Simultaneous Quantification of Forsterite Content and Minor–Trace Elements in Olivine by LA–ICP–MS and Geological Applications in Emeishan Large Igneous Province

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Received: 9 June 2020; Accepted: 14 July 2020; Published: 17 July 2020

Abstract: Olivine forsterite contents \([\text{Fo} = 100 \times \text{Mg}/(\text{Mg} + \text{Fe})]\) in mol\% and minor–trace element concentrations can aid our understanding of the Earth’s mantle. Traditionally, these data are obtained by electron probe microanalysis for Fo contents and minor elements, and then by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) for trace elements. In this study, we demonstrate that LA–ICP–MS, with a simplified 100% quantification approach, allows the calculation of Fo contents simultaneously with minor–trace elements. The approach proceeds as follows: (1) calculation of Fo contents from measured Fe/Mg ratios; (2) according to the olivine stoichiometric formula \([(\text{Mg, Fe})_2\text{SiO}_4]\) and known Fo contents, contents of Mg, Fe and Si can be computed, which are used as internal standards for minor–trace element quantification. The Fo content of the MongOLSh 11-2 olivine reference material is 89.55 ± 0.15 (2 s; N = 120), which agrees with the recommended values of 89.53 ± 0.05 (2 s). For minor–trace elements, the results matched well with the recommended values, apart from P and Zn data. This technique was applied to olivine phenocrysts in the Lijiang picrites from the Emeishan large igneous province. The olivine compositions suggest that the Lijiang picrites have a peridotitic mantle source.

Keywords: olivine geochemistry; LA–ICP–MS; forsterite content; minor-trace elements; data reduction approach

1. Introduction

Olivine is the most abundant mineral in the Earth’s upper mantle; it is a common mineral in many mafic rocks and mantle peridotites, and also occurs in diamonds [1]. Thus, it has a special significance in our understanding of mantle geodynamics and melting processes [2,3]. Olivine has a simple major element composition consisting of MgO, FeO and SiO$_2$, with a molecular formula of $(\text{Mg, Fe})_2\text{SiO}_4$. These three oxides commonly comprise > 99% of the olivine mass. The forsterite (Fo) content, as expressed by the molar ratio $100 \times \text{Mg}/(\text{Mg} + \text{Fe})$, is an important compositional indicator, and is widely used to identify primary mantle-derived melts, assess the degree of evolution experienced by magmas [2–4], and estimate magma crystallization and mantle potential temperatures [5,6]. Despite its simple major element composition, olivine contains a number of petrogenetically significant minor–trace elements [1], such as Ni, Mn, Ca, Al, Sc, Cr, Co, Zn, V and Y. The mass fraction of these
elements varies by several orders of magnitude, from a few ng/g to several thousand µg/g. Olivine minor–trace element data have been increasingly used as a tool to understand mantle lithologies and melting processes [1–3,6–9], track magma evolution processes [10,11], and estimate oxygen fugacities and magma temperatures [12–16].

Electron probe microanalysis (EPMA) in combination with laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) has been traditionally used to acquire such analytical data for olivine [17]. Commonly, minor elements (e.g., Ni, Mn and Cr) along with the major elements (Si, Mg and Fe) are measured by EPMA [7], and then other trace elements (usually < 200 µg/g; e.g., Sc, Zn and Y) are determined by LA–ICP–MS [18–20]. However, this combined technique is time-consuming and requires a strict match of the analyzed locations. In addition, EPMA has a spatial resolution of 1–5 µm, whereas LA–ICP–MS has a spatial resolution of 15–100 µm. This mismatch in sampling volume can also lead to a bias in the analytical data, particularly for olivine that shows diffusion profiles. To avoid this issue, a high-precision (HP) EPMA technique was developed by Sobolev et al. [2,3], and further modified by Batanova et al. [21] and Su et al. [22]. This technique allows the analysis of a range of trace elements (e.g., Ni, Mn, Ca, Al, Cr, Na, P, Zn and Ti) with a limit of detection (LODs) of tens of µg/g. Advances in HP-EPMA have been achieved by using a high electron beam current (ca. 900 nA), increased accelerating voltage (ca. 25 kV) and extended counting times (ca. 15 min per analysis) [2,3,21–24]. However, this technique is time-consuming (>15 min per spot analysis) and requires careful laboratory procedures, which may limit its use in routine analyses.

The LA–ICP–MS technique is rapid (<2 min per spot analysis), has low LODs (sub-ng/g), and is widely available [25]. This technique has been used to simultaneously quantify major and trace element in silicate glasses and minerals using the conventional 100% oxide normalization approach [26–29]. However, its applicability to olivine has not been well investigated. In this study, we demonstrate that a single LA–ICP–MS, along with a simplified 100% method, is able to simultaneously determine the Fo contents and minor–trace elements contents of olivine samples. The accuracy and precision of these Fo contents were experimentally and theoretically evaluated based on the measured Fe/Mg ratios. This technique was further validated by analyzing a well-characterized olivine reference material (RM) MongOLS 11-2 [30], an in-house olivine RM XEN [21], and a large suite of natural olivines (N = 154) with Fo contents of 81–93. This method was applied to olivine phenocrysts in the Lijiang picrites from the Emeishan large igneous province. With the advantages of low LODs, high sample throughput and being simple to undertake, the LA–ICP–MS method may have the potential of wide applicability in the field of olivine geochemistry.

2. Materials and Methods

2.1. Reference Materials and Olivine Samples

GOR132-G glass is one of the MPI–DING series RMs. It has been well-characterized in previous studies [31,32]. This glass was made from a komatiitic rock powder, and has a chemical composition closer to olivine than any other available glass RMs. In this study, GOR132-G glass was used as the primary calibration standard for quantifying Fo contents and minor–trace element concentrations in olivine. Reference values for GOR132-G were taken from the GeoReM database (http://georem.mpch-mainz.gwdg.de/) [32,33], and are provided in Electronic Supplementary Material (ESI) Table S1 for method traceability. Recently, a new olivine RM (MongOLS11-2) for in situ analysis has been developed [30]. This olivine RM was prepared from the central portion of a large (20 cm × 20 cm × 10 cm) mantle peridotite xenolith, in a ca. 0.5-Ma basaltic breccia from Shavaryn–Tsaram, Tariat region, central Mongolia. A total of 27 major and trace elements were characterized by various techniques, including Electron probe microanalysis (EPMA), X-Ray fluorescence spectrometer (XRF), LA–ICP–MS, secondary ion mass spectrometry (SIMS) and isotope dilution (ID)–ICP–MS. Another internal laboratory olivine RM (XEN) was also used in this study. This olivine has previously been characterized by Batanova et al. [21] using EPMA and LA–ICP–MS techniques. To further confirm the
robustness and usefulness of LA–ICP–MS and this simplified 100% approach, a large set of natural olivines \((N = 154)\) was analyzed. These olivine crystals were hand-picked from the Dali, Pingchuan and Lijiang picrites from the Emeishan large igneous province (LIP). Prior to LA–ICP–MS analysis, the Fo contents of the olivine samples were determined by EPMA. The details of EPMA analysis are given in ESI S1.

### 2.2. LA–ICP–MS

These analyses were carried out using a GeolasHD 193 nm ArF excimer LA system (Coherent; Göttingen, Germany) coupled to an Element XR sector field (SF)–ICP–MS (Thermo Fisher Scientific; Bremen, Germany) at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS), Beijing, China. Details of the LA–ICP–MS analysis technique are given in Wu et al. [34,35]. Helium was used as the carrier gas to improve the transport efficiency of the ablated aerosols [36,37]. A novel “wave” signal-smoothing device was used to improve the signal stability [38,39]. Daily optimization of instrumental performance with the USGS BCR-2G standard involved maximizing the signal to background intensity ratios for \(^{25}\text{Mg}^+\), \(^{57}\text{Fe}^+\) and \(^{89}\text{Y}^+\), while maintaining low oxide production \((\text{ThO}^+/\text{Th}^+ < 0.1\%)\), low doubly charged ion production \((\text{Ca}^2+/\text{Ca}^+ < 1.0\%)\), and minimal ICP-induced elemental fractionation \([\text{sensitivity ratio } S(\text{U}^+)/S(\text{Th}^+) = 0.95/1.05]\). In this study, the SF–ICP–MS was running without using the guard electrode to maintain a low level of oxide spectral interference \((e.g., ^{29}\text{Si}^{16}\text{O}^+ \text{on } ^{45}\text{Sc}^+)\). Table 1 summarizes the LA–ICP–MS instrumental conditions. Since the SF–ICP–MS is running at low mass resolution \((M/ΔM = 300)\), the method described in this study should be readily applicable to quadrupole ICP–MS instruments.

| Table 1. Typical instrument conditions for LA–ICP–MS analyses. |
|-------------------------------------------------------------|
| **Laser Ablation System**                                    |
| Make, model and type                                        | Coherent, Geolas HD |
| Ablation cell and volume                                    | Cell developed in-house; aerosol dispersion volume of < 3 cm\(^3\) |
| Laser wavelength                                            | 193 nm |
| Pulse width                                                 | 20 ns |
| Energy density/fluence                                      | ca. 3 J/cm |
| Repetition rate                                              | 5 Hz |
| Spot size                                                   | 44 μm |
| Sampling mode/pattern                                        | Single hole drilling; three cleaning pulses |
| Ablation gas flow                                            | ca. 0.75 L/min (He) |
| Ablation duration                                            | 40 s |
| SF–ICP–MS                                                   | |
| Make, model and type                                        | Thermo Fisher Scientific Element XR |
| RF power                                                    | 1320 W |
| Guard electrode                                             | off |
| Sample cone                                                 | Nickel Standard |
| Skimmer cone                                                | Nickel H |
| Coolant gas flow (Ar)                                       | 15.0 L/min |
| Auxiliary gas flow (Ar)                                     | 0.80 L/min |
| Carrier gas flow (Ar)                                       | 0.95 L/min |
| Enhancement gas flow (N\(_2\))                              | None |
| Scan mode                                                   | E-scan |
| Isotopes measured (m/z) + dwell times                       | 7\_Li, 23Na, 25Mg, 27Al, 28Si, 31P, 43Ca, 45Sc, 49Ti, 51V, 53Cr, 55Mn, 57Fe, 59Co, 60Ni, 63Cu, 65Zn, 69Ga and 89Y; 10 ms for each isotope |
| Mass window                                                 | 20% |
| Sample per peak                                             | 20 |
| Detection system                                            | Single SEM detector in triple mode (pulse counting, analog and Faraday cup) |
| Resolution (M/ΔM)                                            | Low (ca. 300) |
| Total integration time per reading                          | 0.90 s |
2.3. Data Acquisition

The locations of laser spots were selected after careful binocular microscopic examination of the samples so as to avoid cracks and inclusions. We also suggest checking the locations with the support of SEM images. The signal intensities of $^7\text{Li}$, $^{23}\text{Na}$, $^{25}\text{Mg}$, $^{27}\text{Al}$, $^{29}\text{Si}$, $^{31}\text{P}$, $^{43}\text{Ca}$, $^{45}\text{Sc}$, $^{49}\text{Ti}$, $^{51}\text{V}$, $^{53}\text{Cr}$, $^{55}\text{Mn}$, $^{57}\text{Fe}$, $^{59}\text{Co}$, $^{60}\text{Ni}$, $^{63}\text{Cu}$, $^{67}\text{Zn}$, $^{69}\text{Ga}$ and $^{89}\text{Y}$ were monitored during each analysis. A total of six analytical sessions were performed during a period of six months (ESI Table S2). All data were acquired by firing the laser for 40 s, after 10 s of gas background measurement, which was followed by 10 s of monitoring the signal “washout”. Prior to analysis, possible surface contamination was removed in a pre-ablation step with three laser pulses. GOR132-G reference glass was used to correct for the instrument- and time-dependent fractionations of $\text{Fe}/\text{Mg}$ ratios and all minor–trace elements. We selected GOR132-G reference glass as the primary calibrator for three reasons, as follows: (1) this glass is widely distributed and used in LA–ICP–MS laboratories around world; (2) its compositions of major and some trace elements are comparable to those of nature olivines; (3) compared to natural olivines, this glass has high abundances of Cu, Ga and Y, and therefore it is more suitable for use as the calibrator for low-content trace elements. Olivine RM MongOLSh11-2 and XEN were analyzed for data quality control purposes. A standard–sample bracketing approach was adopted, which involved the analysis of eight unknown samples followed by one analysis each of GOR132-G, MongOLSh11-2 and XEN.

2.4. Data Reduction Approach

The 100% oxide normalization approach is documented elsewhere [26–28,40,41]. This strategy requires the measurement of all major, minor and trace elements, and then quantifies major and trace elements based on the total matrix normalized to 100%. Olivine has a predictably simple chemistry. Therefore, this conventional 100% method can be simplified as follows: (1) calculation of Fo contents from the measured $\text{Fe}/\text{Mg}$ ratios; (2) according to the olivine stoichiometric formula $[(\text{Mg, Fe})_2\text{SiO}_4]$ and known Fo contents, the contents of Mg, Fe and Si can be computed, which are used as internal standards for minor–trace element quantification. Details are shown below:

The $\text{Fe}/\text{Mg}$ ratios in the olivine samples were calculated by standardization to GOR132-G glass, as follows:

$$
\frac{\text{Fe}}{\text{Mg}}_{\text{olivine}} = \frac{\text{intensity} \ (\frac{\text{Fe}}{\text{Mg}}_{\text{olivine}})}{\text{intensity} \ (\frac{\text{Fe}}{\text{Mg}}_{\text{GOR132-G}})} \times 0.5812
$$

(1)

The $\text{Fe}/\text{Mg}$ ratio is given as a weight ratio, and 0.5812 is the recommended $\text{Fe}/\text{Mg}$ ratio for GOR132-G glass. The molar Fo content can be rewritten in a weight format:

$$
\text{Fo} = \frac{100}{1 + \frac{\text{Fe}}{\text{Mg}} \times 0.4352}
$$

(2)

The constant 0.4352 is the coefficient between the molar- and weight-based $\text{Fe}/\text{Mg}$ ratios. This shows that the Fo content can be obtained once the $\text{Fe}/\text{Mg}$ ratio is known.

For olivine, three major oxide components ($\text{MgO}$, $\text{SiO}_2$ and $\text{FeO}$) commonly comprise $>99\%$ of the mass. Therefore, we assumed that the sum of $\text{MgO}$, $\text{SiO}_2$ and $\text{FeO}$ is 100%, as follows:

$$
\text{MgO} + \text{FeO} + \text{SiO}_2 = 100\%.
$$

(3)

Based on the molecular formula $[(\text{Mg, Fe})_2\text{SiO}_4]$ of olivine, we have

$$
\frac{\text{MgO}}{80.608} + \frac{\text{FeO}}{143.688} = \frac{\text{SiO}_2}{60.084}
$$

(4)
The molar Fo content can be rewritten in an oxide format (i.e., FeO and MgO) as follows:

\[
\frac{\text{FeO}}{\text{MgO}} = \left( \frac{100}{\text{Fo}} - 1 \right) \times 1.7826 \tag{5}
\]

Combining Equations (3), (4) and (5) yields

\[
\text{Mg} = \frac{100 \times \text{Fo}}{252.79 - 0.7826 \times \text{Fo}} / 1.6583 \tag{6}
\]

\[
\text{Fe} = \frac{17826 - 178.26 \times \text{Fo}}{252.79 - 0.7826 \times \text{Fo}} / 1.2865 \tag{7}
\]

\[
\text{Si} = \frac{7453}{252.79 - 0.7826 \times \text{Fo}} / 2.1393 \tag{8}
\]

Here, 1.6583, 1.2865 and 2.1393 in the denominator are the coefficients between element and oxide for Mg, Fe and Si, respectively. Using this approach, the accuracies of the Mg, Fe and Si are better than 1.5%, relative to the recommended values. All minor–trace element data were quantified using the internal standardization approach \[42\], as follows:

\[
C_{\text{element}} = \frac{\text{intensity (el)}}{\text{intensity (Mg, Fe, Si)}} \times \frac{\text{intensity (Mg, Fe, Si)}}{\text{intensity (el)}} \times \frac{C_{\text{Mg}}}{C_{\text{Mg}}} \times \frac{\text{COR132-G}}{\text{COR132-G} \times C_{\text{Mg, Fe, Si}} \text{sample}} \tag{9}
\]

Where C represents the concentration of a target element and el is the element. The mass fractions of Mg, Fe and Si were calculated from Equations (6)–(8).

A DRS code in Iolite software was programmed to facilitate this simplified 100% strategy (see supplementary files). It should be noted that the conventional 100% method \[40\] using only Si, Mg and Fe yields results nearly identical to this simplified 100% method. To a certain extent, this simplified 100% method is repackaged from that conventional 100% method \[40\]. We repackaged it in a way that allows the easier evaluation of the precision and accuracy of Fo contents.

### 3. Results and Discussion

#### 3.1. Precision of the Fe/Mg Ratio and its Influence on Fo Content

As shown in Equation (2), the analytical precision of Fe/Mg ratios directly depends on the Fo contents. There are two main sources controlling the analytical precision of the Fe/Mg ratios: (1) Down-hole fractionation (DHF), and (2) the counting statistics of signal intensity. DHF is defined as the progressive, volatility-controlled fractionation between a pair of elements as the laser pit deepens \[43,44\]. A severe DHF can significantly degrade the analytical precision. The DHF effect has been widely documented in zircon U–Pb geochronology studies \[45,46\]. Jochum et al. \[47\] reported a detectable DHF between refractory lithophile and chalcophile-siderophile elements. Iron is a refractory siderophile element based on the cosmochemical classification of this element, while Mg is a refractory lithophile element. Figure 1 shows the DHF behavior of the $^{57}$Fe/$^{25}$Mg ratio in COR132-G glass and MongOLS11-2 olivine. A slightly larger scatter of $^{57}$Fe/$^{25}$Mg ratios was observed for COR132-G glass, which is mainly due to the relatively low concentration of Fe and Mg. The results illustrate that Fe/Mg ratios slightly increase with a longer ablation time, illustrating the different fractionation behavior of Fe and Mg. However, these fractionations are almost identical in both sample matrices, indicating a very limited DHF-induced bias for the Fe/Mg ratio between the COR132-G glass and the MongOLS11-2 olivine. This slight DHF has a negligible effect (<1%) on the analytical precision of the measured Fe/Mg ratios. Based on these observations, we did not conduct any DHF corrections on the Fe/Mg ratios.
Mg is a refractory lithophile element. Figure 1 shows the DHF behavior of the $^{57}\text{Fe}/^{25}\text{Mg}$ ratio in GOR132-G glass and MongOLSh11-2 olivine. A slightly larger scatter of $^{57}\text{Fe}/^{25}\text{Mg}$ ratios was observed for GOR132-G glass, which is mainly due to the relatively low concentration of Fe and Mg. The results illustrate that Fe/Mg ratios slightly increase with a longer ablation time, illustrating the different fractionation behavior of Fe and Mg. However, these fractionations are almost identical in both sample matrices, indicating a very limited DHF-induced bias for the Fe/Mg ratio between the GOR132-G glass and the MongOLSh11-2 olivine. This slight DHF has a negligible effect (<1%) on the analytical precision of the measured Fe/Mg ratios. Based on these observations, we did not conduct any DHF corrections on the Fe/Mg ratios.

Figure 1. Comparison of down-hole fractionation (DHF) of Fe/Mg in GOR132-G glass and MongOL Sh11-2 olivine. Laser spot size is 44 $\mu$m. In order to compare at the same scale, the $^{57}\text{Fe}/^{25}\text{Mg}$ ratios are normalized to the mean value of the initial two seconds. The observed large scatter of $^{57}\text{Fe}/^{25}\text{Mg}$ ratios in GOR132-G glass is mainly attributed to the relatively low concentrations of Fe and Mg. The signal intensity of $^{57}\text{Fe}$ and $^{25}\text{Mg}$ is another factor influencing the measured precision due to counting statistics. The signal intensity of $^{25}\text{Mg}$ is one order of magnitude greater than that of $^{57}\text{Fe}$, which is mainly due to its higher concentration (MgO: ca. 48 wt.%) and abundance of measured isotopes ($^{25}\text{Mg}$: 10 atom%). Figure 2 shows the precision of the Fe/Mg ratios as a function of the $^{57}\text{Fe}$ intensity for MongOLSh11-2 olivine. The variation in $^{57}\text{Fe}$ intensity was simply achieved by changing the laser spot size (10, 16, 24, 32, 44 and 60 $\mu$m). Figure 2a illustrates that the precision of the Fe/Mg ratio improves with greater $^{57}\text{Fe}$ signal intensity. In general, the precision is <2% with a $^{57}\text{Fe}$ signal intensity of >300,000 cps (or a laser spot size of >24 $\mu$m). A laser spot size of 44 $\mu$m was used in this study, yielding an analytical precision of <1.5%. It should be emphasized that the instrument sensitivity can vary depending on the daily instrument tuning, different samples, the condition of the skimmer cones, and the state of the secondary electron multiplier (SEM) detector. These factors may slightly affect the precision of the Fe/Mg ratios.
These results indicate that the uncertainty of Fo contents obtained from the LA–ICP–MS technique (spot size: 44 µm) is 0.10–0.20 for Fo = 80–90, and 0.20–0.22 for Fo = 70–80. These uncertainties are inferior to those obtained using HP-EPMA (0.05–0.10) [2,3], but comparable to those obtained using the normal EPMA technique. Figure 3 also indicates that when using a spot size of 44 µm, the Fo uncertainty is calculated based on the below Equation (10).

$$\delta_{Fo} \sim k \times \frac{\delta_{Fe}}{Mg} = \sqrt{\delta_{Olivine}^2 + \delta_{GOR-132O}^2}$$  \tag{10}

As shown in Equation (2), the uncertainty on the Fo content from the precision of the Fe/Mg ratios can be modeled based on their reciprocal relationship. Figure 2b shows the modeled uncertainty of Fo content as a function of laser spot size (10, 16, 24, 32, 44 and 60 µm). The modeled Fo uncertainty is calculated based on the below Equation (10). $k$ is the conversion factor between the Fo and Fe/Mg ratio.

In general, a high Fo content is less affected than a low Fo content by a specific laser spot size. Figure 3 also indicates that when using a spot size of 44 µm, the Fo uncertainty is ≤0.15 for Fo > 90, 0.15–0.20 for Fo = 80–90, and 0.20–0.22 for Fo = 70–80. These uncertainties are inferior to those obtained using HP-EPMA (0.05–0.10) [2,3], but comparable to those obtained using the normal EPMA technique (0.10–0.30) [7]. These results indicate that the uncertainty of Fo contents obtained from the LA–ICP–MS technique (spot size: 44 µm) is sufficient for olivine geochemical studies.
3.2. Accuracy of Fo Contents and Long-Term Reproducibility

To evaluate the accuracy of the LA–ICP–MS technique for Fo determinations, MongOLSh11-2 samples were analyzed. The Fo values were calculated based on Equations (1) and (2). The results are summarized in Figure 3 and the ESI Table S2. The plotted error bars are the internal precision calculated from Equation (10). The average of the internal precision is 0.15. MongOLSh11-2 was analyzed as the data quality control material in six analytical sessions over a period of six months. A total of 120 analyses yielded a mean value of 89.53 ± 0.05 (2s), which is in agreement with the recommended value of 89.53 ± 0.14 (2s) [30]. The long-term reproducibility of the LA–ICP–MS technique was established by repeated measurements of MongOLSh11-2 over six months. Figure 3a shows that the long-term analytical reproducibility for Fo (given as 2 Relative Standard Deviation R.S.D.%) is ± 0.17%, which is similar to that reported by the normal EPMA technique [7]. Figure 3b shows a histogram of Fo contents (N = 120), which is clearly a Gaussian distribution, further demonstrating the stability of the LA–ICP–MS technique for the determination of Fo contents.

To further confirm the accuracy of the LA–ICP–MS technique for Fo determinations, XEN and a large suite of natural olivine grains (N = 154) were measured. XEN was repeatedly analyzed in five analytical sessions over a period of five months. A total of 98 analyses yielded a mean value of 90.73 ± 0.14 (2s), which is comparable to the published value of 90.78 ± 0.06 (2s) [21]. The natural olivines are from the Dali, Pingchuan and Lijiang picrites, which are part of the Emeishan LIP. These olivine phenocrysts have variable Fo contents (from 81 to 93). Figure 4 shows that the LA–ICP–MS results match the EPMA results with an R² value of 0.993. Some small scatter from the 1:1 line was observed, which is probably related to the compositional heterogeneity of the olivine phenocrysts and the different sampling volumes of the EPMA and LA–ICP–MS techniques. Using this simplified 100% approach, LA–ICP–MS is robust and reliable in quantifying Fo contents over a wide range of Fo compositions. Despite its different chemical and physical composition, our results indicate the GOR132-G glass is a suitable RM for quantifying olivine Fo contents. This is due to the similar fractionations of Fe and Mg during ablation (Figure 1).

![Figure 4](image)

**Figure 4.** Plots of one-to-one lines of Fo values (N = 154) obtained via EPMA and LA–ICP–MS. Samples shown here are the natural olivines present in the Dali, Pingchuan and Lijiang picrites, Emeishan large igneous province (LIP).

3.3. Accuracy of Minor–Trace Elements

In this study, the well-characterized MongOLSh11-2 olivine RM and the in-house XEN RM were analyzed for minor–trace elements, and the accuracies of the measurements were evaluated. The accuracy is given as the relative deviation (%), which is defined as the discrepancy (%) from the recommended value. Figure 5 plots the data of MongOLSh11-2 and XEN, which were calculated using...
the simplified 100% method with Mg, Fe and Si as internal standards. The complete dataset is given in ESI Table S2. The accuracies of the Mg, Fe and Si are better than 1.5%, relative to the recommended value (ESI Table S2). The LODs are calculated as three times the standard deviation of a sample that contains zero analyte (here, we used the gas blank), as proposed by Longerich et al. [42]. Figure 5c shows that, for most elements, the LODs from the LA–ICP–MS is < 0.1 µg/g, which is clearly better than these of HP–EPMA.

As shown in Figure 5, the results for most minor–trace elements agree with the recommended values, except for those of Li, Na, P, Zn and Ga. These results demonstrate that LA–ICP–MS, along with this simplified 100% method, is practical for the quantification of minor–trace elements. Figure 5 also illustrates that the accuracies are not affected by the used internal standards (Mg, Fe, and Si) with GOR132-G as calibrator, which can be interpreted via the similar DHF behaviors of Mg, Fe and Si in GOR132-G and the olivine samples (Figure 1 and ESI Figure S1). Bussweiler et al. [20] reported a detectable laser-induced inter-element fractionation (e.g., Na, Zn, Ni, Co and P) between olivine and commonly used silicate glass calibration materials (NISt SRM 612, GSD-1G and BHVO-2G).
using a laser spot size smaller than 100 µm. Here, we evaluated the laser-induced inter-element fractionation between GOR132-G and olivine samples. Figure 6 plots the fractionation factors (FI, as proposed by Fryer et al. [43]) of GOR132-G, MongOLSh11-2 and XEN olivines. Fractionation factors describe the degree of fractionation during ablation of a given isotope relative to an internal standard (25Mg, 56Fe and 29Si). The observed FIs for the investigated elements are in the range of 0.9 to 1.1. Importantly, the trends of the FIs for individual elements (except for Zn) are very similar (within 10%) for GOR132-G, MongOLSh11-2 and XEN, indicating the negligible laser-induced bias between GOR132-G glass and olivine samples. Compared with NIST SRM 612, the chemical composition of GOR132-G glass is more similar to olivine, which likely minimizes the laser-induced inter-element fractionations, and thus reduces the matrix effects. ESI Figure S2 compares the results for the Fo content and minor–trace elements of one Lijiang olivine quantified using GOR132-G and MongOLSh11-2 as calibration standards. The results show that the data calibrated by GOR132-G match with the data by MongOLSh11-2 within 10%, except for Li, Na, P, Zn and Ga.

Figure 6. Plots of the fractionation factors for GOR132-G, MongOLSh11-2 and XEN olivines. Fractionation factors describe the degree of fractionation during ablation of a given isotope relative to an internal standard (25Mg, 56Fe and 29Si).

Large variations for Li, Na and Ga are mainly attributed to their low concentrations, which are close to the LODs (Figure 5c). The results for these elements can be improved with a longer dwell time (e.g., 30 ms). The results for P in MongOLSh11-2 are systematically higher than the recommended values.
value (Figure 5a), which may be related to the interference of $^{30}$Si on $^{31}$P. We have investigated this issue using the SF–ICP–MS middle resolution, and the results indicate that the effect of $^{30}$Si on $^{31}$P is limited and can be ignored. Instead, the P value in GOR132-G is given as the information value (Figure 5a), which may be related to the interference of Zn and refractory Mg. MongOLSh11-2 exhibits greater DHF compared with GOR132-G (Figure 6). A bias factor (1.38) derived from the MongOLSh 11-2 was used to correct the P data from XEN and the other olivine samples. Table 2 shows that the corrected P result for XEN (42.6 ± 12.2 µg/g) agrees well with the value from the literature (37.0 ± 2.0 µg/g), obtained by LA–ICP–MS [21].

### Table 2. Minor and trace element concentrations in MongOL Sh11-2 and XEN olivine reference materials.

| Element | MongOL Sh11-2 | XEN |
|---------|---------------|-----|
|        | Recommended Values | This Study ($N = 120$) | Recommended Values | This Study ($N = 98$) |
|        | Mass Fraction (µg/g) | 2 S.D. (µg/g) | Mean (µg/g) | 2 S.D. (µg/g) | Mass Fraction (µg/g) | 2 S.D. (µg/g) | Mean (µg/g) | 2 S.D. (µg/g) |
| Li      | 2.18          | 0.40          | 1.56       | 0.30          | -       | -           | 1.21       | 0.34          |
| Na      | 130           | 24           | 101        | 26             | 15       | 15           | -         | -             |
| Al      | 245           | 34           | 266        | 14             | 46.0 /43.0 | b | 60 /8.0 | b | 43.4 | 4.0 |
| P       | 66.4          | 20           | 706        | 32             | 37.0 /17.0 | b | 5.0 /5.0 | b | 42.6* | 12.2 |
| Ca      | 688           | 59           | 706        | 32             | 246 /239 | b | 19 /7 | b | 252 | 10 |
| Sc      | 3.40          | 0.20          | 3.39       | 0.10           | -       | -           | 2.03       | 0.14          |
| Ti      | 40.2          | 6.0           | 41.7       | 1.3            | 11.0 /10.0 | b | 1.0 /4.0 | b | 10.8 | 1.1 |
| V       | 5.5           | 0.5           | 5.2        | 0.1            | -       | -           | 1.87       | 0.16          |
| Cr      | 125           | 9             | 123        | 5              | 40.0       | b | 5.0       | b | 40.0 | 1.7 |
| Mn      | 1119          | 47           | 1133       | 33             | 1043 /1032 | b | 15 /6 | b | 1050 | 34 |
| Co      | 148           | 12           | 139        | 3              | 145 /149 | b | 2 /8 | b | 135 | 6 |
| Ni      | 2822          | 87           | 2717       | 57             | 3166 /3132 | b | 55 /31 | b | 2995 | 63 |
| Cu      | 1.13          | 0.18          | 1.09       | 0.06           | -       | -           | 0.59       | 0.06          |
| Zn      | 56.3          | 4.6           | -          | -              | 44.0 /43.0 | b | 2.0 /6.0 | b | 41.0* | 3.2* |
| Ga      | 0.10          | 0.02          | 0.12       | 0.02           | -       | -           | 0.060      | 0.060         |
| Y       | 0.079         | 0.014         | 0.074      | 0.005          | -       | -           | 0.030      | 0.030         |

Three Zn isotopes have potential overlaps between Mg or Si. $^{24}$Mg $^{40}$Ar$^+$ on $^{64}$Zn$^+$, $^{26}$Mg $^{40}$Ar$^+$ on $^{66}$Zn$^+$, and $^{28}$Si $^{40}$Ar$^+$ on $^{68}$Zn$^+$. De Hoog et al. [7] recommended the use of $^{66}$Zn, because their tests showed only limited formation of $^{26}$Mg $^{40}$Ar$^+$ in the plasma. Foley et al. [17] suggested using the $^{67}$Zn isotope because it is free of interferences from argides of the major element Si, Mg and Fe, whereas the $^{67}$Zn isotope has only a 4% abundance. In this study, the Zn data for MongOLSh11-2, calculated from $^{64}$Zn, $^{66}$Zn and $^{67}$Zn, are 104.1 µg/g, 71.0 µg/g and 64.0 µg/g, respectively. The data from $^{67}$Zn is the closest one to the recommended value (56.3 ± 4.6 µg/g–1), indicating $^{67}$Zn is preferable for Zn quantification. However, even using the $^{67}$Zn isotope, the Zn data for MongOLSh11-2 are still systematically high, by 8–15%, which is probably related to the DHF effect between volatile the Zn and refractory Mg. MongOLSh11-2 exhibits greater DHF compared with GOR132-G (Figure 6). The corrected Zn result for XEN is in agreement with the recommended value (Table 2), demonstrating the robustness of this correction. Currently, only a few data have been reported for XEN. Table 2 summarizes the major and minor–trace elements data using LA–ICP–MS. This data may be useful for the certification of XEN.

#### 3.4. Olivine Phenocrysts in the Lijiang Picrites from the Emeishan Large Igneous Province

Using the LA–ICP–MS technique and the simplified 100% approach, we analyzed olivine phenocrysts in the Lijiang picrites from the Emeishan LIP. The picrites have high Ti/Y ratios (Ti/Y = 650)
and are belong to high-Ti-type rocks (Ti/Y > 500) [48]. These olivine compositions were also compared with those from other high-Ti picrites (Yongsheng picrites [49], Emeishan LIP, with Ti/Y = 782, and Nuanetsi picrites [50], Karoo LIP, with Ti/Y = 650). Olivines from the Lijiang picrites have relatively low Ni contents and Fe/Mn ratios, and high Ca contents, consistent with the olivines that crystallize from peridotite-derived melts (Figure 7). These features, combined with the high Mn/Zn ratios [51] of the Lijiang olivines, indicate derivation from a peridotite source. In contrast, olivines from the Yongsheng and Nuanetsi picrites have systematically higher Ni contents and Fe/Mn ratios, and lower Ca contents, than those from the Lijiang picrites, which indicates the involvement of a pyroxenite component in their mantle sources (Figure 7). The different olivine compositions observed in these picrites require multiple mantle sources for high-Ti picrites, as proposed by Kamenetsky et al. [51].

**Figure 7.** Chemistry of olivine phenocrysts in the Lijiang picrites, Emeishan LIP. Data for olivine from Yongsheng 50 and Nuanetsi picrites 51 are plotted for comparison. (a) Fo value versus Ni (µg/g) illustrating Ni depletion in Lijiang olivine relative to Yongsheng and Nuanetsi. (b) Fo value versus Ca (µg/g) illustrating Ca enrichment in Lijiang olivine relative to Yongsheng and Nuanetsi. (c) Fo value versus Fe/Mn ratios illustrating lower Fe/Mn ratios in Lijiang olivine relative to Yongsheng and Nuanetsi. (d) Fo value versus Mn/Zn ratios illustrating sources of peridotite-derived melts for Lijiang olivine.

### 3.5. Advantages and Limitations

Compared with HP-EPMA, the main advantage of the LA–ICP–MS technique is the low LODs. For most trace elements, the LODs are < 0.1 µg/g (Figure 5c). This provides more reliable data for elements with concentrations near to or below the LODs of HP–EPMA (ca. 10 µg/g). This is particularly important for some incompatible elements (e.g., Sc and Y). Another advantage is the high sample throughput. Routinely, a single spot can be analyzed in 2 min, which is much faster than HP-EPMA (>15 min per spot analysis). As such, this technique is suitable for analyzing a large number of samples;
for example, in the field of diamond indicator mineral research, where tens of thousands of olivines need to be analyzed. However, LA–ICP–MS has a spatial resolution of 15–100 µm, which limits its application to fine-grained olivine (<15 µm), and/or compositional zonation crystals, or the small-size olivine inclusions in host minerals. However, LA–ICP–MS with this simplified 100% strategy is robust, and may have a wide range of applications in the field of olivine geochemistry.

4. Conclusions

In this study, we demonstrate that LA–ICP–MS is a suitable technique for the routine, in situ, simultaneous determination of Fo contents and minor–trace element contents in olivine. The robustness and usefulness of this technique were validated by analyzing a well-characterized olivine RM (MongOLSh 11-2) and an internal olivine RM (XEN), and further verified by analysis of a large suite of natural olivines (N = 154) with a wide range of Fo contents (81–93). The accuracy and precision of the Fo contents obtained by LA–ICP–MS are comparable to those obtained by conventional EPMA.

For minor–trace elements, most results are in agreement with the recommended values given to the analytical uncertainties, apart from P and Zn data. A bias factor derived from analyses of MongOLSh11-2 needs to be corrected for other olivine samples. We also demonstrate that GOR132-G is a suitable calibration material for the quantification of Fo contents and minor–trace elements in olivine. This technique was initially applied to olivine phenocrysts in the Lijiang picrites from the Emeishan LIP, which showed that these rocks have a peridotitic mantle source. LA–ICP–MS with this simplified 100% method, for the simultaneous determination of Fo contents and minor–trace elements, has the advantage of low LODs, a high sample throughput, and is simple to undertake. Thus, it may have a wide range of applications in the field of olivine geochemistry, particularly for the field where tens of thousands of olivines need to be analyzed.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-163X/10/7/634/s1,
ESI1: Details of EPMA analysis; Table S1: Reference values for GOR132-G glass; Figure S1: Comparison of down-hole fractionation of $^{29}$Si/$^{25}$Mg ratios in GOR132-G and MongOLSh 11-2; Figure S2: Results of Fo contents and minor–trace element in one Lijiang olivine quantified using GOR132-G and MongOLSh11-2 as calibration standards. ESI2: Table S2: Data of Fo content and minor–trace elements of MongOLSh 11-2 and XEN from six sessions. ESI3: The programmed Iolite DRS code for the simplified 100% strategy.

Author Contributions: Conceptualization, S.W.; methodology, Y.W.; formal analysis, Y.Y., H.W., C.H., L.X., J.Y.; writing—original draft preparation, S.W. and Y.W.; writing—review and editing, S.W. and Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the open funding of the State Key Laboratory of Lithospheric Evolution (No. SKL-K201805), National Natural Science Foundation of China (Nos. 41903024 and 41525012), China Postdoctoral Science Foundation (2020M670450) and National Key R&D Program of China (2018YFA0702602).

Acknowledgments: We thank Bin Wu for assistance with EPMA analyses. Valentina G. Batanova is thanked for kindly providing us with the MongOLSh11-2 and XEN olivine reference materials. Klaus Peter Jochum is thanked for providing the GOR132-G glass reference material. Aaron Stallard is thanked for the polishing of language.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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