an ideal peak/background ratio.6 An accelerating voltage of 15 kV is often used for analyzing oxides in geological samples, while 20 kV is used for sulfide analysis (such as analyzing Cu and Zn in sulfide). Low and high accelerating voltages can be applied for light16,17 and trace elements,18 respectively, to obtain high counts.

Beam current. A high beam current increases the X-rays generated in the samples, thereby improving the precision of the analysis. However, the X-ray counts could exceed the upper limit of the X-ray counter in WDS when the beam current is high, leading to incorrect results. A beam current of 2×10^5 A is effective for analyzing major elements in geological samples. However, a low beam current should be used when the migration of element occurs during the analysis, such as Na in feldspar. In contrast, a high beam current, up to 5×10^7 A or 9×10^7 A,18,19 can be used for analyzing trace elements.

Beam diameter. Beam diameter is often small (such as a focused beam or 1 μm spot size) to improve spatial resolution. However, in some cases, a small beam spot could potentially damage the sample or cause the migration of the element. A large beam spot size is generally used when the element migration occurs during the analysis. Beam diameter used for the sample and standard analysis can be different when it is smaller than 20 μm. However, the beam diameter should be similar when it is larger than 20 μm because a large beam spot reduces the characteristic X-ray intensity (Fig. 6).20

Additionally, the analytical area should be homogeneous. A heterogeneous area can yield inaccurate analytical results when a large beam is employed, partly because EPMA considers the analysis area homogeneous in the matrix correction process.2 For a heterogeneous area, the actual matrix where the emitted characteristic X-rays travel through is different from that used in the matrix correction procedure,6 leading to additional errors.10 Counting time. Counting time is the time used for measuring a peak or background. Background counting time is usually half of the peak counting time; however, it can be extended properly to improve the detection limit. Counting time varies depending on the concentrations of the elements. Peak counting time of major elements is usually from 10 s to 30 s, while that of minor or trace elements can be from 30 s to 120 s to improve the precision. However, the counting time for migratory elements should be shorter.

Background. Continuous X-rays generated by bremsstrahlung radiation contribute to the background intensity in the WDS X-ray spectra. These background X-rays are subtracted to obtain the net intensity of the characteristic X-rays. In a routine analysis, the background intensity is usually obtained through linear fitting according to the intensity measured on one side or both sides of the peak (Fig. 7a). However, the actual background may be curved (Fig. 7b), and a two-point linear fitting often results in errors, especially for light or trace element analyses. Methods such as two-point exponential, polynomial, or multi-point fittings19,21,22 can be applied for a better estimation of the background intensity. In addition, the mean atomic number
Fig. 6 A graph showing the changes in the detected characteristic X-ray intensity with the increasing beam diameter.\(^{20}\) (a) Na, Mg, Al, and Si with a thallium acid phthalate (TAP) crystal and (b) Si in olivine and jadeite with a TAP and polyethylene terephthalate (PET) crystal. The gray area in the graph ranges from 98 wt% to 102 wt% on the vertical axis.

Fig. 7 A schematic diagram demonstrating the background intensity obtained by interpolation (Bg1 and Bg2): (a) linear fitting applicable when the background curvature is small; (b) linear fitting not applicable when the background curvature is large (after Reed\(^{6}\)).

**Standard.** Chemical compositions of standards are obtained through different analytical techniques, such as wet chemical analysis, X-ray fluorescence spectroscopy, and EPMA. It is ideal to select standards with the same chemical composition as the sample to minimize matrix effect. The concentrations of the elements to be calibrated in the standard should be sufficiently high to generate enough characteristic X-rays and ideally higher than that in the samples. In addition, the quality of a standard must be evaluated. For EPMA applications in geosciences, natural minerals are the most commonly used standards.\(^{24}\) Although these standards were previously evaluated as homogeneous by various analytical techniques, the quality, especially the homogeneity, may not be guaranteed. Thus, EPMA operators should examine the quality of standards in their laboratory and select appropriate standards accordingly.

**DATA EVALUATION AND INTERPRETATION**

Assuming all major elements are analyzed, and results are not normalized to 100 wt%, the data quality of the quantitative EPMA is first evaluated by examining whether the total content of all measured elements is approximately 100 wt%. Generally, the total analytical error of an EPMA instrument provided by the manufacturer is approximately 2 wt%. Therefore, a total of 98 wt%–102 wt% is considered as a good result.

Theoretically, the total is 100 wt% when all elements are correctly measured during the quantitative EPMA. For example, the total for olivine, pyroxene, feldspar, and garnet is approximately 100 wt%. However, the theoretical total is less than 100 wt% when some elements, such as H and Li, are not measured. For example, hornblende and mica contain approximately 2.5 wt% and 4.5 wt% H\(_2\)O, respectively, and the

**Diffracting crystals.** Diffracting crystals with different interplanar d spacings (Tables 1 and 2) are used to analyze different elements. A smaller d spacing is essential to obtain a better peak resolution in WDS. Counting rate and peak resolution should also be considered when selecting diffracting crystals. Counting rate increases when the diffraction angle is large, although the peak resolution may be poor. For example, distinguishing Ce L\(\beta\)\(_1\) from Nd L\(\alpha\)\(_1\) is difficult with PET crystals and easy with LIF crystals in the JEOL EPMA (Fig. 8).

**Analysis sequence of elements.** Elements that easily migrate under electron beam bombardments, such as Na, K, and F, should be analyzed first. In addition, the analysis sequence of the elements should be arranged based on the diffraction angles from large to small or vice versa to improve the analytical efficiency and minimize movement and wearing of the WDS spectrometer.

**Fig. 8** The effect of the diffracting crystal on resolution in a wavelength dispersive (WD) spectra: peaks are recognizable with LIF (a); peaks are unrecognizable with PET (b) (after Reed\(^{6}\)).
theoretical total is approximately 97.5 wt% and 95.5 wt%, respectively. An analytical total within the range of “theoretical total - 2 wt%” and “theoretical total + 1 wt%” is deemed suitable. The good analytical total is closer to the lower side due to the possible presence of unmeasured minor or trace elements.

Another criterion to evaluate the analytical results is by examining the atomic ratios or atomic % according to the chemical formula of minerals. For example, the S atoms in pyrite (FeS₂) is 2/3 of the total atoms. Additionally, the Si atoms in olivine ((Mg, Fe)₂SiO₄) is 1/3 of the total cations.

Minor or trace elements have slight effect on the analytical total and atomic ratio. Therefore, it is difficult to determine the quality of their analytical result. A proper secondary standard containing the minor or trace elements analyzed in the sample can be measured during the sample analysis to evaluate the analytical quality of the minor or trace elements.

**ANALYTICAL PRECAUTIONS FOR SPECIAL MINERALS**

In geosciences, some minerals are special and require additional attention during the quantitative EPMA. They include: (1) minerals with migrant elements and time-dependent X-ray intensities (TDI) during the analysis, such as feldspar, carbonates, apatite, glass, and hydrous minerals; (2) minerals containing light elements that are difficult to analyze, such as C in carbonate, Be in beryl, B in tourmaline, and hydrous minerals; and (3) minerals with variable oxidation-state oxides, such as magnetite, hematite, and cuprite. The precautions essential for these “special” minerals during the quantitative EPMA are described below.

**Feldspar.** Sodium and potassium in feldspar can easily migrate during EPMA, leading to underestimated Na and K contents and an overestimated Si and Al contents. Therefore, a low beam current (10 nA) and a large beam spot (10 μm or more), is preferred during the analysis. Additionally, Na and K should be analyzed first. In addition to examining the analytical total, the atomic ratios should also be checked to evaluate the data quality. The atomic ratio of feldspar that can be used for the data quality evaluation includes Na + K+ 2xCa = Al and 3xNa + 3xK + 2xCa = Si (in cation number). The minerals or materials without TDI (such as homogenous jadeite standard) are preferred as the standard for Na. However, when albite minerals are selected as standards, it is necessary to decrease the beam current and increase the beam diameter to ensure that there are no TDI for Na during the standard analysis.

**Carbonate minerals.** Significant element migration under electron beam irradiation was also discovered in carbonate minerals.25–27 The optimized analytical conditions for carbonate minerals include a beam current of 5 nA and beam diameter of 10 μm for calcite; 10 nA and 10 μm for dolomite; 10 nA and 5 μm or 20 nA and 10 μm for siderite; and 20 nA and 5 μm for other carbonates.25 Additionally, the easily migrated elements should be analyzed first. The carbon content is stoichiometrically calculated (such as the ratio of C:O = 1:3) based on their chemical formula (MCO₃, where M is a metal cation) or by fixing the CO₂ content from the difference between 100 wt% and the MO content, and subsequently the CO₂ content is included in the matrix correction. In addition, silicate minerals are more suitable than carbonate minerals to serve as standards for the carbonate mineral analysis. When carbonate minerals are selected as standards, it is also necessary to ensure that there are no TDI during the standard analysis.

**Apatite.** Fluorine in apatite shows strong TDI during the electron beam irradiation,28–30 especially when the incident electron beam is parallel to the c-axis of apatite (Fig. 9). A TDI correction model based on the mathematical relationship between the characteristic X-ray intensity and time was proposed to measure the F content in apatite.31,32 The model extrapolates the X-ray intensity to the moment when the electron beam just arrives at the sample surface (time=0). In addition, it was proposed that cooling the samples with a liquid nitrogen cold trap in EPMA could reduce the TDI effect.31

However, not all laboratories can perform automated TDI correction and use liquid nitrogen cold traps due to software and hardware limitations. The following are the considerations for the quantitative EPMA of apatite:

1. Avoid exposing apatite to a high electron beam current before analysis. Observe it with a low beam current and minimize the observation time.

2. A low beam current and large beam diameter can be used to minimize the F migration. Analyze F and Cl first, with a short analytical time.30

![Fig. 9 The variation in the X-ray intensity of different crystal planes of fluorapatite with the exposure time of electron beam (Modified after Stormer et al.31).](image-url)
(3) Polish apatite crystal such that its c axis is parallel to the polished surface since apatite exhibits less TDI effect in this direction.28

(4) Select diffracting crystals LDE1 (JEOL), PC1 ( Cameca), and LSA55 (Shimadzu) for analyzing F since they have higher count rates than the traditional TAP crystals. It is necessary to select an appropriate background position for the measurement because the peak shape of F is broad when using these diffracting crystals.

(5) Utilize topaz, BaF2, MgF2, or materials with a weak TDI as the standard for analyzing F. Fluorine in apatite has strong TDI effect, which is not a good choice as a standard for analyzing F in apatite.30 Fluorite is also unsuitable as a standard for F in apatite because F in fluorite shows significant TDI.

(6) Examine the F concentration. According to the apatite chemical formula, the F concentration in the end member of fluorapatite is 3.77 wt%. Thus, the F concentration in apatite higher than 3.77 wt% should be treated carefully.

Glass. Sodium and potassium in silicate glass also exhibit TDI under electron beam bombardment, particularly those in rhyolite or H2O-bearing glass.34 Experimental conditions suitable for analyzing glass include reducing the current density by a lower beam current and utilizing a larger beam diameter,20,34,35 conducting TDI correction,34 and analyzing at cryogenic temperatures.36

The following are the considerations for the EPMA of glass:

(1) Use a low beam current and a large beam diameter. When the beam diameter exceeds 20 µm, use the same beam diameter for both standards and samples.

(2) Determine whether the sample exhibits TDI under the selected conditions before analysis. Reduce the beam current and/or increase the beam diameter till the TDI is negligible when the sample demonstrates TDI effect.

(3) Analyze a secondary glass standard with a composition similar to the sample for data quality control or evaluation. Difference between 100 wt% and an actual total content obtained is often used to determine the concentrations of H2O or volatiles in glass. However, the difference may also arise due to the surface discharge of the sample37 or TDI. The H2O content calculated by the difference method must be involved in the matrix correction for glass samples with high H2O content.

Hydrous minerals. All the components in a sample, including H2O, should be considered for the matrix corrections in quantitative EPMA. The total of hydrous minerals obtained by EPMA is less than 100 wt% because EPMA does not measure the H2O content. Matrix correction factors can be incorrect when H2O is not included in the matrix correction. However, the effect can be ignored for minerals with low H2O content, such as mica and hornblende. In contrast, inaccurate results can be obtained for minerals with high H2O content, such as chlorite, serpentine, and turquoise, when H2O is not considered in the matrix correction.

Tourmaline and beryl. The accurate EMPA of light elements is problematic due to the high absorption of the low energy X-rays and spectral interferences from higher-order X-ray lines of heavier elements.10 During the EPMA of tourmaline and beryl, B and Be are calculated instead of being measured. The chemical formula of tourmaline is (Na,Ca,K)R[Al(SiO3)](BO3)2(O,OH,F) (R = Mg, Fe, Li, Mn, Cr, V, or Al) with approximately 10 wt% B2O3 while that of beryl is Be3Al2[Si6O18] with approximately 14 wt% BeO. The contents of B2O3 and BeO can be calculated according to the atomic ratio B:Si=1:2 and Be:O=1:6 with B2O3 and BeO included in the matrix correction when B and Be are not measured directly by EPMA.

Variable oxidation state oxides. Concentrations obtained by quantitative EPMA are usually expressed as oxides of elements with oxygen calculated by stoichiometry, i.e., proportioning O according to the valence state of a cation and then participating in the matrix correction. Therefore, the valence states of the cations are determined before the analysis.

When a preset valence state of an element (such as Fe) does not match the actual valence state of the element in a mineral (such as magnetite), the calculated O content and the total will be incorrect. For example, the total obtained will be 1.6 wt% less than the theoretical total 100 wt% when the Fe valence is incorrectly set as +2 for hematite (Fe2O3). In contrast, an accurate result is obtained when the Fe valence state is correctly set to +3.38 Iron in minerals of the spinel group, such as magnetite Fe3+Fe2+O4, exists as both Fe3+ and Fe2+ in different proportions. It has been demonstrated that careful electron microprobe analyses with stoichiometry and charge balance for Fe-bearing minerals such as magnetite and ilmenite yield Fe3+(Fe2++Fe3+) ratio similar to those from Mössbauer analyses, albeit with larger relative errors.39 However, the software provided by the instrument manufacturers may only allow an integer value to be input, creating an obstacle for analyzing oxides with variable oxidation states. In this case, cations with variable oxidation states can be analyzed and determined as a simple substance (setting the valence state to 0), and O can be calculated from difference and included in the matrix correction.38

RECENT ADVANCES AND CHALLENGES IN EPMA

Light element analysis. Light elements, such as Be, B, C, N, O, and F, emit low energy “soft X-rays” (energy less than 1 keV) (Table 3). Detection of these low energy soft X-rays, thereby
determining light element concentrations by EPMA is challenging and is often less efficient and less accurate. These challenges include: (1) samples, diffracting crystals, and detector windows that absorb the low energy characteristic X-rays strongly; (2) reliable mass absorption coefficients of light elements remain to be determined; (3) low energy characteristic X-rays are interfered by the X-rays generated from heavier elements; (4) peaks of characteristic X-rays from light elements shift and the peak shapes of the light elements change too in different matrices or compounds; (5) the lack of suitable light element standards; and (6) the carbon contamination and thickness difference of the carbon film on the sample surface.

Nevertheless, the accuracy and precision of the light element analysis can be improved through the following steps:

(1) Use a diffracting crystal with large d spacings, such as layered dispersion element (LDE, Table 2), to obtain significantly high counts and peak/background ratios.

(2) Use a suitable acceleration voltage for the light element analyses. For example, the intensity of Be in beryllium metal is the highest when the acceleration voltage is 12 kV. Although the intensity of the characteristic X-rays increases with increasing the acceleration voltage, a higher acceleration voltage also increases the depth of characteristic X-rays, causing a high absorption effect.

(3) Minimize the effect of coating material, primarily carbon, on the characteristic X-rays of light elements. The conductive thin film coated on a sample surface can significantly absorb low-energy characteristic X-rays emitted by the light elements. Carbon contamination on the sample surface due to the heat from electron beam bombardment make the absorption effect even worse. Differences in the carbon film thickness between the standards and samples also lead to errors in the analytical results. Therefore, it is strongly recommended to use a liquid nitrogen cold trap for cooling, coat standards and samples with the same thickness of the carbon film, and correct uncertainties from carbon film thickness and counting rate to effectively alleviate the above-mentioned problems.

(4) Consider effects of the peak shift and peak shape on the measured intensities. Changes in the peak shift and peak shape of a light element have been observed in a different matrix (Fig. 10a). Changes in the peak shape also occur in different crystallographic planes within the same mineral (Fig. 10b), such as peak area integral intensity and area/peak factor, which is crucial for the light element analysis.

In addition, utilizing pulse height analysis for alleviating interference from heavier elements and developing ultra-soft X-ray spectrometer technology will also assist in analyzing light elements.

**Trace element analysis.** Trace element analysis using EPMA has gained extensive attention in recent years. The principal challenge is to effectively improve the detection limit and increase the accuracy and precision of the analytical results. The precision of the analysis is improved by increasing the accelerating voltage, beam current, and counting time. In most cases, a high accelerating voltage also helps improve the detection limit. Although a high beam current and long counting time improve precision, they can also cause TDI.

Nevertheless, allocating the counting time to different locations on the homogeneous sample surface reduces the TDI effect, which is well utilized for analyzing glass and quartz. In addition, using large diffracting crystals and simultaneously analyzing the same element with multiple spectrometers improve the precision and detection limit.

Factors affecting the trace element analysis include peak, background fitting, and secondary fluorescence effect. The peak interference is mainly caused by the low-order X-rays of some elements (Fig. 11a) and may be separated by overlapping the peak deconvolution and correction. A “step” is a sharp decline in the X-ray continuum background (Fig. 11b) and a “hole” is a negative peak in the X-ray continuum background (Fig. 12). The “steps” and “holes” observed in the background or underneath the peak also

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**Table 3. Characteristics of the light element Kα lines (after Goldstein et al.)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Z</th>
<th>λ(Å)</th>
<th>E(keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>4</td>
<td>114.0</td>
<td>0.109</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>5</td>
<td>67.6</td>
<td>0.183</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>6</td>
<td>44.7</td>
<td>0.277</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>7</td>
<td>31.6</td>
<td>0.392</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>8</td>
<td>23.62</td>
<td>0.525</td>
</tr>
<tr>
<td>Fluorine</td>
<td>F</td>
<td>9</td>
<td>18.32</td>
<td>0.677</td>
</tr>
</tbody>
</table>

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**Fig. 10** (a) The peak shape of C Kα peaks recorded from SiC and FeC with differences in position and shape (after Bastin and Heijligers); (b) Two extremes of the B Kα peak shape recorded from ZrB₂ with the rotation of the specimen (after Bastin and Heijligers).
significant affect the trace element analysis. Therefore, the interference peaks, “steps”, “holes” and other interfering factors present in the background need to be avoided when selecting the background positions for analysis. The secondary fluorescence is the excitation of an element in an adjacent phase by the primary X-rays from the measurement spot. This phenomenon can occur far away from the original measurement spot since X-rays penetrate very far, for example, a chromeite host with an olivine inclusion when analyzing Cr in the olivine, or a neighboring rutile close to quartz when analyzing Ti in the quartz. This results in an overestimation of the concentration of the analyzed element. Therefore, it is essential to select the measurement spots with a sufficient distance from the neighboring mineral or utilize simulation software for correcting the secondary fluorescence effect to avoid or reduce secondary fluorescence effect. For elements with a curved background shape rather than a straight line, such as Al Kα in quartz (Fig. 11a), a two-point exponential curve fitting for the background or a blank correction (measure a zero concentration standard with a matrix similar to the unknown to obtain an accurate background intensity) is superior to a two-point background interpolation method. The multipoint background fitting is another effective method for fitting a curved background. In addition, the MAN method adopted by the Probe Software, an EMPA application software, is also a reliable fitting method for the background intensities. In an analytical procedure, a suitable secondary standard and a sample can be analyzed simultaneously to effectively monitor the accuracy of the results.

**EPMA U-Th-Pbtotal dating.** The EPMA U-Th-Pbtotal dating, also known as the chemical U-Th-Pbtotal isochron method (CHIME), is widely applied for accessory minerals rich in U and Th, such as zircon, monazite, xenotime, thorianite, and uraninite. This method assumes that the dating mineral system is closed (without the Pb loss), and the initial Pb content is negligible. The basic dating equation was continuously improved, and several methods were proposed, including isochron, average apparent age, three-dimensional fitting, and two-dimensional fitting methods. Theoretically, the initial Pb content can be estimated and corrected by applying isochron and three-dimensional fitting methods. However, its applications become problematic when the initial Pb is heterogeneously distributed in the minerals.

Since most accessory minerals have low contents of U, Th, and Pb (mainly Pb), high-quality measurements of these elements play a vital role in the CHIME dating method. However, analyzing U, Th, and Pb is a challenge for rare earth element-rich (REE-rich) minerals (such as zircon, monazite, and xenotime) due to the complex spectral characteristics of REEs that affect the Pb analysis. Hence, interference correction is essential when interferential elements exist in a sample. Some methods such as shared background measurement, multipoint background analysis, and MAN method can be used for background interference to obtain accurate backgrounds.

**Combined analysis with WDS/EDS.** EDS and WDS are widely used in the microanalysis of major elements in minerals and materials. The application of silicon drift detector EDS (SDD-EDS) has greatly improved the EDS performance with the development of semiconductor detectors and improvement of EDS energy resolution. The SDD-EDS has high counts throughput and extremely high stability in terms of peak shape (resolution) and peak position (calibration), making it possible to utilize EDS for accurate quantitative analysis. Thus, EDS has become an analytical tool for the precise quantification of major elements (>1 wt%) even when severe peak interference occurs. Moreover, trace elements analysis with EDS can obtain a detection limit of 250 ppm or less in the absence of peak interference.

The peak resolution of SDD-EDS is lower than that of the WDS, thereby limiting the determination of trace element content by EDS. However, the simultaneous analysis, short measurement time, and simple operation make EDS suitable for analyzing major elements, especially for easily migrated elements. A rapid and accurate component information of the sample can be obtained when a WDS with high resolution and low detection limit is combined with the simple and fast EDS.

In order to combine WDS and EDS, it is necessary to meet the...
requirements of the operating software to control the simultaneous working of WDS and EDS. In addition, suitable operation conditions should be established. The normal working conditions of WDS and EDS are different. WDS requires a large beam current to obtain a higher count rate, which generates high counts in EDS and leads to a long dead time. When WDS and EDS are combined, WDS can be used to analyze trace elements (0.01 wt%-1 wt%) and elements with overlapping peaks in EDS (such as the L line of Ni, Cu, and Zn), while EDS can be used to analyze major elements. Thus, the advantages of WDS and EDS can be availed to improve the efficiency of analysis.\(^{72}\)

Quantitative analysis at low accelerating voltages for improved spatial resolution. With field emission guns equipped in EPMA, large and steady beam currents under low accelerating voltages become available,\(^{2,6}\) leading to an improved spatial resolution down to submicron scale. The low accelerating voltage EPMA has been applied to study volcanic processes by diffusion chronometry across submicron crystal zones,\(^{73}\) and for developing alloy materials with desirable properties.\(^{2}\) However, the following challenges remain for this technology:

1. Carbon accumulation and contamination due to the polymerization and deposition of hydrocarbon molecules around the analysis point absorbs the low energy X-rays.\(^{15,74}\) Plasma cleaning, gas cleaning, liquid nitrogen traps, and Peltier thermoelectric devices can be used to mitigate the impact of carbon contamination.\(^{15,42,75,76}\) Replacing oil pumps with oil-free vacuum pumps can eliminate carbon contaminations at the source.\(^{2}\) In addition, some correction methods can be used to correct the carbon contamination effect.\(^{15}\)

2. The surface morphology of the samples, such as polishing quality, coating, and surface oxidation, can significantly affect analyses at low voltages because the electron beam cannot penetrate the sample deeply enough.\(^{74,77}\)

3. The L and M X-ray lines should be used at low voltages because high-energy X-ray lines of elements are not generated at low accelerating voltages. The L and M lines are severely overlapped and interfered by the second and third order X-rays of other elements,\(^{78,79}\) making background analysis more difficult (Fig. 13). In addition, low X-ray intensity requires a long counting time and/or high beam current for the trace element analysis.\(^{2}\)

4. For the first-row transition elements in the periodic table, their L lines are mostly low-energy X-rays that do not have well-determined mass absorption coefficients. Moreover, the chemical bonding and self-absorption result in severe peak shift for the Lα signal, invalidating the traditional absorption correction.\(^{79,82}\) The methods proposed to address this issue include: a) correcting the matrix correction coefficient,\(^{83}\) b) replacing Lα with L1 (M1-L3 transition),\(^{79,80,84}\) and c) combining curve correction with the area integration of Lα and Lβ.\(^{77,85}\) However, these solutions are only applicable for samples with simple compositions, such as olivine and ferroalloy, and the validity of samples with complex compositions still requires verification.

Iron oxidation state. The peak shift of Fe Lα and Fe Lβ X-ray lines and change of Fe Lα/Lβ intensity ratio were observed in the Fe\(^{2+}\)/Fe\(^{3+}\) analysis with EPMA. The peak shift and intensity variation differ with the oxidation state.\(^{86}\) Hence, the Lα and Lβ of Fe\(^{2+}\) (such as almandine) and Fe\(^{3+}\) (such as andradite) may be distinguished and quantified in terms of their energies of L lines (Fig. 14). The quantitative analysis of Fe oxides is based on the self-absorption correction, improved peak resolution, and matrix effect correction. Among these, self-absorption is the main influencing factor that depends on the Fe concentration and Fe L-line X-ray path length in the sample.\(^{87}\)

The most commonly used method to obtain Fe\(^{3+}\)/Fe\(^{2+}\) of samples is known as the “flank method,” which involves a
careful consideration of the peak positions of Lβ and La lines and Lβ/La intensity ratio.\textsuperscript{86,93} The WDS spectrometers used are recalibrated based on the standards to strengthen the EPMA sensitivity for the “flank method”.\textsuperscript{93} This calibration can avoid the Fe\textsubscript{total} content interference and the self-absorption effect.\textsuperscript{93} Furthermore, this method measures the intensity ratios on the high- and the low-energy sides of La and Lβ, respectively, and analyzes the Lα and Lβ peaks at the locations where the spectral differences are most significant (Fig. 14), thus considerably improve the sensitivity.\textsuperscript{87}

Because the Fe\textsuperscript{3+} and Fe\textsuperscript{2+} self-absorption effects vary with minerals, the self-absorption effect of different minerals should be individually determined to establish a valid empirical correction model. The chemical composition of different end-members for garnet group minerals has no obvious effect on the Lβ/La ratio, indicating that the matrix effect is the same, and the “flank method” can be applied to different garnet end-members.\textsuperscript{87} The studies on the self-absorption effect of different minerals facilitates the application of the “flank method” to other materials, such as glass,\textsuperscript{88-92} hornblende,\textsuperscript{88} and biotite.\textsuperscript{88} However, suitable and appropriate standards with accurate Fe\textsuperscript{3+}/ΣFe values and establishment of specific “flank method” for different minerals are urgently required to promote the application of the “flank method” in determining Fe\textsuperscript{3+}/ΣFe by EPMA.

Standard reference materials. The standard reference materials used in EPMA include the primary standards and secondary standards. The primary standards are essential for every EPMA laboratory. Nevertheless, the primary standards used in different EPMA laboratories could vary. There are currently insufficient primary standards that can be applied in all EPMA laboratories. The absence of a global primary standards leads to a situation where we cannot reliably compare the quality of the quantitative results from different EPMA laboratories. Therefore, it is necessary to establish globally adopted, high-quality primary standards for most elements on the periodic table.

As discussed before, the quality of the EPMA results can be assessed using the analytical total or atomic ratios. However, it becomes difficult to use this approach to evaluate the quality of the trace element analyses. Therefore, suitable secondary standards are necessary for evaluating the analytical results. Moreover, it is effective to evaluate the results and find the problems by analyzing the secondary standards used under the same analytical conditions and sessions as the samples, for example, cross analyzing the secondary standards and unknown samples. In addition, blank references can be used for accurate background measurements.\textsuperscript{22,23}

Utilizing a secondary standard with its giving compositions similar to an unknown sample is always preferred. Unfortunately, such secondary standards are often missing, especially for the trace and light elements and for EPMA U-Th-Pb\textsubscript{total} dating. For example, for Ti analysis in quartz, a blank quartz reference\textsuperscript{22} with approximately 0 ppm of Ti and a quartz reference material\textsuperscript{94} with 57±4 ppm of Ti can be used to measure the background and monitor the quality of the analytical results, respectively.

However, it could be beneficial to monitor the accuracy of the Ti analysis in quartz with secondary standards having low (such as 5 ppm) or relatively high (such as 100 ppm and 500 ppm) Ti content.

CONCLUSIONS AND OUTLOOKS

The past 70 years have witnessed widespread applications of EPMA in analyzing minerals or other materials for major, minor, trace, and light elements, for U-Th-Pb\textsubscript{total} dating, and for determining the iron oxidation state. Improvement of hardware and software promotes the development of the analytical techniques of EPMA. For example, the availability of large diffracting crystals promotes the analyses of trace elements. Field emission gun enables high spatial resolution analysis, and implementing the latest soft X-ray analysis improves the analysis of light elements. The future progress of EPMA technology lies in: 1) further improvement of the instrument hardware and software, 2) optimization of the existing analysis methods, 3) development of practical methods for individual minerals and elements, 4) understanding the mechanism of interference factors and related issues, and 5) optimized matrix correction model. Developments, advances, and novel applications of EPMA techniques also require hardware manufacturers and instrument users to work together to address the challenges and difficulties encountered.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENT
This research was funded by the National Key R&D Program of China (2017YFC0601404), Natural Science Foundation of China (41773040), and Fundamental Research Funds for the Central University, China University of Geosciences (Wuhan) (CUGCJ1818). We are grateful to Prof. Wei Guo and four anonymous reviewers for providing valuable comments and suggestions, which helped in significantly improving this manuscript.

REFERENCES


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- Purity certification up to 99.99999%.
- Depth analysis of elements distribution in materials.

Typical LOD for 99.99999% Indium

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