Supplementary information file for: ''LA-ICP-MS analyses of trace elements in Fe-rich alloys: quantification of matrix effects for 193 nm excimer laser systems'' by E.S. Steenstra, J. Berndt, S. Klemme and W. van Westrenen.

A.1 Accuracy and precision of element concentrations measured using electron microprobe analyses (EPMA)

To demonstrate the accuracy and precision of the EPMA method applied here, we analysed the NIST 610 glass for the various major and trace elements of interests using a JEOL JXA 8530F field emission electron microprobe at the University of Münster while using a spot size of 10 μm and an accelerating voltage of 15 kV. These conditions are equivalent to those used to obtain the EPMA data on the experimental charges in our previous studies[36–41] that form the basis of this study. As in our previous studies, interference corrections were applied for over 34 elements to address spectral overlaps. Fig. S.1 and Table S.1 show the results and confirm the accuracy and precision of the EPMA approach used throughout our studies[36–41]. The measured concentrations of most elements are generally within 10% of the GeoRem reference values[50] (Fig. S.1), despite their low abundance in the NIST 610 glass of mostly <500 ppm and the use of an only moderate beam current (15 nA) due to the beam sensitivity of the glass. Notable exceptions are S and Te. It should be noted that the concentration of Te in NIST 610 is deemed uncertain, given the absence of an uncertainty in the GeoRem database[50]. In case of S, the discrepancy could be a result of its heterogeneous distribution in the NIST 610 reference material given the large range of published values (Table S.1).

A.2 Accuracy and precision of element concentrations in silicate reference materials measured by LA-ICP-MS

To illustrate the general accuracy and precision of the LA-ICP-MS method applied here, 12 well-characterized silicate reference materials were analysed. To investigate the possible effects of variable spot sizes, four different spot sizes (25, 35, 50 and 85 μm, respectively) were used for each of these reference materials. Figures S.2–7 and Table S.2 show a comparison of the new and previous analyses, that were carried out using a wide range of analytical techniques (GeoReM database, Application Version 19, and references therein[50]).

NIST 610

The NIST-610 glass is one of the best characterized silicate reference materials and contains relatively high abundances of the various volatile and refractory elements. For this glass concentrations measured by LA-ICP-MS are generally within 10% of the reference values from the GeoRem database[50]. Measured concentrations of Mg, Fe, As are somewhat higher and show a positive offset ranging between 10-20% relative deviation. The latter values are within the range of previously reported concentrations[50].

Concentrations of Ge, Te and Bi are on average slightly underestimated relative to the reference concentrations (<20 %), but are also still well within the published ranges.

GSD-1G

Our results generally agree within 10% of the reference values reported for GSD-1G in the GeoRem database[50]. Notable exceptions include Ge, As, Cd and Sn, for which we obtain slightly higher concentrations relative to reference values. Concentrations found for Bi and Sb are slightly lower than reference values, but plot well within the range of published and/or reference concentrations[50] if the uncertainties are taken into account.

GSE-1G

Measured concentrations of the various elements in the GSE-1G glass are generally also in good agreement relative to reference values[50] (Fig. S.3) However, both As and Se concentrations are higher than the reported reference values. This could be a result of the heterogeneous distribution of these elements within this reference material, perhaps due to volatility-related issues during the synthesis of GSE-1G or their heterogeneous distribution with the silicate calibrant materials[51-53]. The heterogeneous distribution in the GSE-1G glass may also be reflected from the very large range of both reference and published concentrations for these elements[50]. The reported reference concentrations of elements Se, Cd and Sb have uncertainties of approx. 75, 33 and 25%. Alternatively, it could reflect the increased analytical uncertainties with decreasing concentrations[54]. Besides Se, the measured concentrations of the other elements are generally within 10% of the reference values, especially if the individual uncertainties of each group of measurements are taken into account.

GOR132-G

Measured concentrations of the various elements are generally within 10 and occasionally 20% of the reference values determined for this glass[50] (Fig. S.3). Notable exceptions are Sn and to a lesser extent Pb, which concentrations are lower than the reference values. However, errors on the low Sn concentrations are also very large, suggesting it could be heterogeneously distributed in the GOR132-G glass or the NIST 612 calibrant glass. A heterogeneous distribution of Sn in the GOR132-G glass also seems to be reflected from the relatively large range of published values. Alternatively, it could be related to the relatively low concentration of Sn in this particular glass[54].

NIST 614

Measured element concentrations of the overall majority of the element considered here in the NIST 614 glass are also in good agreement (< 20% relative deviation, usually <10%) with published reference values[50] (Fig. S.4). An exception is Fe, for which measured concentrations are in some cases lower than reference values. However, the data still plots within the published range, and it may reflect some heterogeneity of Fe in this reference material or simply its low abundance, as proposed for other elements for the same glass[54].

NIST 616

Measured element concentrations vary considerably more, relative to reference values, in the NIST 616 reference glass (Fig. S.4). This most likely reflects the very low concentrations of most of the elements considered here (usually <1 ppm)[54]. As a result, most data points still plot within the reference range if uncertainties are taken into account.

T1-G

Measured element concentrations of Cr, Bi and Tl are consistently underestimated relative to reference values[50], but are still within the published range. It should be noted that Bi and Tl are present in very low concentrations (< 0.1 ppm), which results in very large uncertainties (Fig. S.5). Measured concentrations of Ge and Mo are slightly higher than reference values, which could be a result of their relative low concentrations in the silicate glass (<6 ppm) and related analytical uncertainties or because of their heterogeneous distribution within this glass and/or in the NIST 612 glass used for calibration[53].

BIR-1G

Concentrations derived for Sn in the BIR-1G glass from the literature vary substantially, suggesting it could be heterogeneously distributed in the glass (Fig. S.5). Alternatively, it simply reflects the low concentration of Sn in this glass and related analytical uncertainties, as previously proposed[54]. The relatively larger deviations for Ge, In and Mo are most likely related to their very low concentrations in the BIR-1G reference material (<1.5 ppm for Ge, <0.1 ppm for In and Mo)[54].

ATHO-G

Concentrations of most elements of interest are low in this reference material (usually <10 ppm). Errors and relative uncertainties are therefore significant for a number of elements, including Cr, Co, Ga, Ge, Sb and Pb (Fig. S.6). Elemental concentrations of Ga and Ge are overestimated relative to reference values. Given the high concentration of Ga in this glass, we attribute this significant difference to compositional heterogeneity in terms of Ga, as proposed for other elements[55] and which is suggested from the larger spread of published concentrations of Ga. The overestimation of Ge and underestimation of Cr, Co, Sb and Pb is most likely a result of their low concentrations in the ATHO-G glass material and/or compositional heterogeneity in terms of these elements[55].

ML3B-G

Measured concentrations of most elements agree well with reference values (Fig. S.6), although some of the measurements have relatively large errors due to low concentrations. A notable exception is Cr, for which we measured slightly lower concentrations than the reference values presented in the GeoRem database[50]. This difference can be explained by the heterogeneous distribution of Cr within this reference material[53].

BHVO-2G

The measured concentrations for the majority of the elements agree well with those reported in the GeoRem database[50] (Fig. S.7). Exceptions are again Ge and Sn, presumably due to their heterogeneous distribution in BHVO-2G[54] in case of Sn and/or because of relatively low concentrations in case of Ge.

BCR-2G

Our results yield an underestimation of the concentrations of Cu, Sn, Tl and an overestimation of Zn and Ga, relative to reference concentrations, for the BCR-2G glass. Note that all of these values are well within the published ranges, and that relative large deviations (> 10%) from reference concentrations for Zn, Sn and Tl[50] for the BCR-2G glass were also reported by ref. (45).

All in all, the results show that virtually all concentrations of the investigated elements in silicate reference materials are reproduced within 20 % relative deviation by LA-ICP-MS, and usually within <10 % relative deviation. Although detection limits increase with decreasing beam size, we found no evidence for volatility-related fractionation effects on volatile and/or refractory elements in silicate materials, as a function of beam size.

Supplementary references

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Fig. S.1 Relative deviations between reference concentrations of silicate reference material NIST 610 (taken from the GeoRem database website[50]) and those measured by electron microprobe in this study. Shaded area represents the range of published data, dotted lines define 10% relative deviation. All uncertainties are 1 standard deviation.

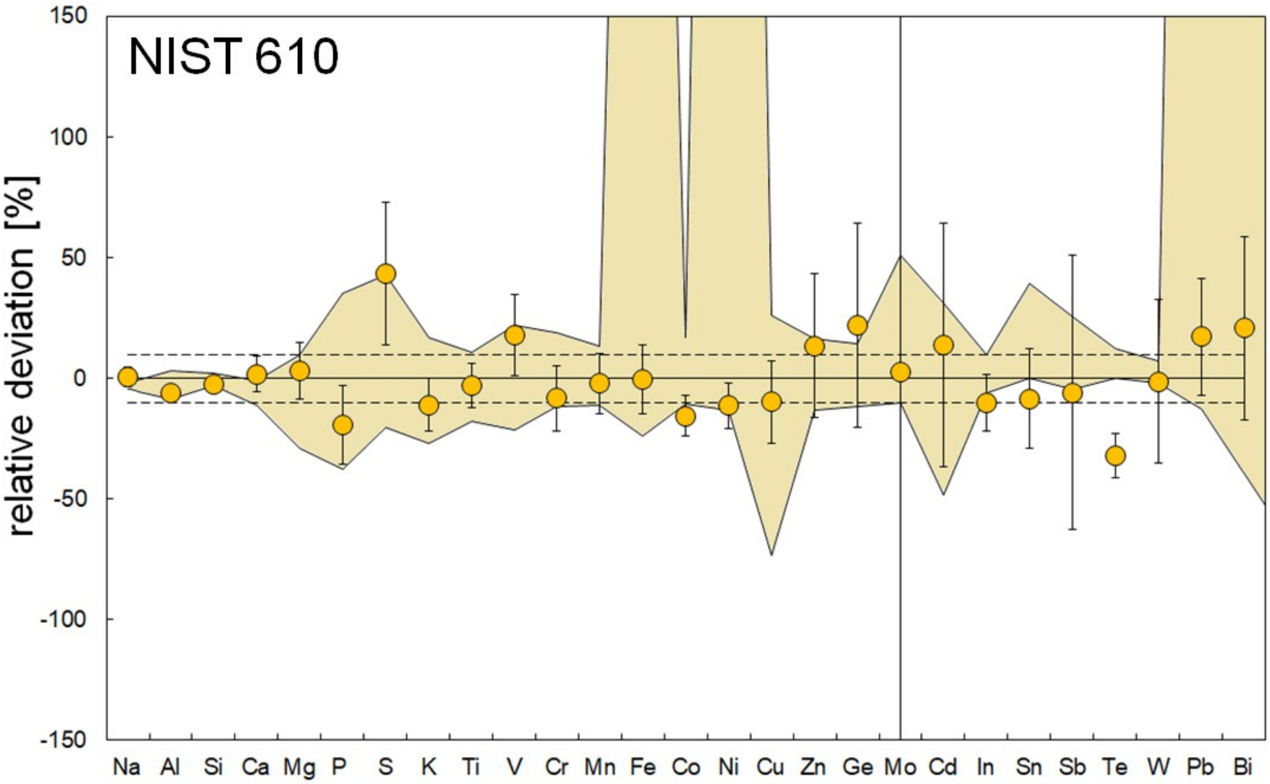

Fig. S.2 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials NIST 610 and GSD-1G (from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

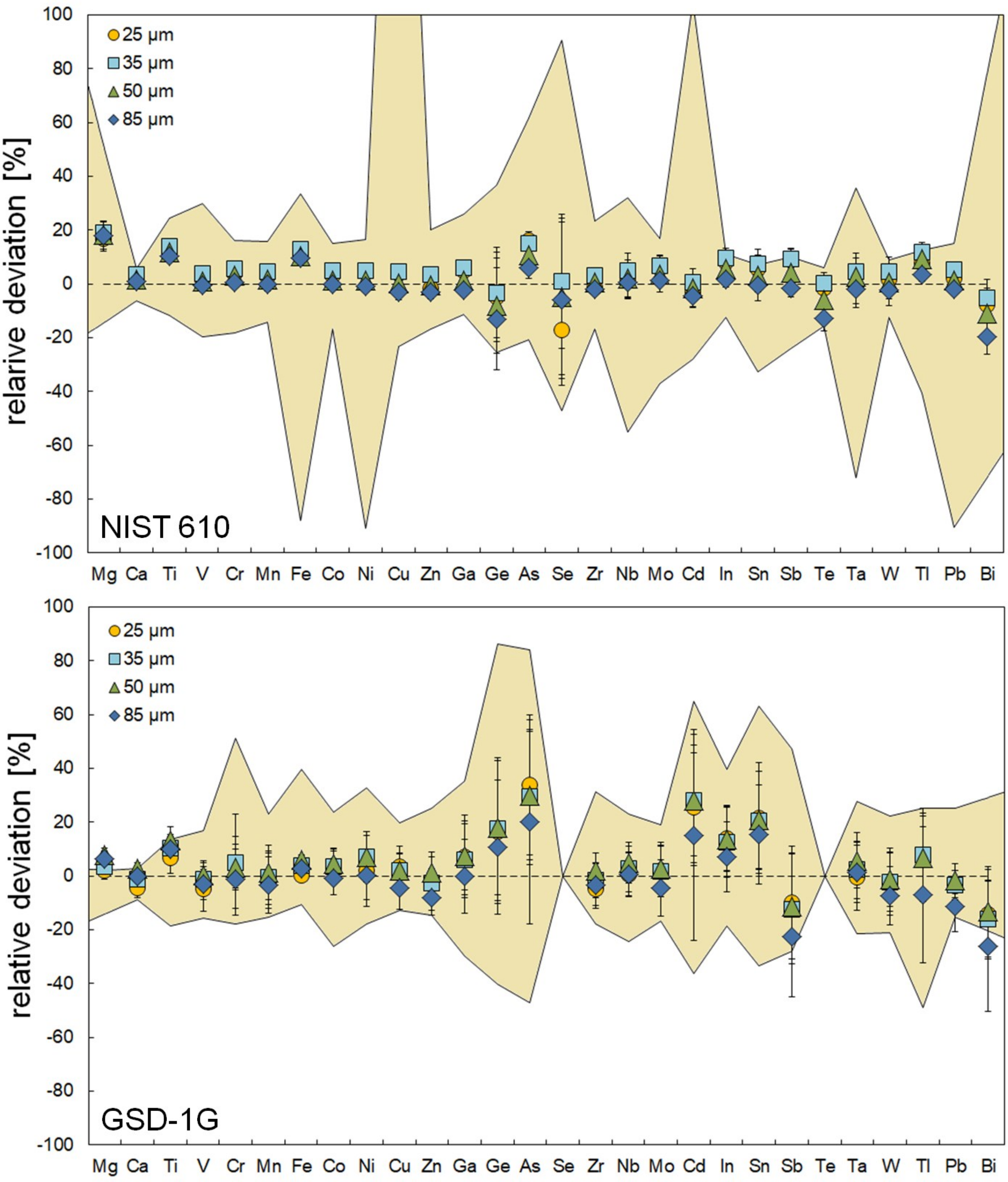

Fig. S.3 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials GSE-1G and GOR132-G (from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

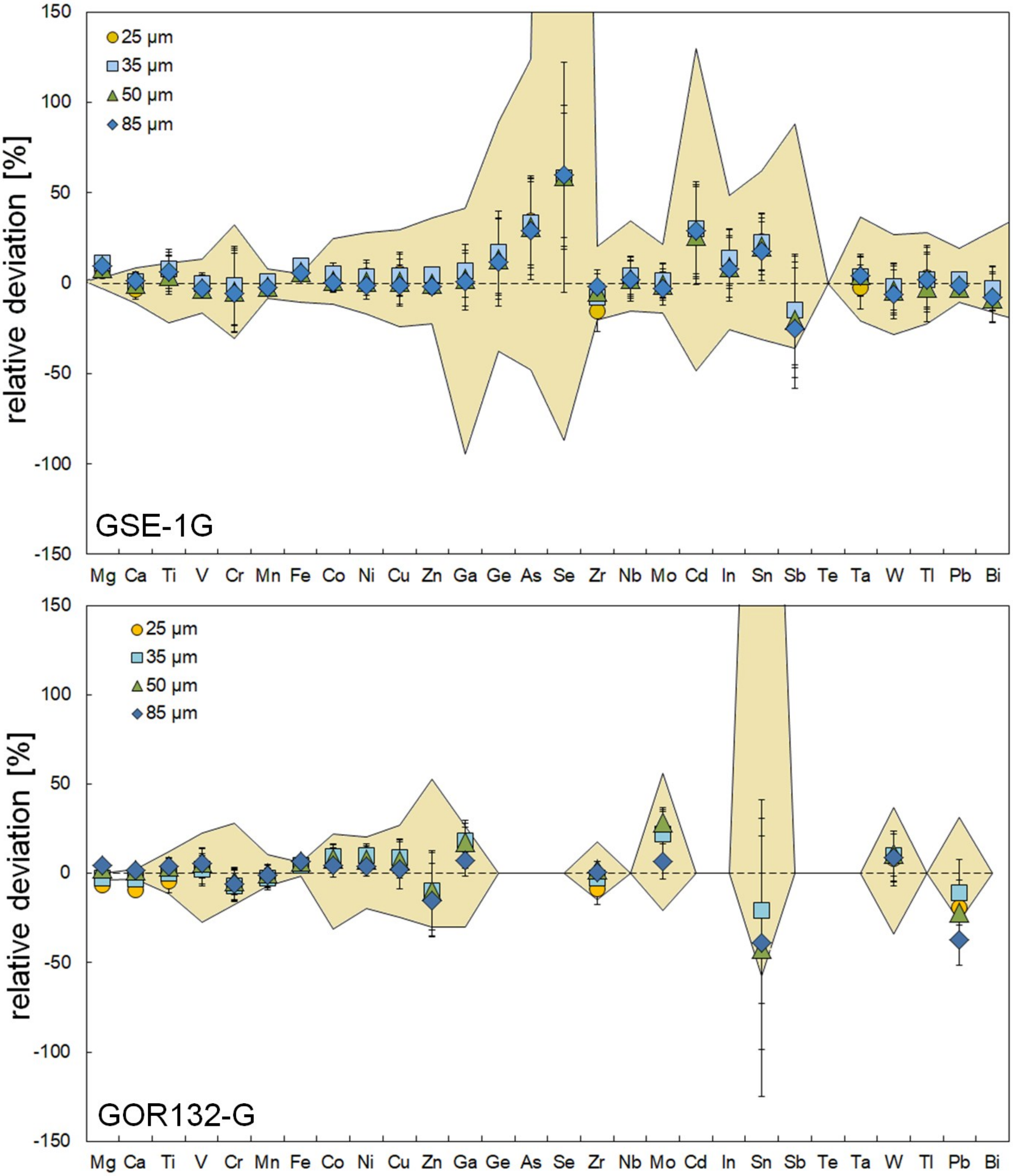

Fig. S.4 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials NIST 616 and NIST 616 from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

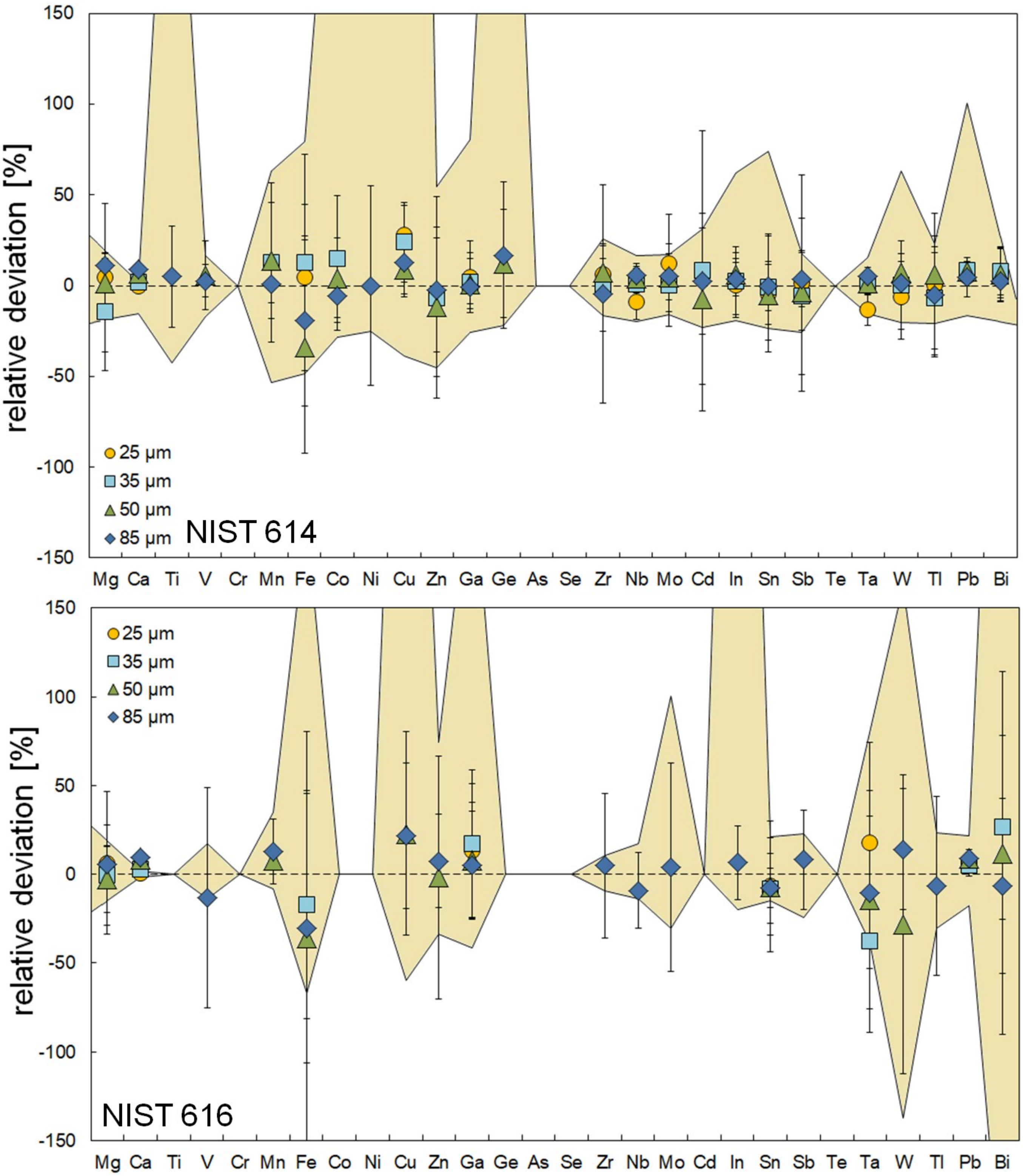

Fig. S.5 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials T1-G and BIR-1G (from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

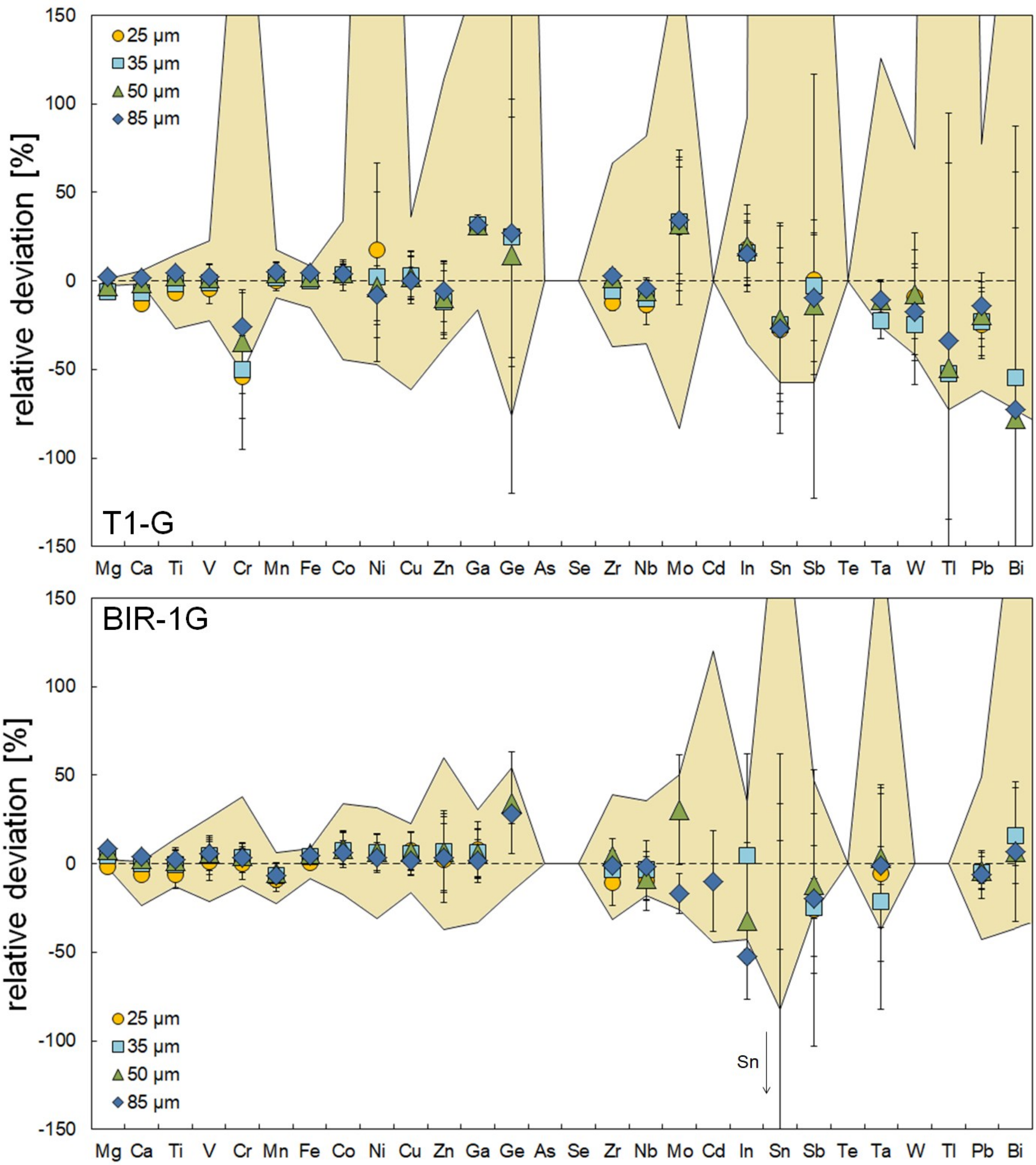

Fig. S.6 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials ATHO-G and ML3B-G (from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

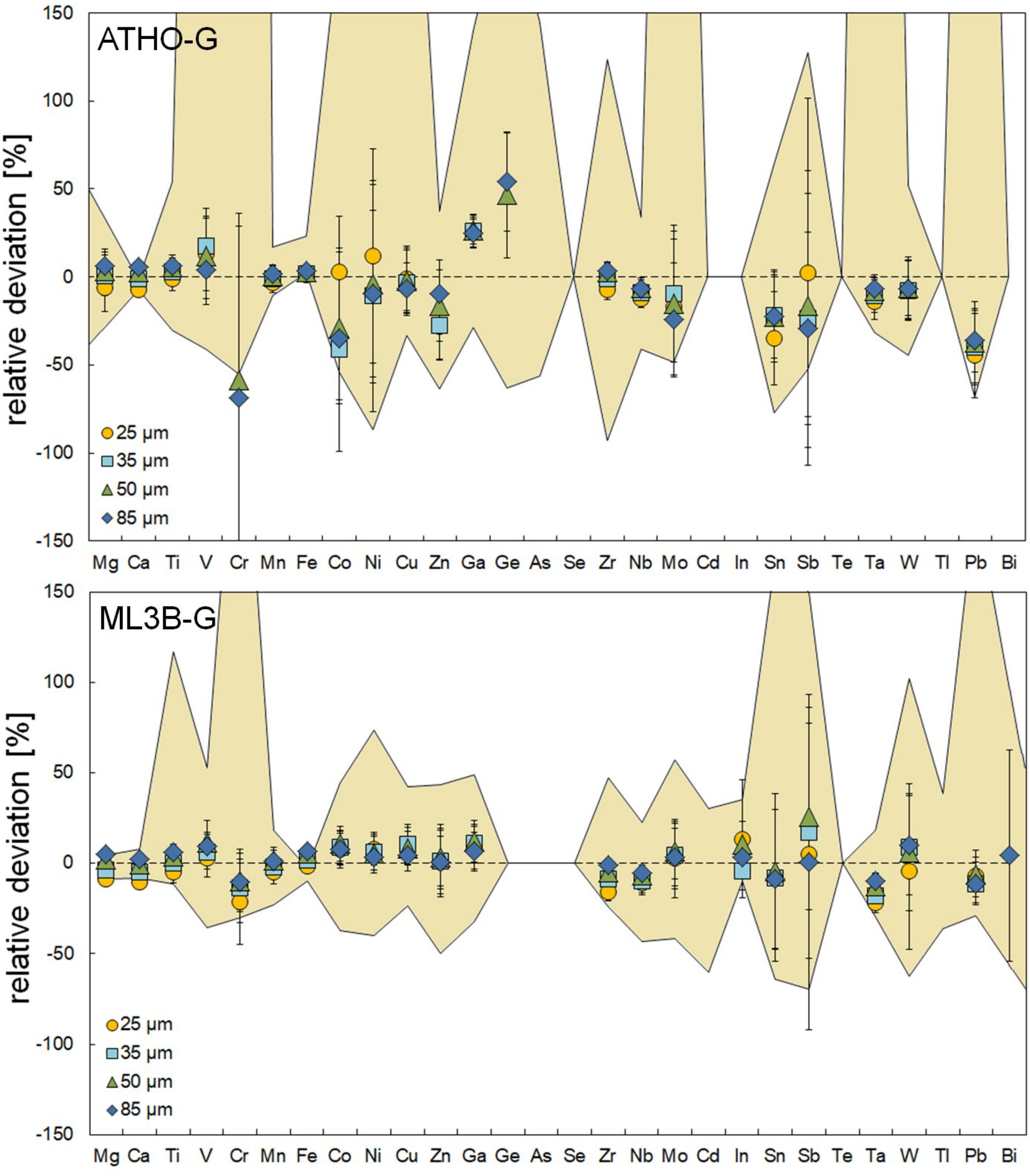

Fig. S.7 Relative deviations between reference element concentrations measured by LA-ICP-MS in silicate reference materials BHVO-2G and BCR-2G (from the GeoReM database[50] and references therein) and those measured in this study using 25, 35, 50 or 85 µm spot sizes. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. See Table S.1 for additional details.

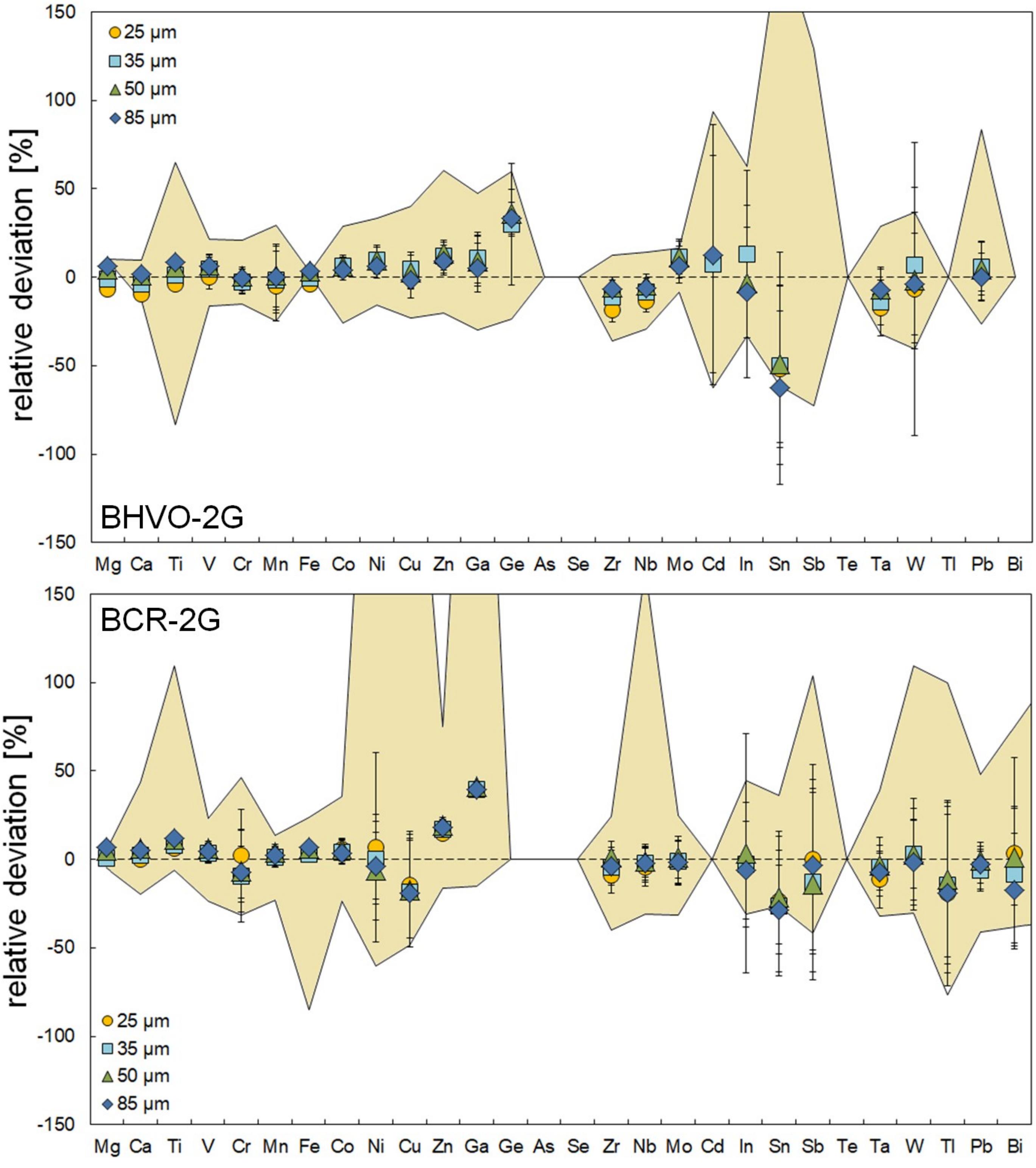

Table S.1 Concentrations in the NIST 610 reference glass measured using EMPA (*N = 15*) and those from the GeoRem database[50] and references therein. Each of the 15 measurements are based on 10 replicate analyses. Numbers in parentheses represent 1 standard deviation.

	Measured (this study)	**GeoRem (preferred values)[50]**	**GeoRem (published range)[50]**
Na_2O (wt.%)	13.30(23)	13.4(3)	13.35–14.00
Al_2O_3	2.07(2)	1.95(4)	1.89–2.13
SiO_2	71.3(4)	69.7(5)	68.1–72.0
CaO	11.2(6)	11.4(2)	11.3–12.8
Mg (ppm)	419(20)	432(29)	393–610
P	512(45)	413(46)	305–661
S	401(58)	575(32)	403–720
K	521(40)	464(21)	397–633
Ti	466(33)	452(10)	408–550
V	381(46)	450(9)	369–573
Cr	445(53)	408(10)	343–462
Mn	453(44)	444(13)	392–499
Fe	460(55)	458(9)	57–600
Co	485(35)	410(10)	351–459
Ni	517(50)	459(4)	43–530
Cu	489(73)	441(15)	350–1648
Zn	405(85)	460(18)	396–531
Ge	367(60)	447(78)	391–505
As	b.d.l.[a]	325(18)	272–496
Se	b.d.l.[a]	138(42)	95–183
Mo	407(369)[a]	417(21)	276–463
Cd	237(79)	270(16)	206–521
In	483(41)	434(19)	396–461
Sn	470(72)	430(29)	309–430
Sb	421(185)	396(19)	315–414
Te	444(58)	302[b]	269–302
W	450(115)[a]	444(29)	415–452
Pb	363(71)	426(1)	40–489
Bi	318(73)	384(26)	114–638

[a] Detection limits of As, Se, Mo and W are approximately 670, 325, 800 and 450 ppm, respectively [b] Value marked as uncertain in the GeoRem database

Table S.2 Measured concentrations in various silicate reference materials, for 5 replicate analyses, with a 50 μm spot size. Numbers in parentheses represent 1 standard deviation. All measurements were obtained using the NIST 612 as a reference material for external calibration and Si as internal standard, using the Si contents from the GeoRem database[50]. Reference values from the GeoRem database are included for comparison purposes. All values are in ppm.

	ATHO-G		**GOR132-G**		**T1-G**		**ML3B-G**		**NIST 610**		**NIST 614**	
	This study	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***
Mg24	656(8)	632(61)	141331(780)	137514(1228)	22467(286)	23021(246)	41402(328)	40456(491)	528(3)	432(29)	34(2)	34(2)
Ca43	12552(78)	12153(214)	61597(188)	60409(858)	50137(434)	50758(643)	74699(1158)	75065(715)	82763(379)	81499(1430)	91143(1058)	85073(1430)
Ti49	1614(16)	1529(96)	1920(14)	1834(78)	4656(25)	4526(102)	13343(247)	12769(540)	503(3)	452(10)	<4.6	3.6(3)
V51	4.4(8)	3.9(3)	228(1)	214(17)	194(2)	190(11)	303(14)	268(23)	454(2)	450(9)	1.07(14)	1.01(4)
Cr53	3.9(9)	6.1(14)	2421(6)	2528(183)	16(2)	21(2)	162(4)	177(23)	422(3)	408(10)	<2.1	1.2(1)
Mn55	828(5)	821(39)	1191(4)	1193(54)	1030(11)	984(46)	1342(24)	1317(70)	451(3)	444(13)	1.7(4)	1.4(1)
Fe56	26119(137)	25418(777)	84356(379)	78508(777)	51385(341)	50058(466)	89847(1304)	84726(777)	510(2)	458(9)	14(1)	19(6)
Co59	1.7(1)	2.1(5)	101(1)	93(6)	19.8(5)	19(1)	46(1)	41(4)	415(2)	410(10)	0.83(8)	0.79(9)
Ni60	13(1)	13(5)	1288(5)	1187(58)	10(1)	11(1)	114(2)	107(9)	465(3)	459(4)	b.d.l.	1.1(1)
Cu63	18(1)	19(2)	221(1)	205(21)	19.3(2)	19(2)	122(1)	112(10)	442(3)	441(15)	1.5(2)	1.4(1)
Zn66	121(7)	141(15)	70(2)	77(13)	68(3)	74(10)	112(4)	108(14)	458(2)	460(18)	2.5(4)	2.8(4)
Ga69	34.3(3)	25(2)	12.6(2)	10(1)	28(1)	19(1)	24.4(5)	20(2)	438(3)	433(13)	1.33(8)	1.31(9)
Ge73	3.4(4)	1.8(9)*	1.2(1)	0.7*	2.1(6)	1.8(15)*	1.6(5)	1.1(11)	414(5)	447(78)	1.07(19)	0.94(10)
As75	b.d.l.[a]	1.4(5)	b.d.l.	0.16*	b.d.l.	1.0(4)	b.d.l.	1.0(4)	364(3)	325(18)	b.d.l.	0.74(23)
Se82	b.d.l.	0.1*	b.d.l.	0.03*	b.d.l.	0.05*	b.d.l.	0.06*	132(5)	138(42)	b.d.l.	0.40(8)
Zr90	529(6)	512(20)	10.1(2)	9.9(3)	146(2)	144(4)	116(2)	122(3)	450(3)	448(9)	0.91(10)	0.85(3)
Nb93	59(6)	62(3)	0.24(1)	0.07(1)	8.4(1)	8.9(4)	8.1(2)	8.6(2)	475(2)	465(34)	0.86(4)	0.82(3)
Mo95	4.2(5)	4.8(1)	43(1)	31(3)	6.2(5)	4.2(18)	17.9(4)	17(2)	432(4)	417(21)	0.84(7)	0.80(3)
Cd111	b.d.l.	0.5*	b.d.l.	0.08*	b.d.l.	0.2*	b.d.l.	0.1*	266(4)	270(16)	0.52(13)	0.56(5)
In115	0.11(4)	0.17*	0.12(1)	0.09*	0.37(3)	0.30(30)*	<0.22	0.2*	459(2)	434(19)	0.84(2)	0.79(5)
Sn118	4.4(3)	5.4(7)	0.24(5)	0.34(9)*	1.7(2)	2.0(5)	1.09(9)	1.14(33)	444(2)	430(29)	1.60(9)	1.68(15)
Sb121	0.28(4)	0.32(10)	0.07(2)	0.06(4)	0.22(2)	0.25(5)	0.15(2)	0.11(5)	413(3)	396(19)	0.77(8)	0.79(6)
Te125	0.13(7)*	–	0.06(3)	–	0.14(7)	–	0.13(9)	–	285(4)	302*	0.57(15)	–
Ta181	3.6(1)	3.9(2)	0.044(4)	0.031(2)	0.42(2)	0.46(2)	0.49(2)	0.55(1)	458(2)	446(33)	0.82(2)	0.81(3)
W182	8.8(3)	9.3(12)	28.5(2)	25(3)	0.64(3)	0.69(12)	0.37(2)	0.35(9)	446(3)	444(29)	0.87(2)	0.81(7)
Tl205	0.06(1)	0.07*	0.0011(5)	0.001*	0.09(1)	0.13(8)*	0.006(1)	0.008*	66(1)	60(3)	0.29(1)	0.27(2)
Pb208	4.1(2)	5.7(6)	16.0(4)	20(2)	9.8(2)	12(2)	1.31(4)	1.38(7)	432(3)	426(1)	2.5(1)	2.32(4)
Bi209	0.022(3)	0.05*	<0.01	0.007(3)*	0.06(1)	0.10(5)*	<0.007	0.006(9)*	346(2)	384(26)	0.62(5)	0.58(4)

	NIST 616		**BIR-1G**		**BHVO-2G**		**BCR-2G**		**GSD-1G**		**GSE-1G**	
	This study	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***	***This study***	***GeoReM pref.***
Mg24	34(3)	35(3)	62613(243)	57707(614)	45791(127)	437711(123)	23078(111)	21855(553)	23930(66)	22100(553)	23429(335)	21487(184)
Ca43	92078(463)	84358(715)	97779(537)	95082(1430)	82544(720)	81499(715)	53823(202)	50472(786)	52919(321)	51473(786)	52795(574)	52903(2145)
Ti49	b.d.l.	2.7(3)	6354(22)	6235(420)	17716(109)	16726(12)	15338(59)	13608(240)	8569(61)	7434(360)	469(3)	450(42)
V51	<0.48	0.23(2)	347(2)	326(32)	330(2)	308(19)	453(1)	425(18)	44.1(3)	44(2)	427(3)	440(20)
Cr53	b.d.l.	0.40(13)	411(4)	392(24)	296(2)	293(12)	16(1)	17(2)*	43(1)	42(3)	383(5)	400(80)
Mn55	<0.66	0.61(3)	1400(6)	1471(77)	1330(4)	1317(232)	1614(7)	1550(70)	223(2)	220(20)	581(7)	590(20)
Fe56	12(2)	16(8)	86006(432)	80839(777)	91093(376)	87835(777)	102766(184)	96386(2332)	110111(1157)	103381(777)	105353(1369)	98717(2332)
Co59	b.d.l.	0.05(2)	56.9(3)	52(5)	46.9(5)	44(2)	40.4(3)	38(2)	42(1)	40(2)	386(4)	380(20)
Ni60	b.d.l.	0.44(10)	191(2)	178(18)	128(2)	116(7)	12(1)	13(2)	62(2)	58(4)	443(3)	440(30)
Cu63	0.91(16)	0.7(3)	128(2)	119(12)	131(2)	127(11)	17.9(5)	21(5)	43(1)	42(2)	383(7)	380(40)
Zn66	1.3(4)	1.3(3)	84(1)	78(17)	118(3)	102(6)	155(2)	125(5)	55(1)	54(2)	460(7)	460(10)
Ga69	0.54(4)	0.50(13)	15.9(2)	15(2)	24.2(4)	22(3)	39.2(2)	23(1)	58(1)	54(7)	503(7)	490(70)
Ge73	b.d.l.	0.28(4)	1.8(5)	1.2(1)	2.5(3)	1.6(1)*	<2.4	1.5(1)*	39(2)	32(8)	370(3)	320(80)
As75	b.d.l.	0.2*	b.d.l.	–	b.d.l.	–	b.d.l.	–	38(1)	27(8)	378(10)	260(90)
Se82	b.d.l.	0.22*	b.d.l.	–	b.d.l.	–	b.d.l.	–	b.d.l.	2(1)	49(4)	20(16)
Zr90	<0.17	0.10(1)	14.7(2)	14(1)	161(2)	170(7)	187(1)	184(15)	43(1)	42(2)	393(7)	410(30)
Nb93	0.029(3)	0.019(2)	0.48(2)	0.52(4)	17.6(2)	18.3(8)	12.3(1)	12.5(10)	44.1(3)	42(3)	432(3)	420(40)

Mo95	<0.12	0.09(1)	0.11(2)	0.08(1)*	4.3(2)	3.8(2)*	273(2)	270(30)	40(1)	39(3)	387(3)	390(30)
Cd111	b.d.l.	0.036*	b.d.l.	0.14(4)*	b.d.l.	0.10(2)*	0.33(6)	0.2*	25(2)	18(4)	218(9)	160(50)
In115	<0.040	0.030(4)	0.07(1)	0.09(1)*	0.10(1)	0.10(2)*	0.11(3)	0.11(2)*	44.0(4)	38(5)	407(9)	370(60)
Sn118	1.1(2)	1.2(1)	0.84(6)	2.3(13)*	1.7(1)	2.6(6)*	2.1(1)	2.6(4)*	37(1)	29(6)	352(5)	280(50)
Sb121	<0.12	0.08(1)	0.50(7)	0.56(9)	0.13(3)	0.30(13)	0.31(5)	0.35(8)	39(1)	43(7)	374(6)	450(110)
Te125	b.d.l.	–	0.18(9)	–	0.21(7)	–	0.13(10)	–	26(1)	–	255(13)	–
Ta181	0.026(6)	0.03(1)	0.037(6)	0.036(6)	1.08(3)	1.15(10)	0.76(22)	0.78(6)	42.5(4)	40(4)	410(5)	390(40)
W182	0.034(11)	0.043(4)	0.0198(1)	–	0.23(3)	0.23(4)*	0.52(2)	0.50(7)	42.5(3)	43(4)	413(5)	430(50)
Tl205	0.013(1)	0.008(1)	0.004(1)	–	0.024(9)	–	0.27(1)	–	0.97(5)	0.9(1)	1.9(1)	2.0(2)
Pb208	2.03(3)	1.85(4)	3.6(1)	3.7(3)	1.8(6)	3.7(3)	11.0(10)	11(1)	49(1)	50(2)	369(8)	378(12)
Bi209	0.024(10)	0.021(6)	0.0097(14)	0.009(2)*	0.018(2)	0.009(2)*	0.051(3)	0.05(1)*	31(1)	35(4)	296(8)	320(30)

[a] b.d.l. = below detection limit, where the minimum detection limit (MDL) at the 99% confidence level was determined by Poisson counting statistics, or MDL = 2.3 * $\sqrt{2B}$, where B is the total counts in the background interval [b] (*) Denotes concentrations that are close to detection limits or values marked as ‘‘uncertain’’ in the GeoRem database[50]