

## Electronic Supplementary Information (ESI)

# **A new olivine reference material by a novel synthesized method for *in situ* iron and magnesium isotope analysis using laser ablation MC-ICP-MS**

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## Supplementary information

### (1) Solution Fe and Mg isotope analyses

**Solution MC-ICP-MS Fe isotope analyses:** Solution Fe isotope measurements were performed on a Nu Plasma 1700 MC-ICP-MS (Nu Instruments, Wrexham, UK) at the GPMR. Compared to other standard-size MC-ICP-MS instruments, the Nu Plasma 1700 boasts a natural dispersion close to 1700 mm, offering an exceptional measurement range. It features 16 Faraday cups, each equipped with  $10^{11} \Omega$  resistors, and each detector has independently adjustable slits for width and center position, allowing for different resolutions on a single detector. These capabilities enable the Nu Plasma 1700 provides high mass resolution for fully separating polyatomic interference ions.<sup>1</sup>

The dissolution procedure is as follows: weigh olivine powder (containing 50–100  $\mu\text{g}$  of iron) into a PTFE-lined stainless steel bomb, and add 1 ml of  $\text{HNO}_3$  and 1 ml of HF. The bomb is then heated to 190 °C in an electric oven for 24 hours. After cooling, the bomb is opened, and the solution is evaporated to dryness at 120 °C on a hotplate. The residue is redissolved twice with 1 ml of  $\text{HNO}_3$  to remove HF. Following this, 1 ml of  $\text{HNO}_3$  and 2 ml of Milli-Q water are added, and the sample is heated again at 190 °C for 24 hours to ensure complete dissolution of the olivine. Once fully dissolved, the sample is dried and redissolved in 1 ml of HCl, a process repeated twice to convert the sample entirely into chloride form. The solution is finally dissolved in 0.5 ml of 8 mol  $\text{L}^{-1}$  HCl containing 0.001%  $\text{H}_2\text{O}_2$ , ready for separation and purification following the method described by Huang et al.<sup>2</sup> This process uses 0.8 mL of AG-MP-1M resin in a

Bio-Rad column, with a sequence of elution solutions employed to thoroughly clean and separate the sample. Iron is eluted with 4 ml of 0.5 mol L<sup>-1</sup> HCl and water. The eluate is then dried and conditioned in 0.3 mol L<sup>-1</sup> HNO<sub>3</sub> for Fe isotope analysis. The whole procedural blank of Fe was ~20 ng, which was considered negligible for analysis. The geological reference materials, BCR-2 and BHVO-2 were used as unknown samples.

Fe isotopic ratios were determined using the Standard Sample Bracketing (SSB) method. All test solutions were systematically diluted with 2% HNO<sub>3</sub> to achieve a precise Fe concentration of 5.00 ± 0.25 µg g<sup>-1</sup>. A 60 s acid blank was measured before each isotopic analysis to subtract from the analyte signal. Each isotopic analysis consisted of an integration of 25 cycles with a duration of 8 s per cycle, achieving an internal precision better than 15×10<sup>-6</sup> (relative standard error) for the <sup>56</sup>Fe/<sup>54</sup>Fe ratio. The δ<sup>56</sup>Fe<sub>IRMM-014</sub> results of reference materials for BCR-2 and BHVO-2 were 0.07‰ ± 0.03 (2SD, n = 9), 0.11‰ ± 0.05 (2SD, n = 9), respectively, which are in agreement with the reference values (Table S1). Instrument settings and operational parameters were adjusted following the methodology described by Lei et al.<sup>3</sup>

Figure 2 presents the iron isotope test results conducted on the olivine solution. The figure demonstrates that the solution values are consistent and repeatable. Therefore, we obtained the δ<sup>56</sup>Fe<sub>IRMM-014</sub> isotope values for the olivine powder 0.00 ± 0.02‰ (2SD, n = 9).

**Solution MC-ICP-MS Mg isotope analyses:** Magnesium isotope solution analyses were performed in two different laboratories: the GPMR Laboratory, and the State Key

Laboratory of Continental Dynamics (SKLCD) at Northwest University, Xi'an, China.

Major element analysis of the olivine powder yielded K and Mg concentrations of 0.0015 wt% and 49 wt%, respectively (Table S2). Given the negligible K content, coprecipitation pretreatment was deemed unnecessary prior to the purification step.<sup>1</sup> Calcium was measured at 0.055 wt%, with a Ca/Mg ratio below 2, suggesting that calcium does not impact magnesium tests, and no additional separation steps were required.<sup>4</sup> The magnesium purification process follows the method by Bao et al.,<sup>5</sup> using two stages of cation exchange chromatography with Bio-Rad AG50W-X12 resin. Initially, 25  $\mu\text{g}$  of Mg from the dissolved olivine sample was loaded onto a column containing 2 mL of AG50W-X12 resin conditioned with 5 mL of 12 mol L<sup>-1</sup>. After loading, 5 mL of 12 mol L<sup>-1</sup> HCl was used to elute major cations (Mg, Na, Al), followed by washing with 20 mL of 6 mol L<sup>-1</sup> HCl and 5 mL of Milli-Q H<sub>2</sub>O to remove remaining elements (e.g., Ca, Fe). The eluate was evaporated to dryness and re-dissolved in 0.5 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.5 mol L<sup>-1</sup> HF before being loaded onto a second column containing 0.5 mL of AG50W-X12 resin preconditioned with 5 mL of 12 mol L<sup>-1</sup> HCl and Milli-Q H<sub>2</sub>O. The second resin was conditioned with 5 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.5 mol L<sup>-1</sup> HF, and the sample was loaded, followed by 1 mL and 3 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> + 0.5 mol L<sup>-1</sup> HF to elute Al, Fe, Na, Ti, and other matrix elements. Finally, 3 mL of 6 mol L<sup>-1</sup> HCl was used to elute Mg, and the eluate was collected, evaporated to dryness at 80 °C, and dissolved in 2% HNO<sub>3</sub> for Mg isotope analysis. The whole procedural blank of Mg was ~20 ng, which was considered negligible for analysis. The geological reference materials, BCR-2, GSR-1, and GSP-2 were used as unknown

samples. The measured  $\delta^{25}\text{Mg}_{\text{DSM-3}}$  values for reference materials BCR-2, GSR-1 and GSP-2 were  $-0.10\text{‰} \pm 0.02$  (2SD, n = 7),  $0.12\text{‰} \pm 0.03$  (2SD, n = 7),  $0.02\text{‰} \pm 0.02$  (2SD, n = 7) respectively, all of which are consistent with previously reported values (Table S4).

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## (2) The F-ratio calculation based on ISO GUIDE (2017)

The experimental F-ratio is the ratio of the between-pellet variance ( $M_{between}$ ) to the within-pellet variance ( $M_{within}$ ):

$$F = \frac{M_{between}}{M_{within}} \quad (1)$$

where  $M_{between}$  is the ratio of between-pellet sums of squares ( $S_{between}^2$ ) to the associated between-pellet degrees of freedom ( $V_{between}$ ), and  $M_{within}$  is the ratio of within-pellet sums of squares ( $S_{within}^2$ ) to the associated within-pellet degrees of freedom ( $V_{within}$ ):

$$S_{between}^2 = \frac{SS_{between}}{V_{between}} \quad (2)$$

$$S_{within}^2 = \frac{SS_{within}}{V_{within}} \quad (3)$$

where  $V_{between}$  and  $V_{within}$  depend on the number of pellets from which samples are taken ( $m$ , 10 in this study) and the number of replicate measurements for each pellet ( $n$ , 20 in this study), and are calculated as follows:

$$V_{between} = m - 1 \quad (4)$$

$$V_{within} = m \times n - m \quad (5)$$

### (3) The uncertainty evaluation based on ISO GUIDE (2017)

For the uncertainty evaluation of the assigned value in prepared reference materials, we use the following equation:

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{hom}^2 + u_{lts}^2} \quad (6)$$

where k is a coverage factor; in many cases, the distribution can be assumed to be approximately normal, and the required coverage probability is 95 %; this leads to a coverage factor k= 2.

The uncertainty  $u_{hom}$  associated with heterogeneity is then given by Formula (7):

$$u_{hom}^2 = \sqrt{u_{bb}^2 + u_{wb}^2} \quad (7)$$

There is no significant within-unit uncertainty,  $u_{wb}^2$  is 0. The between-unit standard deviation  $S_{bb}$  is calculated from the between-group mean square  $M_{between}$  and  $n$ , and it is introduced as the uncertainty component due to between-unit non-uniformity  $u_{bb}$ , given by Formula(8)

$$u_{bb} = S_{bb} \quad (8)$$

$$S_{bb}^2 = \frac{s_1^2 - s_2^2}{n} \quad (9)$$

Where

$$n = \frac{\sum_{i=1}^a n_i}{a} \quad (10)$$

For a simple linear model applied to a classical stability study over several points in time, the uncertainty  $U_{ts}$  associated with the predicted change is given by Formula (11)

$$u_{ts}^2 = s(\beta_1) \cdot (t_{m1} + t_{cert}) \quad (11)$$

where  $s(\beta_1)$  is the standard error for the estimated slope, calculated as in Formula (15),  $t_{m1}$  is the time interval between value assignment and the initial stability monitoring point, and  $t_{cert}$  is the period of validity of a certificate issued during that time.

Linear regression is used in reference material studies to determine simple rates of change and test their statistical significance. This clause describes the simplest case.

The simple linear model can be expressed as in Formula (12):

$$y_i = \beta_0 + \beta_1 x_i + \varepsilon \quad (12)$$

where  $\beta_0$  and  $\beta_1$  are the intercept and slope, respectively, and  $\varepsilon$  denotes the random error component, usually assumed to be normally distributed with a mean of zero.

The regression parameters can be computed from Formulae (13) and (14):



$$\beta_1 = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad (13)$$

$$\beta_0 = \bar{y} - \beta_1 \bar{x} \quad (14)$$

where  $\beta_0$  and  $\beta_1$  are the estimated intercept and slope, respectively, and  $\bar{x}$  and  $\bar{y}$  are the mean of the respective observations.

The standard errors  $s(\beta_1)$  and  $S(\beta_0)$  and  $\beta_0$  and  $\beta_1$  can be computed using Formulae (15) to (17):

$$s(\beta_1) = \frac{s}{\sqrt{\sum_{i=1}^n (X_i - \bar{X})^2}} \quad (15)$$

Where

$$s^2 = \frac{\sum_{i=1}^n (Y_i - \beta_0 - \beta_1 X_i)^2}{n - 2} \quad (16)$$

And

$$S(\beta_0) = s(\beta_1) \sqrt{\frac{\sum_{i=1}^n x^2}{n}} \quad (17)$$

Where Formula (16) was used to calculate the certified value, where the data set means follow an approximately normal distribution and no weighting is applied, the

standard deviation of the mean of the p data set means  $y_i$  can be applied as  $u_{char}$

$$u_{char} = \frac{s(y)}{\sqrt{p}} = \frac{1}{\sqrt{p}} \cdot \sqrt{\frac{\sum (y_i - y_{char})^2}{p-1}} \quad (18)$$

Where

$$y_{char} = \bar{x} = \frac{1}{\sum_{i=1}^m n_i} \sum_{i=1}^m \sum_{j=1}^{n_i} x_{ij} \quad (19)$$

where  $s(y)$  denotes the standard deviation of the p data set mean values.

(4) Fig.S1 Sintered olivine sample using a tube furnace at different air conditions



(5) Fig.S2 Sintered olivine samples at optimized conditions (1300 °C, 2 h in argon gas)  
in different batches.



(6) Table S1. The measurement results of  $\delta^{56}\text{Fe}_{\text{IRMM-014}}$  for BCR-2 and BHVO-2 obtained from solution-MC-ICP-MS in this study and reference values

Name	$\delta^{56}\text{Fe}_{\text{IRMM-014}}$ (‰)	2SD	$\delta^{57}\text{Fe}_{\text{IRMM-014}}$ (‰)	2SD	Reference
BCR-2	0.072	0.029	0.112	0.062	This study
	0.090	0.021	0.133	0.040	Chen <i>et al.</i> <sup>1</sup>
	0.091	0.025	0.133	0.031	Dauphas <i>et al.</i> <sup>2</sup>
	0.091	0.011	0.126	0.017	Craddock <i>et al.</i> <sup>3</sup>
	0.084	0.029	0.130	0.048	He <i>et al.</i> <sup>4</sup>
BHVO-2	0.113	0.047	0.149	0.089	This study
	0.102	0.026	0.149	0.056	Chen <i>et al.</i> <sup>1</sup>
	0.114	0.011	0.174	0.016	Craddock <i>et al.</i> <sup>3</sup>
	0.109	0.028	0.160	0.058	He <i>et al.</i> <sup>4</sup>

References:

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(7) Table S2. The results of major elements in olivine ultrafine powder obtained by XRF

Element	Contents	Olivine powder	
		Round 1	Round 2
SiO <sub>2</sub>	wt%	40.92	40.75
TiO <sub>2</sub>	wt%	0.007	0.005
Al <sub>2</sub> O <sub>3</sub>	wt%	0.08	0.08
TFe <sub>2</sub> O <sub>3</sub>	wt%	9.70	9.69
MnO	wt%	0.12	0.12
MgO	wt%	49.06	48.94
CaO	wt%	0.06	0.05
Na <sub>2</sub> O	wt%	0.014	0.016
K <sub>2</sub> O	wt%	0.001	0.002
P <sub>2</sub> O <sub>5</sub>	wt%	0.005	0.006
LOI	wt%	-0.04	-0.02
SUM	wt%	99.94	99.64

**(8)** Table S3. The results of trace elements in olivine ultrafine powder obtained by ICP-MS (Agilent 7700e). ICP-MS measurement results for BHVO-2, BCR-2 and RGM-2 reference materials, together with their reference values from GeoReM (<http://georem.mpch-mainz.gwdg.de/>)

	BHVO-2		BCR-2		RGM-2		Olivine powder	
	Meas. value	Ref. value	Meas. value	Ref. value	Meas. value	Ref. value	Round 1	Round 2
Li	4.30	4.80	8.99	9.00	59.67	57.00	1.61	1.57
Be	1.00	1.00	2.36	-	2.42	2.37	0.01	0.02
Sc	31.97	32.00	33.03	33.00	4.39	4.40	2.50	2.48
V	322.52	317.00	410.68	416.00	11.90	13.00	3.59	3.80
Cr	285.06	280.00	14.20	16.50	4.82	5.90	89.84	89.72
Co	45.58	45.00	37.26	37.00	1.83	2.00	137.35	138.07
Ni	122.43	119.00	11.81	13.00	3.35	5.20	2936.58	2987.13
Cu	129.30	127.00	18.41	19.66	9.71	9.60	1.30	1.29
Zn	103.87	103.00	132.07	133.00	31.05	32.00	40.44	40.06
Ga	21.85	21.70	22.03	23.00	16.44	16.55	0.16	0.17
Rb	9.17	9.11	46.91	46.90	147.71	150.00	0.03	0.03
Sr	398.24	396.00	338.80	340.00	107.05	107.50	0.26	0.27
Y	26.72	26.00	35.96	37.00	23.45	23.16	0.04	0.04
Zr	168.50	172.00	179.29	184.00	228.51	220.00	0.27	0.26
Nb	18.75	18.10	12.45	12.60	8.91	9.30	0.02	0.02
Sn	1.71	1.70	1.94	2.03	3.30	3.34	0.12	0.12
Cs	0.10	0.10	1.09	1.10	9.63	9.60	0.00	0.00
Ba	129.73	131.00	658.78	677.00	826.61	810.00	0.27	0.31
La	15.26	15.20	24.59	24.90	23.36	24.00	0.03	0.03
Ce	37.52	37.50	51.72	52.90	45.65	47.00	0.03	0.03
Pr	5.20	5.35	6.64	6.70	5.29	5.36	0.00	0.00
Nd	24.05	24.50	27.90	28.70	19.37	19.00	0.01	0.01
Sm	6.03	6.07	6.56	6.58	4.09	4.30	0.01	0.01
Eu	2.02	2.07	1.97	1.96	0.64	0.66	0.00	0.00
Gd	6.23	6.24	6.65	6.75	3.67	3.70	0.01	0.01
Tb	0.96	0.92	1.06	1.07	0.61	0.66	0.00	0.00
Dy	5.39	5.31	6.60	6.41	3.68	4.10	0.01	0.01
Ho	0.96	0.98	1.30	1.28	0.79	0.82	0.00	0.00
Er	2.54	2.54	3.61	3.66	2.32	2.35	0.01	0.00
Tm	0.33	0.33	0.53	0.54	0.38	0.37	0.00	0.00
Yb	2.02	2.00	3.36	3.38	2.54	2.60	0.01	0.02
Lu	0.28	0.27	0.50	0.50	0.39	0.40	0.00	0.00
Hf	4.41	4.36	4.86	4.90	6.02	6.20	0.01	0.01

	BHVO-2		BCR-2		RGM-2		Olivine powder	
	Meas.	Ref.	Meas.	Ref.	Meas.	Ref.	Meas.	
	value	value	value	value	value	value	Round 1	Round 2
Ta	1.16	1.14	0.79	0.78	0.92	0.95	0.00	0.00
Tl	0.05	0.06	0.29	-	0.91	0.93	0.01	0.01
Pb	1.47	1.60	10.21	11.00	19.97	19.27	0.02	0.02
Th	1.17	1.22	5.83	5.70	14.95	15.10	0.00	0.00
U	0.40	0.40	1.69	1.69	5.69	5.80	0.01	0.01



(9) Table S4. The measurement results  $\delta^{25}\text{Mg}_{\text{DSM-3}}$  for BCR-2, GSR-1 and GSP-2 using SN-MC-ICP-MS in this study and reference values

Name	$\delta^{25}\text{Mg}_{\text{DSM-3}}$ (‰)	2SD	$\delta^{26}\text{Mg}_{\text{DSM-3}}$ (‰)	2SD	Reference
BCR-2	-0.097	0.025	-0.187	0.027	This study
	-0.085	0.023	-0.168	0.029	An <i>et al.</i> <sup>1</sup>
	-0.110	0.050	-0.200	0.100	Bao <i>et al.</i> <sup>2</sup>
GSR-1	-0.124	0.032	-0.233	0.049	This study
	-0.130	0.030	-0.260	0.040	Wang <i>et al.</i> <sup>3</sup>
	-0.123	0.011	-0.234	0.016	An <i>et al.</i> <sup>1</sup>
GSP-2	0.020	0.018	0.034	0.040	This study
	0.030	0.011	0.042	0.020	An <i>et al.</i> <sup>1</sup>

References:

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