Supplementary information file for: ''Addressing matrix effects for 193 nm excimer LA-ICP-MS analyses of Fe-rich sulfides and a new predictive model'' by E.S. Steenstra, J. Berndt, S. Klemme, W. van Westrenen, E.S. Bullock and A. Shahar.

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

To demonstrate the accuracy and precision of the EPMA method used in this study, we re-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 comparable to those used to obtain the EPMA data on the experimental charges in our previous studies[6,27–30] that form the basis of this study. Interference corrections were applied for over 34 elements to address spectral overlaps, as has been done in our previous studies. Fig. S.2 and Table S.3 show the results from Steenstra et al.[26] (measured at the onset of the measurements on the synthetic samples presented in this study, N = 15) and from this study (measured at the end of the measurements time-frame; N = 19). The results generally confirm the accuracy and precision of the EPMA approach used throughout this study and our previous studies[6,27–30]. The measured concentrations of most elements are generally within 10% of the GeoRem reference values[41] (Fig. S.2; Table S.3), despite their very low abundance in the NIST 610 glass of mostly <500 ppm and the use of only a moderate beam current (15 nA). The second analysis session of NIST 610 at the end of this study yielded larger average deviations (>10%) of V, Ni, Co, Ge, Sb and Pb, relative to preferred GeoRem values[41], similar to the first set of analyses (Fig. S.2). In the case of S, our results are not affected by potential analytical issues related to EPMA analyses, as we did not measure S using LA-ICP-MS and did not consider this element in the fitting procedures. The EPMA analyses of V in NIST 610 are slightly lower than preferred values[41], but V was also not considered in this study due to its low concentrations in the sulfides. The average concentrations Ge and Pb in NIST 610 measured by EPMA are lower than preferred, but within error of the latter values[41], reflecting the challenges of measuring their abundances at the 300-500 ppm level (Fig. S.2). The concentrations of Ni, Co and Sb in the NIST 610 glass measured at the beginning and end of this study are slightly higher than preferred values, but close to or within error of published/preferred values (Fig. S.2).

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, well-characterized reference materials NIST 610, BIR-1G and BHVO-2G were analysed. For this purpose, Si was used as the internal standard in conjunction with the

NIST 612 glass. Fig. S.3 shows the results, compared to preferred values and/or published values from the GeoRem database (GeoReM database, Application Version 19, and references therein[41]). As in our previous study[26], we observe that there is good agreement (i.e. within 10% RD) between measured concentrations of a variety of major and trace elements and the preferred values listed in the GeoRem database (Fig. S.3). This is especially the case for NIST 610, in which the elements of interest are more abundant relative to BIR-1G and BHVO-2G. For BIR-1G and BHVO-2G, measured Ge concentrations are higher than preferred values - presumably due to the production of $^{56}Fe^{16}O^{+}$ and lesser amounts of $^{57}Fe^{16}O^{+}$ and $^{56}Fe^{16}O^{1}H^{+}$ on ^{72}Ge and ^{73}Ge, respectively[42]. This analytical issue becomes negligible at the high concentrations of the synthetic sulfides[41].

It also should be noted that ^{63}Cu and ^{69}Ga have a potential interference from $^{23}Na^{40}Ar$ and $^{138}Ba^{2+}$, respectively. Fig. S.3 shows that there is good agreement between measured concentrations of both Cu in the BIR-1G, BHVO-2G and NIST 610 glasses, suggesting that the measured concentrations of Cu are not significantly affected by this interference. Fig. S.3 also shows that the measured abundances of Ga in the BHVO-2G glass is higher than the preferred value[41]. The latter discrepancy is most likely a result of the substantially greater Ba/Ga (~6) of BHVO-2G compared to NIST 610 (~1.05) and BIR-1G (~0.45), resulting in overestimation of the Ga content in BHVO-2G because of interference from $^{138}Ba^{2+}$ on $^{69}Ga^{+}$.

Supplementary references

[41] K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll and A. W. Hofmann, *Geost. Geoanal. Res.*, 2005, **29,** 333–338.

[42] P.A. Sossi, S. Klemme, H. St.C. O’Neill, J. Berndt, F. Moynier. *Geochim. Cosmochim. Acta*, 2019, **260,** 204–231.

Fig. S.1 Backscattered electron images of typical run products ESS-85 and ESS-82. Close-up of run ESS-82 shows the smaller-scale heterogeneities typical for Fe-rich sulfide liquids.

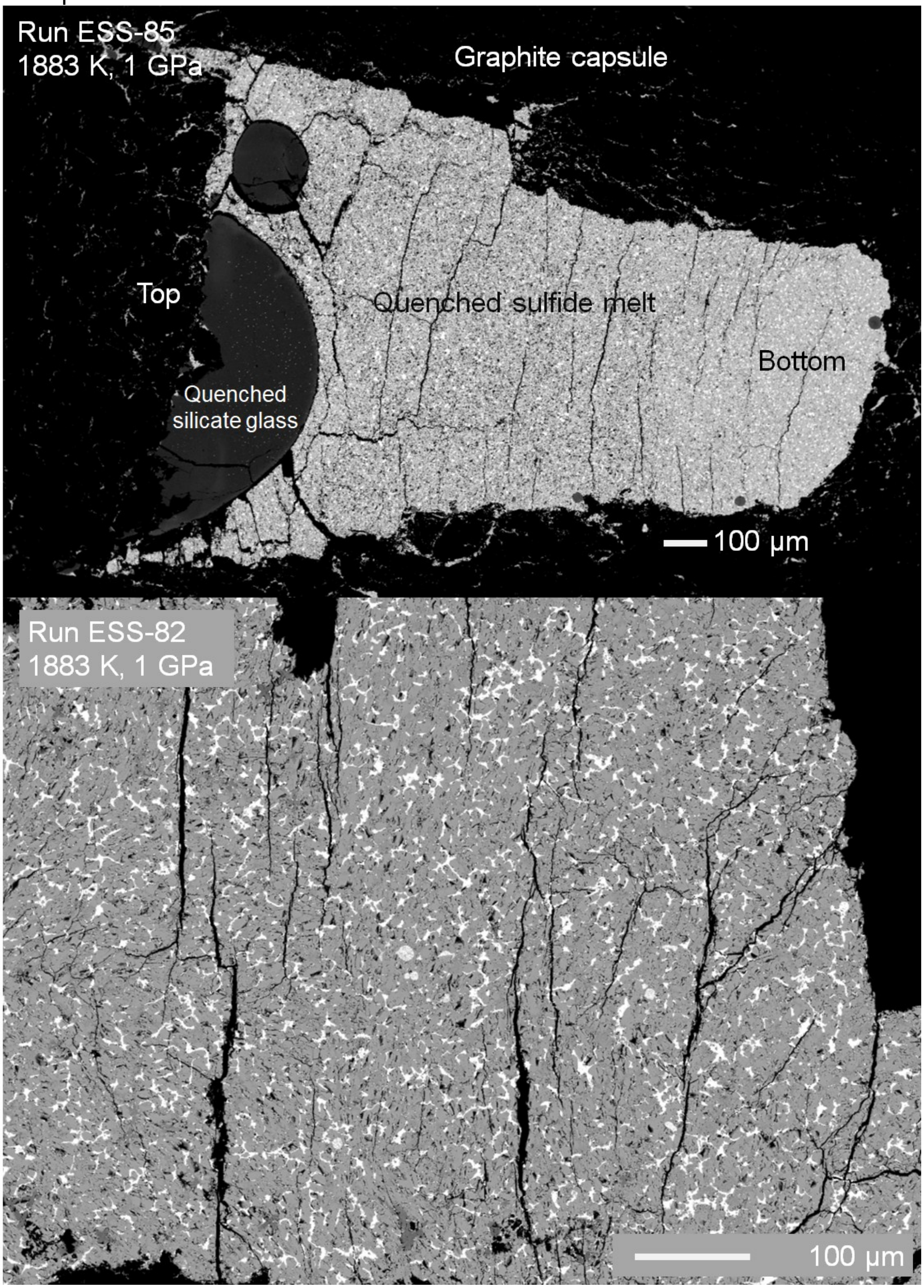

Fig. S.2 Relative deviations between reference concentrations of silicate reference material NIST 610 (taken from the GeoRem database website[41]) and those measured by electron microprobe. Data from (a) Steenstra et al.[26], measured within a similar time-frame of the EPMA measurements presented in this study and (b) this study. Shaded area represents the range of published data, dotted lines define 10% relative deviation. All uncertainties are 1 standard deviation.

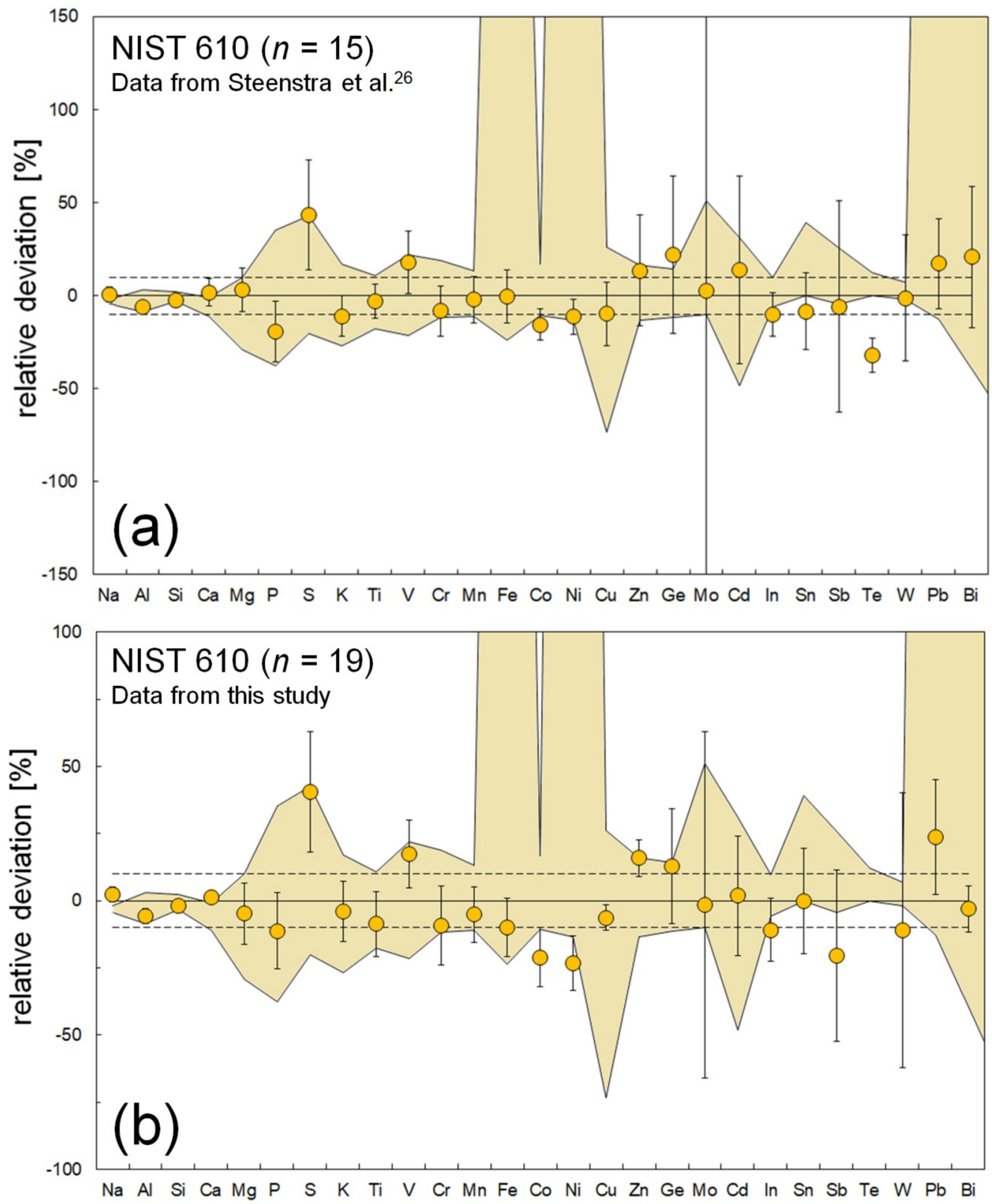

Fig. S.3 Relative deviations between reference concentrations of silicate reference material NIST 610, BHVO-2G and BIR-1G (taken from the GeoRem database website[41]) and those measured by LA-ICP-MS in this study. Shaded area represents the range of published data. All uncertainties are 1 standard deviation. Blue and yellow symbols denote data obtained with a Thermo Element XR ICP-MS and with a Thermo Element II, respectively.

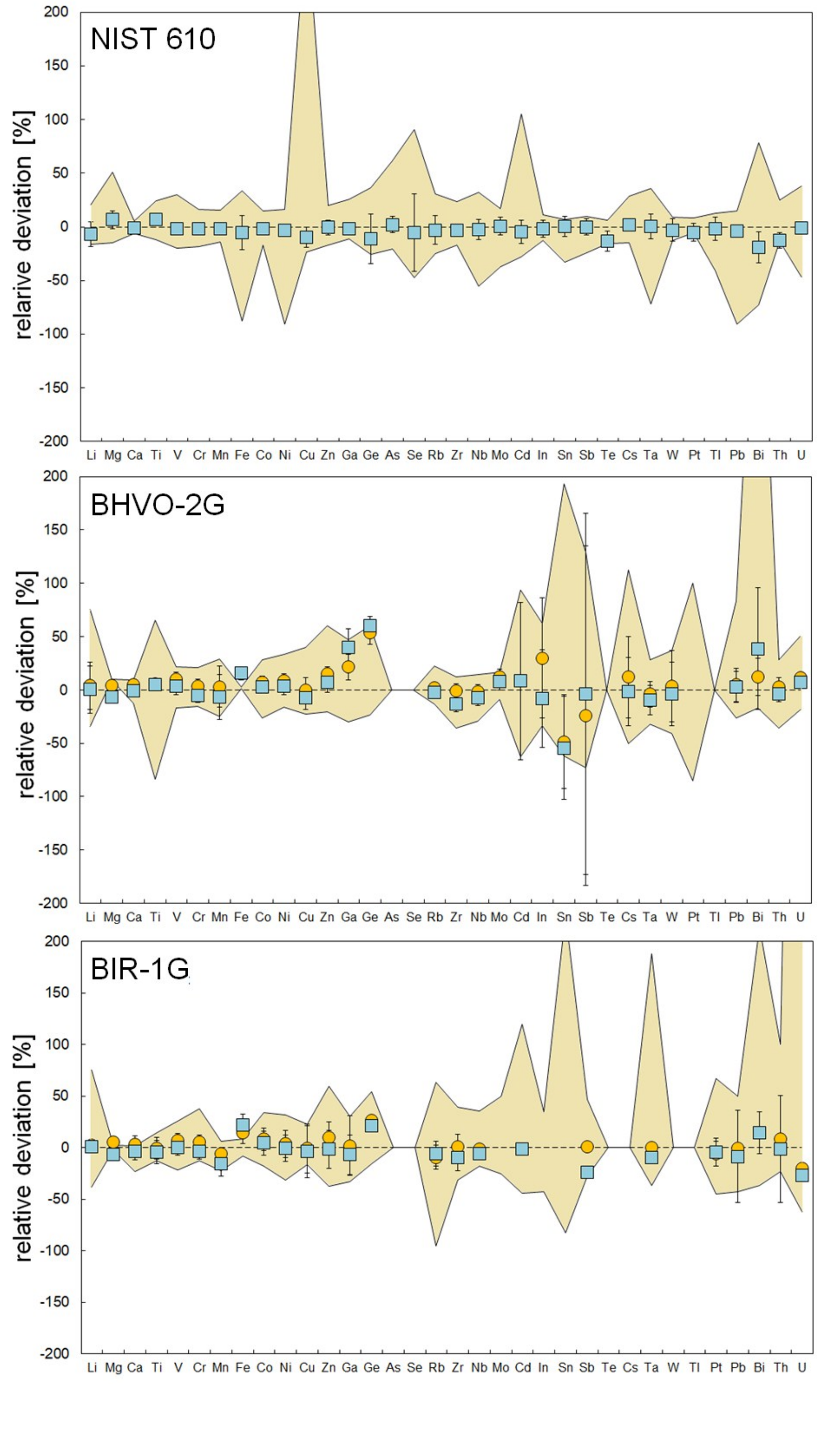

Table S.1 Experimental starting compositions. All quenched sulfides were synthesized at 1 GPa and 1883 K for 20 to 40 minutes.

Run	**Composition** [a]
ESS-66-C1	GG + FeS-C1 (FeS + 1 wt.% In, Ni, W, Cd, Mo, Bi + 0.5 wt.% Cr, Sb, Cu, Co
ESS-67-C2	GG + FeS-C2 (FeS + 1 wt.% Cr, Ni, Sb, Cu, Co, Cd + 0.5 wt.% In, W, Mo, Bi
ESS-70-C3	GG + FeS-C3 (FeS + 1 wt.% Se, Ni, V, Sn, Te + 0.5 wt.% Zn, Pb, As, Ge
ESS-71-C4	GG + FeS-C4 (FeS + 1 wt.% Zn, Ni, Pb, As, Ge + 0.5 wt.% Se, V, Sn, Te
ESS-86-C1	GG + FeS-C1 (FeS + 1 wt.% In, Ni, W, Cd, Mo, Bi + 0.5 wt.% Cr, Sb, Cu, Co
ESS-88-C3	GG + FeS-C3 (FeS + 1 wt.% Se, Ni, V, Sn, Te + 0.5 wt.% Zn, Pb, As, Ge
ESS-89-C4	GG + FeS-C4 (FeS + 1 wt.% Zn, Ni, Pb, As, Ge + 0.5 wt.% Se, V, Sn, Te
ESS-72-D1	GG + FeS-D1 (FeS + 2 wt.% In, Ni, W, Cd + 0.5 wt.% Cr, Sb, Cu, Mo
ESS-75-D2	GG + FeS-D2 (FeS + 2 wt.% Cr, Sb, Cu, Mo + 1.5 wt.% In + 0.5 wt.% Ni, W, Cd
ESS-73-D3	GG + FeS-D3 (FeS + 2 wt.% Bi, Se, Ge, Co + 0.5 wt.% Ni, Zn, Pb, As
ESS-74-D4	GG + FeS-D4 (FeS + 2 wt.% Zn, Pb, As + 0.5 wt.% Bi, Se, Ge, Co, Ni
ESS-81-D4	GG + FeS-D4 (FeS + 2 wt.% Zn, Pb, As + 0.5 wt.% Bi, Se, Ge, Co, Ni
ESS-82-D1	GG + FeS-D1 (FeS + 2 wt.% In, Ni, W, Cd + 0.5 wt.% Cr, Sb, Cu, Mo
ESS-83-D2	GG + FeS-D2 (FeS + 2 wt.% Cr, Sb, Cu, Mo + 1.5 wt.% In + 0.5 wt.% Ni, W, Cd
ESS-85-D4	GG + FeS-D4 (FeS + 2 wt.% Zn, Pb, As + 0.5 wt.% Bi, Se, Ge, Co, Ni

[a] Descriptions of the various synthetic bulk sulfide compositions and related doping levels; GG = synthetic silicate Apollo 15 lunar green glass[6]

Table S.2 Compositions of experimentally produced synthetic sulfides measured using electron microprobe and LA-ICP-MS. All sulfides were measured with LA-ICP-MS using a 65 µm spot size. Numbers in parentheses represent 2 standard errors. All LA-ICP-MS measurements were obtained using the NIST 612 as a reference material for external calibration and Fe, Ni or Cu as the internal standard.

EPMA wt.%	**ESS-35** *N = 31*	**ESS-66** *N = 94*	**ESS-67** *N = 63*	**ESS-70** *N = 66*	**ESS-71** *N = 82*	**ESS-72** *N = 84*	**ESS-73** *N = 97*	**ESS-74** *N = 65*	**ESS-75** *N = 93*
Ca	b.d.l.	0.04(2)	0.02(1)	0.10(4)	0.11(4)	b.d.l.	0.09(2)	0.04(1)	b.d.l.
S	30.34(66)	30.66(40)	31.40(75)	30.07(96)	31.76(41)	31.49(69)	30.72(39)	31.33(52)	30.76(52)
V	n.d.	–	–	0.36(33)	0.40(23)	–	–	–	–
Cr	0.05(1)	0.57(20)	0.41(17)	0.04(1)	0.08(3)	0.42(15)	0.07(1)	0.08(1)	0.34(26)
Mn	0.012(3)	0.029(3)	0.037(4)	0.035(5)	0.036(3)	0.029(3)	0.035(3)	0.031(3)	0.026(3)
Fe	63.47(63)	57.66(46)	58.89(48)	58.85(65)	59.42(45)	57.75(63)	56.19(43)	56.54(82)	57.39(73)
Co	n.d.	0.85(6)	1.16(11)	–	–	–	1.76(10)	1.61(9)	–
Ni	0.09(1)	1.02(12)	0.64(15)	0.61(24)	0.48(11)	2.78(56)	1.16(22)	0.78(17)	0.48(12)
Cu	0.22(1)	0.61(5)	1.04(5)	0.05(1)	0.049(4)	0.41(2)	0.10(1)	0.064(5)	2.32(25)
Zn	0.05(1)	–	0.07(1)	0.47(7)	0.65(9)	–	1.09(14)	1.69(49)	–
Ge	n.d.	–	–	0.12(6)	0.39(17)	–	0.81(16)	–	–
As	n.d.	–	–	0.34(14)	0.25(7)	–	0.89(20)	0.89(21)	–
Se	0.046(4)	–	–	1.25(5)	0.60(2)	–	1.70(4)	0.60(2)	–
Mo	n.d.	0.84(5)	0.23(3)	0.03(1)	0.03(1)	0.25(3)	0.03(1)	0.02(1)	1.75(27)
Cd	0.08(1)	0.73(16)	0.62(20)	–	–	0.81(34)	–	–	0.39(11)
In	–	0.78(14)	–	–	–	0.65(19)	–	–	0.59(16)
Sn	n.d.	–	–	0.85(43)	0.27(9)	–	–	–	–
Sb	n.d.	0.18(4)	0.45(17)	–	–	0.12(4)	–	–	1.31(38)
Te	0.09(2)	–	–	0.82(28)	0.46(10)	–	–	–	–
W	n.d.	0.18(8)	0.04(2)	–	–	0.10(6)	–	–	0.07(2)
Pb	0.04(2)	–	–	0.33(15)	0.35(9)	–	0.10(2)	1.29(46)	–
Bi	0.05(2)	0.25(5)	0.27(10)	–	–	–	0.32(10)	0.28(12)	–
O	0.55(6)	3.32(42)	3.02(84)	2.90(67)	2.25(38)	2.48(49)	2.04(27)	1.93(39)	3.28(40)
Total	95.14	97.94(62)	98.48(35)	97.24(43)	97.64(73)	97.46(38)	97.14(32)	97.49(30)	98.71(74)
LA-ICP-MS	*N = 8*	*N = 14*	*N = 16*	*N = 13*	*N = 17*	*N = 18*	*N = 15*	*N = 17*	*N = 7*
Fe int. stand.									
Mg24 (ppm)	<13	380(28)	243(127)	458(52)	471(36)	310(72)	264(89)	539(332)	46(13)
Si29	524(29)	524(31)	548(153)	566(56)	554(31)	701(267)	418(32)	1321(707)	462(61)
Ca43	155(25)	990(80)	788(102)	2450(135)	1507(66)	1203(385)	1305(248)	1993(757)	460(137)
V51	416(13)	11(1)	9(2)	8252(890)	5647(309)	12(1)	21(1)	12(1)	1.7(4)
Cr53	533(16)	4955(382)	7971(1286)	617(72)	840(46)	4604(361)	745(11)	881(22)	2739(922)
Mn55	158(7)	344(5)	443(5)	465(5)	455(4)	384(4)	465(12)	429(7)	282(5)
Fe56	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Co59	1140(38)	8542(95)	12723(179)	26.3(3)	26.2(3)	23.2(4)	19508(294)	18216(318)	25(1)
Ni60	1197(33)	11577(171)	7554(221)	9063(207)	5930(152)	27228(1085)	13060(430)	9149(219)	6166(485)
Ni61	1190(29)	10224(252)	6738(178)	8502(228)	5576(131)	25443(993)	11947(325)	8640(262)	6191(431)
Cu63	2653(46)	6860(96)	11332(221)	484(7)	612(10)	4289(113)	1117(12)	685(16)	17856(454)
Zn66	632(19)	52(1)	1011(30)	6482(158)	7935(297)	49(2)	13528(525)	19001(1316)	57(8)
Ge73	421(12)	12(1)	12(1)	2715(131)	6923(327)	12(1)	9872(546)	4422(231)	10(1)
As75	42(2)	68(2)	64(2)	5325(177)	3390(128)	66(2)	9712(486)	10618(479)	57(4)
Se82	287(3)	<6	<6	7010(87)	3258(31)	<6	8862(153)	3237(88)	<5

Mo95	841(10)	8671(141)	2526(63)	165(3)	147(1)	2399(53)	162(1)	140(4)	13321(1177)
Cd111	876(30)	7870(318)	7540(345)	12(1)	19(1)	12127(760)	9(1)	62(4)	4031(127)
In115	<2	9814(301)	3104(112)	45(2)	15(1)	7388(402)	2.9(1)	50(2)	7001(252)
Sn118	646(22)	31(1)	34(1)	9102(315)	3017(130)	30(1)	48(1)	32(1)	23(2)
Sb121	387(12)	2417(90)	5954(219)	19(1)	5.8(3)	1324(54)	6.3(2)	8.0(3)	16072(1269)
Te125	1194(48)	5(1)	15(1)	10093(501)	5362(210)	6.2(5)	4.4(3)	6(1)	5.1(4)
W182	546(26)	2308(190)	797(123)	9(1)	5(1)	3738(623)	1.2(4)	1.5(4)	1007(92)
Pb208	800(28)	3.1(1)	56(2)	4760(285)	4551(221)	12(8)	1710(92)	18576(633)	13(1)
Bi209	590(22)	2957(112)	3121(66)	3.9(2)	2.6(1)	0.6(1)	3752158)	3640(170)	11(1)
Ni int. stand.	*N = 8*	*N = 14*	*N = 16*	*N = 13*	*N = 17*	*N = 18*	*N = 15*	*N = 17*	*N = 7*
Mg24 (ppm)	<10	338(26)	214(116)	316(36)	390(25)	336(97)	238(80)	474(299)	36(10)
Si29	409(28)	436(28)	443(132)	341(30)	406(22)	697(308)	344(29)	1051(575)	357(26)
Ca43	123(20)	825(71)	635(98)	1462(70)	1095(46)	1172(441)	1069(203)	1575(619)	352(80)
V51	325(12)	9(1)	8(1)	5172(607)	4288(222)	12(1)	18(1)	10.0(5)	1.3(4)
Cr53	417(13)	4450(373)	7015(1279)	436(55)	712(36)	4957(523)	684(22)	782(25)	2151(846)
Mn55	124(6)	292(5)	363(13)	294(7)	349(9)	375(18)	394(16)	350(10)	221(21)
Fe56 (wt.%)	49.98(135)	63.47(97)	63.31(188)	53.51(127)	64.75(152)	78.47(341)	64.45(195)	63.25(151)	48.41(384)
Co59 (ppm)	888(12)	7233(116)	10369(207)	16.5(3)	19.9(4)	22(1)	16454(314)	14774(270)	19(1)
Ni60	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Ni61	934(18)	10060(124)	6398(86)	6361(132)	5043(86)	28982(213)	11836(228)	8266(260)	4907(132)
Cu63	2073(33)	5918(42)	9431(256)	313(5)	480(13)	4252(85)	967(30)	571(19)	13996(952)
Zn66	494(21)	472)	894(51)	4662(101)	6873(270)	54(4)	12602(665)	17179(1335)	45(9)
Ge73	329(5)	11(1)	10(1)	1938(64)	5962(192)	13(2)	9259(553)	4011(223)	8(1)
As75	32(1)	65(2)	59(1)	3850(86)	2964(77)	74(3)	9337(291)	9853(380)	45(3)
Se82	225(6)	b.d.l.	b.d.l.	5103(112)	2886(75)	<6	8801(327)	3165(101)	4(2)
Mo95	657(18)	7482(182)	2106(100)	107(4)	115(3)	2384(98)	140(4)	116(4)	10365(659)
Cd111	686(25)	7354(312)	6836(430)	9(1)	17(1)	13365(996)	9(1)	57(4)	3149(239)
In115	1.7(3)	8286(200)	2526(98)	28(1)	11.8(5)	7106(177)	2.4(1)	41(2)	5475(406)
Sn118	503(15)	26(1)	28(1)	5892(138)	2363(83)	30(1)	41(2)	26(1)	18(1)
Sb121	302(7)	2087(62)	4961(138)	12(1)	4.6(1)	1326(41)	5,5(1)	6.7(2)	12516(319)
Te125	936(37)	5(1)	14(1)	7248(324)	4662(206)	6.8(7)	4.2(4)	6(1)	4.0(4)
W182	426(19)	1963(170)	660117)	6(1)	4(1)	3706(744)	1.1(3)	1.3(3)	791(95)
Pb208	624(21)	2.6(1)	45(2)	2960(153)	3438(185)	11(8)	1430(92)	14928(583)	10(1)
Bi209	460(17)	2493(79)	2643(92)	2.5(1)	2.0(1)	0.6(1)	3178(154)	2963(112)	8.3(2)
Cu int. stand.	*N = 8*	*N = 14*	*N = 16*	*N = 13*	*N = 17*	*N = 18*	*N = 15*	*N = 17*	*N = 7*
Mg24 (ppm)	<11	353(27)	240(130)	458(52)	399(27)	320(83)	254(85)	543(348)	59(17)
Si29	440(27)	455(28)	498(149)	495(47)	415(22)	656(272)	368(28)	1219(687)	597(76)
Ca43	131(20)	861(72)	711(100)	2121(111)	1117(38)	1111(390)	1141(211)	1804(747)	596(174)
V51	350(10)	10(1)	9(2)	7490(844)	4375(244)	12(1)	19(1)	11(1)	2.2(6)
Cr53	448(12)	4666(396)	7885(1351)	631(76)	728(40)	4780(441)	734(12)	878(37)	3503(1218)
Mn55	133(5)	305(5)	408(10)	426(6)	356(6)	362(11)	422(9)	392(9)	365(13)
Fe56 (wt.%)	53.76(93)	64.03(95)	68.87(136)	75.68(109)	64.46(102)	73.81(204)	67.04(73)	68.82(161)	79.38(200)
Co59 (ppm)	956(22)	7543(127)	11659(251)	23.9(3)	20.3(3)	21.6(4)	17626(287)	16521(374)	32(1)
Ni60	1007(16)	10665(75)	7247(191)	8850(155)	4933(129)	27015(521)	12471(426)	8810(303)	7978(540)
Ni61	1005(21)	10498(161)	7204(143)	9246(217)	5168(136)	28134(553)	12714(337)	9285(451)	8189(470)
Cu63	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Zn66	532(14)	49(2)	1001(36)	6758(132)	7014(242)	52(3)	13459(447)	19174(1369)	74(12)
Ge73	354(6)	11(1)	12(1)	2814(119)	6096(251)	13(1)	9872(504)	4490(313)	13(1)
As75	35(1)	68(2)	67(2)	5581(176)	3032(122)	71(3)	10048(487)	11077(661)	74(5)

Se82	242(4)	<6	<6	7420(93)	2956(49)	<6	9463(118)	3555(90)	7(2)
Mo95	708(13)	7827(195)	2371(94)	155(4)	117(2)	2307(72)	151(2)	130(2)	17239(1543)
Cd111	738(21)	7669(305)	7659(304)	12(1)	17(1)	12925(856)	9(1)	64(4)	5218(148)
In115	1.92(2)	8642(192)	2836(67)	41(1)	12.1(4)	6888(241)	2.6(1)	46(2)	9042(147)
Sn118	542(16)	28(1)	32(1)	8543(233)	2415(101)	29(1)	44(1)	30(1)	30(2)
Sb121	326(9)	2178(61)	5590(212)	18(1)	4.7(2)	1283(35)	5.9(2)	7.5(4)	20820(1464)
Te125	1007(34)	5(1)	16(1)	10522(439)	4764(158)	6.6(6)	4.4(3)	6(1)	6.6(5)
W182	458(21)	2053(175)	740(121)	8(1)	4(1)	3555(644)	1.1(3)	1.4(4)	1303(127)
Pb208	672(21)	2.7(1)	51(1)	4287(222)	3504(148)	11(8)	1532(74)	16721(537)	17.2(4)
Bi209	496(19)	2611(79)	2867(57)	3.6(2)	2.0(1)	0.5(1)	3408(123)	3336(215)	14(1)

EPMA	**ESS-81**	**ESS-82**	**ESS-83**	**ESS-85**	**ESS-86**	**ESS-88**	**ESS-89**
wt.%	*N = 44*	*N = 68*	*N = 56*	*N = 85*	*N = 92*	*N = 49*	*N = 64*
Ca	0.01(1)	b.d.l.	0.02(2)	0.09(4)	0.05(6)	0.07(7)	0.04(2)
S	32.92(40)	30.77(113)	31.03(40)	31.30(48)	31.44(63)	33.42(58)	30.37(89)
V	–	–	–	–	–	n.d.	n.d.
Cr	0.10(1)	0.11(1)	0.12(2)	0.06(1)	0.49(17)	0.05(1)	0.03(1)
Mn	0.024(4)	0.026(4)	0.026(4)	0.029(3)	0.034(4)	0.023(3)	0.039(4)
Fe	55.33(97)	58.15(82)	57.27(58)	56.56(56)	57.89(47)	58.80(46)	59.09(65)
Co	1.05(7)	–	–	0.88(4)	0.71(2)	–	–
Ni	0.55(7)	1.46(32)	0.48(14)	0.48(8)	0.76(10)	0.74(17)	0.46(19)
Cu	0.057(5)	0.49(7)	2.32(15)	0.043(6)	0.53(4)	0.027(9)	0.042(7)
Zn	3.84(97)	–	–	2.03(49)	0.03(1)	0.42(10)	1.35(27)
Ge	0.22(9)	–	–	0.30(11)	–	0.17(11)	0.49(18)
As	1.72(40)	–	–	1.21(22)	–	0.55(18)	0.49(16)
Se	0.47(2)	–	–	0.43(1)	–	0.82(4)	0.53(3)
Mo	0.05(1)	0.30(5)	1.29(9)	0.027(5)	0.86(6)	–	–
Cd	–	1.37(59)	0.46(9)	–	0.44(12)	–	–
In	–	1.60(40)	1.05(14)	–	0.70(12)	–	–
Sn	–	–	–	n.d	n.d.	n.d.	n.d.
Sb	–	0.36(11)	1.26(51)	–	0.12(4)	–	–
Te	–	–	–	–	–	0.42(18)	0.83(29)
W	–	0.17(6)	0.05(1)	–	0.32(26)	–	–
Pb	0.86(13)	–	–	1.04(26)	–	0.37(18)	0.88(33)
Bi	0.32(14)	–	–	0.31(14)	0.24(7)	–	–
O	1.57(31)	3.36(79)	3.65(33)	3.04(32)	3.44(50)	1.53(42)	3.25(54)
Total	99.19(19)	98.24(28)	99.17(16)	98.04(22)	97.85(23)	97.63(19)	98.12(22)
LA-ICP-MS	*N = 3*	*N = 26*	*N = 23*	*N = 27*	*N = 24*	*N = 25*	*N = 23*
Fe int. stand.							
Mg24 (ppm)	300(238)	198(90)	104(115)	351(18)	213(42)	359(62)	269(54)
Si29	426(448)	452(120)	510(377)	256(8)	277(32)	199(74)	390(51)
Ca43	398(51)	405(164)	675(272)	775(25)	407(82)	996(72)	695(67)
V51	7(1)	3(1)	1.5(1)	6.8(3)	6(1)	5349(363)	3618(331)
Cr53	854(59)	1738(488)	735(54)	398(7)	2868(276)	368(23)	281(22)
Mn55	272(23)	248(5)	289(5)	277(3)	293(11)	225(3)	358(10)
Fe56	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Co59	10070(27)	14(1)	17.6(3)	5948(106)	5277(67)	16.4(2)	15.6(3)
Ni60	6303(67)	12699(322)	5352(273)	3618(138)	7262(190)	5694(132)	3180(115)
Ni61	6285(46)	12797(403)	5713(275)	3630(147)	7528(201)	5508(159)	3332(153)
Cu63	507(23)	3907(137)	17311(501)	380(5)	4285(94)	240(4)	371(8)

Zn66	32677(3628)	51(4)	55(2)	24230(1303)	195(6)	5007(236)	11569(536)
Ge73	2948(422)	9(1)	8.5(4)	3041(203)	35(2)	2752(159)	6702(1442)
As75	17681(426)	52(3)	56(3)	11961(796)	87(3)	5739(265)	5362(720)
Se82	3494(307)	1.5(2)	3.6(2)	2726(88)	34(1)	4688(112)	3714(325)
Mo95	126(1)	1712(59)	8720(1250)	87(3)	4836(85)	82(2)	117(10)
Cd111	28(3)	23501(2988)	5120(518)	42(3)	5634(325)	4.2(4)	30(5)
In115	19(2)	18820(1297)	11455(510)	27(2)	9080(412)	23(1)	25(3)
Sn118	18(2)	28(2)	29(2)	25(2)	24(1)	4997(323)	4965(624)
Sb121	5.0(5)	4023(231)	17625(1285)	6.3(4)	1790(96)	5.2(3)	8.6(9)
Te125	3.1(5)	4.4(3)	4.8(3)	2.8(2)	4.1(3)	6260(407)	13310(1608)
W182	7(1)	3747(870)	562(146)	1.6(1)	1809(334)	2.1(2)	6.7(11)
Pb208	10869(2388)	7(1)	12(1)	13680(735)	124(8)	4757(381)	13176(1877)
Bi209	3980(550)	5.3(4)	10(1)	4321(313)	2807(202)	3.1(2)	99(13)
Ni int. stand.	*N = 3*	*N = 26*	*N = 23*	*N = 27*	*N = 24*	*N = 25*	*N = 23*
Mg24	264(212)	240(118)	<80	356(24)	227(47)	471(78)	399(84)
Si29	377(399)	535(160)	414(270)	259(14)	291(36)	260(94)	577(83)
Ca43	350(42)	488(217)	575(189)	788(40)	434(91)	1310(81)	1025(109)
V51	6(1)	3(1)	1.3(1)	6.9(4)	6(1)	7035(487)	5363(550)
Cr53	753(45)	2038(594)	668(54)	401(18)	3007(324)	482(30)	415(37)
Mn55	239(18)	287(11)	263(12)	280(11)	307(16)	297(6)	527(25)
Fe56 (wt.%)	49.16(5193)	66.22(173)	52.25(244)	56.65(212)	59.53(156)	77.71(185)	86.15(307)
Co59	8848(115)	16.6(3)	15.9(6)	5992(141)	5506(97)	22(1)	23(1)
Ni60	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Ni61	5563(67)	14718(139)	5112(67)	3611(33)	7835(64)	7152(83)	4863(137)
Cu63	445(16)	4497(66)	15692(851)	384(14)	4456(54)	317(5)	544(22)
Zn66	28752(2954)	59(3)	50(4)	24597(1698)	204(9)	6595(222)	16933(848)
Ge73	2590(343)	11(1)	7.6(4)	3082(243)	36(3)	3614(168)	9810(2195)
As75	15522(241)	60(2)	51(1)	11898(534)	91(2)	7463(221)	7888(1095)
Se82	3091(254)	1.7(2)	3.2(14)	2728(133)	36(1)	6089(117)	5449(536)
Mo95	111(1)	1997(93)	7838(1147)	88(4)	5075(142)	109(4)	173(18)
Cd111	25(3)	26969(2783)	4690(591)	42(4)	5874(307)	5.5(4)	44(8)
In115	17(2)	21677(1054)	10280(741)	27(2)	9429(296)	30(1)	36(5)
Sn118	16(2)	32(2)	26(2)	25(2)	25(1)	6556(331)	7309(959)
Sb121	4.4(4)	4624(179)	15691(687)	6.3(3)	1854(68)	6.8(3)	13(1)
Te125	2.7(4)	5.1(3)	4.4(4)	2.8(2)	4.3(3)	8262(422)	19467(2445)
W182	7(1)	4458(1188)	485(99)	1.7(2)	1922(372)	2.8(2)	10(2)
Pb208	9519(2001)	8(1)	11(1)	13923(970)	129(7)	6242(428)	19404(2847)
Bi209	3481(464)	6.2(3)	8.7(5)	4393(365)	2926(189)	4.0(3)	145(20)
Cu int. stand.	*N = 3*	*N = 26*	*N = 23*	*N = 27*	*N = 24*	*N = 25*	*N = 23*
Mg24	305(256)	263(132)	37(16)	351(19)	267(54)	359(62)	270(55)
Si29	436(477)	583(180)	348(80)	255(9)	344(43)	198(73)	391(51)
Ca43	397(47)	535(243)	655(69)	777(22)	509(105)	995(69)	698(70)
V51	7(1)	3(1)	2.0(2)	6.8(3)	7(1)	5336(388)	3626(325)
Cr53	855(54)	2198(638)	994(83)	395(9)	3546(369)	365(24)	281(23)
Mn55	270(11)	310(14)	388(10)	277(3)	362(17)	225(3)	357(10)
Fe56 (wt.%)	55.86(255)	71.60(235)	77.08(228)	55.96(73)	70.34(151)	58.98(104)	58.42(125)
Co59	10041(471)	17.9(5)	24(1)	5937(92)	6511(99)	16(1)	15.6(5)
Ni60	6280(234)	15791(218)	7191(469)	3602(127)	8929(109)	5667(96)	3171(134)
Ni61	6313(313)	15911(227)	7652(448)	3604(136)	9279(142)	5439(111)	3323(152)

Cu63	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*	*Int.*
Zn66	32560(2223)	64(3)	74(3)	24231(1266)	241(9)	4996(163)	11505(498)
Ge73	2935(324)	11(1)	11(1)	3042(210)	43(3)	2743(143)	6666(1460)
As75	17611(379)	65(2)	76(5)	11888(770)	108(2)	5668(226)	5371(740)
Se82	3506(166)	1.8(2)	4.8(3)	2696(84)	42(1)	4622(90)	3683(316)
Mo95	125(6)	2157(109)	11771(1862)	87(3)	6000(162)	83(3)	116(10)
Cd111	28(2)	28966(2628)	6807(645)	42(3)	6945(352)	4.2(3)	30(5)
In115	19(2)	23353(981)	15105(652)	27(2)	11149(364)	23(1)	24(3)
Sn118	18(2)	35(2)	39(3)	25(2)	30(1)	4976(278)	4940(601)
Sb121	4.9(3)	4985(174)	23625(2160)	6.3(4)	2195(90)	5.2(3)	8.5(9)
Te125	3.1(3)	5.5(3)	6.4(4)	2.8(2)	5.1(4)	6264(343)	13136(1501)
W182	7(1)	4846(1342)	761(230)	1.6(1)	2256(427)	2.1(2)	6.6(10)
Pb208	10770(1952)	9(1)	16(1)	13718(726)	153(8)	4733(328)	13050(1714)
Bi209	3943(391)	6.6(3)	13(1)	4339(318)	3463(230)	3.1(2)	97(12)

[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

Table S.3 Concentrations in the NIST 610 reference glass measured using EMPA (1) at the start of the study (*N = 15*), as previously reported in ref.[26], (2) measured in this study at the end of the study (*N = 19*), and those from the GeoRem database[41] and references therein. Each of the 15 and 19 measurements are based on 10 replicate analyses. Numbers in parentheses represent 1 standard deviation.

	Measured (this study)	**Detection limit (ppm)**	**GeoRem (preferred values)[41]**	**Deviation (in %) of GeoRem preferred values to measured values**		**GeoRem (published range)[41]**
				Beginning of study[26]	End of study	
Na_2O (wt.%)	13.09(33)	113	13.4(3)	+1±4	+2±3	13.35–14.00
Al_2O_3	2.07(2)	138	1.95(4)	–6±3	–6±3	1.89–2.13
SiO_2	71.06(104)	445	69.7(5)	–2±2	–4±1	68.1–72.0
CaO	11.24(5)	127	11.4(2)	+2±7	+2±2	11.3–12.8
Mg (ppm)	454(23)	78	432(29)	+3±12	–5±11	393–610
P	465(23)	118	413(46)	–19±16	–11±14	305–661
S	409(42)	145	575(32)	+43±29	+41±22	403–720
K	483(34)	66	464(21)	–11±11	–4±11	397–633
Ti	495(54)	132	452(10)	–3±9	–9±12	408–550
V	383(33)	123	450(9)	+18±17	+17±13	369–573
Cr	450(61)	122	408(10)	–8±13	–9±15	343–462
Mn	468(37)	119	444(13)	–2±13	–5±10	392–499
Fe	508(51)	114	458(9)	0±14	–10±11	57–600
Co	519(59)	124	410(10)	–15±8	–23±8	351–459
Ni	598(73)	134	459(4)	–11±9	–23±10	43–530
Cu	471(8)	146	441(15)	–10±17	–6±5	350–1648
Zn	397(8)	211	460(18)	+14±30	+16±7	396–531
Ge	396(6)	130	447(78)	+22±42	+13±21	391–505
As	b.d.l.[a]	123	325(18)	n.d.	–	272–496
Se	b.d.l.[a]	253	138(42)	–	–	95–183
Mo	423(196)[a]	529	417(21)	+2±551	–1±64	276–463
Cd	265(41)	139	270(16)	+14±50	+2±22	206–521
In	487(42)	83	434(19)	–10±12	–11±12	396–461
Sn	430(54)	164	430(29)	–9±21	0±20	309–430
Sb	498(156)[a]	403	396(19)	–6±57	–20±32	315–414
Te	b.d.l.[a]	67	302[b]	–32±9	–	269–302
W	499(206)	331	444(29)	–1±34	–11±51	415–452
Pb	344(57)	142	426(1)	+17±24	+24±21	40–489
Bi	396(8)	112	384(26)	+21±38	–3±9	114–638

[a] Close to or below detection limit [b] Value marked as uncertain in the GeoRem database