

Applications of LA-ICP-MS in the elemental analyses of geological samples

LIU YongSheng*, HU ZhaoChu, LI Ming & GAO Shan

State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China

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Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), which is a rapidly developing analytical technique for the analyses of trace elements and isotopes, plays an important role in advancing the study of Earth science, especially with respect to micro-geochemistry. This article reviews the application of LA-ICP-MS in the elemental analysis of solid geological samples. Although LA-ICP-MS has been widely used in the spatial resolution analysis of element compositions and rapid bulk analysis of whole-rock and soil samples, the analysis accuracy is restricted by numerous factors, including the instrumental conditions, the elemental fractionation and matrix effects, the lack of sufficient matrix-matched reference materials, and the strategies for quantitative calibration and sensitivity drift correction. According to the type of samples and the analyte elements, the analysis accuracy can be improved through the optimization of instrument conditions and the adoption of suitable correction strategies and reference materials.

LA-ICP-MS, geological sample, elemental analysis, quantitative strategy

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The *in situ* analyses of trace elements and isotope compositions of solid samples using methods that do not involve complex and time-consuming wet-chemical digestion is a key point that has been attracting the attention of chemists. The micro-analysis of elemental concentrations in solid samples has been an attractive frontier in the development of analytical science. Micro-geochemistry has recently been suggested to perhaps lead the development of geochemistry in the future. In 1984, soon after the first commercial ICP-MS appeared, Gray [1] analyzed the elemental and Pb-isotope compositions of granites by combining ICP-MS and LA, thereby introducing the micro-analytical technique of laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Jackson et al. [2] fully demonstrated the strong potential of LA-ICP-MS in analyzing the trace-element compositions of geological samples, and LA-ICP-MS were subsequently used to measure the partition coefficients of the trace elements [3]. Fryer et al. [4] were the first to

adopt LA-ICP-MS to the *in situ* analysis of the U-Pb geochronology of U-rich minerals. Li et al. [5] developed a method to simultaneously conduct U-Pb dating and trace-element analysis for a single zircon grain using LA-ICP-MS. In recent years, the technique of *in situ* analysis of trace elements and isotopes using LA-ICP-MS has been quickly developed and widely used in numerous fields, including geology, metallurgy, environmental science, biology, chemistry, materials science and archeology (Figure 1).

The fundamental operating principle of LA-ICP-MS is that a laser beam is focused onto the surface of a sample contained in an ablation cell, the sample is ablated and gasified and is then carried, as particulates (i.e. an aerosol), by the carrier gas (He or/and Ar) into the ICP to be ionized; after ionization, the ions with different mass-to-charge ratios are then filtered by the mass spectrum system and are detected by the detector. Compared with solution nebulization (SN)-ICP-MS, LA-ICP-MS has the advantages of greater spatial resolution (typically greater than 5 μm for profile analysis and $n\times 100$ nm for depth analysis), lower

*Corresponding author (email: yshliu@cug.edu.cn)

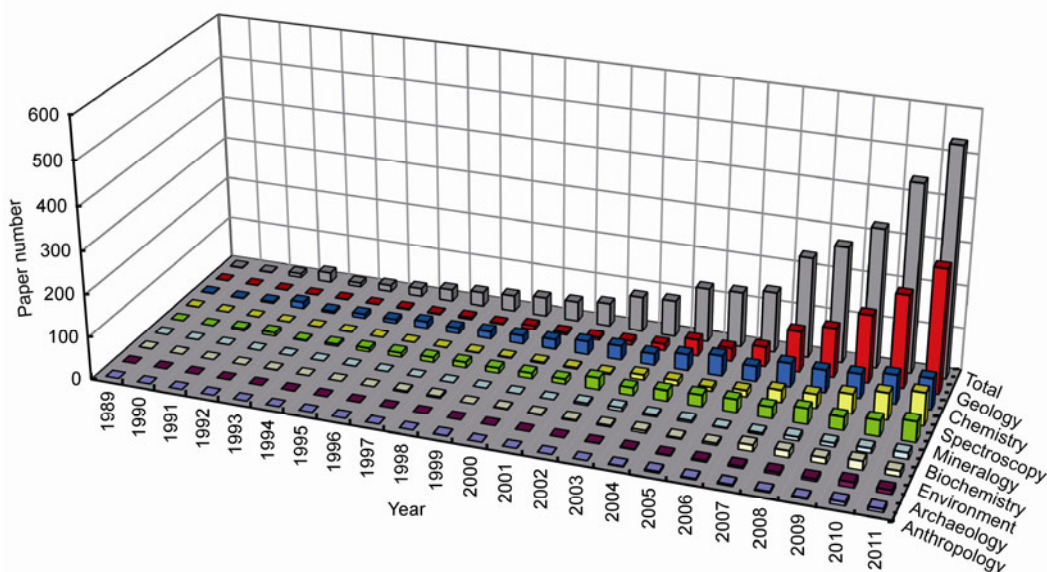


Figure 1 The application of LA-ICP-MS in different academic fields over the past 20 years. The data were extracted from the Web of Science.

sample consumption, faster and more efficient (less than 3 min for a single-point analysis), a lower background and fewer interferences from oxides and hydroxides [6]. Furthermore, the use of LA-ICP-MS avoids the time-consuming sample digestion process and sample-digestion-related problems (e.g. incomplete digestion of some minerals and poor stability of some elements in dilute acid solutions) faced by SN-ICP-MS [7,8]. As a consequence, LA-ICP-MS has been used in the geosciences not only as a single-spot analysis method, especially where trace element or isotope concentrations are required at high spatial resolution (e.g. the analysis of a single fluid/melt inclusion, a single zircon grain, or the zonation of a mineral) [2,4,5,9–16] or distribution analyses of elements and isotopes of rocks and minerals are required [17–21], but also for bulk analyses of rocks and soils [22–29].

Several factors affect the accuracy of an analysis of elemental content; these factors primarily include the instrumental conditions (i.e. the wavelength and pulse width of the laser and the sensitivity and resolution of ICP-MS), the quantitative calibration strategy, the standards used for calibration, the matrix and fractionation effects, and the sensitivity drift of the instrument. With the application of a suitable calibration strategy and optimized instrument conditions, better precision (better than 5%) and accuracy (better than 5%–10%) could be obtained using LA-ICP-MS analysis compared to that achieved using SN-ICP-MS. Many early LA-ICP-MS systems utilized the fundamental infrared wavelength of Nd:YAG lasers (1064 nm), which is poorly absorbed by many rock-forming minerals. The application of a UV laser in LA-ICP-MS systems resulted in significant improvements in the spatial resolution, better material absorptivity, reduced elemental fractionation and improved analytical precision. The use of shorter-wavelength lasers

[30] (i.e. the replacement of 1064 nm wavelength with 266 nm) (frequency-quadrupled output) or 213 nm (frequency-quintupled output) wavelength harmonic generators [31] or the use of 157 nm [32] or 193 nm [33] wavelengths produced by excimer gas lasers) and shorter pulse (e.g. femtosecond lasers) [34] can produce aerosols with smaller particle sizes and thereby reduce the non-stoichiometric effect. The shortcomings of 157 nm laser irradiation, which include the strong absorptivity of this wavelength by oxygen and its inherently low energy, have restricted its wide use. The properties of the 213 and 193 nm wavelengths with respect to the previously mentioned characteristics, are better than those of the 266 nm wavelength [35,36] and have thus been used more widely in laser ablation systems. Compared to nanosecond-laser ablation systems, the femtosecond-laser ablation systems provide significantly improved analytical performance, including a stronger signal intensity for a similar fluence, reduced matrix effects, better particle-size distributions, and negligible thermally induced fractionation; the femtosecond-laser systems are thus regarded as a more versatile analytical technique [34,37,38].

In addition to the instrumental hardware, other critical factors that affect analyses, including the choice of suitable reference materials and a calibration strategy for quantification, the optimization of instrumental parameters, the adaptation of reasonable correction strategies for sensitivity drift, and elemental fractionation, need to be taken into consideration for obtaining accurate analysis data via LA-ICP-MS.

1 Quantitative calibration of elemental contents analyzed by LA-ICP-MS

When LA-ICP-MS is used to perform quantitative analysis,

the method of combining external calibration and internal normalization is generally used [39], as demonstrated in eq. (1),

$$\begin{cases} C_{\text{sam}}^i = (cps_{\text{sam}}^i \times l^i) \times k_{is}, \\ l^i = C_{\text{rm}}^i / cps_{\text{rm}}^i, \\ k_{is} = (cps_{\text{rm}}^{is} / C_{\text{rm}}^{is}) / (cps_{\text{sam}}^{is} / C_{\text{sam}}^{is}), \end{cases} \quad (1)$$

where C_{sam}^i is the concentration of analyte element i in the sample, C_{rm}^i is the concentration of analyte element i in the reference material for calibration, cps_{sam}^i is the net count rate (sample signal minus background) of i in the sample, cps_{rm}^i is the net count rate of i in the reference material for calibration, cps_{sam}^{is} is the net count rate of internal standard element is in the sample, cps_{rm}^{is} is the net count rate of is in the reference material for calibration, C_{sam}^{is} is the concentration of is in the sample, and C_{rm}^{is} is the concentration of is in the reference material for calibration. The concentration of the internal standard element (regularly refer to one major element) must be obtained using other independent approaches (e.g. measured using EMP or calculated according to the stoichiometric formula). The use of the fixed stoichiometric formula method may introduce extra error if the internal standard element is heterogeneous in the sample, whereas the adoption of other independent ways of measuring the internal standard element can increase costs and workload. Moreover, diverse analytical results can be obtained when different elements are used as the internal standard [40]; the concentration of the analyte element can only be accurately measured when the internal standard element and the analyte element behave similarly during ablation. Different fractionation effects of the internal standard element and the analyte element are key factors that limit accurate calibration with this method. Jackson [41] found that, in general, a linear correlation exists between the fractionation index (FI) and the achieved accuracy when non-matrix-matched calibration is used; the FI therefore provides a simple means of correcting fractionation-related errors. Based on the linear relationship between accuracy and FI, Jackson [41] suggested a multiple internal standard correction procedure, as shown in the following equation:

$$C_{\text{SamCORR}}^i = C_{\text{Sam}_{is1}}^i - (C_{\text{Sam}_{is1}}^i - C_{\text{Sam}_{is2}}^i) \times \frac{\text{FI}^i - \text{FI}^{is1}}{\text{FI}^{is2} - \text{FI}^{is1}}, \quad (2)$$

where C_{SamCORR}^i is the corrected concentration of analyte element i in the sample; $C_{\text{Sam}_{is1}}^i$ is the concentration of analyte element i in the sample determined using internal standard $is1$; $C_{\text{Sam}_{is2}}^i$ is the concentration of analyte element i in the sample determined using internal standard $is2$;

FI^i is the fractionation index of analyte element i ; FI^{is1} is the fractionation index of internal standard element $is1$; and FI^{is2} is the fractionation index of internal standard element $is2$. The advantages of this procedure are that it is not predicated on near-linear analyte/internal standard intensity ratios and that it relies on data for major elements, which are generally homogeneously distributed within geological samples and can be measured accurately. Therefore, the accuracy of the analytical result can generally be enhanced when this method is used. The disadvantages are that the method requires accurate information on two or more major elements (i.e. those used as internal standards) and that the FIs of these major elements must differ greatly. A larger error will be generated as error propagation if the difference in the FI between the major elements used as internal standards is small.

Leach and Hieftje [42] explored a summed-spectrum normalization calibration procedure to determine elements in alloys using LAICP-MS without applying internal standardization. Although this technique is most likely feasible for alloys, it is not practical for silicate minerals with a variable matrix. Irrespective of the outcome of the sum normalization calibration procedure, the work of Leach and Hieftje [42] rekindled an interest in major- and trace-element analyses of solid materials using LA-ICP-MS without internal standardization. As an improvement to the summed signal normalization technique, Halicz and Günther [43] calculated the concentration of the internal standard based on normalization of the sum of all metal oxides to 100 wt.% to determine the trace-element compositions of anhydrous silicates. This method has been used to analyze the major and trace elements of silicate glasses [40,43,44], silicate minerals [40,45,46], carbonate minerals [47], silicate whole-rocks [23,24] and metal oxides [48]. The generic formula for this calibration method is demonstrated as follows:

$$\begin{cases} C_{\text{sam}}^i = (cps_{\text{sam}}^i \times l^i) \times k_{\text{total}}, \\ l^i = \sum_{s=1}^n \left((C_{\text{rm}^s}^i / cps_{\text{rm}^s}^i) \times \left(C_{\text{rm}^s}^i / \sum_{s=1}^n C_{\text{rm}^s}^i \right) \right), \\ k_{\text{total}} = (100 - C_{\text{sam}}^v) / \sum_{j=1}^N (cps_{\text{sam}}^j \times l^j), \end{cases} \quad (3)$$

where cps_{sam}^i (cps_{sam}^j) is the net signal intensity of analyte element i (j) in the sample; $cps_{\text{rm}^s}^i$ is the net signal intensity of analyte element i (j) in the reference material s for calibration; C_{sam}^i (and $C_{\text{rm}^s}^i$) is the concentration of analyte element i (in the form of a simple substance for the analysis of metals and/or alloys [49], in the form of an oxide for the analysis of silicate minerals and glasses [40], in the form of a carbonate for the analysis of carbonate minerals [47] or in the form of a sulfide for the analysis of sulfide minerals) in the sample (and reference material s); C_{sam}^v is the content

of the unmeasured volatile component or complex anion in the sample; n is the number of reference materials used for calibration, N is the number of elements that can be measured by LA-ICP-MS (elements should be analyzed as many as possible). The essence of the summed component normalization technique is to calculate the concentration of the analyte element using all components in the sample as internal standards. When a single external standard is used, the slope (I^i) of the calibration curve is the same as that in eq. (1); when multiple external standards are used, the slope (I^i) of the calibration curve can be calculated based on the concentration-weighted average, which leads to the greatest reduction in uncertainty introduced through the relatively high uncertainties of those elements with low concentrations in the reference materials [40] because, for a given element, high concentrations can be determined more precisely than low concentrations, and the reference values of high concentrations are typically more accurate than those of low concentrations.

Isotopic dilution method, which avoids the use of external standards, can also be adopted to analyze bulk rock and soil samples via LA-ICP-MS [50]. In some special cases, meaningful results can be obtained through simple calibration against matrix-matched external standards. For example, McCandless et al. [51] analyzed the trace elements of individual fluid inclusion in quartz using a simple external calibration against artificially prepared fluid inclusions. Despite the low accuracy of the simple external calibration method, it is simple and effective to understand the variation or distribution of elements in a small solid sample when there is no matrix-matched reference material or internal standard available. For example, Butler and Nesbitt [52] adopted this method to investigate the distributions of trace elements in the chalcopyrite wall of a black smoker chimney.

2 Factors affecting accurate elemental analysis with LA-ICP-MS

The accuracy and precision of elemental analyses performed with LA-ICP-MS are limited by many factors, including the laser ablation conditions, the ICP-MS analytical conditions, instrumental sensitivity drift, matrix effects between the sample and standards, fractionation effects, the accuracy of the recommended values for reference materials used for calibration, and the internal standard used for normalization.

2.1 Reference materials and matrix effects

Reference materials play an important role in LA-ICP-MS analysis. They are used as samples for quantitative calibration, quality control and assurance, and the development of methods and for inter-laboratory comparisons of analysis data. A credible reference material is a prerequisite to the acquisition of accurate data with LA-ICP-MS. The refer-

ence materials can be divided into four types: synthetic reference glasses, geological reference glasses with natural compositions, synthetic minerals and natural minerals [53].

Synthetic reference glasses consist mainly of the standard reference materials (SRM) of the 600 series (SRM 610–617) of the National Institute of Standards and Technology (NIST) and the GS reference glasses (GSC-1G, GSD-1G and GSE-1G) of the United States Geological Survey (USGS). The compositions of the NIST SRM 61x series differ from those of natural rocks and minerals; they contain 61 trace elements and four major elements (SiO_2 , Al_2O_3 , CaO and Na_2O) [54–57]. SRM 610 and SRM 612 are the most widely used NIST glasses. They have the advantages that the concentrations of all of the trace elements are similar and high (ca. 400–500 ppm for SRM 610 and 30–40 ppm for SRM 612). The USGS GS reference glasses have major element compositions of basalt and many trace elements in similar abundance at different concentrations (ca. 4–5 ppm for GSC-1G, ca. 40–50 ppm for GSD-1G and ca. 400–500 ppm for GSE-1G) [44,58]. Reference glasses with natural composition are produced by the direct melting of natural rocks and soil powders. They mainly include USGS reference glasses (BCR-2G, BHVO-2G and BIR-1G), MPI-DING reference glasses (KL2-G, ML3B-G, StHs6/80-G, GOR128-G, GOR132-G, BM90/21-G, ATHO-G and T1-G) and Chinese Geological Standard Glasses (CGSG) (CGSG-1, CGSG-2, CGSG-4 and CGSG-5). The USGS reference glasses have natural basaltic compositions [27,58–60], whereas the MPI-DING reference glasses comprise basalt (KL2-G and ML3B-G), andesite (StHs6/80-G), komatiite (GOR128-G, GOR132-G), peridotite (BM90/21-G), rhyolite (ATHO-G) and quartz diorite (T1-G) [61,62], and the CGSG reference glasses comprise basalt (CGSG-1), syenite (CGSG-2), andesite (CGSG-5) and soil (CGSG-4) [63].

Except for reference materials with silicate compositions, reference materials with compositions of sulfide, carbonate and phosphate are very limited. In-house reference materials of sulfide are typically used in most laboratories; these materials are synthesized by the following methods: (1) NiS fire assay [14,64], (2) a welding technique at high temperature and high pressure [65–69] and (3) pressed powder pellets [70,71]. Gilbert et al. [72] evaluated the homogeneity of the PGE and Au in six sulfide-matrix reference materials (synthetic pyrrhotite 8b [73], Po724-T and Po727-T1 [74], fused nickel sulfides PGE-A [75] and NiS-3 [72], and Lombard iron meteorite [76]) and the consistency of concentrations against different reference materials via cross-calibration. They found that Po727-T1 and 8b produced results that were comparable, within uncertainty, for all elements. Po727-T1 also produced consistent results with NiS-3 for all elements. All other RMs showed differences for some elements, especially Ru in Po724-T and Os, Ir and Au in PGE-A. Po724-T, Po727-T1 and the Lombard meteorite were found to be homogeneous with respect to all elements; however, 8b, PGEA and NiS-3 were heterogene-

ous with respect to only some elements. MASS-3 is a commercially available pressed-powder pellet of sulfide produced by the USGS for trace element analysis. The welding technique and pressed-powder pellets were generally used to develop reference materials with other special matrixes. Bédard et al. [77] developed a reference material for analyzing trace element concentrations in zircon by welding a mixture of zircon and albite powders. Klemme et al. [78] prepared 11 synthetic silicate and phosphate glasses to serve as reference materials for the *in situ* microanalysis of clinopyroxene, apatite, titanite and other phosphate and titanite phases. In addition, synthetic Ca-phosphate pellets MAPS-4 and MAPS-5 have been produced by USGS. Pressed-powder pellets of carbonate have been used in many laboratories as in-house reference materials for the analysis of samples with a carbonate matrix [79–83]. Calcium carbonate pressed pellets MACS-1, MACS-2 and MACS-3, which contain >60 trace elements with high concentrations, have been developed by the USGS.

Suitable reference materials and accurate knowledge of their compositions are necessary to achieve accurate analyses using LA-ICP-MS. NIST glasses SRM 610 and SRM 612 are mostly used as primary calibration standards because they contain many trace elements in high concentrations; furthermore, most of the trace elements are homogeneously distributed [84]. Despite the many advantages of the NIST glasses, their compositions differ from those of natural minerals and rocks, and thus different fractionation effects from the MPI-DING and USGS silicate glasses are observed. The NIST glasses have been shown to not be suitable external standards for the correction of natural silicate minerals and glasses [40,46,85,86]. For example, the relative deviation of REE in zircon is as high as 20% when calibrated against SRM 610 when Si is used as an internal standard, whereas the analysis accuracy can be improved remarkably if Zr is used as an internal standard [46]. Without doubt, the deviation caused by matrix effects between the standard and sample can be reduced to some degree through optimization of the instrument conditions (e.g. an increase in the energy density of the laser) [87]. MPI-DING glasses and USGS glasses have been shown to exhibit similar relative sensitivities, and they showed no obvious matrix-related fractionation effect when a 193 nm laser [40] or a 213 nm laser [87] was used. The disadvantage of using a calibration standard with low concentrations of some elements (i.e. the uncertainties of recommended values and instrument counting may be large) could be overcome through the use of multiple external standards, as previously discussed. Our experiments indicate that calibration against these reference glasses with natural compositions results in accuracies for the analysis of silicate minerals or glasses typically better than 10% [40,46,88]. Jochum et al. [85] have suggested that a matrix-matched external standard must be used for the accurate analysis of Pb.

In addition, both the recommended (or reference) values

and homogeneity of reference materials can significantly affect the analytical accuracy. Eggins and Shelley [84] found that 24 elements (Ag, As, Au, B, Bi, Cd, Cr, Cs, Mo, Pb, Re, (Rh), Sb, Se, Te, Tl, W, Cu, Pt, Cd, Fe and Mn) are distributed heterogeneously in the NIST glasses, whereas Be, Mg, Sr, Ba, Sc, Y, REE, V, Zr, Hf, Nb, Ta, Th, U, Ga, In, Sn, Co, Ni and Zn show no evidence of significant heterogeneity. Many researchers have adopted various methods to obtain the best possible estimate of the “true” values of trace elements in the NIST glasses [54–57,89–91]. The USGS and MPI-DING reference glasses with natural compositions have also been extensively analyzed by laboratories that used different techniques, and the preferred values typically have a high degree of confidence [27,58,60–62,90,92–94]. However, research on the synthetic USGS GS series standard glasses [44,58] is insufficient, and the uncertainties of some reference values are high. Recently, Chen et al. [47] and Jochum et al. [95] revised the reference value of Nb in carbonate-pellet MACS-3 (the revised value is 53.4–53.8 ppm).

2.2 Elemental fractionation in ablation, transport and excitation processes

Many authors have reported results related to the non-representative sampling of laser ablation (or non-stoichiometric ablation) and temporal changes in elemental responses during laser ablation, both of which are commonly referred to as “elemental fractionation” and could severely affect the accuracy of quantification. Elemental fractionation can occur during the ablation process, the aerosol transport process or the excitation process in ICP [86,96–101]. The intensity of the fractionation effect caused by temporal changes in elemental responses during laser ablation can be measured by the fractionation index (FI):

$$\left(FI^i = \frac{cps_{\text{Secondhalf}}^i / cps_{\text{Secondhalf}}^{ns}}{cps_{\text{Firsthalf}}^i / cps_{\text{Secondhalf}}^{ns}} \right) \quad [102].$$

The classification of elements based on the FI roughly follows the Goldschmidt geochemical classification of elements [86,97,102]. Košler et al. [95] found that the formation of phases of different mineralogy and/or chemical composition from the original sample at the ablation site can result in elemental fractionation (non-stoichiometric sampling) in material delivered to an ICP-MS for quantitative analysis. For example, both larger spherical particles and agglomerates of smaller particles produced by the ablation of zircon ($ZrSiO_4$) are mixtures of amorphous and crystalline materials—most likely zircon, baddeleyite (ZrO_2) and SiO_2 . U and Th are highly compatible with the structure of ZrO_2 (baddeleyite) and $ZrSiO_4$, whereas Pb is normally not present in large quantities, and significant quantities of the Pb would be excluded from either ZrO_2 or from the thermally affected $ZrSiO_4$. The difference in the transport efficiencies of the ZrO_2 and $ZrSiO_4$ particles and that of Pb and the degree of gasifica-

tion and ionization of two types of particles may be the critical reason for the elemental fractionation of Pb and U [100]. Míková et al. [98] found that the fractionation trends of the alkali elements are different from those of other lithophile elements and that a combination of thermally driven diffusion and size-dependent particle fractionation are responsible for the observed fractionation of alkali elements during laser ablation of silicate samples. Kuhn and Günther [103] and Hu et al. [104] found that the trace-element patterns of aerosols vary significantly with particle size; for example, small aerosol particles are rich in chalcophile elements (i.e. Cu, Zn, Ag, Cd, Sn, Sb, Pb and Bi). Moreover, the particle-size-related fractionation effects are different for aerosols ablated by a 266 nm laser and those ablated by a 193 nm laser. REE and HFSE tend to be enriched in the smaller aerosol particles when a 266 nm laser is used [103]; however, they tend to be enriched in the larger aerosol particles when a 193 nm laser is used [104].

Researchers can reduce or suppress the influence of the fractionation effect on the analysis accuracy by changing the laser system, optimizing the instrument conditions and applying a suitable data-reduction strategy. Ablation using a laser with a shorter wavelength or shorter pulse (e.g. using femtosecond instead of nanosecond laser pulses) could diminish the fractionation effect due to reduced thermal alteration of the sample material [105]. Guillong et al. [35] demonstrated that ablating silicate glass using a laser with a shorter wavelength could produce smaller particles and thus reduce elemental fractionation by comparing laser ablation using wavelengths of 266, 213 or 193 nm. Günther and Heinrich [96] suggested that elemental fractionation was insignificant (<10%) when a 193 nm laser was used. Shorter laser pulses result in weaker thermal effects of laser ablation and a thinner heated layer in the ablation pit. A femtosecond laser is not only predominantly non-thermal and causes less collateral damage than a laser with longer pulses, but it also provides smaller particle sizes for aerosols and no laser-plasma interactions and has the potential to eliminate fractionation effects and matrix dependence [34]. The fractionation effect could also be diminished through optimization of the volume and geometry of an ablation cell to improve the efficiency and stability of aerosol transportation and to decrease the particle sizes and their distribution [104,106–108].

Elemental fractionation can also be reduced through optimization of the instrumental conditions. Mank and Mason [109] showed that large-diameter craters, if ablated with sufficient laser energy density, reduce elemental fractionation and give a more intense signal for a longer period of time. The carrier gas is a key factor that affects elemental fractionation. Using helium instead of argon as a carrier gas leads to smaller fractionation effects in silicate matrices and to a 2- to 4-fold signal enhancement when 193 nm lasers are used [101,110]. The purity of the carrier gas used in LA-ICP-MS as well as the amount of oxygen released from silicate and oxide samples during the ablation in an “oxy-

gen-free” ambient gas were shown to contribute significantly to elemental fractionation [111]. Hirata [112] used a chemically assisted laser ablation technique (a Freon R-134a gas was introduced into the ablation cell as a fluorination reactant) to minimize the elemental fractionation. In addition, the energy density of the laser must be maintained at a sufficiently high and stable level; elemental fractionation in both ns- and fs-laser ablation systems can be reduced if the laser energy density exceeds the ablation threshold of the material being analyzed [113]. Furthermore, the ICP analytical conditions need to be optimized to achieve an improved degree of atomization and ionization (and thus a reduction in the degree of elemental fractionation), which can be monitored by the U^+/Th^+ signal ratio in SRM 610 glass [105]. Both ions have similar ionization energies and masses, and both of their major isotopes have a relative abundance of >99%. If full atomization is achieved, an intensity ratio close to the concentration ratio in the ablated material can be expected.

To reduce the influence of elemental fractionation on the analysis accuracy, Sylvester and Ghaderi [15] suggested an ‘intercept’ method to calculate the ratio between the signal intensity for each isotope of interest and that of an internal standard element (cps^s/cps^{is}) by linear fitting under the assumptions that the intrinsic value for cps^s/cps^{is} in an analyzed material is that measured at the start of laser ablation and that all subsequent measured ratios are progressively fractionated. In addition, the adoption of matrix-matched calibration standards and the selection of the same signal integration intervals for reference materials and unknown samples are important to reduce the influence of elemental fractionation on the accuracy of quantification.

2.3 Laser ablation conditions

The laser ablation conditions include the ablated spot size (D), the laser frequency (F), the energy density (Ed), the laser ablation mode and the carrier gas. The spot size can not only affect sensitivity and elemental fractionation but also the matrix effects, depending on the mass load of the ICP [23]. For a given sample and energy density, if the average laser ablation rate (r , measured by the sample depth ablated by a single laser pulse) is relatively stable, then the average volume of sample ablated per unit time (V) is approximately dependent on the spot size (i.e. $V = F \times r \times \pi \times (D/2)^2$). Therefore, the sensitivity should show an exponential relationship with the diameter of the laser beam spot. The use of a relatively larger spot size can generally not only improve the accuracy and precision of the analysis, but can also reduce the detection limit. Moreover, a larger spot size increases the diameter/depth ratio of the ablation pit and thus reduces elemental fractionation [86,109]. However, the use of an excessively large spot size may enhance the mass-load-induced matrix effects in the ICP and the elemental fractionation because the amount of dry aerosol in-

troduced into the ICP will increase significantly (depending on the laser energy density) [114,115] and thus hamper the accurate determination of some elements [23]. Spatial-resolved analysis using a laser beam spot as small as possible is necessary for solving many problems in Earth science [116]. The use of a small laser beam spot can avoid the matrix effects that depend on the mass load of the ICP, but it will increase the analytical detection limits and require greater sensitivity of the ICP-MS instrumentation. Although accurate analysis data can be obtained through optimization of the instrument conditions when a small laser beam spot is used [116,117], the use of an excessively small laser beam spot (such as $<24\ \mu\text{m}$) could cause severe fractionation effects and thereby hinder the analysis via LA-ICP-MS [86].

The ablation rates vary with the sample matrix and are roughly positively correlated with the energy density for a given mineral/glass as a whole [110] (Figure 2). At a given energy density, the ablation rates of NIST glasses are significantly greater than that of the silicate minerals (e.g. zircon, olivine and garnet) and glasses with natural compositions. For example, the average ablation rates of NIST glasses are greater than that of zircon by a factor of approximately 50%. Experiments have shown that the linear correlations between the sensitivity and F, as previously discussed, was not observed during the analysis of zircons [116], which implies that the ablation rate and/or spot size for each single pulse could vary with an increase in the ablation depth. The adoption of a lower pulse frequency can reduce the elemental fractionation by increasing the diameter/depth ratio of the ablation pit; however, some measures (e.g. the addition of a small amount of N_2) should be taken to compensate for the reduced sensitivity [116]. Gaboardi and Humayun [87] suggested that the volatility effects (especially for transparent minerals or glasses) could be minimized and possibly negated by an increase in the laser energy output. However, Horn and Günther [110] showed that, as the energy density is increased, the particle size distribution

shifts towards larger particles, at least for a Nd: YAG laser ablation system.

Although the type of carrier gas does not obviously affect the ablation rate [36], it can remarkably affect the particle size distribution, the transport efficiency and, thus, the sensitivity when a 193 nm laser is used [101,118]. The use of helium instead of argon as a carrier gas led to a 2- to 4-fold signal enhancement with 193 nm lasers [101,110,118]. Horn and Günther [110] showed that the ablation carrier gas strongly influences the particle size distribution when a 193 nm laser is used, whereas this effect is far less pronounced for ablations where a 266 nm laser is used. Their experiments also show that a 266 nm laser produces a larger proportion of primary particles that are not significantly influenced by the ablation carrier gas environment, whereas a 193 nm laser produces a larger proportion of vapor during irradiation with the 193 nm laser beam, and this vapor subsequently condenses to form larger aggregates [110]. The addition of a small amount of N_2 or H_2 into the carrier gas can increase the sensitivity and reduce the background and polyatomic ion yield [119–121]. Hu et al. [120] found that the addition of $5\text{--}10\ \text{mL}\ \text{min}^{-1}$ of nitrogen into the central channel gas during LA-ICP-MS analyses increases the sensitivity for most of the 65 investigated elements by a factor of 2–3.

The single-point mode and the line-scanning mode are generally used in LA-ICP-MS analyses. Laser ablation in the line-scanning mode is generally understood to produce a more stable signal and thus improve the analytical precision; in addition, it also provides a more representative sampling due to the larger area ablated compared with the area ablated during spot analysis [23]. However, material ablated in scanning mode is confined to the surface of the sample and has been shown to produce larger particles than spot ablations, which may result in more pronounced matrix effects, significant element fractionation due to incomplete ionization [99] and, thus, larger relative deviations for some elements [23].

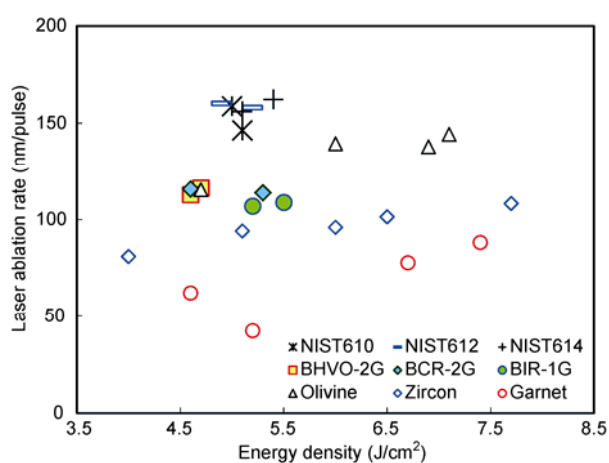


Figure 2 Variations of the ablation rates with the energy density using a 193 nm laser.

2.4 Sensitivity drift correction and internal standards

Sensitivity drift in LA-ICP-MS analysis is one of the most important factors that influences the uncertainty of an analysis [122]. Sensitivity drift can be caused during laser ablation and ICP-MS analysis processes. Internal normalization is a classic method for correcting the ICP-MS sensitivity drift. However, the sensitivity drift is usually non-linear, the degree of drift differs from one mass to the next [123], and the drift rates are mass-dependent [40,124]; i.e. it is impossible to correct the sensitivity drift of all other elements using any single element (or isotope) as the internal standard. Therefore, Eggin et al. [124] developed a method that combines enriched isotopes and conventional elemental internal standards to precisely analyze trace elements by

ICP-MS. The use of enriched isotopes expands the suite of available reference isotopes spaced through the mass spectrum so that the complex mass-dependent variations in sensitivity encountered during ICP-MS analysis can be monitored and corrected. However, this method is not applicable for the analysis of natural solid samples (such as natural minerals) via LA-ICP-MS. Gaboardi and Humayun [87] found that the elemental relative sensitivity shows an additional dependence on the temperature of condensation for the NIST glasses in addition to the dependences on the element mass and the first ionization potential. Therefore, with the use of NIST glasses as external calibration standards, analytical results for natural minerals or glasses could vary significantly based on the selection of different internal standard elements [40,41]. Successful matrix-independent standardization of refractory elements is possible if the condensing temperature of the internal standard element is approximately the same as that of the analyte element (such as the case with Ca and REE) [87]. The difference caused by the use of different major elements as internal standards can be measured by the variations in the k values in eqs. (1) and (3) [40] (Figure 3).

Cheatham et al. [123] developed an analytical procedure and an off-line data reduction algorithm to correct the non-linear sensitivity drift during SN-ICP-MS analyses, and this procedure resulted in a significant improvement in analytical accuracy and precision. In this technique, a “drift correction” standard is analyzed after every four or five samples. A polynomial curve is fitted for each isotope analyzed, and a correction based on this curve is applied to the measured intensity of the respective isotopes in the samples and standards. Eggins et al. [10], Sinclair et al. [125] and Liu et al. [40] combined this method and the internal standard normalization to correct the sensitivity drift during LA-ICP-MS analysis, where they analyzed the “drift correction” standard SRM 610 after every 5–10 samples (i.e. SRM 610

+ 5–10 samples + SRM 610) and then used the variations in the signal intensities [10] or signals normalized to a major element (such as Si in a silicate mineral) [40] of SRM 610 to correct the sensitivity drift. The possible contributions of sample position and laser focusing or imaging to the variations in the measurements of a “drift correction” standard can be partially corrected through normalization to a major element [40].

3 Applications of LA-ICP-MS in the elemental analysis of geological samples

3.1 Bulk analyses of whole-rock and soil samples

Compared with SN-ICP-MS for the bulk analysis of geological samples, LA-ICP-MS has several outstanding advantages, including a lower background, lower oxide and hydroxide interferences, a simpler sample preparation procedure, faster analyses, and cost effectiveness. Based on the sample preparation technique, LA-ICP-MS methods have been applied to the bulk analysis of various samples, including (1) the direct analysis of a rock slice [24,126], (2) the analysis of pressed-powder pellets both with binders [1,26,127] and without binders [128], and (3) the analysis of fused glasses fused both with a flux agent [6,129,130] and without a flux agent [22,23,25,61,131–134].

The homogeneous distribution of major and trace elements in the sample to be analyzed is a fundamental requirement for bulk analysis using LA-ICP-MS because of the relatively small ablation spot used (generally < 160 μm). The direct analysis of a rock slice using LA-ICP-MS can only be performed on cryptocrystalline volcanic rock, volcanic glass or fine-grained pelite because of the selective ablation of different minerals [24]. The pressing of a powder pellet without binders simplified the sample preparation and avoided any undesirable dilution of the sample; however, the particle size of the samples needs to be sufficiently reduced (e.g. to <1 μm) [128]. If the particle size of the sample powder is relatively large or if the pellet is not sufficiently compacted, selective ablation of different minerals, signal variations caused by powder outbreak during ablation and the incomplete vaporization of particles could result in poor precision and accuracy [28,135]. The addition of binders could result in the production of discs with greater mechanical stability than that of discs obtained by pressing the sample alone, and the use of such discs could reduce signal instability caused by powder outbreak ablation [127,136]. Furthermore, pellets prepared with vanillic acid as a binder exhibited the greatest optical absorbance at a wavelength of 213 nm, which resulted in a lower ablation depth and in improved signal sensitivity, most likely through the formation of smaller particles during the ablation process [127]. The disadvantage of the addition of a chemical binder is that the dilution effect may lead to the concentration of some elements in pressed pellets being lower than the detection

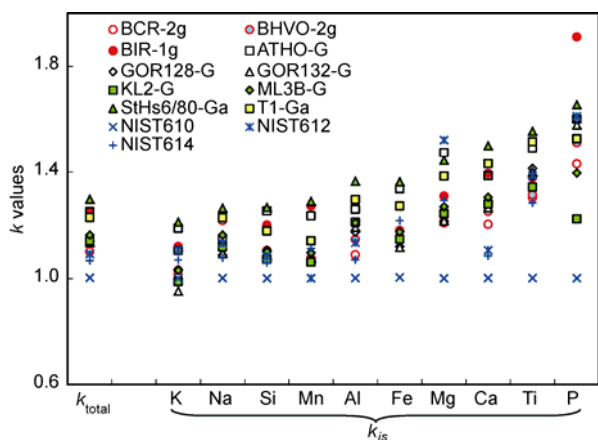


Figure 3 The k values calculated using the internal standardization (eq. (1)) and summed metal oxide normalization techniques when SRM 610 was used as an external standard.

limit. Fused glass is generally more homogeneous than a pressed-powder pellet and is therefore preferable for laser ablation analysis. The addition of a properly chosen flux (e.g. $\text{Li}_2\text{B}_4\text{O}_7$) significantly lowers the temperatures required for fusion of the rock powder, thereby improving the homogeneity of the fused glass and reducing the loss of volatile elements during the melting process. However, the introduction of the flux agents not only dilutes the trace-element contents but also increases the backgrounds for some elements (e.g. B, Li and REE) [137]. A flux-free fusion technique involves the direct melting of the rock powders in an Ar environment into homogeneous glasses at 1300–1800°C using an iridium strip heater [22,25,133,134], a tungsten strip heater (Hf and Ta pollution may exist) [132] or a molybdenum strip heater [23,138], which avoids the above problems caused by the flux agent. For high- SiO_2 rocks, high-purity MgO needs to be added to reduce the melt viscosity and result in homogeneous glasses [134]. Although this method seems to be simple, the high melting temperature may result in a severe loss of volatile elements (e.g. Pb) [22,25]. To minimize the volatilization of elements during high-temperature melting, the sample can be melted in a sealed platinum capsule, although this method is inherently expensive and not suitable for routine analysis [131] or in a BN crucible, which may result in metal segregation caused by the reduction of BN and result in the loss of Cr, Ni and Cu [23]. The loss of volatile elements could be suppressed through the use of a sandwich-like heater with a double-filament [139].

The quantitative calculations for bulk analyses can be performed using an external standard calibration and internal standard (or summed metal oxide) normalization technique or an isotopic dilution method. If internal standard normalization is used, the element used as an internal standard should be analyzed using other independent methods (e.g. XRF or wet chemical methods) or added into the powder sample during the preparation of the pressed pellet or whole-rock glass [28,136]. The bulk content of volatile components (such as H_2O and CO_2) in the sample should be accurately measured using other independent methods if the summed metal oxide normalization technique is used. With the isotopic dilution method, an isotopic spike can be added into the powdered sample during the preparation of the pressed pellet [29,50,140] or whole-rock glass [133]; trace elements can then be accurately measured without the use of any external standard.

3.2 Silicate and carbonate minerals

The method for analyzing silicate minerals is similar to that for silicate whole rocks. The frequently used calibration strategies include (1) Calibration against reference glasses SRM 610 or SRM 612, combined with normalization using a single (or multiple) internal standard (typically Ca, Si and Mg depending on the type of mineral) [2,3,10,59,141] or the

summed metal oxide normalization method [142]. This method has the advantage that most elements can be calibrated against only one reference glass (i.e. the workload is small); however, the special matrix of NIST glasses may impede the accurate analysis of some samples (e.g. zircon) [46]. (2) Calibration against (multiple) silicate reference glasses with natural compositions (e.g. the MPI-DING and USGS glasses) and the application of the summed metal oxide normalization or internal standardization method [40,45]. Through the use of the summed metal oxide normalization technique, we can not only accurately analyze the trace elements in silicate minerals but can also determine the major element concentrations with accuracies comparable to that provided by EMP analysis and even better than that provided by EMP analysis for some major components (such as MnO) [45]. Nevertheless, several reference glasses need to be analyzed (i.e. the workload is greater) to reduce the effect caused by the low concentrations of some elements in some individual reference glasses [40]. (3) Calibration against liquid standards, combined with the summed major element oxide normalization and internal standardization methods, where the calibration solutions are introduced into the ICP using an Aridus liquid sample introduction system with aerosol desolvation [43]. However, the composition of the solution used for the calibration can lead to losses of some elements during the desolvation process in the Aridus or during aerosol transfer to the ICP, which has been demonstrated for Cu [43].

Unlike the silicate reference materials, significantly fewer reference materials with carbonate matrix can be used for analysis of carbonate minerals by LA-ICP-MS. At present, the commercially available carbonate reference material for LA-ICP-MS analysis is the Ca-carbonate pellet MACS-3 developed by Dr. Stephen Wilson at the USGS; the concentrations of more than 50 trace elements in this reference material are greater than 1 ppm. Given the influence of the matrix effect on the accuracy of quantifications, numerous researchers have performed a substantial amount of work in preparing carbonate-matrix reference materials, such as CaSiO_3 glass synthesized from coral powder [125], Ca-Mg carbonate glass with a lithium tetraborate flux [79] and pressed pellets of carbonate powders [79–83]. In general, the production of a homogeneous pressed pellet of a carbonate powder is difficult; a few elements in MACS-3 are even slightly heterogeneous [47]. The combination of external standard calibration and internal standard (generally Ca) normalization is often used to quantitatively analyze trace elements in carbonate materials using LA-ICP-MS [81, 143–145]. Chen et al. [47] proposed a method that combines an external-standard (silicate glass) calibration with the total normalization technique to analyze the major and trace elements in carbonate minerals and biological crusts. This method is based on the bulk components in carbonate materials consisting entirely of carbonate forms ($\text{M}_{2/x}\text{CO}_3$, where x is the ion valence of element M). Strnad et al. [145] and

Chen et al. [47] reported that the analysis results of carbonate samples calibrated against silicate reference glasses and those of carbonate samples calibrated against reference carbonate pellets exhibited no significant difference. However, Jochum et al. [95] suggested that accurate results can be obtained through calibration against silicate reference glasses for large ion lithophile elements but that matrix-matched standard calibration may be required for chalcophile and siderophile elements.

3.3 Metal oxides and metal sulfides

Trace elements in metal oxides can, in general, be accurately analyzed by calibration against silicate reference glasses. Xu et al. [146] and Huelin et al. [147] analyzed the trace elements in Fe-Mn oxides calibrated against SRM 610 in combination with internal-standard normalization. Nadoll and Koenig [148] found that the results of some trace elements calibrated against silicate reference glasses (SRM 610 and GSE-1G) agree well with results analyzed by EMP and suggested that magnetite can be accurately analyzed using silicate reference glasses as an external standard. Donohue et al. [149] analyzed thirteen trace elements in ilmenite (FeTiO_3) megacrysts using LA-ICP-MS (calibrated against SRM 610 with Ti used as internal standard) and reported good agreement between the results determined by LA-ICP-MS and SN-ICP-MS for most elements, except in cases where megacrysts with a titano-magnetite exsolution phase were present. With calibration against SRM 610 and the use of Ti as an internal standard [150] or with the application of multiple standards (BCR-2G, BHVO-2G and BIR-1G) for calibration in combination with the summed metal oxide normalization technique [48], trace elements in rutiles can be accurately analyzed by LA-ICP-MS, and the results are comparable with the results of SIMS and/or EMP analyses.

Both synthetic sulfide reference materials and silicate reference glasses have been used as external calibration standards for the analysis of sulfides by LA-ICP-MS. Because the concentrations of noble-metal elements (such as Os, Ir, Ru, Rh, Pt, Pd, and Au) in silicate reference glasses are, in general, very low and heterogeneous, synthetic sulfide reference materials were prepared for the analysis of noble-metal elements in sulfides [14,65,72,73,151,152]. With the exception of the noble metal elements, the trace elements in sulfides could be calibrated against pressed-powder pellets of sulfide (e.g. MASS-1 or MASS-3) [153], glasses of sulfide fused with a lithium borate flux [68,154,155], silicate reference glasses [156,157] or multi-element standard solutions [158]. Košler et al. [111] found that a small amount of oxygen released from the sample during the laser ablation process can also affect the elemental fractionation. Therefore, the influence of such different matrixes on the analytical accuracy needs to be further evaluated in cases where trace elements in sulfide are calibrated

against silicate reference glasses.

In general, the lack of matrix-matched homogeneous reference materials is a bottleneck for accurate analyses of trace elements and the evaluation of the reliability of LA-ICP-MS analysis data for metal oxides and sulfides.

3.4 Individual melt inclusion and fluid inclusion

Heinrich et al. [159] and Pettke et al. [160] systematically reviewed the influencing factors, the calibration methods, the accuracy and the detection limits for the analysis of single melt/fluid inclusion by LA-ICP-MS. Shepherd and Chenery [161] were the first to study the feasibility of analyzing element compositions of single fluid inclusions by LA-ICP-MS. Moissette et al. [162] proposed a calibration strategy for the analysis of single fluid inclusions based on the use of the synthetic fluid inclusion in halite as an external standard. Applying a simple external calibration method, Ghazi et al. [163] and McCandless et al. [51] analyzed the single fluid inclusions in halite and quartz calibrated against a standard solution sealed in a glass capillary. However, the internal pressures of the natural inclusions are different from that of the artificial ones, which can lead to different release rates of volatile substances when the inclusions are opened. The error caused by the different ablation yields cannot be corrected using a simple external calibration. Thus, Shepherd et al. [164] tried to analyze the single fluid inclusions by using artificial inclusions as external standards and Cl determined by cryo-SEM-EDS as an internal standard. In addition, the direct ablation of a fluid inclusion with a pit size similar to the diameter of an inclusion commonly leads to an explosion and the splashing of material onto the sample surface [162] and into the chamber, which increases the danger of selective loss of solid internal precipitates. Therefore, Günther et al. [11] adopted a stepwise opening procedure for complex poly-phase inclusions. They first drilled a small hole (4–10 μm pit) for the partial release of liquid and vapor, then completely drilled out a pit that covered the entire inclusion. A high laser energy density needs to be used to analyze fluid inclusions in quartz due to the poor absorption of quartz at the wavelengths typically used in laser ablation. The quantification of trace element concentrations could be calibrated against the NIST reference glasses or standard solutions with Na (or Cl) used as an internal standard calculated according to the salinity [11,159]. The total salinity was generally determined by microthermometric measurements of phase transitions from known phase diagrams via measurements of either the depression of the ice-melting temperature or the temperature of dissolution of NaCl crystals. The methods used to estimate the Na (or Cl) content by salinity may affect the analysis accuracy of single fluid inclusions [160,165]. Allan et al. [166] demonstrated that precision and accuracy are insensitive to inclusion size and depth. Analytical precision in the determination of K, Rb, and

Cs is typically better than 15% RSD, whereas that for the determination of Li, Mg, Ca, Sr, Ba, Mn, Fe, Cu, Zn, and Cl are typically reproducible within 30% RSD. The analyses of most elements are accurate to within 15%. The limits of detection vary widely according to the inclusion volume, but range from 1 to 100 ppm for most elements [166]. In recent years, important progress has been made in the analyses of S, Cl and Br in single fluid inclusions by LA-ICP-MS. Guillong et al. [13] developed a method to analyze the S content in individual fluid inclusions using scapolite as an external standard and found that the factor that affected the precision and accuracy was not interference, but rather S pollution from an unknown source. Seo et al. [167] and Leisen et al. [168] reported a method for the analysis of Cl and Br concentrations in single fluid inclusions that involves calibration against NIST glass and/or scapolite.

The technique of analyzing element compositions in single melt inclusions using LA-ICP-MS was first applied to glassy melt inclusions exposed at the surface [169–171]. The method was later applied to recrystallized silicate melt inclusions in minerals with simple chemical compositions, such as quartz and topaz [172,173], and then to the unexposed and recrystallized melt inclusions in chemically complex minerals, such as amphibole, olivine, pyroxene, plagioclase and apatite [12,174–179]. At present, two analysis strategies have been generally used to analyze multiphase silicate melt inclusions using LA-ICP-MS: (1) The inclusion can be first homogenized and quenched to a homogeneous glass and then ablated using a spot size smaller than the inclusion. Element concentrations could be quantified using the same method as that used for silicate minerals, which have been previously described. However, the homogenization of silicate melt inclusions can often be rather difficult or impossible due to potential decrepitation or leakage of the silicate melt inclusions upon heating. In addition, both diffusive exchange of certain elements between the host and the silicate melt inclusion and, if the homogenization temperature is excessively high, possible partial melting of the host mineral might modify the composition of the inclusion [175]. Furthermore, a sulfide in an inclusion is difficult to quench into glass using a fast cooling rate. (2) Ablation of the entire silicate melt inclusion along with its host mineral and subsequent deconvolution of the mixed ablation signal can be used [12,174,175]. This approach offers a unique opportunity to analyze the bulk composition of the unexposed and recrystallized silicate melt inclusion without homogenization through heating and greatly increases the number of inclusions that can be analyzed in the same crystal. The disadvantage of this method is that the content of one element in the inclusion or the content ratio of one element between the host mineral and the inclusion should be obtained through another independent method of quantification.

4 What should we do in the future?

The technique of analyzing element concentrations with LA-ICP-MS has been widely and maturely applied to numerous geological samples. Given the research status and problems associated with elemental analysis using LA-ICP-MS, the following work could be conducted in the future: (1) the development of matrix-matched reference materials for different minerals (especially for metal oxides and sulfides); (2) the elucidation of the formation mechanisms of matrix-dependent and time-dependent elemental fractionations and the development of methods to eliminate or improve these mechanisms; (3) the establishment of accurate analysis methods with a high spatial resolution for natural minerals; (4) the development of a quantitative calibration strategy for single melt/fluid inclusions in complex minerals; (5) the development of a common protocol for data reduction and reporting for scientists to be able to compare and interpret these data accurately; and (6) the expansion of the application areas of element analysis using LA-ICP-MS.

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