Supplemental Information

Quantitative verification of 1:100 diluted fused glass beads for X-ray fluorescence analysis of geological specimens

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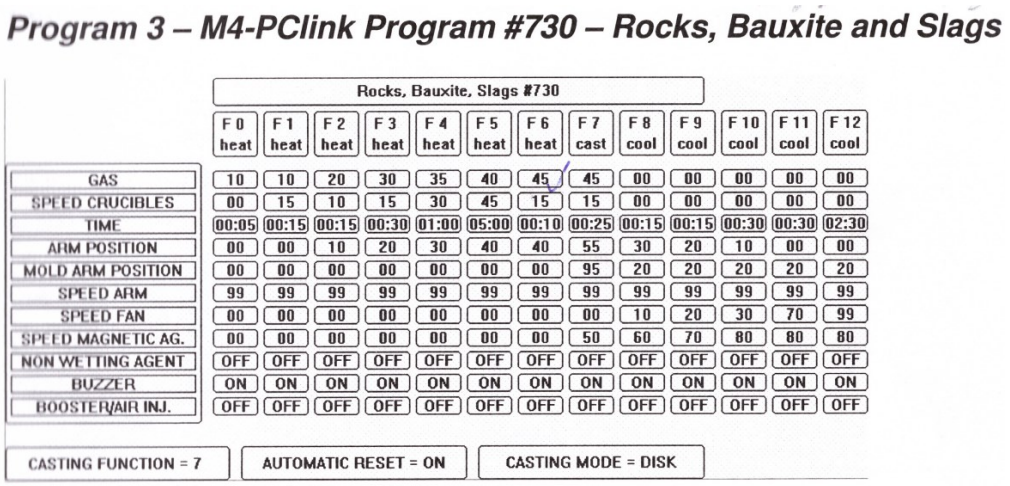
Figure S1. The program of Claisse M4 automatic fluxer used in the fusion of glass disk.



Program 3 – M4-PClink Program #730 – Rocks, Bauxite and Slags

Rocks, Bauxite, Slags #730

	F 0 heat	F 1 heat	F 2 heat	F 3 heat	F 4 heat	F 5 heat	F 6 heat	F 7 cast	F 8 cool	F 9 cool	F 10 cool	F 11 cool	F 12 cool
GAS	10	10	20	30	35	40	45	45	00	00	00	00	00
SPEED CRUCIBLES	00	15	10	15	30	45	15	15	00	00	00	00	00
TIME	00:05	00:15	00:15	00:30	01:00	05:00	00:10	00:25	00:15	00:15	00:30	00:30	02:30
ARM POSITION	00	00	10	20	30	40	40	55	30	20	10	00	00
MOLD ARM POSITION	00	00	00	00	00	00	00	95	20	20	20	20	20
SPEED ARM	99	99	99	99	99	99	99	99	99	99	99	99	99
SPEED FAN	00	00	00	00	00	00	00	00	10	20	30	70	99
SPEED MAGNETIC AG.	00	00	00	00	00	00	00	50	60	70	80	80	80
NON WETTING AGENT	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF
BUZZER	ON	ON	ON	ON	ON	ON	ON	ON	ON	ON	ON	ON	ON
BOOSTER/AIR INJ.	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF	OFF

CASTING FUNCTION = 7 | AUTOMATIC RESET = ON | CASTING MODE = DISK

Figure S2. Sketch diagram of the proposed swirl procedure**.**

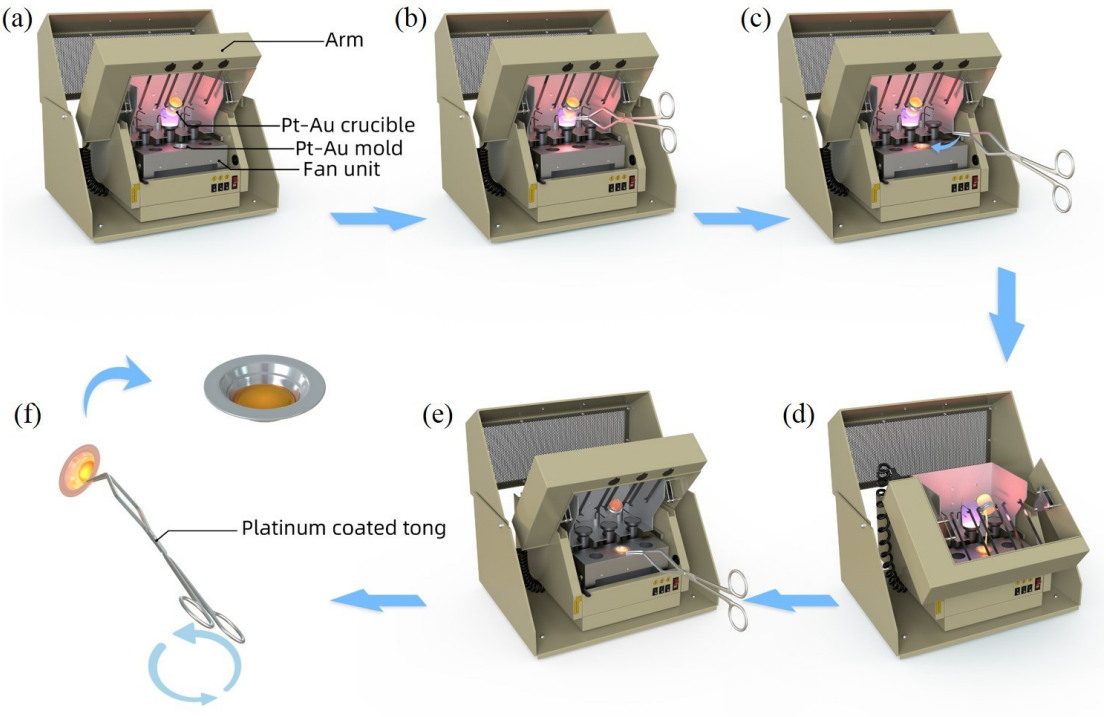


Figure S3. Input information through bar code or quick response (QR) code scanning.

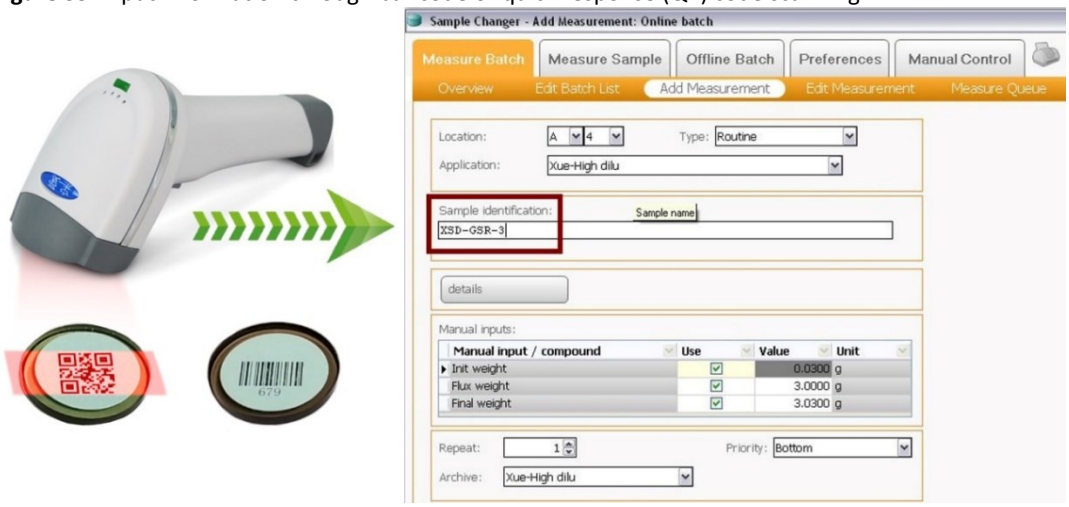
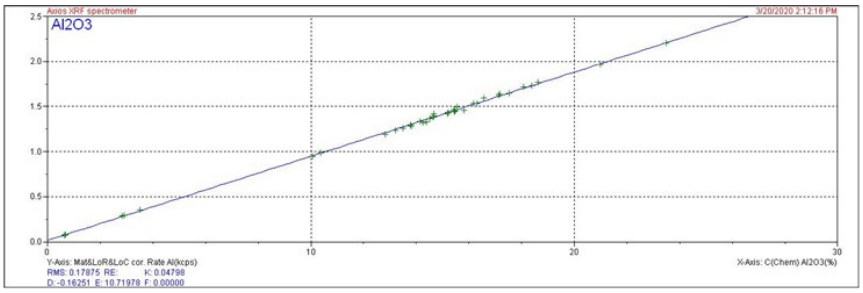
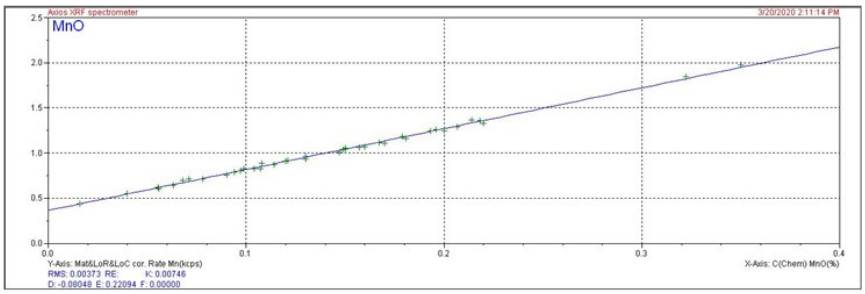
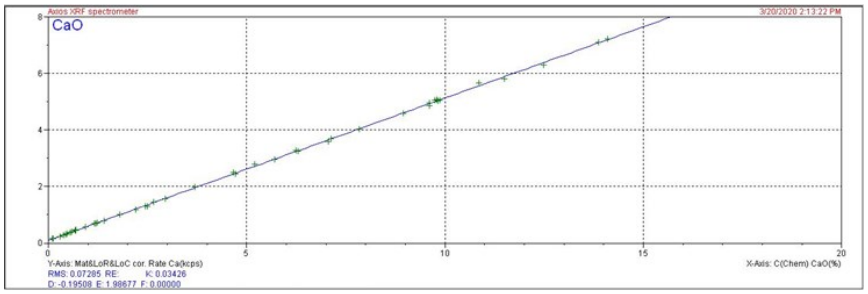
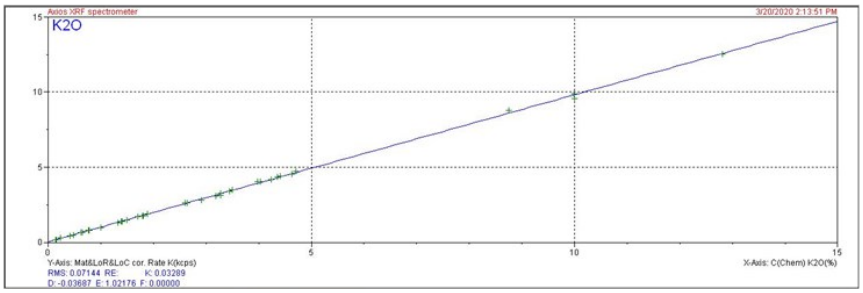


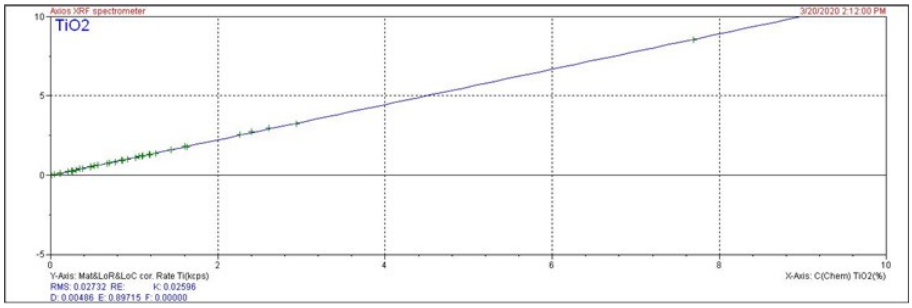
Figure S4. Calibration curves of major and minor element oxides with 1:100 glass beads

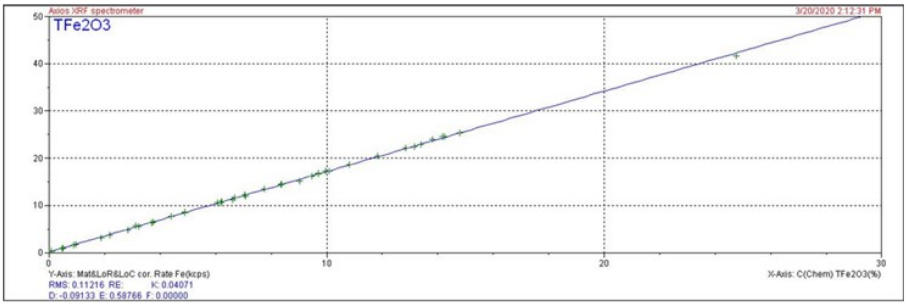


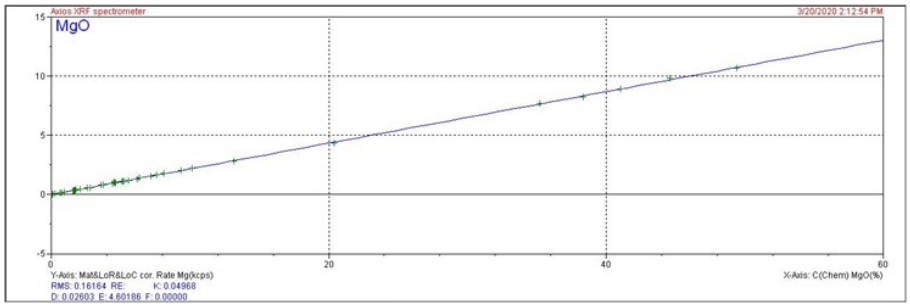


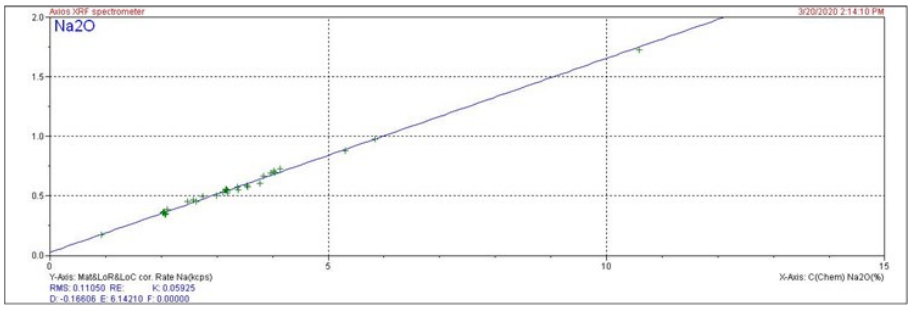


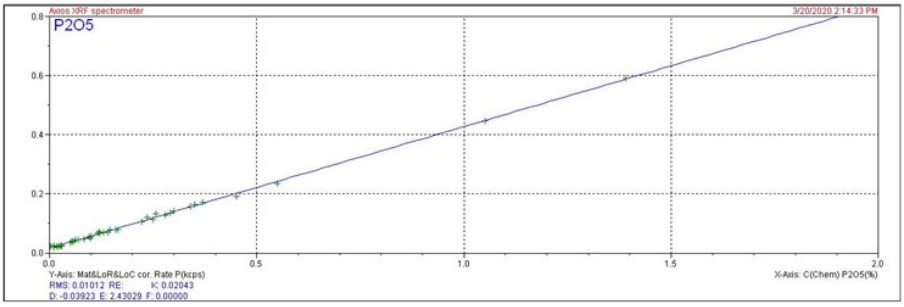


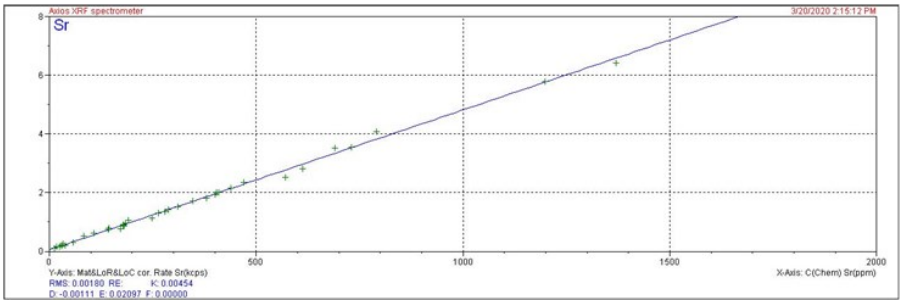

Axios XRF spectrometer
3/20/2020 2:12:00 PM
TiO2
Y-Axis: Mat&LoR&LoC cor. Rate Ti(kcps)
RMS: 0.02732 RE: K: 0.02596
D: 0.00486 E: 0.09715 F: 0.00000
X-Axis: C(Chem) TiO2(%)


Axios XRF spectrometer
3/20/2020 2:12:31 PM
TFe2O3
Y-Axis: Mat&LoR&LoC cor. Rate Fe(kcps)
RMS: 0.11216 RE: K: 0.04071
D: -0.09133 E: 0.58766 F: 0.00000
X-Axis: C(Chem) TFe2O3(%)


Axios XRF spectrometer
3/20/2020 2:12:54 PM
MgO
Y-Axis: Mat&LoR&LoC cor. Rate Mg(kcps)
RMS: 0.16164 RE: K: 0.04968
D: 0.02603 E: 4.60186 F: 0.00000
X-Axis: C(Chem) MgO(%)


Axios XRF spectrometer
3/20/2020 2:14:10 PM
Na2O
Y-Axis: Mat&LoR&LoC cor. Rate Na(kcps)
RMS: 0.11050 RE: K: 0.05925
D: -0.16606 E: 6.14210 F: 0.00000
X-Axis: C(Chem) Na2O(%)


Axios XRF spectrometer
3/20/2020 2:14:33 PM
P2O5
Y-Axis: Mat&LoR&LoC cor. Rate P(kcps)
RMS: 0.01012 RE: K: 0.02043
D: -0.03923 E: 2.43029 F: 0.00000
X-Axis: C(Chem) P2O5(%)


Axios XRF spectrometer
3/20/2020 2:15:12 PM
Sr
Y-Axis: Mat&LoR&LoC cor. Rate Sr(kcps)
RMS: 0.00180 RE: K: 0.00454
D: -0.00111 E: 0.02097 F: 0.00000
X-Axis: C(Chem) Sr(ppm)

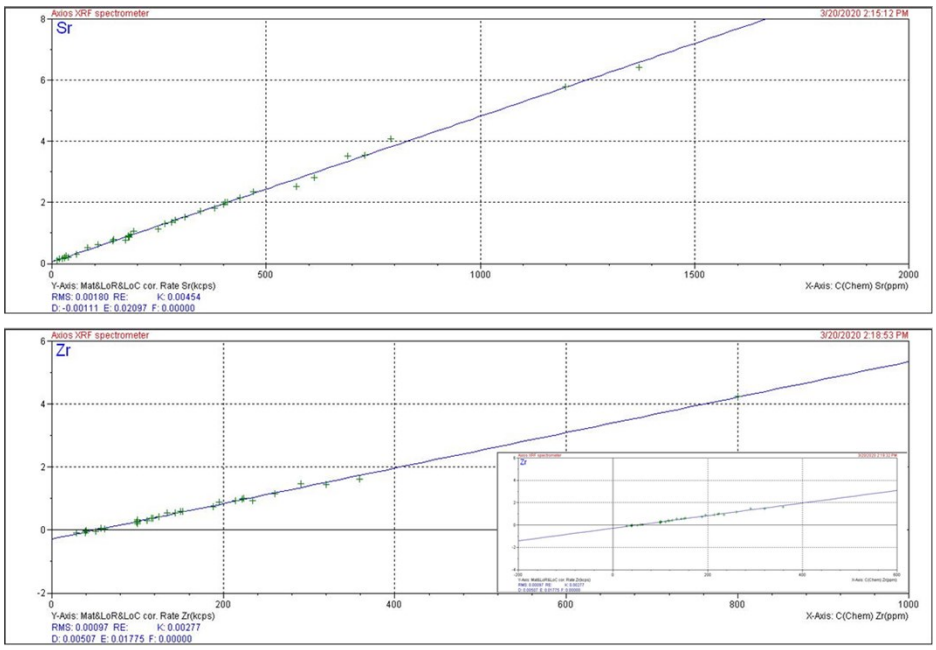
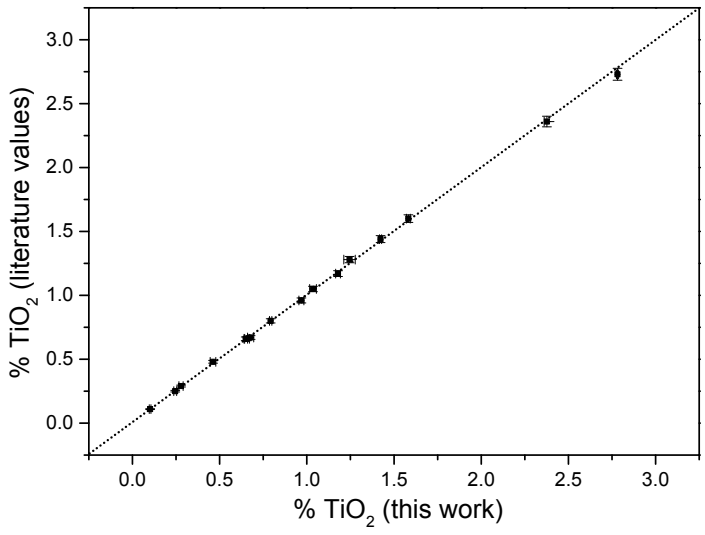
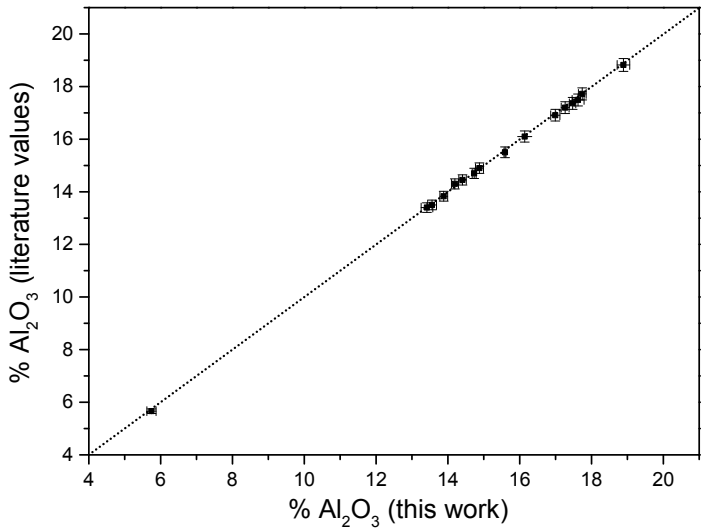
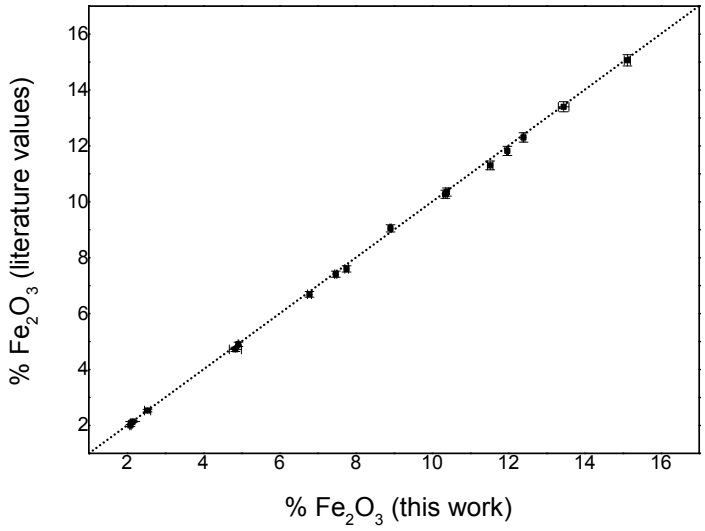
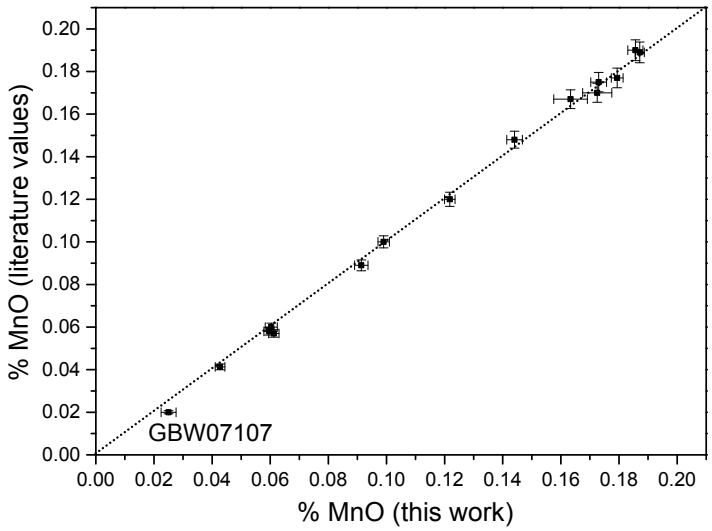


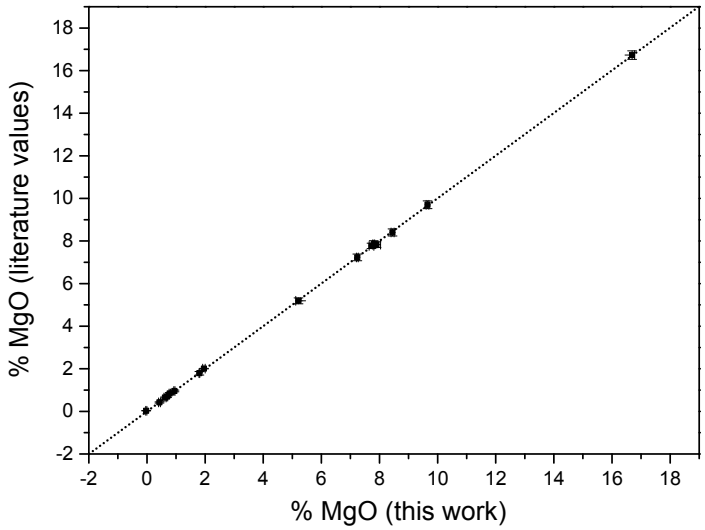
Figure S5. Statistical comparison of the analytical values obtained by the proposed procedure with the recommended values. The diagonal line shows equal values of x-y parameters. The error bar is the standard deviation.

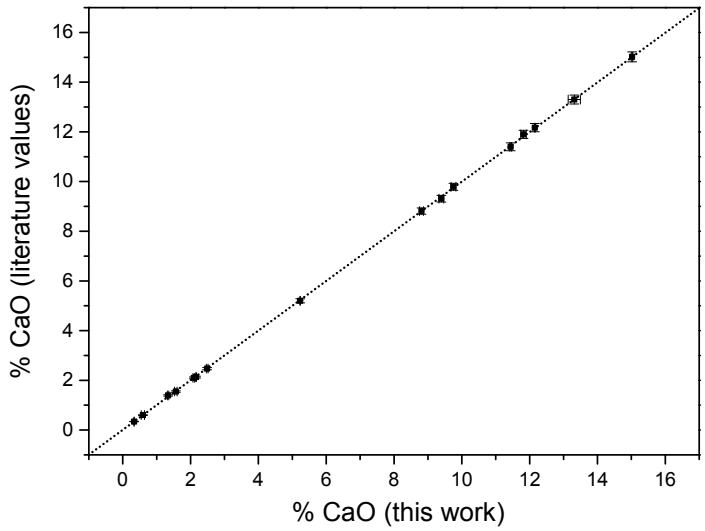


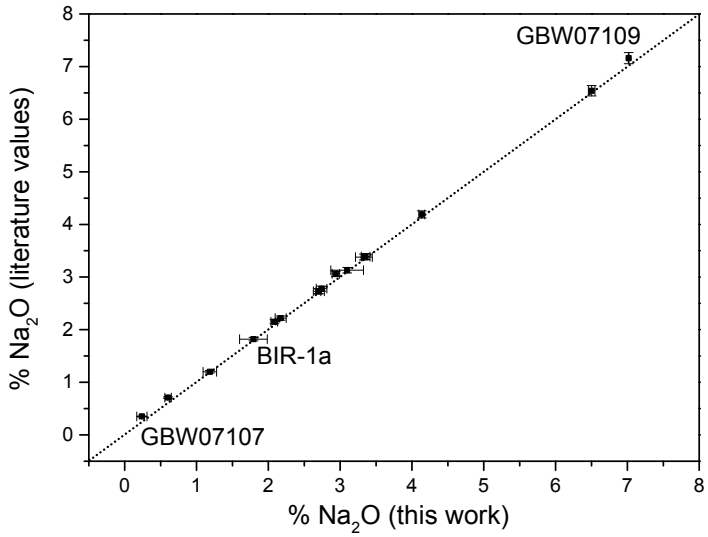

% Al_2O_3 (literature values)
% Al_2O_3 (this work)
4
6
8
10
12
14
16
18
20

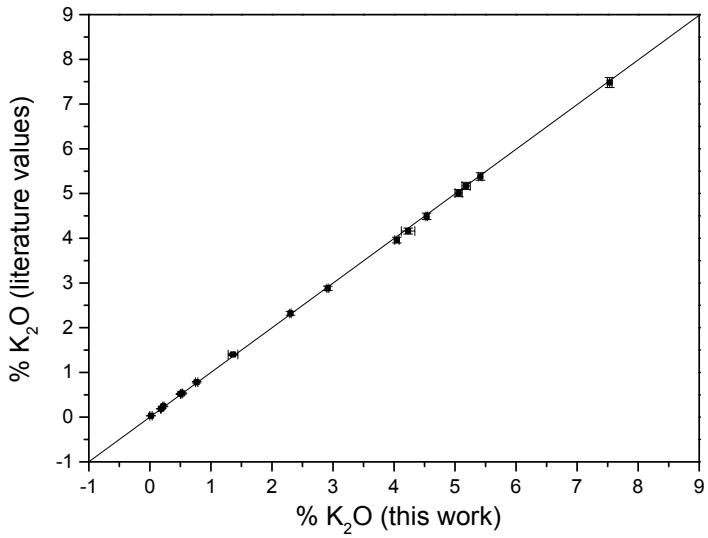

% Fe_2O_3 (literature values)
% Fe_2O_3 (this work)
2
4
6
8
10
12
14
16

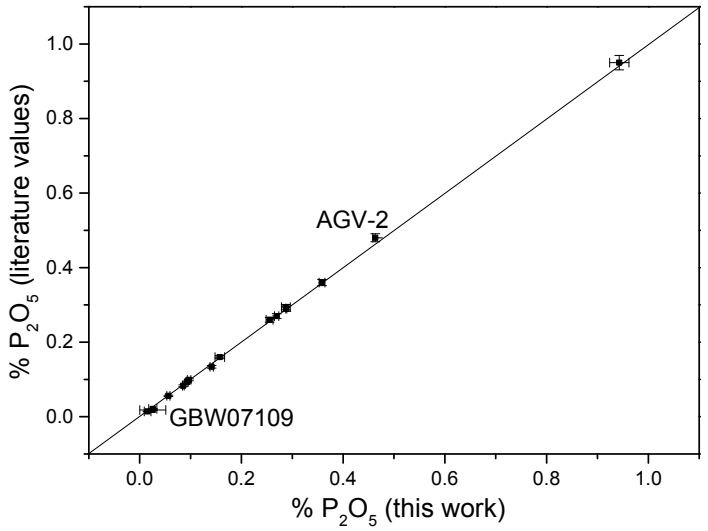

% MnO (literature values)
% MnO (this work)
GBW07107
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0.20

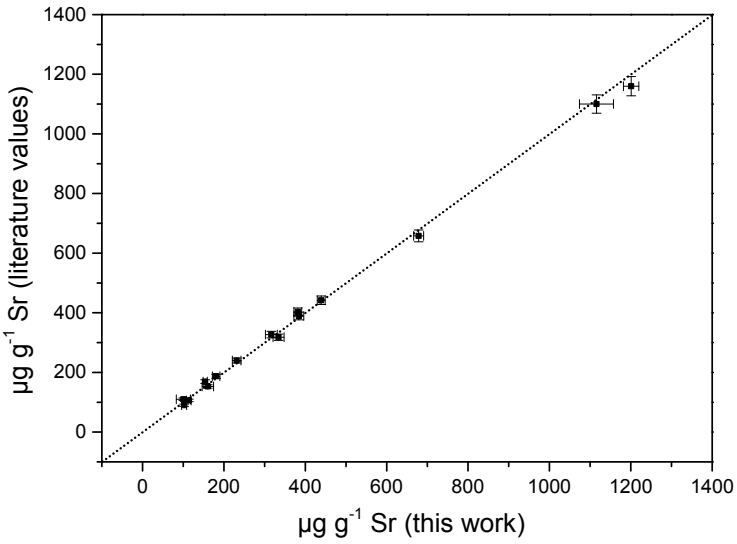

% MgO (literature values)
% MgO (this work)
-2
0
2
4
6
8
10
12
14
16
18


% CaO (literature values)
% CaO (this work)
0
2
4
6
8
10
12
14
16


% Na2O (literature values)
% Na2O (this work)
GBW07109
BIR-1a
GBW07107
0
1
2
3
4
5
6
7
8


% K_2O (literature values)
% K_2O (this work)
9
8
7
6
5
4
3
2
1
0
-1
-1
0
1
2
3
4
5
6
7
8
9


% P_2O_5 (literature values)
% P_2O_5 (this work)
AGV-2
GBW07109
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0


1400
1200
1000
800
600
400
200
0
µg g-1 Sr (literature values)
0
200
400
600
800
1000
1200
1400
µg g-1 Sr (this work)

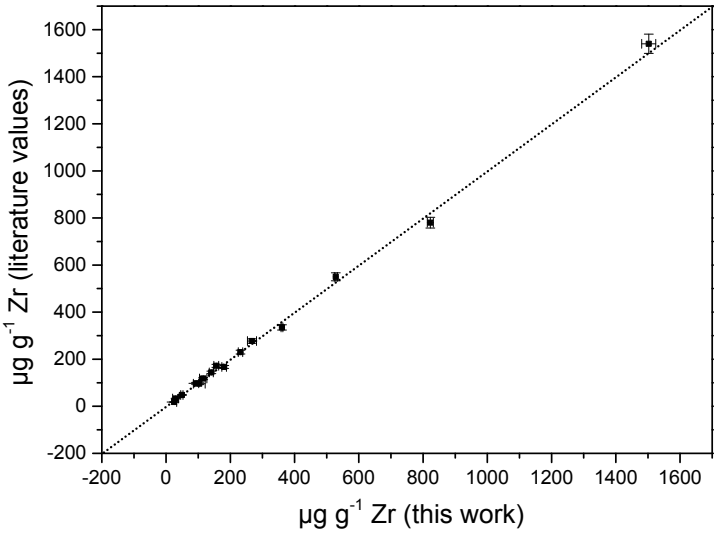
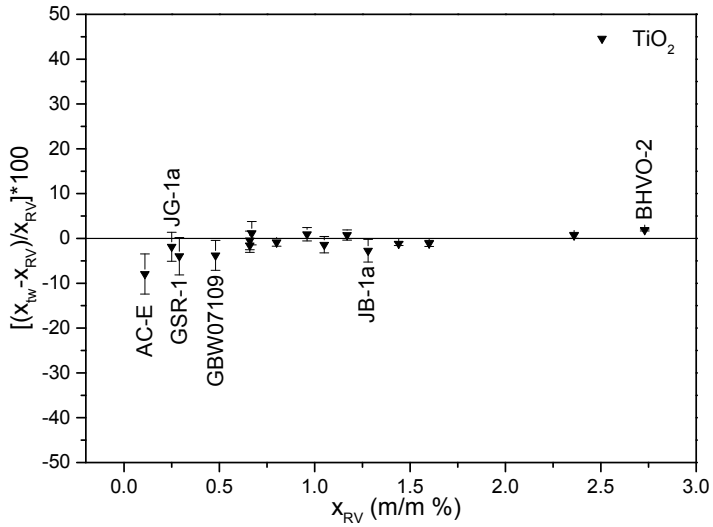
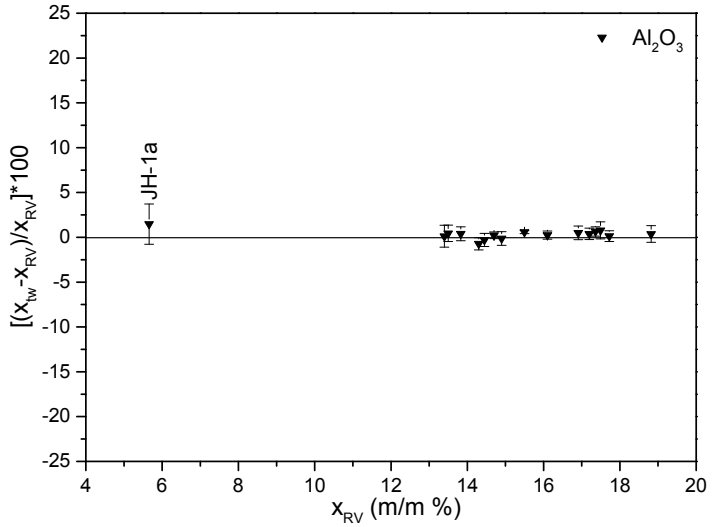
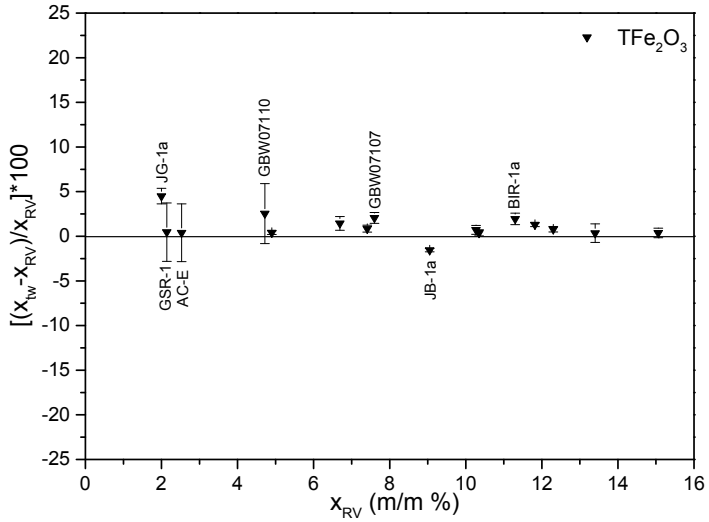
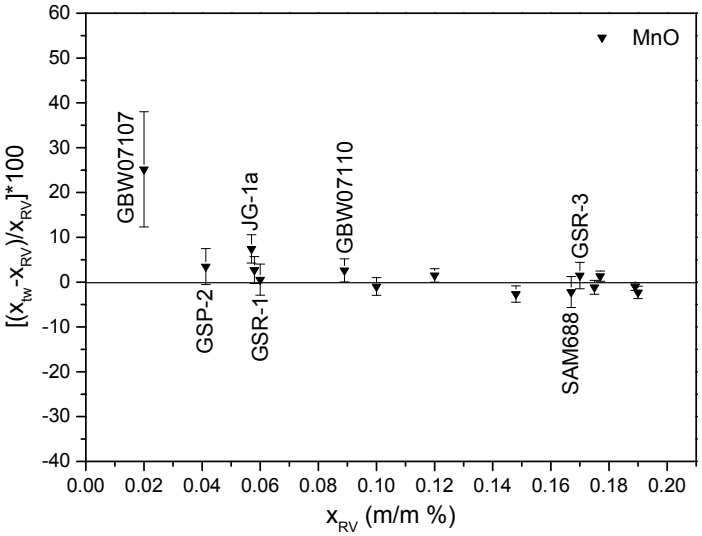

1600
1400
1200
1000
800
600
400
200
0
-200
µg g-1 Zr (literature values)
-200
0
200
400
600
800
1000
1200
1400
1600
µg g-1 Zr (this work)

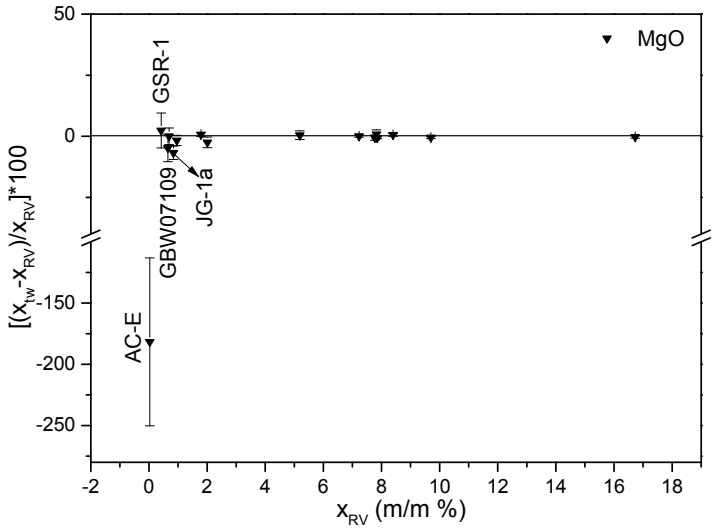
Figure S6. Percentage difference ((X_{RV} - X_m)/X_{RV}] ·100) of recommended value (X_{RV}) as a function of the mean value (X_m) for the present work. The error bar is the relative standard deviation

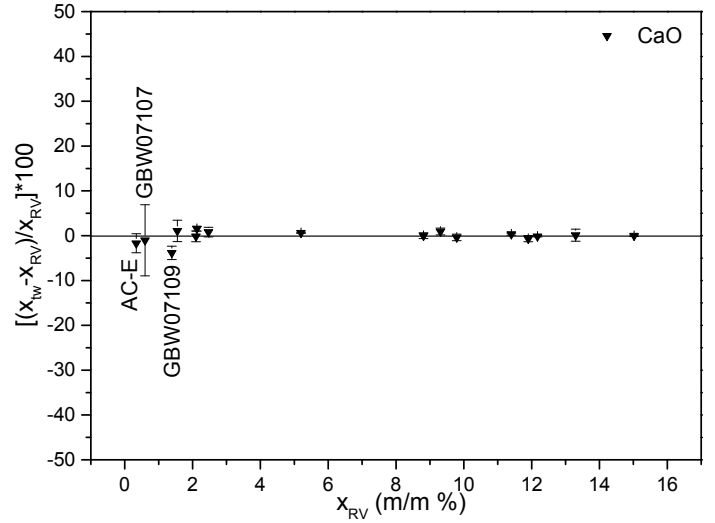


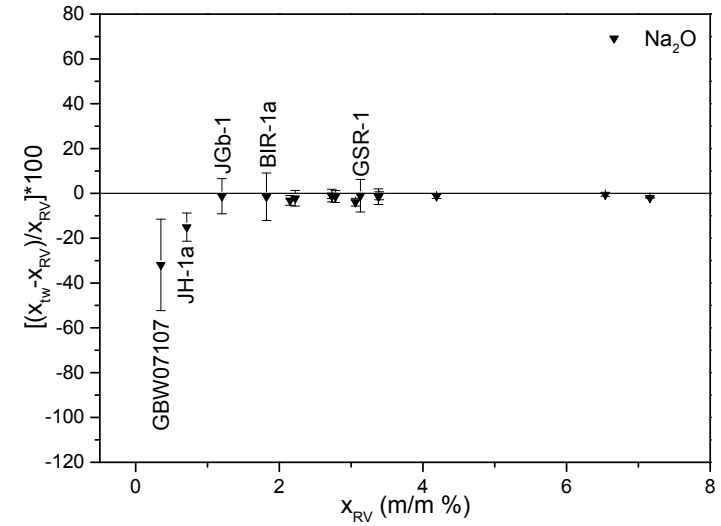


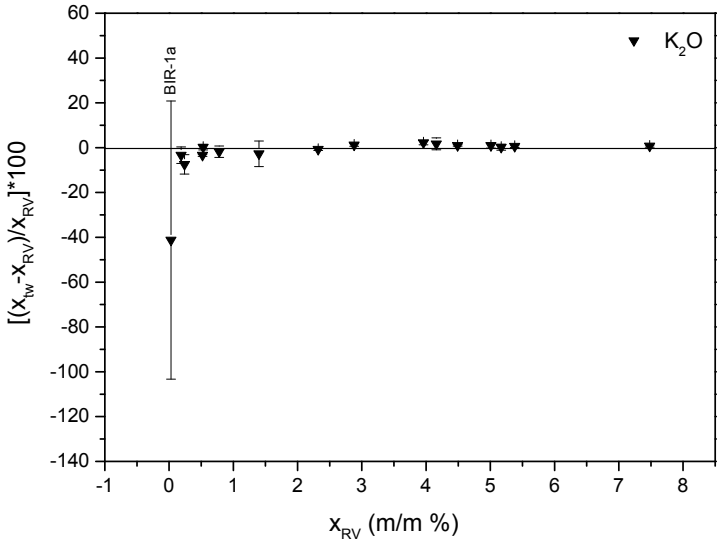

TFe2O3
JG-1a
GSR-1
AC-E
GBW07110
GBW07107
JB-1a
BIR-1a
[(xtw-xRV)/xRV]*100
xRV (m/m %)

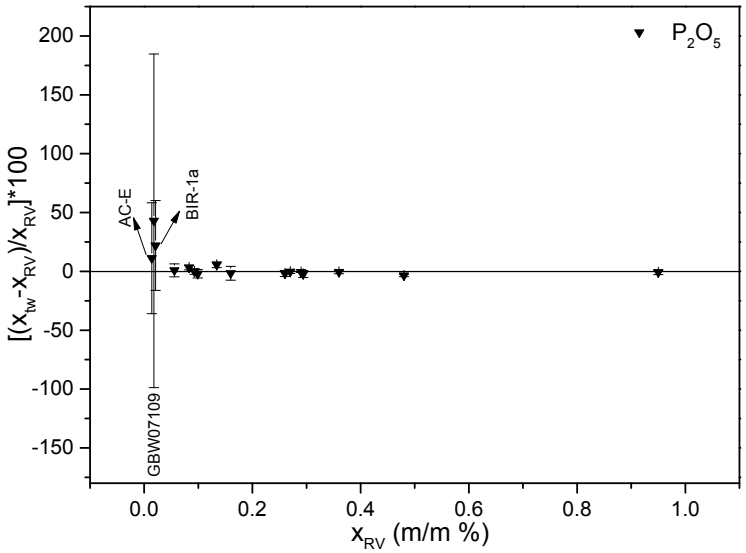

MnO
GBW07107
GSP-2
GSR-1
JG-1a
GBW07110
SAM688
GSR-3
[(xtw-xRV)/xRV]*100
xRV (m/m %)

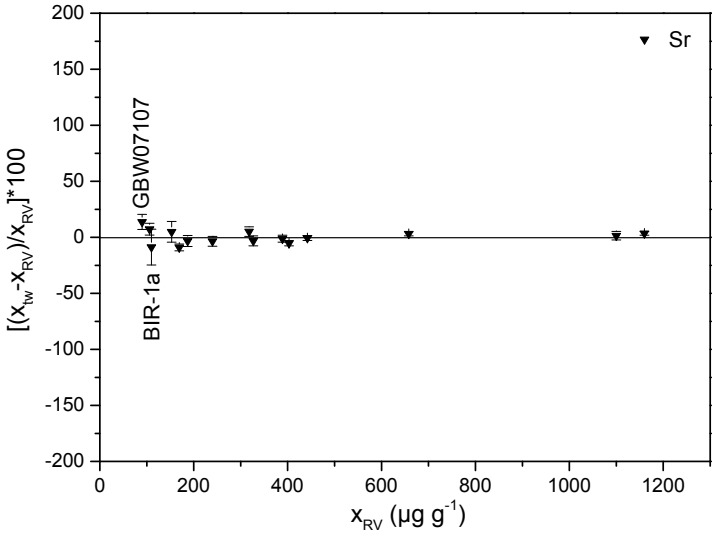

MgO
GSR-1
GBW07109
JG-1a
AC-E
$[(x_{tw}-x_{RV})/x_{RV}]*100$
x_{RV} (m/m %)


CaO
GBW07107
AC-E
GBW07109
$[(x_{tw}-x_{RV})/x_{RV}]*100$
x_{RV} (m/m %)


Na2O
GBW07107
JH-1a
JGb-1
BIR-1a
GSR-1
[(xtw-xRV)/xRV]*100
xRV (m/m %)


K2O
BIR-1a
[(xtw-xRV)/xRV]*100
xRV (m/m %)


P2O5
AC-E
BIR-1a
GBW07109
[(xtw-xRV)/xRV]*100
xRV (m/m %)


Sr
GBW07107
BIR-1a
[(xtw-xRV)/xRV]*100
xRV (µg g-1)

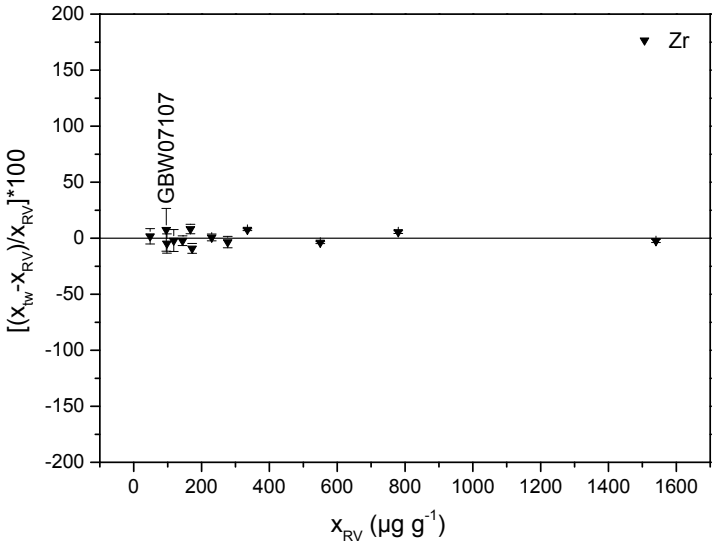

Zr
GBW07107
200
150
100
50
0
-50
-100
-150
-200
0
200
400
600
800
1000
1200
1400
1600
[(x_tw-x_RV)/x_RV]*100
x_RV (μg g^-1)

Figure S7. Instrumental conditions of µ-XRF instrument (M4 Tornado).

MAP INFORMATION

Mapping parameters		
Width:	635	pixel
	31.739	mm
Height:	614	pixel
	30.686	mm
Pixel Size:	50	µm
Total number of pixel:	389890	pixel
Acquisition parameters		
Frame count:	1	
Pixel time:	100	ms/pixel
Measure time:	9:55 h	
Overall time:	12:16 h	
Stage speed:	500	µm/s
Stage position (X,Y,Z):	101.815;63.459;117.015	mm
Tube parameter		
High voltage:	50	kV
Anode current:	600	µA
Filter:	Al 640 µm	
Optic:	Lens	
Collimator diameter:	0	
SpotSize:	20	
Chamber at:	Air 2	mbar
Flow rate:	---	l/min
Anode:	Rh	
Detector parameters		
Selected detectors:	1,2	
Max. pulse throughput:	275000	cps

Table S1 Details of CRMs used for the calibration and validation of the methods.

Provider	CRMs used for the calibration	Rock type	CRMs used for the validation	Rock type
ANRT[a]	DR-N	Diorite		
	FK-N	Feldspar		
	GS-N	Granite		
	UB-N	Serpentinite		
CRPG[b]	GA	Granite		
	Mica-Fe	Biotite		
	Mica-Mg	Phlogopite		
GIT-IWG[c]	AL-I	Albite	AC-E	Granite
	BE-N	Basalt		
	MA-N	Granite		
	MDO-G	Trachyte		
	PM-S	Gabbro		
	WS-E	Diabase		
CGL[d]	MGL-OShBO	Alkaline granite		
GSJ[e]	JA-1	Andesite	JB-1a	Basalt
	JA-2	Andesite	JB-3	Basalt
	JA-3	Andesite	JG-1a	Granodiorite
	JB-1b	Basalt	JGb-1	Gabbro
	JB-2	Basalt	JH-1a	Hornblendite
	JB-2a	Basalt		
	JB-3a	Basalt		
	JF-1	Feldspar		
	JG-2	Granite		
	JG-3	Granodiorite		
	JGb-2	Gabbro		
	JP-1	Peridotite		
	JR-1	Rhyolite		
IGGE[f]	GBW07101	Ultramafic rock	GBW07103 (GSR-1)	Granite
	GBW07102	Ultramafic rock	GBW07105 (GSR-3)	Basalt
	GBW07104	Andesite	GBW07107	Shale
	GBW07106	Sandstone	GBW07109	Syenite
	GBW07111	Diorite	GBW07110	Trachyte
	GBW07112	Gabbro		
	GBW07121	Granite-gneiss		
	GBW07122	Hornblendite		
	GBW07123	Diabase		

	GBW07310	Stream sediment		
	GBW07311	Stream sediment		
	GBW07312	Stream sediment		
USGS[g]	BCR-2	Basalt	AGV-2	Andesite
	DNC-1a	Diabase	BHVO-2	Basalt
	DST-2b	Dunite	BIR-1a	Basalt
	RGM-2*	Rhyolite	GSP-2	Granodiorite
	SBC-1*	Shale		
	SDC-1	Mica schist		
	W-2a	Diabase		
NIST[h]			SAM688	Basalt

[a] ANRT is Association Nationale de la Recherche Technique;

[b] CRPG is Centre de Recherches Pétrographiques et Géochimiques;

[c] GIT-IWG is Groupe International de Travail–International Working Group;

[d] CGL is Central Geological Laboratory of Mongolia;

[e] GSJ is Geological Survey of Japan;

[f] IGGE is Institute of Geophysical and Geochemical Exploration;

[g] USGS is United States Geological Survey;

[h] NIST is US National Institute of Standards and Technology.

Table S2 Typical operating parameters of ICP-OES

Instrumentation	Setting
IRIS Advantage ICP-OES	
RF power	1150 W
Cooling gas	15 L min^{-1}
Auxiliary gas	0.5 L min^{-1}
Nebulizing gas pressure	25 PSI
Exposure time	Low wave: 15 s
	High wave: 8 s
Sample uptake rate	1.85 mL min^{-1}
Emission lines measured (nm)	
Analytes	Si (251.611)
	Ti (336.121)
	Al (308.215)
	Fe (259.940)
	Mn (257.610)
	Mg (285.213)
	Ca (317.933)
	Na (589.592)
	K (766.491)
	P (213.617)
	Ni (231.604)
	Sr (346.446)
	Zr (343.823)

Table S3 Procedure used in the proposed swirl procedure

1	heat the Pt–Au crucible weighed the sample on the M4 fluxer
2	clamp the Pt–Au mold with a platinum coated tong and preheat 30 seconds in the fire
3	place the Pt–Au mold in the blow hole of the fan unit
4	the instrument pours the molten liquid into the preheated Pt–Au mold
5	quickly raise the arm of the instrument and clip the Pt–Au mold contained the melt
6	quickly swirled the Pt–Au mold with the platinum coated tong until the circular disk was formed

Table S4 Instrumental conditions of the wavelength dispersive X-ray fluorescence spectrometry

Element	Line	Crystal	Collimator (µm)	Detector	Tube filter	X-ray tube		Angle (2θ)			Counting Time (s)	PHD[a]	
						kV	mA	Line	Bg1[b]	Bg2		LL[c]	UL[d]
Major													
SiO_2	Si Kα	PE 002	150	Flow	None	30	120	109.083	-2.332	2.417	60	28	62
TiO_2	Ti Kα	LiF 200	300	Flow	None	40	90	86.119	-0.910		50	27	58
Al_2O_3	Al Kα	PE 002	550	Flow	None	30	120	144.782	-1.434		60	24	63
TFe_2O_3[e]	Fe Kα	LiF 200	300	Flow	Al (200 µm)	60	60	57.510	1.312		50	18	61
MnO	Mn Kα	LiF 200	300	Flow	None	60	60	62.961	0.641		50	15	55
MgO	Mg Kα	PX1	300	Flow	None	30	120	23.236	-2.327	2.421	60	24	63
CaO	Ca Kα	LiF 200	150	Flow	None	30	120	113.067	1.485		60	27	57
Na_2O	Na Kα	PX1	700	Flow	None	30	120	28.065	-2.151	2.389	60	24	61
K_2O	K Kα	LiF 200	300	Flow	None	30	120	136.663	1.761		50	27	56
P_2O_5	P Kα	Ge 111	300	Flow	None	30	120	141.146	2.656		50	28	58
Minor													
Rh	Rh Kα-C[f]	LiF 200	150	Scint.	None	60	60	18.370			10	26	71
Ni	Ni Kα	LiF 200	150	Flow	Al (200 µm)	60	60	48.656	0.875		60	20	61
Sr	Sr Kα	LiF 200	150	Scint.	Al (200 µm)	60	60	25.103	-0.915	0.880	60	27	70
Zr	Zr Kα	LiF 200	150	Scint.	Al (200 µm)	60	60	22.483	-0.932	0.998	60	24	70

The PANalytical WD-XRF instrument was equipped with a 4 kW Rh anode Super Sharp X-ray Tube and the SuperQ 4.0 software. The mask selected in this experiment was 27 mm in diameter and the temperature of the monochromator chamber was maintained at vacuum and 35.0 ℃. The PR gas flow rate was 1.0 L $hour^{-1}$. The sample measurement process was maintained at the 'spinner on' state (sample spinning was used for all the samples).

[a] PHD = pulse height distribution; [b] Bg = background; [c] LL = lower limit; [d] UL = upper limit; Flow = gas flow proportional detector; Scint. = scintillation detector; [e] TFe_2O_3 = total iron oxide as Fe_2O_3; [f] Kα-C = Kα-compton scattered tube line.

Table S5 Data for the range of standard sample composition, root means square, K-factor, lower limits of detection, and line overlap correction.

Number	Element	Range of standard sample composition	RMS	K-factor	LLD[a] (μg g^{-1})	Line overlap correction
	Major	(m/m %[b])	(m/m %)			
1	SiO_2	34.34–90.36	0.34	0.047	639.3	
2	TiO_2	0.004–7.69	0.027	0.026	239.2	Ba Lα
3	Al_2O_3	0.21–23.48	0.18	0.048	1430.5	Br Lα, Ba Lα, Cr Kβ
4	TFe_2O_3[c]	0.075–26.45	0.11	0.041	100.5	Mn Kβ
5	MnO	0.001–0.36	0.0037	0.0075	92.2	V Kβ
6	MgO	0.006–49.40	0.16	0.049	386.9	Ca Kα
7	CaO	0.08–14.10	0.073	0.034	319.5	
8	Na_2O	0.008–10.59	0.11	0.059	576.6	Zn Lβ
9	K_2O	0.003–12.81	0.071	0.033	171.8	
10	P_2O_5	0.002–1.39	0.010	0.020	179.4	
	Minor	(μg g^{-1})	(μg g^{-1})			
11	Ni	1–3780	0.0034	0.0095	27.5	
12	Sr	2.3–1370	0.0018	0.0045	95.4	
13	Zr	1–800	0.00097	0.0028	18.2	Sr Kβ

[a] LLD is the lower limits of detection; [b] m/m % is the mass percentage; [c] TFe_2O_3, total iron oxide as ferric iron.

Table S6 Results of GRS-1 and GSR-3 measured using XRF, ICP-OES (fusion) and ICP-OES (acid attack) (n=6[a])

	XRF		**ICP-OES (alkali fusion)**		**ICP-OES (acid attack)**		**Certified values**	
Element	GSR-1	GSR-3	GSR-1	GSR-3	GSR-1	GSR-3	GSR-1	GSR-3
	Mean ± 1s	Mean ± 1s	Mean ± 1s	Mean ± 1s	Mean ± 1s	Mean ± 1s	Mean ± 1s	Mean ± 1s
Major (m/m %)								
SiO_2	72.94 ± 0.17	44.46 ± 0.22	72.68 ± 0.31	44.51 ± 0.26	NA[b]	NA	72.83 ± 0.15	44.64 ± 0.16
TiO_2	0.278 ± 0.012	2.38 ± 0.02	0.301 ± 0.010	2.35 ± 0.06	0.281 ± 0.009	2.32 ± 0.06	0.287 ± 0.017	2.36 ± 0.10
Al_2O_3	13.42 ± 0.16	13.89 ± 0.11	13.34 ± 0.21	13.7 ± 0.18	13.29 ± 0.20	13.82 ± 0.22	13.40 ± 0.11	13.83 ± 0.20
TFe_2O_3	2.15 ± 0.07	13.45 ± 0.14	2.12 ± 0.05	13.34 ± 0.18	2.23 ± 0.08	13.26 ± 0.21	2.14 ± 0.08	13.40 ± 0.29
MnO	0.060 ± 0.002	0.171 ± 0.003	0.061 ± 0.001	0.174 ± 0.004	0.057 ± 0.002	0.165 ± 0.005	0.060 ± 0.002	0.169 ± 0.012
MgO	0.43 ± 0.03	7.73 ± 0.08	0.44 ± 0.03	7.74 ± 0.08	0.41 ± 0.04	7.68 ± 0.07	0.42 ± 0.05	7.77 ± 0.26
CaO	1.57 ± 0.04	8.81 ± 0.06	1.56 ± 0.04	8.79 ± 0.12	1.53 ± 0.05	8.73 ± 0.09	1.55 ± 0.07	8.81 ± 0.14
Na_2O	3.08 ± 0.11	3.33 ± 0.12	3.1 ± 0.06	3.41 ± 0.09	3.20 ± 0.08	3.32 ± 0.08	3.13 ± 0.09	3.38 ± 0.07
K_2O	5.06 ± 0.06	2.30 ± 0.02	5.04 ± 0.08	2.38 ± 0.05	4.97 ± 0.09	2.26 ± 0.06	5.01 ± 0.10	2.32 ± 0.08
P_2O_5	0.093 ± 0.002	0.943 ± 0.019	0.097 ± 0.007	0.956 ± 0.04	0.091 ± 0.007	0.976 ± 0.03	0.093 ± 0.005	0.946 ± 0.044
LOI	0.78 ± 0.07	2.40 ± 0.04					0.69 ± 0.09	2.24 ± 0.14
TOTAL	99.87	99.85					99.61	99.87
Minor (μg g^{-1})								
Ni	–[c]	147.1 ± 9.2	–	142.0 ± 7	–	136.2 ± 6	2.3 ± 1.2	140 ± 11
Sr	113.7 ± 5.5	1115 ± 42	112.0 ± 4	1074 ± 36	108.0 ± 6	1113 ± 34	106.0 ± 9	1100 ± 100
Zr	180.7 ± 7.0	267.3 ± 14.1	172.8 ± 12	282.4 ± 18	163.6 ± 9	272.0 ± 15	167.0 ± 14	277 ± 30

The recommed values of GRS-1 and GSR-3 are obtained from Xie, 1989 [1]; [a] n is the number of replicates; [b] NA is not applicable; [c] no detected

Table S7 Method detection limit (µg g^{-1}) for various instruments (n=10)

	XRF	ICP-OES* (Acid digestion)	ICP-OES (Alkaline fusion)
Major			
SiO_2	639.3	—	30.0
TiO_2	239.2	5.0	10.0
Al_2O_3	1430.5	20.0	66.7
TFe_2O_3[c]	100.5	10.0	16.7
MnO	92.2	0.3	1.0
MgO	386.9	6.7	13.3
CaO	319.5	25.0	53.3
Na_2O	576.6	21.7	108.3
K_2O	171.8	10.0	36.7
P_2O_5	179.4	56.7	91.7
Minor			
Ni	27.5	6.7	15.0
Sr	95.4	10.0	18.3
Zr	18.2	13.3	21.7

***** LOD calculation of ICP-OES in agreement with Gold Book of IUPAC (mean of blanks + 3 times the standard deviation).

Table S8 Mean of results of three replicate samples analysis (± 1s) of reference materials (this work) compared to recommended values (RV), as issued by their producers, plus and minus the Horwitz expression interval (Hc). Missing data refer to results less than the detection limits or to unknown values (n=3[a]).

	AC-E			**JB-1a**			**JB-3**			**JG-1a**		
Element	**Mean ± 1*s***	***U***	**RV ± H_c**	**Mean ± 1*s***	***U***	**RV ± H_c**	**Mean ± 1*s***	***U***	**RV ± H_c**	**Mean ± 1*s***	***U***	**RV ± H_c**
Major (m/m %)												
SiO_2	70.42 ± 0.14	0.36	70.35 ± 0.74	52.27 ± 0.32	0.49	52.41 ± 0.58	50.89 ± 0.22	0.41	50.96 ± 0.56	72.43 ± 0.18	0.38	72.30 ± 0.76
TiO_2	0.101 ± 0.005	0.056	0.110 ± 0.003	1.25 ± 0.03	0.065	1.28 ± 0.03	1.42 ± 0.01	0.057	1.44 ± 0.03	0.245 ± 0.008	0.05	0.250 ± 0.006
Al_2O_3	14.73 ± 0.06	0.17	14.70 ± 0.20	14.41 ± 0.11	0.2	14.45 ± 0.19	17.27 ± 0.11	0.2	17.20 ± 0.22	14.20 ± 0.10	0.19	14.30 ± 0.19
TFe_2O_3	2.54 ± 0.08	0.27	2.53 ± 0.04	8.91 ± 0.02	0.33	9.05 ± 0.13	11.97 ± 0.03	0.33	11.82 ± 0.16	2.09 ± 0.02	0.33	2.00 ± 0.04
MnO	0.060 ± 0.002	0.026	0.058 ± 0.002	0.144 ± 0.003	0.028	0.148 ± 0.004	0.179 ± 0.002	0.027	0.177 ± 0.005	0.061 ± 0.003	0.028	0.057 ± 0.002
MgO	*-0.024 ± 0.020*	*0.35*	0.03 ± 0.001	7.90 ± 0.14	0.38	7.83 ± 0.11	5.21 ± 0.09	0.36	5.19 ± 0.08	0.690 ± 0.023	0.35	0.69 ± 0.014
CaO	0.334 ± 0.007	0.094	0.34 ± 0.008	9.40 ± 0.07	0.13	9.31 ± 0.13	9.75 ± 0.07	0.12	9.79 ± 0.14	2.16 ± 0.01	0.1	2.13 ± 0.04
Na_2O	6.50 ± 0.05	0.11	6.54 ± 0.10	2.70 ± 0.08	0.13	2.73 ± 0.05	2.70 ± 0.03	0.11	2.73 ± 0.05	3.35 ± 0.06	0.12	3.39 ± 0.06
K_2O	4.54 ± 0.01	0.15	4.49 ± 0.07	1.36 ± 0.08	0.16	1.40 ± 0.03	0.766 ± 0.02	0.13	0.780 ± 0.016	4.05 ± 0.04	0.13	3.96 ± 0.06
P_2O_5	0.016 ± 0.007	0.044	0.014 ± 0.001	0.255 ± 0.007	0.044	0.26 ± 0.006	0.287 ± 0.009	0.045	0.294 ± 0.007	0.086 ± 0.002	0.044	0.083 ± 0.002
LOI[b]	0.29 ± 0.07		0.37 ± 0.12	1.92 ± 0.06		2.07	-0.39 ± 0.03		0.50	0.67 ± 0.06		0.5
TOTAL	99.51		99.53	100.51		98.87	100.06		100.88	100.03		99.71
Minor (µg g^{-1})												
Ni	*38.5 ± 41.4*	*81.7*	1.5 ± 0.1	134.8 ± 6.5	66.6	139 ± 5.3	*44.5 ± 25.7*	*72.5*	36.2 ± 1.7	ND[c]		6.91 ± 0.4
Sr	ND		3 ± 0.2	439.2 ± 9.7	16.7	442 ± 14.1	381.6 ± 9.5	16.6	403 ± 13.1	180.9 ± 9.2	16.4	187 ± 6.8
Zr	803.6 ± 13.2	24.8	780 ± 22.9	140.7 ± 6.2	20.9	144 ± 5.5	93.2 ± 8.4	21.9	97.8 ± 3.9	115.6 ± 11.5	23.7	118 ± 4.6
	JGb-1			**JH-1a**			**GSR-1**			**GSR-3**		
Element	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**
Major (m/m %)												
SiO_2	43.58 ± 0.32	0.49	43.66 ± 0.49	48.01 ± 0.18	0.38	48.18 ± 0.54	72.94 ± 0.17	0.37	72.83 ± 0.76	44.46 ± 0.22	0.41	44.64 ± 0.50
TiO_2	1.58 ± 0.01	0.056	1.60 ± 0.03	0.678 ± 0.018	0.052	0.670 ± 0.014	0.278 ± 0.012	0.045	0.290 ± 0.007	2.38 ± 0.02	0.045	2.36 ± 0.04
Al_2O_3	17.63 ± 0.17	0.25	17.49 ± 0.23	5.74 ± 0.13	0.21	5.66 ± 0.09	13.42 ± 0.16	0.24	13.40 ± 0.18	13.89 ± 0.11	0.2	13.83 ± 0.19
TFe_2O_3	15.12 ± 0.08	0.3	15.06 ± 0.20	10.34 ± 0.05	0.32	10.27 ± 0.14	2.15 ± 0.07	0.22	2.14 ± 0.04	13.45 ± 0.14	0.26	13.40 ± 0.18
MnO	0.187 ± 0.002	0.027	0.189 ± 0.005	0.186 ± 0.003	0.028	0.19 ± 0.005	0.060 ± 0.002	0.018	0.06 ± 0.002	0.171 ± 0.003	0.018	0.170 ± 0.004
MgO	7.80 ± 0.03	0.35	7.85 ± 0.12	16.69 ± 0.09	0.36	16.73 ± 0.22	0.43 ± 0.03	0.36	0.42 ± 0.01	7.73 ± 0.08	0.36	7.77 ± 0.11
CaO	11.82 ± 0.08	0.13	11.90 ± 0.16	15.02 ± 0.03	0.09	15.02 ± 0.20	1.57 ± 0.04	0.09	1.55 ± 0.03	8.81 ± 0.06	0.11	8.81 ± 0.13
Na_2O	1.18 ± 0.09	0.15	1.20 ± 0.02	0.603 ± 0.045	0.11	0.710 ± 0.015	3.08 ± 0.11	0.28	3.13 ± 0.05	3.33 ± 0.12	0.17	3.38 ± 0.06
K_2O	0.222 ± 0.010	0.14	0.240 ± 0.006	0.531 ± 0.006	0.12	0.530 ± 0.012	5.06 ± 0.06	0.14	5.01 ± 0.08	2.30 ± 0.02	0.18	2.32 ± 0.04

P_2O_5	0.057 ± 0.003	0.043	0.056 ± 0.002	0.097 ± 0.004	0.044	0.099 ± 0.003	0.093 ± 0.002	0.043	0.093 ± 0.003	0.943 ± 0.019	0.048	0.950 ± 0.019
LOI	0.64 ± 0.08		0.85	2.13 ± 0.10		NA[d]	0.78 ± 0.07		0.69 ± 0.09	2.40 ± 0.04		2.24 ± 0.14
TOTAL	99.82		100.1	100.03		NA	99.87		99.61	99.85		99.87
Minor (µg g^{-1})												
Ni	*30.5 ± 11.5*	*67.5*	25.4 ± 1.2	*58.3 ± 13.3*	*67.9*	58.2 ± 2.5	ND		2 ± 0.1	147.1 ± 9.2	67	140 ± 5.3
Sr	316.5 ± 14.5	20.8	327 ±10.9	160.5 ± 14.1	20.5	153 ± 5.7	113.7 ± 5.5	14	106 ± 4.2	1115 ± 42	49.8	1100 ± 30.7
Zr	*29.8 ± 9.5*	*22.4*	32.8 ± 1.6	49.1 ± 3.3	19.9	48.3 ± 2.2	180.7 ± 7.0	21.2	167 ± 6.2	267.3 ± 14.1	25.5	277 ± 9.5
	GBW07107			**GBW07109**			**GBW07110**			**AGV-2**		
Element	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**
Major (m/m %)												
SiO_2	59.09 ± 0.30	0.47	59.23 ± 0.64	54.38 ± 0.16	0.37	54.48 ± 0.60	63.13 ± 0.21	0.4	63.06 ± 0.68	59.45 ± 0.13	0.35	59.30 ± 0.64
TiO_2	0.650 ± 0.010	0.054	0.660 ± 0.014	0.462 ± 0.016	0.057	0.480 ± 0.011	0.793 ± 0.007	0.054	0.80 ± 0.016	1.04 ± 0.02	0.056	1.05 ± 0.02
Al_2O_3	18.89 ± 0.18	0.26	18.82 ± 0.24	17.74 ± 0.11	0.2	17.72 ± 0.23	16.14 ± 0.07	0.18	16.10 ± 0.22	16.99 ± 0.13	0.22	16.91 ± 0.22
TFe_2O_3	7.76 ± 0.05	0.33	7.60 ± 0.11	7.47 ± 0.03	0.32	7.41 ± 0.11	4.84 ± 0.16	0.34	4.72 ± 0.07	6.79 ± 0.05	0.33	6.69 ± 0.10
MnO	0.025 ± 0.003	0.028	0.020 ± 0.001	0.122 ± 0.002	0.027	0.120 ± 0.003	0.091 ± 0.002	0.027	0.089 ± 0.002	0.099 ± 0.002	0.024	0.10 ± 0.003
MgO	1.96 ± 0.04	0.35	2.01 ± 0.04	0.62 ± 0.04	0.35	0.65 ± 0.01	0.78 ± 0.02	0.35	0.840 ± 0.017	1.80 ± 0.02	0.35	1.79 ± 0.03
CaO	0.594 ± 0.048	0.1	0.60 ± 0.01	1.34 ± 0.02	0.1	1.39 ± 0.03	2.49 ± 0.03	0.1	2.47 ± 0.04	5.23 ± 0.01	0.1	5.20 ± 0.08
Na_2O	0.238 ± 0.071	0.13	0.350 ± 0.008	7.02 ± 0.01	0.1	7.16 ± 0.11	2.94 ± 0.05	0.12	3.06 ± 0.05	4.14 ± 0.04	0.11	4.19 ± 0.07
K_2O	4.23 ± 0.11	0.18	4.16 ± 0.07	7.53 ± 0.04	0.15	7.48 ± 0.11	5.18 ± 0.07	0.15	5.17 ± 0.08	2.92 ± 0.02	0.14	2.88 ± 0.05
P_2O_5	0.158 ± 0.009	0.045	0.160 ± 0.004	0.026 ± 0.026	0.052	0.018 ± 0.001	0.358 ± 0.006	0.044	0.360 ± 0.008	0.463 ± 0.005	0.044	0.480 ± 0.011
LOI	6.19 ± 0.07		5.97 ± 0.55	2.81 ± 0.01		NA	2.79 ± 0.02		NA	1.00 ± 0.06		1.05
TOTAL	99.78		99.58	99.52		NA	99.53		NA	99.92		99.7
Minor (µg g^{-1})												
Ni	ND		37 ± 1.7	ND		2 ± 0.1	ND		13 ± 0.7	ND		19 ± 1.0
Sr	102.4 ± 6.1	14.2	90 ± 3.7	1200.8 ± 19.0	25.2	1160 ± 32.1	334.3 ± 13.6	20	318 ± 10.7	678.6 ± 12.2	18.7	658 ± 19.8
Zr	103.2 ± 18.3	28.8	96 ± 3.9	1502.4 ± 21.9	32	1540 ± 40.8	360.6 ± 2.8	19.8	335 ± 11.2	231.6 ± 7.0	21.2	230 ± 8.1
	BHVO-2			**BIR-1a**			**GSP-2**			**SAM688**		
Element	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**	**Mean ± 1s**	***U***	**RV ± H_c**
Major (m/m %)												
SiO_2	50.12 ± 0.23	0.42	49.90 ± 0.55	47.83 ± 0.22	0.41	47.96 ± 0.54	66.74 ± 0.25	0.43	66.60 ± 0.71	48.27 ± 0.08	0.33	48.40 ± 0.54
TiO_2	2.78 ± 0.01	0.057	2.73 ± 0.05	0.969 ± 0.014	0.053	0.960 ± 0.019	0.657 ± 0.014	0.049	0.660 ± 0.014	1.18 ± 0.01	0.053	1.17 ± 0.02
Al_2O_3	13.56 ± 0.12	0.21	13.50 ± 0.18	15.59 ± 0.03	0.16	15.50 ± 0.21	14.88 ± 0.11	0.2	14.90 ± 0.20	17.47 ± 0.09	0.19	17.36 ± 0.23
TFe_2O_3	12.40 ± 0.04	0.33	12.30 ± 0.17	11.52 ± 0.07	0.34	11.30 ± 0.16	4.92 ± 0.01	0.32	4.90 ± 0.08	10.39 ± 0.04	0.31	10.35 ± 0.15

MnO	0.171 ± 0.002	0.028	0.167 ± 0.004	0.173 ± 0.003	0.026	0.175 ± 0.005	0.043 ± 0.002	0.026	0.041 ± 0.001	0.163 ± 0.006	0.025	0.167 ± 0.004
MgO	7.24 ± 0.03	0.35	7.23 ± 0.11	9.65 ± 0.05	0.35	9.70 ± 0.14	0.94 ± 0.02	0.35	0.96 ± 0.02	8.45 ± 0.05	0.35	8.40 ± 0.12
CaO	11.44 ± 0.03	0.1	11.40 ± 0.16	13.32 ± 0.18	0.23	13.30 ± 0.18	2.10 ± 0.03	0.09	2.10 ± 0.04	12.15 ± 0.02	0.1	12.17 ± 0.17
Na_2O	2.17 ± 0.08	0.13	2.22 ± 0.04	1.79 ± 0.19	0.24	1.82 ± 0.03	2.74 ± 0.07	0.13	2.78 ± 0.05	2.08 ± 0.05	0.11	2.15 ± 0.04
K_2O	0.502 ± 0.003	0.15	0.520 ± 0.011	0.018 ± 0.019	0.13	0.030 ± 0.001	5.42 ± 0.03	0.14	5.38 ± 0.08	0.181 ± 0.007	0.14	0.187 ± 0.005
P_2O_5	0.269 ± 0.004	0.044	0.270 ± 0.007	0.026 ± 0.008	0.044	0.021 ± 0.001	0.288 ± 0.001	0.044	0.290 ± 0.007	0.141 ± 0.003	0.044	0.134 ± 0.004
LOI	-0.55 ± 0.03		-0.54	-0.52 ± 0.05		-0.54	0.88 ± 0.11		0.8	-0.24 ± 0.01		NA
TOTAL	100.1		99.53	100.37		100.23	99.6		99.41	100.24		NA
Minor ($\mu g\ g^{-1}$)												
Ni	104.0 ± 0.9	66.2	119 ± 4.6	154.8 ± 13.3	67.9	170 ± 6.3	ND		17 ± 0.9	144.1 ± 7.5	66.7	150 ± 5.6
Sr	384.2 ± 12.0	18.6	389 ± 12.7	*100.4 ± 17.6*	*23.8*	110 ± 4.3	231.4 ± 10.6	17.4	240 ± 8.4	154.0 ± 5.2	13.8	169.2 ± 6.3
Zr	156.4 ± 7.6	21.4	172 ± 6.3	*25.1 ± 8.1*	*21.7*	18 ± 0.9	528.4 ± 4.7	20.3	550 ± 17.0	59.3 ± 3.3	19.6	NA

[a] n is the number of replicates; the replicates of GRS-1 and GSR-3 are six, respectively; [b] Standard deviation are used for the LOI of Recommended values of RMs; some of RMs only mean values of LOI are provided by the author, including: J JB-3, JB-1a, JG-1a, JGB-1, AGV-2, BHVO-2, BIR-1a and GSP-2 (Table S10). [c] ND is no determined; [d] NA is no available data; Recommended values of RMs of GIT-IWG, GSJ, and IGGE are obtained from these literature, including Govindaraju (1995) (AC-E) [2], Imai (1995) (JB-1a, JB-3, JG-1a, JGb-1) [3], Imai (1998) (JH-1a) [4], Xie (1989) (GBW07103, GBW07105, GBW07107) [1], and Wang (2013) (GBW07109, GBW07110) [5], respectively. Recommended values of RMs of USGS (AGV-2, BHVO-2, BIR-1a, GSP-2) and SAM688 (NIST) are from their certificates. ***U*** is the expanded uncertainty at 95% confidence level.

Table S9 Z-score results for major and minor elements determination by proposed procedure.

	AC-E	JB-1a	JB-3	JG-1a	JGb-1	JH-1a	GSR-1	GSR-3	GBW07107
SiO_2	0.09	-0.24	-0.12	0.17	-0.15	-0.31	0.15	-0.36	-0.22
TiO_2	***-2.85***	-1.42	-0.62	-0.75	-0.60	0.55	-1.65	0.40	-0.73
Al_2O_3	0.17	-0.22	0.30	-0.54	0.60	0.96	0.09	0.30	0.29
TFe_2O_3	0.23	-1.08	0.94	2.50	0.28	0.51	0.26	0.26	1.40
MnO	0.88	-1.00	0.52	2.41	-0.38	-0.89	0.18	0.56	***6.98***
MgO	***-53.59***	0.58	0.29	0.01	-0.41	-0.18	1.04	-0.39	-1.38
CaO	-0.72	0.65	-0.26	0.88	-0.49	0.00	0.57	0.00	-0.47
Na_2O	-0.38	-0.58	-0.66	-0.63	-0.65	***-7.16***	-0.62	-0.87	***-13.63***
K_2O	0.63	-1.43	-0.86	1.35	***-3.00***	0.09	0.62	-0.41	1.06
P_2O_5	2.94	-0.73	-0.96	1.12	0.29	-0.71	-0.05	-0.37	-0.60
Ni	***327.00***	-0.79	4.90	NA	4.08	0.03	NA	1.32	NA
Sr	NA	-0.20	-1.63	-0.90	-0.96	1.31	1.83	0.51	***3.38***
Zr	1.03	-0.60	-1.17	-0.53	-1.93	0.39	***2.22***	-1.02	1.85

	GBW07109	GBW07110	AGV-2	BHVO-2	BIR-1a	GSP-2	SAM688
SiO_2	-0.17	0.10	0.23	0.39	-0.24	0.19	-0.24
TiO_2	-1.69	-0.43	-0.70	1.10	0.47	-0.20	0.38
Al_2O_3	0.10	0.19	0.38	0.33	0.44	-0.10	0.50
TFe_2O_3	0.58	1.61	0.96	0.57	1.40	0.26	0.27
MnO	0.55	0.91	-0.34	0.95	-0.44	1.07	-0.84
MgO	***-2.23***	***-3.29***	0.41	0.06	-0.34	-0.85	0.41
CaO	-2.02	0.46	0.41	0.25	0.09	-0.09	-0.10
Na_2O	-1.34	-2.32	-0.79	-1.24	-0.83	-0.83	-1.76
K_2O	0.49	0.13	0.72	-1.53	***-12.16***	0.42	-1.30
P_2O_5	***11.73***	-0.19	-1.56	-0.10	6.17	-0.25	2.05
Ni	NA	NA	NA	***-3.24***	***-2.42***	NA	-1.04
Sr	1.27	1.53	1.04	-0.38	***-2.22***	-1.02	***-2.44***
Zr	-0.92	2.29	0.19	***-2.47***	***7.62***	-1.27	NA

NA is no available data

Table S10. Loss of ignitions of Recommended values of JB-3, JB-1a, JG-1a, JGB-1, AGV-2, BHVO-2, BIR-1a and GSP-2

Certified reference materials	Loss of ignition	Source
JB-3	0.5	[6]
JB-1a	2.07	[6]
JG-1a	0.5	[7]
JGB-1	0.85	[8]
AGV-2	1.05	[9]
BHVO-2	-0.54	[10]
BIR-1a	-0.54	[11]
GSP-2	0.8	[7]

The LOIs of JH-1a (2.13), GBW07109 (2.81), GBW07110 (2.79), and SAM688 (-0.24) are reported first in our work. The LOI of JB-3 was corrected from 0.5[6] to -0.39 in our work, because the total percentage of major elements (including the LOI) of JB-3 was within the 99.5—100.5% range,[12] i.e., indicating high-quality data in geological research when the value we obtained was adopted. In contrast, the total exceeded 100.5 when the value 0.5 was adopted

Lithium metaborate fusion procedure for ICP-OES: A 30.0 mg sample and 0.30 g lithium metaborate were weighed, mixed thoroughly, transferred into a glassy carbon crucible (10 mL), and fused at 1050 ℃ for 30 minutes in a muffle furnace. The crucible was cooled and the separated bead transferred into a beaker with 30 mL of 10% v/v HNO_3. The solution was continuously stirred with a magnetic stir bar for about 20 minutes for complete dissolution of the bead, then the solutions were made up to 50 mL with 2% v/v HNO_3 and filtered to remove any suspended carbon particles and stored in polyethene bottles.

Acid attack procedure for ICP-OES: 30.0 mg of each sample is weighed into a PTFE vessel, along with 0.5 ml 8 M HNO_3 and 1 ml 28 M HF. Then, the vessel is placed on a hot plate at 140℃, and the solution evaporates next to dryness. Thereafter, 0.5 ml 8 M HNO_3 and 1 ml 28 M HF are added again into the vessel, after covered the lid on the vessel, the vessel is put in the autoclave, placed in an oven and heated to 200℃ for 5 days. After cooling, the vessel taken from the autoclave was placed on the hot plate at 140℃ and the solution again evaporates next to dryness. After that, 2 ml 8 M HNO_3 is added to the vessel, placed into the autoclave and put in to the oven at 150℃ for 1 day. This procedure is repeated once. When the vessel is taken from the autoclave, the solution in the vessel is transferred into 50 mL volumetric flask and made up to the volume with 3% HNO_3 solution.

References:

1. X. Xie, M. Yan, C. Wang, L. Li and H. Shen, *Geostandards Newsletter*, 1989, **13**, 83-179.
2. K. Govindaraju, *Geostandards Newsletter*, 1995, **19**, 1-32.
3. N. Imai, S. Terashima, S. Itoh and A. Ando, *Geostandards Newsletter*, 1995, **19**, 135-213.
4. N. Imai, S. Terashima, S. Itoh and A. Ando, *Geostandards Newsletter*, 1999, **23**, 223-250.
5. G. T. Wang Y., Wang X., Gao Y., Jochum K.P. and Müller W.E.G., *Geological Publishing House(Beijing)*, 2013, 589pp. (in Chinese/English).
6. J. Stix, M. P. Gorton and E. Fontaine, *Geostandards Newsletter*, 1996, **20**, 87-94.
7. Z. Yu, M. D. Norman and P. Robinson, *Geostandards Newsletter*, 2003, **27**, 67-89.
8. A. Herbrich, F. Hauff, K. Hoernle, R. Werner, D. Garbe-Schönberg and S. White, *Geochimica et Cosmochimica Acta*, 2016, **185**, 141-159.
9. M. I. Varas-Reus, C. J. Garrido, C. Marchesi, D. Bosch and K. Hidas, *Geochimica et Cosmochimica Acta*, 2018, **232**, 303-328.
10. G. Zhang, C. Smith-Duque, S. Tang, H. Li, C. Zarikian, S. D'Hondt and F. Inagaki, *Lithos*, 2012, **144-145**, 73-87.
11. F. Wei, J. Prytulak, J. Xu, W. Wei, J. O. S. Hammond and B. Zhao, *Lithos*, 2017, **288-289**, 175-190.
12. R. Gill, *Modern Analytical Geochemistry*, 2014, p 6.