

Electronic supplementary information

**Quantitative Analysis of Fe³⁺/ΣFe in Silicate Glasses Based on XPS Fe
3p Core-Level Spectroscopy**

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval
to the final version of the manuscript.

Table.S1 Composition of Initial Materials Selected for the Experiment

	MORBa	HBb
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SiO ₂	49.57±0.47	34.65±0.42
TiO ₂	1.72±0.06	3.68±0.09
Al ₂ O ₃	16.95±0.11	25.60±0.20
CaO	11.05±0.18	4.04±0.05
MgO	7.11±0.11	7.70±0.17
FeO _T	9.77±0.28	22.83±0.36
Na ₂ O	2.74±0.18	1.25±0.10
K ₂ O	0.16±0.02	0.17±0.04
P ₂ O ₅	0.24±0.04	/
Total	99.31±0.60	99.91±0.73

***Data sources: a Shimizu et al. (1980). MORB AII-92-29-1. Average composition of samples prepared under air conditions; b from other studies within Professor Hongluo Zhang research group. Average composition of samples prepared under air conditions. “/” indicates that the content has not been added.**

Table.S2 Conditions of the Vertical Gas-Mixing Furnace

Sample	wire	Gas flow	logfO ₂	ΔFMQ	rate(ml/min)	Duration(h)
MORB series						
M13	Pt	CO ₂ /CO	-6.31	0.37	240:10	24
M19	Pt	CO ₂ /CO	-4.39	2.26	247:3	24
M21	Pt	CO ₂ /CO	-5.67	1.05	245.5:4.5	24
M27	Pt	Air	-0.68	6.05	Air	24
M29	Re	CO ₂ /CO	-10.19	-3.52	50:200	8
M31	Re	CO ₂ /CO	-9.22	-2.55	110:140	8
M34	Pt	Air/CO ₂	-2.09	4.56	20:230	24
HB series						
B3	Pt	pure CO ₂	-2.41	2.34	250	24
B7	Pt	CO ₂ /CO	-4.20	0.55	240:10	24
B19	Pt	Air	-0.68	3.97	Air	4
B25	Re	CO ₂ /CO	/	/	50:200	2

Table.S3 Major Element Composition of Experimental Products (wt%)

	Comment	SiO ₂	TiO ₂	Al ₂ O ₃	CaO	MgO	FeO _T	Na ₂ O	K ₂ O	P ₂ O ₅	Total
B3	HB	35.07	3.66±	25.37	4.14±	7.82±	22.74	0.93±	0.13±	-	99.85±0.61
		±0.42	0.10	±0.21	0.10	0.11	±0.32	0.11	0.03		
B25	HB	35.94	3.77±	25.62	4.40±	7.87±	21.58	0.49±	0.08±	-	99.75±0.36
		±0.31	0.07	±0.18	0.08	0.13	±0.23	0.09	0.02		
M13	MORB	50.95	1.74±	16.91	11.11	7.11±	9.07±	2.76±	0.16±	0.22±	100.02±0.54
		±0.29	0.06	±0.13	±0.18	0.14	0.28	0.16	0.03	0.03	
M27	MORB	49.57	1.72±	16.95	11.05	7.11±	9.77±	2.74±	0.16±	0.24±	99.31±0.60
		±0.47	0.06	±0.11	±0.18	0.11	0.28	0.18	0.02	0.04	
M34	MORB	50.33	1.74±	17.42	10.88	6.87±	9.11±	2.74±	0.18±	0.22±	99.49±0.49
		±0.46	0.10	±0.17	±0.13	0.12	0.21	0.17	0.04	0.04	
B7	HB	35.46	3.72±	25.21	4.22±	7.96±	22.56	0.55±	0.11±	-	99.78±0.52
		±0.44	0.11	±0.18	0.10	0.12	±0.36	0.08	0.03		
B19	HB	34.65	3.68±	25.60	4.04±	7.70±	22.83	1.25±	0.17±	-	99.91±0.73
		±0.42	0.09	±0.20	0.05	0.17	±0.36	0.10	0.04		
M19	MORB	50.43	1.78±	17.04	11.02	6.92±	9.20±	2.75±	0.15±	0.21±	99.51±0.48
		±0.39	0.08	±0.10	±0.16	0.09	0.21	0.14	0.04	0.03	
M21	MORB	50.73	1.73±	16.93	10.93	7.11±	9.34±	2.75±	0.17±	0.25±	99.93±0.67
		±0.44	0.08	±0.23	±0.14	0.10	0.26	0.10	0.05	0.04	
M29	MORB	50.89	1.79±	17.55	11.00	7.02±	8.85±	2.17±	0.18±	0.17±	99.61±0.65
		±0.51	0.10	±0.16	±0.10	0.07	0.23	0.12	0.04	0.04	
M31	MORB	51.35	1.75±	17.19	11.07	7.27±	8.71±	1.95±	0.15±	0.16±	99.60±0.71
		±0.52	0.08	±0.15	±0.17	0.14	0.12	0.17	0.03	0.04	

* “-” denotes these components were not measured.

Table.S4. Mössbauer Spectrum Fitting Parameters

Sample	X ²	Background	L HWHM	Fe ³⁺				Fe ²⁺				
				CS	δ _{CS}	QS	δ _{QS}	ρ	CS	δ _{CS}	QS	δ _{QS}
M29	1.09	53839(18)	0.138*	0.410*	0*	1.330*	0.210(19)	0.301(65)	0.965(13)	0.186(89)	1.738(19)	0.372(18)
M31	0.56	54209(15)	0.138(48)	0.410*	0*	1.330*	0.710(47)	0.115(79)	1.092(11)	0.400(20)	1.937(20)	0.321(91)
B25	1.16	30408(18)	0.132(24)	0.390*	0*	1.330*	0.400*	0.209(48)	0.965(82)	0.241(10)	1.831(11)	0.314(33)
M21	1.1	51942(24)	0.157(55)	0.410*	0*	1.150(30)	0.450(44)	0.160(13)	0.989(23)	0.251(21)	1.826(33)	0.180(10)
M13	1.06	62939(27)	0.160(49)	0.410(17)	0*	1.110(17)	0.470(40)	0.270(29)	0.984(15)	0.227(28)	1.790(58)	0.195(77)
B7	1.16	31054(21)	0.163(44)	0.390(11)	0*	1.330(19)	0.400*	0.120(19)	1.018(22)	0.234(34)	1.896(42)	0.304(96)
M19	1.23	49459(33)	0.240(57)	0.276(48)	0*	1.246(70)	0.440(13)	0.250(34)	0.987(14)	0.187(31)	1.850(26)	0.150(10)
B3	1.24	45133(24)	0.151(48)	0.309(84)	0*	1.280(16)	0.456(88)	0.080(34)	0.996(42)	0.241(48)	1.836(90)	0.29(15)
B19	1.12	27527(19)	0.180(36)	0.183(29)	0*	1.176(51)	0.461(80)	0.400(55)	0.897(27)	0.239(52)	1.776(59)	0.120(13)
M34	0.53	53722(20)	0.290(47)	0.320(32)	0*	1.331(72)	0.491(80)	0.400(25)	1.083(44)	0.237(89)	1.970(10)	0.070(13)

M27	1.08	47685(27)	0.226(47)	0.224(20)	0*	1.279(23)	0.358(73)	0.800(21)	0.932(56)	0.197(83)	1.747(79)	0.210(13)
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Table.S5 Comparison of values determined by Mössbauer spectroscopy and measured values by XPS Fe 3*p* standard curve I under 50-100 µm beam spot sizes.

Sample Number	Fe ³⁺ /ΣFe (Mössbauer)	Fe ³⁺ /ΣFe (XPS 50 µm)	Fe ³⁺ /ΣFe (XPS 100 µm)
M29	0.039 (0.024)	0.001	0.010
M31	0.041 (0.028)	0.019	0.048
B25	0.043 (0.021)	0.038	0.076
M21	0.147 (0.044)	0.152	0.181
M13	0.179 (0.066)	0.200	0.200
B7	0.181 (0.018)	0.210	0.219
M19	0.327 (0.023)	0.305	0.362
B3	0.355 (0.021)	0.333	0.352
B19	0.573 (0.024)	0.548	0.570
M34	0.616 (0.017)	0.570	0.582
M27	0.745 (0.050)	0.745	0.761

*The values in parentheses represent one standard deviation from Mössbauer spectroscopy tests.

Table.S6 Comparison of values determined by Mössbauer spectroscopy and measured values by XPS Fe 3*p* standard curve II under 200-300 µm beam spot sizes.

Sample Number	Fe ³⁺ /ΣFe (Mössbauer)	Fe ³⁺ /ΣFe (XPS 200 µm)	Fe ³⁺ /ΣFe (XPS 300 µm)
M29	0.039 (0.024)	0.008	0.017
M31	0.041 (0.028)	0.042	0.051
B25	0.043 (0.021)	0.093	0.059
M21	0.147 (0.044)	0.161	0.127
M13	0.179 (0.066)	0.186	0.169
B7	0.181 (0.018)	0.212	0.178
M19	0.327 (0.023)	0.314	0.280
B3	0.355 (0.021)	0.339	0.305
B19	0.573 (0.024)	0.535	0.535
M34	0.616 (0.017)	0.590	0.614

M27	0.745 (0.050)	0.839	0.754
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Table.S7 The signal-to-noise ratio of samples B25 and M13 under different beam spot sizes and number of scans.

Sample Number	Spot Size (μm)	Number of Scans	S/N
B25	50	25	25.92
B25	50	35	27.35
B25	50	45	27.28
B25	100	25	16.66
B25	100	35	30.81
B25	100	45	42.47
B25	200	25	25.89
B25	200	35	43.89
B25	200	45	45.29
B25	300	25	36.64
B25	300	35	43.47
B25	300	45	56.54
M27	50	25	7.55
M27	50	35	5.91
M27	50	45	7.84
M27	100	25	5.61
M27	100	35	7.71
M27	100	45	12.60
M27	200	25	10.63
M27	200	35	13.17
M27	200	45	14.10
M27	300	25	10.86
M27	300	35	12.33
M27	300	45	13.50

Table.S8 Calculation results and standard deviations of repeated experiments for XPS Fe 3*p* with a beam spot size of 50 μm.

Sample Number	XPS 1	XPS 2	XPS 3	S.D.
M29	0.029	0.010	0.019	0.008
M31	0.010	0.038	0.019	0.012
B25	0.010	0.010	0.038	0.013
M21	0.162	0.181	0.152	0.012
M13	0.210	0.210	0.200	0.004
B7	0.190	0.200	0.210	0.008
M19	0.333	0.286	0.305	0.020
B3	0.362	0.371	0.333	0.016
B19	0.559	0.496	0.548	0.028
M34	0.606	0.658	0.570	0.036
M27	0.729	0.745	0.745	0.007

Table.S9 Calculation results and standard deviations of repeated experiments for XPS Fe 3*p* with a beam spot size of 300 μm .

Sample Number	XPS 1	XPS 2	XPS 3	S.D.
M29	0.034	0.034	0.017	0.008
M31	0.076	0.068	0.051	0.011
B25	0.076	0.076	0.059	0.008
M21	0.136	0.153	0.127	0.011
M13	0.169	0.212	0.169	0.020
B7	0.127	0.195	0.178	0.029
M19	0.246	0.314	0.280	0.028
B3	0.314	0.314	0.305	0.004
B19	0.476	0.556	0.535	0.034
M34	0.590	0.639	0.614	0.020
M27	0.770	0.821	0.754	0.029

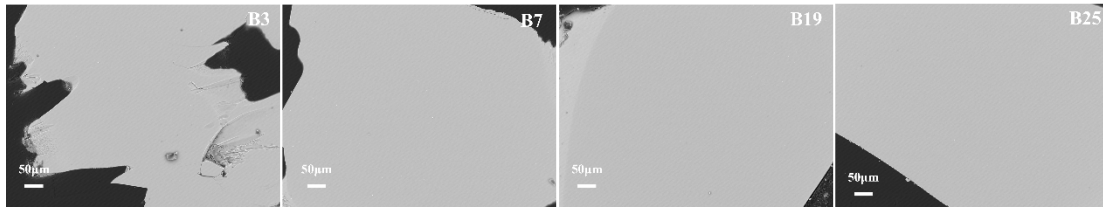


Figure. S1 Backscattered electron images of Reference Sample Series B (B3, B7, B19, B25) under SEM.

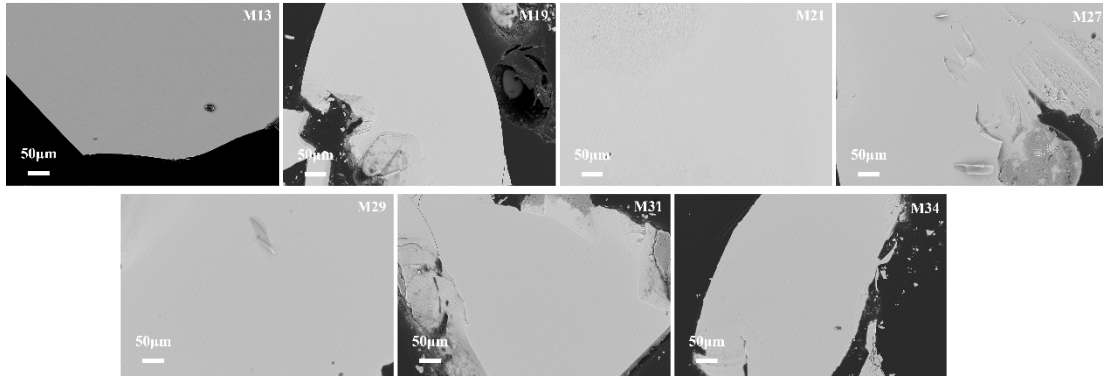


Figure. S2 Backscattered electron images of Reference Sample Series M (M13, M19, M21, M27, M29, M31, M34) under SEM.