Rapid and precise determination of major and trace elements in CCRMP and USGS geochemical reference samples using femtosecond laser ablation ICP-MS

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Summary

We measured 10 major (SiO_2, TiO_2, Al_2O_3, total Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5) and 32 trace (Sc, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, Th, and U) elements in 16 geochemical reference samples (AGV-1, AGV-2, BCR-1, BCR-2, BHVO-2, BIR-1a, DNC-1a, G-2, GSP-1, GSP-2, MAG-1, QLO-1, RGM-1, RGM-2, SGR-1b, and STM-1) distributed by United States Geological Survey (USGS) and three reference rock samples (SY-2, SY-3, and MRG-1) provided by Canadian Certified Reference Materials Project (CCRMP) using inductively coupled plasma–mass spectrometry coupled with the femtosecond laser ablation sample introduction technique (fsLA-ICP-MS). Before the elemental analysis, fused glass-beads were prepared from the mixture of sample powder and high-purity alkali flux with a mixing ratio of 1:10. The abundances of the major and trace elements were externally calibrated by using glass beads containing the major and trace elements prepared from 17 Geological Survey of Japan (GSJ) geochemical reference samples (JB-1, JB-1a, JB-2, JB-3, JA-1, JA-2, JA-3, JR-1, JR-2, JR-3, JP-1, JGb-1, JGb-2, JG-1a, JG-2, JG-3, and JSy-1). Typical analysis repeatabilities for these geochemical reference samples were better than 3% for Al_2O_3 and Na_2O; <5% for SiO_2, TiO_2, total Fe_2O_3, MnO, MgO, CaO, K_2O, P_2O_5, Zn, Rb, Sr, Zr, Nb, Ba, Nd, and U; <8% for Sc, V, Cr, Co, Y, Cs, La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, and Th; <11% for Ni and Cu. These data clearly demonstrate that high analytical repeatability can be achieved by the fsLA-ICP-MS technique with glass beads made from 0.5 g larger samples.

1. Introduction

Series of geochemical reference samples, such as igneous rocks, sedimentary rocks, sediments, and ores are available from institutes such as the Geological Survey of Japan (GSJ; e.g., Ando et al., 1987), the United States Geological Survey (USGS; e.g., Gladney et al., 1990) and the Canadian Certified Reference Materials Project (CCRMP; e.g., Gladney and Roelandts, 1990). These samples are widely used to evaluate the data quality of elemental analyses including critical and strategic materials.

X-ray fluorescence (XRF) spectroscopy is widely used to determine major and trace elements in rock samples. In this technique, pressed rock powder pellets (e.g., Sugisaki et al., 1981) or fused glass beads (e.g., Norrish and Hutton, 1969) are used for the analysis. A major limitation of XRF spectroscopy is that elemental sensitivity may be inadequate to obtain reliable abundance data for some trace elements, including rare earth elements (REEs). With ICP-MS, elemental sensitivity is better, and reliable abundance data for REEs can be obtained (e.g., Hirata et al., 1988). However, incomplete decomposition of refractory minerals such as chromite, monazite, and zircon may cause systematic errors in abundance data (e.g., Hirata et al., 1988; Imai, 1990). To minimize deterioration of data quality due to mass spectrometric interference or incomplete decomposition of the rock samples, the ICP-MS technique combined with a laser ablation sample introduction technique can be applied to the chemical analysis of rocks. With laser-ablation methods, possible analytical errors due to incomplete digestion can be minimized (e.g., Jarvis and Williams, 1993). Despite success in obtaining better precision in elemental determinations, a precise internal standardization procedure is still required. Abundances of the internal standardization elements (e.g., Si, Ca, or Sr) are measured separately by XRF analysis (e.g., Günther et al., 2001). Thus, the precision and accuracy of the abundance values of the analytes can be affected by the reliability of the abundance data for the internal standardization elements obtained by XRF. In this study, we employed a different internal standardization correction technique. We calibrated the abundance values of the analytes based on internal standardization with Li, obviating the use of internal standardization elements whose abundance values are

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obtained separately by another analytical technique (Kon et al., 2011; Kon and Hirata, 2015).

Combination of the internal standardization protocol using Li and laser ablation using the femtosecond lasers, we then successfully determined abundances of 10 major and 32 trace elements in 18 USGS and three CCRMP geochemical reference samples. The data presented here demonstrate that combining Li normalization and the femtosecond-LA-ICP-MS (fsLA-ICP-MS) technique may be a powerful and rapid analytical tool for simultaneous measurement of major and trace elements in concentrations ranging from ppb to wt.%.

2. Analytical procedure
2.1. Sample preparation

Fused-glass beads were prepared from a mixture of 0.5 g of rock powder and 5 g of lithium tetraborate ($Li_2B_4O_7$, Spectromelt A10) flux. The weighing error in the sample-to-flux mixing ratio was not greater than 0.1%. The mixture was heated to 1200°C for 15 minutes in a 95% Pt−5% Au crucible with an inner diameter of 30 mm, using an automatic high-frequency bead sampler (TK-4100; Tokyo Kagaku Co. Ltd., Japan).

2.2. Instruments and analytical conditions of fsLA-ICP-MS

Elemental analysis was conducted by the combination of quadrupole ICP-MS system (Agilent 7500cx; Agilent Technologies Japan Ltd., Japan) and the femtosecond laser-ablation system developed in-house (Hirata and Kon, 2008) and installed at the GSJ, National Institute of Advanced Industrial Science and Technology, Japan. The femtosecond laser-ablation system incorporates a TiS femtosecond laser (IFRIT; Cyber Laser Inc., Japan) as a 260 nm UV light source (third harmonic generation from NIR fundamental wavelength). In this study, a galvanometric optical scanner was employed to move the ablation points within 10 msec without moving the samples (Yokoyama et al., 2011). Present Galvanometric optics allow laser ablation of a 20 mm x 20 mm area. The laser system was operated using a pit diameter of approximately 20 μm, and the laser ablation used a pulse energy of 10 J/cm², an emission repetition rate of 1000 Hz, and a pulse duration of 150 s. To minimize elemental fractionation during ablation and for effective ablation of the glass beads, the ablation spot was moved 10,000 μm/s using the galvanometric optics. Kon and Hirata (2015) present detailed analysis conditions and data processing.

2.3. Reference samples

Elemental compositions of 16 USGS and three CCRMP geochemical reference samples were determined: basalt (BCR-1, BCR-2, BHVO-2, BIR-1a), andesite (AGV-1, AGV-2), rhyolite (RGM-1, RGM-2), gabbro (MRG-1), dolerite (DNC-1a), granite (G-2, GSP-1, GSP-2), syenite (STM-1, SY-2, SY-3), quartz latite (QLO-1), shale (SGR-1b), and marine sediment (MAG-1). We used a calibration line protocol to calculate abundance values. Calibration curves for the analytes were defined using basalt (JB-1, JB-1a, JB-2, and JB-3), andesite (JA-1, JA-2, and JA-3), rhyolite (JR-1, JR-2, and JR-3), peridotite (JP-1), gabbro (JGb-1 and JGb-2), granite (JG-1a, JG-2, and JG-3), and syenite (JSy-1) geochemical reference samples provided by the GSJ. We defined calibration lines by plotting Li-normalized intensities against recent published values of the GSJ samples. The published values were selected preferentially, first using GeoReM preferred values (Jochum et al., 2005); Shimizu et al., (2011); Dulski (2001); Makishima and Nakamura (1999, 2006); Lu et al. (2007) then GSJ recommended values (Imai et al., 1995, 1999).

3. Results and discussion
3.1. Elemental compositions of the USGS and CCRMP geochemical reference samples

We determined the abundances of the major and trace elements in the 16 USGS and three CCRMP geochemical reference samples. The averaged abundance data with repeatabilities (relative standard deviation, %RSD) are listed in Table 1. The quantitative limit (QL) on each element are also listed in Table 1. Typically, the repeatabilities for the geochemical reference samples were better than 3% for Al_2O_3 and Na_2O; <5% for SiO_2, TiO_2, total Fe_2O_3, MnO, MgO, CaO, K_2O, P_2O_5, Zn, Rb, Sr, Zr, Nb, Ba, Nd, and U; <8% for Sc, V, Cr, Co, Y, Cs, La, Ce, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Pb, and Th; <11% for Ni and Cu.

3.2. Reliability of the analyses

We normalized the measured abundance data of major and trace elements in five USGS geochemical reference samples (AGV-1, AGV-2, BCR-1, BCR-2, and BHVO-2) by the abundance values in the GeoReM compilation (Jochum et al., 2005), and plotted the normalized values (Fig. 1).

The relative deviation ranges of the measured abundance values from the GeoReM values were as follows: Pb, –6.1% to 0.8%; Rb, –3.5% to 0.1%; Cs, –4.0% to 4.9%; Ba, 1.2% to 4.8%; Zr, –1.2% to 3.9%; Hf, 0.8% to 5.0%; Nb, –3.3% to -0.6%; and heavy REEs (HREEs), –10.5% to 4.7% (Fig. 1). For almost all trace elements, including volatile elements and zircon-favoured elements, the composition of these five reference samples were consistent with the GeoReM compilation values (Jochum et al., 2005) within the uncertainty of each, indicating good reliability of our procedure. In particular, the abundances of highly volatile (Pb) and relatively volatile (Rb, Cs, and Ba) elements were expected to be lower than the GeoReM values. This is mainly due to the evaporation loss of volatile elements during the high-temperature preparation procedures for glass bead. Abundances of zircon-favoured elements (Zr, Hf, Nb, and HREEs) might also be lower, possibly recording incomplete decomposition of the zircon grains in the rock samples. The lack of any deficiency in the abundance values of these volatile and zircon-favoured elements therefore demonstrates that reliable abundance data can be obtained by the present approach.

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Table 1. Averaged regression values of the standard samples.

	QL	AGV-1 Avg.	AGV-1 RSD	AGV-2 Avg.	AGV-2 RSD	BCR-1 Avg.	BCR-1 RSD	BCR-2 Avg.	BCR-2 RSD	BHVO-2 Avg.	BHVO-2 RSD	BIR-1a Avg.	BIR-1a RSD	DNC-1a Avg.	DNC-1a RSD	G-2 Avg.	G-2 RSD	GSP-1 Avg.	GSP-1 RSD
(wt.%)																			
SiO_2	16	58.1	0.9%	59.1	0.7%	53.5	1.7%	53.1	1.2%	49.8	1.8%	48.0	2.0%	n.d.		69.4	2.7%	67.3	3.2%
TiO_2	0.029	1.04	1.4%	1.04	1.0%	2.26	3.5%	2.26	3.1%	2.78	3.3%	0.973	2.7%	0.479	3.3%	0.487	3.8%	0.672	4.0%
Al_2O_3	0.82	16.8	1.4%	16.8	0.9%	13.3	1.8%	13.3	1.5%	13.4	1.5%	15.4	2.2%	18.2	2.3%	15.4	2.7%	15.1	2.8%
tFe_2O_3	0.25	6.58	2.6%	6.65	1.9%	13.4	3.8%	13.7	2.7%	12.4	3.6%	11.5	3.4%	9.78	3.9%	2.65	3.6%	4.26	3.1%
MnO	0.012	0.0957	1.6%	0.10	0.9%	0.184	4.1%	0.198	3.5%	0.171	3.8%	0.175	3.8%	0.147	4.4%	0.034	8.6%	0.0409	7.2%
MgO	0.15	1.45	3.7%	1.74	2.7%	3.43	1.8%	3.53	1.2%	7.29	1.4%	9.67	1.4%	10.0	1.8%	0.704	7.3%	0.927	6.0%
CaO	0.13	4.73	2.9%	5.06	2.0%	6.82	3.6%	6.95	3.3%	11.4	2.8%	13.3	2.9%	11.1	3.8%	1.83	3.8%	1.90	3.9%
Na_2O	0.26	4.16	1.3%	4.12	0.9%	3.21	1.4%	3.07	1.2%	2.20	1.9%	1.81	2.9%	1.88	2.7%	4.03	1.8%	2.76	2.2%
K_2O	0.12	2.88	1.6%	2.86	0.8%	1.70	1.8%	1.76	1.8%	0.538	5.0%	n.d.		0.255	12.0%	4.44	2.9%	5.46	3.3%
P_2O_5	0.014	0.501	1.4%	0.482	2.2%	0.374	2.2%	0.364	1.3%	0.276	2.5%	0.0157	12.1%	0.0630	3.9%	0.127	3.8%	0.280	4.2%
(ppm)																			
Sc	4.6	12.1	3.1%	12.8	4.4%	32.1	3.6%	32.6	2.8%	31.4	2.8%	42.5	5.0%	30.1	3.3%	4.56	12.5%	7.21	10.6%
V	8.1	121	2.7%	121	2.7%	414	3.7%	417	3.1%	325	3.6%	332	3.9%	151	5.0%	36.6	7.5%	53.8	6.1%
Cr	25	n.d.		n.d.		n.d.		n.d.		290	3.1%	394	2.9%	283	4.1%	n.d.		n.d.	
Co	1.4	14.6	3.8%	15.1	3.6%	37.3	2.8%	37.6	2.6%	45.7	2.4%	54.2	2.8%	58.4	2.9%	n.d.		5.85	8.1%
Ni	3.3	15.0	6.5%	18.9	7.9%	10.5	14.6%	11.8	11.7%	124	2.3%	181	2.3%	274	2.8%	n.d.		n.d.	
Zn	12	93.0	5.2%	91.2	2.6%	133	3.4%	135	1.9%	106	2.6%	74.1	2.7%	67.3	5.8%	85.2	2.0%	104	2.5%
Rb	9.2	65.6	1.8%	66.3	2.1%	45.7	4.7%	45.2	4.7%	n.d.		n.d.		n.d.		166	3.7%	252	3.9%
Sr	4.9	658	3.1%	663	2.2%	335	4.7%	341	4.1%	401	3.8%	111	4.7%	144	5.4%	469	3.9%	228	2.9%
Y	5.4	18.5	5.0%	19.1	3.7%	34.3	2.6%	34.2	2.5%	25.1	3.5%	15.4	8.2%	16.8	6.4%	10.4	9.6%	25.9	3.2%
Zr	21	228	2.0%	234	1.7%	192	2.6%	191	2.3%	175	1.9%	n.d.		40.2	10.9%	347	4.0%	623	5.2%
Nb	3.9	14.1	3.3%	14.1	2.8%	12.6	4.8%	12.4	4.6%	18.0	2.7%	n.d.		n.d.		12.4	4.8%	26.2	3.0%
Cs	0.45	1.27	7.3%	1.15	6.7%	0.976	10.7%	1.14	10.0%	n.d.		n.d.		n.d.		1.33	5.2%	1.01	6.4%
Ba	20	1260	2.3%	1180	1.6%	712	3.8%	705	3.3%	133	6.1%	n.d.		102	9.0%	1920	2.9%	1320	2.5%
La	3.0	37.8	1.9%	37.8	1.8%	25.5	2.9%	25.3	2.4%	15.5	3.4%	n.d.		n.d.		86.5	4.8%	178	5.3%
Ce	5.9	68.1	2.3%	69.0	1.6%	53.3	2.9%	52.7	2.2%	37.6	2.6%	n.d.		n.d.		159	4.4%	426	5.1%
Pr	0.81	8.36	2.5%	8.19	1.5%	6.94	3.1%	6.90	2.7%	5.45	2.7%	n.d.		n.d.		16.2	4.5%	53.4	5.2%
Nd	3.1	31.3	2.4%	30.4	2.1%	28.9	2.7%	28.8	2.7%	24.6	2.1%	n.d.		n.d.		52.1	4.7%	199	5.5%
Sm	0.77	5.69	3.2%	5.43	1.8%	6.62	2.7%	6.62	2.9%	6.08	2.4%	n.d.		1.39	14.3%	6.93	4.0%	25.3	5.4%
Eu	0.016	1.61	5.5%	1.54	5.0%	2.00	6.7%	1.99	6.0%	2.11	5.6%	0.524	5.2%	0.590	8.1%	1.33	3.5%	2.19	3.9%
Gd	0.81	4.74	2.6%	4.54	4.1%	6.98	3.9%	7.07	2.7%	6.46	2.7%	1.81	12.0%	1.92	11.4%	3.99	5.5%	13.0	4.8%
Tb	0.14	0.641	3.7%	0.621	3.4%	1.05	3.1%	1.06	2.7%	0.943	1.6%	0.373	8.2%	0.393	7.4%	0.461	5.7%	1.26	3.7%
Dy	0.96	3.56	4.3%	3.48	3.5%	6.39	3.0%	6.36	3.3%	5.29	2.8%	2.55	9.5%	2.68	8.4%	2.19	7.2%	5.71	3.2%
Ho	0.22	0.666	4.6%	0.656	5.1%	1.28	3.1%	1.27	3.2%	0.978	3.6%	0.566	9.0%	0.613	6.8%	0.372	10.1%	0.931	3.8%
Er	0.55	1.82	4.7%	1.78	5.7%	3.65	3.8%	3.60	3.5%	2.50	4.9%	1.67	7.5%	1.84	7.8%	0.915	12.1%	2.29	3.2%
Tm	0.086	0.251	6.1%	0.251	6.3%	0.516	4.1%	0.521	3.3%	0.332	5.3%	0.248	7.9%	0.283	5.5%	0.123	12.5%	0.291	2.7%
Yb	0.58	1.63	6.3%	1.65	5.4%	3.37	3.4%	3.39	4.9%	2.03	5.0%	1.67	8.4%	1.92	7.6%	n.d.		1.68	6.1%
Lu	0.095	0.246	5.6%	0.245	6.7%	0.499	3.9%	0.500	3.8%	0.278	6.6%	0.244	9.8%	0.287	8.0%	n.d.		0.239	4.9%
Hf	0.76	5.14	2.1%	5.25	1.9%	5.10	3.3%	5.08	3.5%	4.58	2.3%	n.d.		1.13	13.1%	8.27	3.8%	16.0	4.7%
Pb	1.7	35.2	2.8%	13.3	1.3%	13.6	3.1%	10.3	3.7%	n.d.		3.14	12.8%	5.77	7.2%	29.8	3.9%	53.3	4.0%
Th	1.6	6.61	4.0%	6.52	2.9%	6.46	4.5%	6.39	4.3%	n.d.		n.d.		n.d.		24.4	4.6%	105	5.1%
U	0.52	2.02	2.0%	1.99	2.2%	1.82	4.0%	1.80	3.8%	n.d.		n.d.		n.d.		2.12	4.0%	2.51	3.5%

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Table 1. Continued.

(wt.%)	GSP-2 Avg.	RSD	MAG-1 Avg.	RSD	QLO-1 Avg.	RSD	RGM-1 Avg.	RSD	RGM-2 Avg.	RSD	SGR-1b Avg.	RSD	STM-1 Avg.	RSD	SY-2 Avg.	RSD	SY-3 Avg.	RSD	MRG-1 Avg.	RSD
SiO_2	67.0	2.2%	49.9	5.2%	n.d.		73.7	2.6%	n.d.		29.4	11%	60.0	3.2%	59.8	3.4%	59.7	4.4%	39.1	4.2%
TiO_2	0.671	3.3%	0.700	2.8%	0.594	10%	0.278	5.0%	0.271	4.6%	0.238	3.5%	0.132	5.2%	0.136	4.6%	0.150	8.3%	3.81	5.0%
Al_2O_3	14.9	2.7%	16.0	2.1%	16	9.9%	13.7	2.3%	13.7	2.5%	6.36	1.3%	18.5	2.2%	12.0	1.8%	11.5	1.7%	8.21	2.7%
tFe_2O_3	4.85	2.8%	6.71	3.2%	4.21	9.0%	1.84	3.6%	1.84	4.1%	2.59	3.4%	5.19	2.6%	6.19	2.6%	6.40	3.3%	17.9	4.4%
MnO	0.042	6.4%	0.096	2.4%	0.091	9.6%	0.036	7.8%	0.038	7.6%	0.031	9.5%	0.222	2.1%	0.319	1.8%	0.330	2.4%	0.171	5.1%
MgO	0.916	6.2%	2.95	2.2%	0.963	6.8%	n.d.		n.d.		4.48	2.2%	n.d.		2.65	2.3%	2.64	2.4%	13.5	2.0%
CaO	1.99	3.8%	1.27	4.0%	3.02	7.5%	1.13	4.6%	1.09	4.9%	8.32	2.6%	1.05	5.1%	7.90	2.5%	8.20	2.9%	14.8	3.8%
Na_2O	2.78	1.9%	3.84	1.7%	4.08	7.7%	4.11	1.9%	4.04	2.2%	2.98	1.4%	8.82	2.2%	4.26	1.5%	4.05	1.7%	0.732	9.3%
K_2O	5.37	2.7%	3.51	2.8%	3.52	8.1%	4.33	3.1%	4.31	3.0%	1.57	1.7%	4.21	2.4%	4.45	2.4%	4.14	3.1%	n.d.	
P_2O_5	0.286	2.9%	0.157	3.6%	0.251	8.2%	0.041	9.4%	0.040	9.7%	0.249	3.1%	0.154	3.2%	0.430	2.7%	0.538	3.3%	0.058	4.2%
(ppm)																				
Sc	7.39	10%	17.0	4.5%	n.d.		5.92	11%	5.76	14%	n.d.	15%	n.d.		7.72	8.3%	7.36	11%	54.3	5.6%
V	54.3	5.9%	139	2.7%	49	10%	n.d.		n.d.		121	2.6%	n.d.		51.1	4.8%	50.6	6.0%	542	4.8%
Cr	n.d.		101	5.7%	n.d.		n.d.		n.d.		36.7	15%	n.d.		n.d.		n.d.		462	3.9%
Co	6.26	9.1%	20.9	3.2%	6.21	10%	n.d.		n.d.		9.76	5.6%	n.d.		7.25	8.0%	7.48	6.1%	91.8	3.2%
Ni	16.4	8.2%	50.5	4.1%	n.d.		n.d.		n.d.		24.9	5.6%	n.d.		n.d.		n.d.		198	3.3%
Zn	113	1.9%	129	3.5%	58.9	8.0%	32.9	10%	33.7	10%	39.8	6.7%	237	3.7%	252	3.0%	247	4.1%	267	3.6%
Rb	242	3.4%	144	4.1%	68.6	8.7%	149	3.9%	149	3.8%	76.1	3.7%	112	3.3%	220	3.5%	203	5.4%	n.d.	
Sr	232	3.5%	136	3.0%	321	7.7%	105	2.5%	102	2.0%	395	4.1%	685	4.8%	273	3.1%	306	4.8%	280	5.7%
Y	25.6	4.7%	25.7	2.9%	22.6	6.6%	22.5	3.2%	22.4	3.0%	11.0	9.6%	41.9	3.8%	122	3.8%	687	7.3%	13.4	9.8%
Zr	586	4.8%	131	2.8%	186	8.8%	233	4.2%	231	4.3%	51.0	7.4%	1300	4.5%	303	3.1%	358	5.0%	111	4.6%
Nb	25.6	2.7%	15.1	4.1%	10.5	6.4%	9.59	6.6%	9.53	6.6%	6.82	11%	246	4.9%	29.0	2.3%	187	5.5%	19.2	4.0%
Cs	1.16	7.3%	8.10	4.6%	1.61	8.1%	9.72	4.3%	9.66	4.3%	4.79	3.7%	1.50	3.3%	2.68	2.2%	2.63	4.4%	n.d.	
Ba	1370	2.1%	483	3.7%	1400	10%	859	2.8%	842	2.5%	295	3.9%	587	3.4%	462	2.7%	447	5.1%	n.d.	
La	181	5.0%	40.7	4.7%	25.8	9.9%	n.d.		22.7	3.6%	19.0	4.1%	145	4.9%	69.8	4.0%	1330	8.1%	9.4	8.2%
Ce	435	4.8%	83.5	4.7%	48.5	10%	45.3	3.2%	45.0	3.0%	34.5	3.7%	257	5.1%	161	4.3%	2270	7.6%	26.3	5.2%
Pr	54.4	4.6%	9.87	4.8%	5.77	9.5%	5.26	3.5%	5.22	3.1%	4.11	4.0%	25.2	4.9%	20.1	4.3%	224	7.5%	3.95	4.8%
Nd	202	5.0%	36.7	4.7%	22.1	9.7%	18.9	2.9%	18.9	2.7%	14.5	3.6%	78.5	4.8%	76.8	4.3%	728	7.9%	18.5	4.7%
Sm	25.5	5.6%	7.02	4.7%	4.41	9.2%	3.89	3.8%	3.86	4.8%	2.58	3.1%	11.9	5.3%	16.1	4.6%	122	7.8%	4.43	4.8%
Eu	2.21	4.5%	1.38	5.4%	1.24	7.8%	0.622	4.5%	0.607	5.1%	0.50	5.2%	3.37	5.5%	2.47	3.7%	17.7	6.0%	1.47	7.9%
Gd	13.1	4.7%	6.18	4.6%	4.28	9.8%	3.66	3.7%	3.65	4.2%	2.05	8.1%	9.39	4.5%	17.6	4.9%	125	7.5%	4.28	4.9%
Tb	1.26	5.3%	0.892	4.3%	0.642	8.5%	0.599	4.6%	0.598	3.1%	0.316	7.6%	1.37	4.5%	2.98	4.3%	19.8	7.5%	0.589	5.9%
Dy	5.65	4.1%	5.03	3.7%	3.80	7.7%	3.71	3.8%	3.67	2.9%	1.90	8.0%	7.80	4.0%	20.0	4.2%	127	7.5%	3.11	6.7%
Ho	0.930	5.0%	0.971	4.0%	0.799	8.2%	0.763	2.7%	0.765	3.7%	0.370	11%	1.47	4.8%	4.55	4.4%	27.5	7.8%	0.531	9.7%
Er	2.26	5.8%	2.68	3.6%	2.34	8.1%	2.29	4.0%	2.29	4.0%	1.04	11%	4.18	4.6%	15.0	4.5%	82.8	7.7%	1.25	11%
Tm	0.284	5.3%	0.387	3.9%	0.346	7.5%	0.356	3.6%	0.355	2.9%	0.155	11%	0.619	4.8%	2.42	4.3%	11.5	7.6%	0.156	15%
Yb	1.64	8.2%	2.54	3.3%	2.32	7.8%	2.49	4.1%	2.44	2.8%	0.994	13%	4.17	5.3%	17.7	4.9%	66.6	7.9%	n.d.	
Lu	0.228	7.7%	0.373	4.0%	0.366	7.6%	0.388	3.7%	0.390	3.7%	0.155	12%	0.614	3.9%	2.89	5.1%	8.12	8.1%	n.d.	
Hf	14.8	5.2%	3.71	4.3%	4.71	9.9%	6.15	4.4%	6.16	4.4%	1.55	7.4%	27.8	5.4%	8.61	5.4%	9.54	6.6%	4.07	4.3%
Pb	40.4	3.6%	25.2	5.0%	19.5	11%	25.8	3.9%	23.0	3.7%	10.8	3.3%	16.8	3.8%	88.6	3.8%	145	7.5%	5.08	8.2%
Th	106	5.1%	12.2	4.7%	5.00	7.7%	14.8	3.9%	14.8	3.9%	5.25	5.1%	29.9	4.7%	n.d.		n.d.		n.d.	
U	2.55	3.8%	2.82	4.4%	1.89	9.9%	5.64	3.9%	5.61	3.8%	5.31	4.4%	8.52	4.5%	n.d.		n.d.		n.d.	

QL, quantitative limit; Avg., Averaged concentration; %RSD, relative repeatability of the analyses (n = 10); n.d., not detected.

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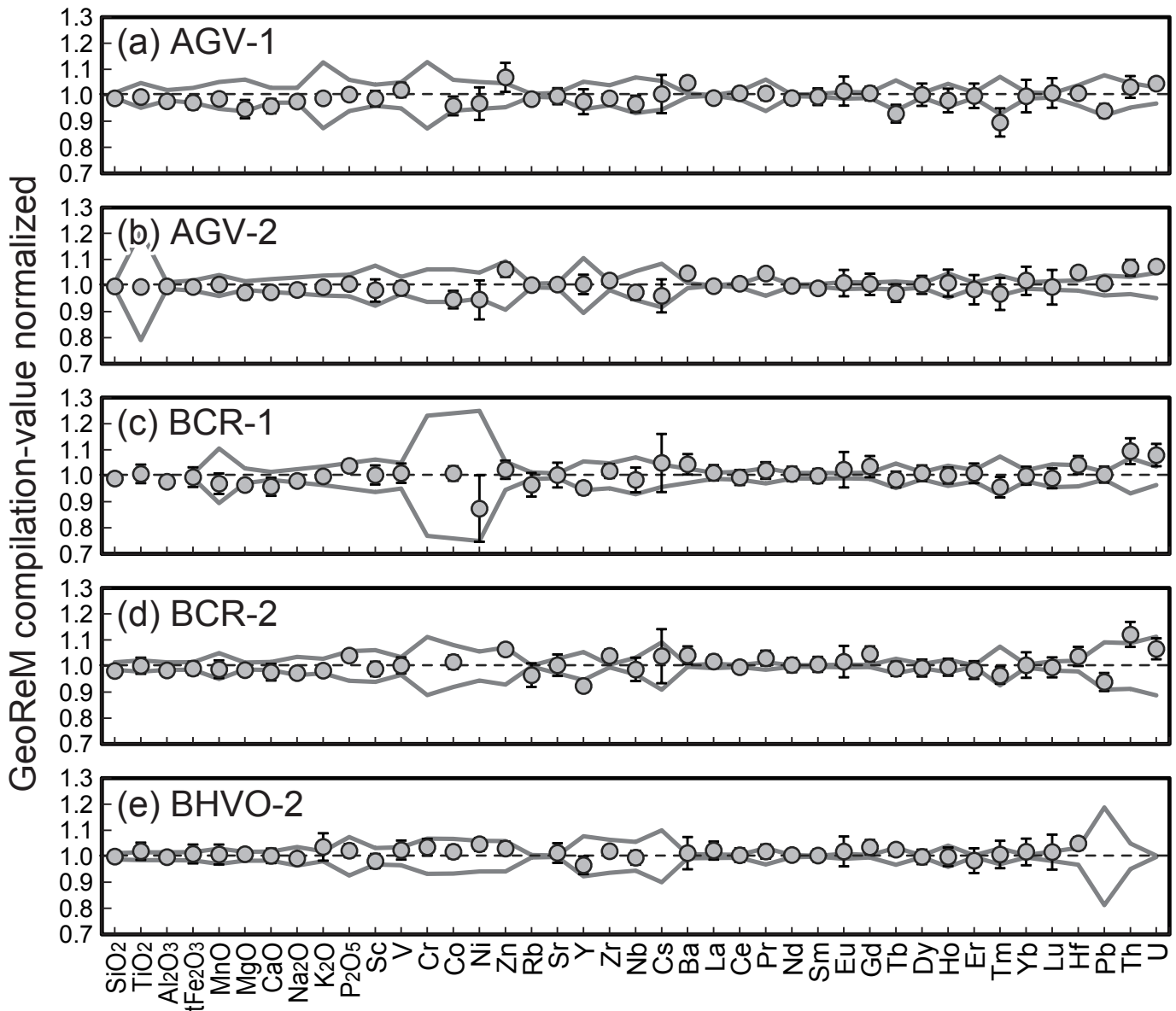
Fig. 1. Comparison of measured abundance data and recently published values for trace elements with GeoReM values (Measured/Reference). **a)** AGV-1, **b)** AGV-2, **c)** BCR-1, **d)** BCR-2, and **e)** BHVO-2. Grey lines show the uncertainties (%RSD) of the GeoReM compilation values (Jochum et al., 2005).

4. Conclusion

We measured the abundances of 10 major and 32 trace elements in 16 USGS and three CCRMP geochemical reference samples. Repeatabilities of the measurements of these samples were better than 5% for almost all major elements, and better than 8% for most trace elements. The reliability of the major and trace element measurements was evaluated by comparison of the measured abundance values with reported values for basaltic and andesitic USGS geochemical reference samples. The data obtained here showed good agreement with recently compiled values.

Acknowledgments

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