Boron isotope fractionation in magma via crustal carbonate dissolution

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Supplementary Information

Contents:

Table S1. Major element composition of Merapi and Vesuvius starting materials used in experiments

	Average composition of hydrous Merapi glass[1,2]	1σ (9)[3]	Average composition of hydrous Vesuvius glass[1,2]	1σ (9)[3]	Whole rock analysis of Merapi limestone added[4]	Whole rock analysis of Vesuvius limestone added[2]	Whole rock analysis of Vesuvius dolostone added[2]
wt%							
SiO_2	51.83	0.43	49.85	0.21	0.28	0.02	0.02
TiO_2	0.89	0.05	1.03	0.08	0.01	-	-
Al_2O_3	18.08	0.24	15.95	0.67	0.13	-	-
FeO_t*	8.17	0.16	7.98	0.25	0.01	0.01	0.00
MnO	0.20	0.03	0.14	0.02	0.00	0.01	0.01
MgO	2.97	0.08	6.03	0.33	0.40	0.79	21.01
CaO	9.19	0.16	9.98	0.29	56.72	54.99	31.34
Na_2O	3.48	0.09	2.35	0.07	0.12	-	-
K_2O	2.05	0.03	4.01	0.19	0.00	-	-
P_2O_5	0.34	0.04	0.70	0.09	0.03	0.02	0.00
Total	97.20		98.29		57.70	55.84	52.38
H_2O	2.23		1.71		0.15	-	-
CO_2	-		-		44.93	44.11	47.59

[1] Merapi hydrous glass was uniformly hydrated at Universität Hannover (Germany) and measured for water content by Karl Fischer Titration (KFT). Vesuvius hydrous glass was uniformly hydrated at INGV (Italy) and the water content estimated by the difference between the total and 100 wt.%.
[2] Analysis carried out by EMP at INGV (Rome, Italy).
[3] 1σ standard deviation. The number in parentheses represents the number of analyses for each sample.
[4] XRF analysis carried out at IFM-GEOMAR (Kiel, Germany).
* Total iron is given as a FeO_t.
Data sources: Deegan *et al.* (2010) and Jolis *et al.* (2013).

Table S2. Representative major element composition of Merapi and Vesuvius experimental glasses (CaO-normal and (MgO)CaO-rich)

	CaO-normal glass					(MgO)CaO-rich glass				
Run-sample	375-7[1]	374-5[1]	V4[2]	V9[2]	V1[2]	375-7[1]	374-5[1]	V4[2]	V9[2]	V1[2]
wt%										
SiO_2	51.83	50.88	49.15	49.21	50.31	35.99	38.11	37.02	24.81	28.77
TiO_2	0.83	0.89	0.93	0.96	0.99	0.44	0.58	0.72	0.66	0.51
Al_2O_3	18.22	18.72	16.61	15.65	15.50	13.04	13.94	12.12	7.93	9.07
FeO_t^*	7.50	6.24	6.58	6.79	6.82	5.85	5.48	5.39	4.49	5.07
MnO	0.22	0.20	0.12	0.14	0.15	0.17	0.14	0.06	0.13	0.12
MgO	2.69	2.73	5.70	5.62	5.96	2.25	2.26	9.04	3.97	4.49
CaO	9.16	8.84	9.14	10.00	9.74	29.77	27.41	20.75	34.99	35.29
Na_2O	4.25	4.48	3.15	2.65	2.51	1.90	2.22	2.41	1.10	1.16
K_2O	2.32	2.26	4.05	4.92	4.28	1.07	1.21	2.31	1.45	1.28
P_2O_5	0.36	0.27	0.58	0.64	0.62	0.25	0.22	0.50	0.38	0.37
Total**	97.38	95.52	96.01	96.76	96.93	90.73	91.58	90.42	80.00	86.24

[1] Merapi series: 375-7, limestone reactant, 150 s duration; 374-5, limestone reactant, 300s duration.
[2] Vesuvius series: V4, dolostone reactant, 60 s duration; V9, limestone reactant, 60 s duration; V1, limestone reactant, 90 s duration.
*Total iron is given as a FeO_t.
**Analysis totals are low due to *a)* microbubbles (cf. Deegan *et al*., 2010), *b)* increased CO_2 solubility in alkaline and ultrapotassic melts in general (Behrens, 1995) or *c)* increased CO_2 solubility in the CaO-rich experimental melt (Moore, 2008).
Data sources: Deegan *et al.* (2010) and Jolis *et al.* (2013).

Table S3. Boron concentration and isotope data for the starting magmatic glasses used in magma-carbonate interaction experiments

SIMS I.D.	B ppm	$\delta^{11}B$ ‰	± ‰
Merapi starting glass			
1141_M94-26_1@1	17	-8.4	1.7
1141_M94-26_2@1	17	-7.0	1.6
1141_M94-26_3@1	15	-7.0	1.6
1141_M94-26_4@1	16	-7.6	1.7
1141_M94-26_5@1	18	-6.8	1.8
1141_M94-26_6@1	18	-5.6	1.7
1141_M94-26_7@1	18	-4.5	1.8
1141_M94-26_5@2	17	-4.9	2.2
1141_M94-26_3@2	16	-8.8	1.6
1141_M94-26_8@1	18	-4.3	1.6
1141_M94-26_2@2	16	-4.6	1.6
1141_M94-26_1@2	18	-3.5	1.6
Vesuvius starting glass			
1141_PC428_1@1	13	-11.8	1.8
1141_PC428_2@1	13	-12.3	1.6
1141_PC428_3@1	13	-13.9	1.5
1141_PC428_4@1	13	-13.0	1.5
1141_PC428_5@1	13	-13.9	1.6
1141_PC428_1@2	12	-7.6	1.5
1141_PC428_6@1	13	-10.7	1.5
1141_PC428_7@1	13	-10.1	1.6
1141_PC428_8@1	14	-12.5	1.5
1141_PC428_5@2	13	-11.3	1.6
1141_PC428_3@2	13	-14.2	1.5
1141_PC428_9@1	13	-12.3	1.6
1141_PC428_9@2	13	-14.6	1.6

Table S4. Boron concentration and isotope data for magma-carbonate interaction experimental glasses

Experiment I.D.	SIMS I.D.	Glass type	B ppm	$\delta^{11}B$ ‰	± ‰
Vesuvius series					
V4, dolostone reactant, 1200°C, 0.5 GPa, 60 s duration					
V4	V4-trav1-1	CaO-normal	72	-7.9	0.6
V4	V4-trav1-2	(MgO)CaO-rich	53	-14.6	0.8
V4	V4-trav1-3	(MgO)CaO-rich	51	-13.6	0.7
V4	V4-trav1-4	(MgO)CaO-rich	30	-20.9	0.8
V4	V4-trav1-5	(MgO)CaO-rich	29	-22.4	0.8
V4	V4-trav1-6	CaO-normal	76	-9.3	0.7
V4	V4-trav1-7	(MgO)CaO-rich	41	-14.6	0.8
V9, limestone reactant, 1200°C, 0.5 GPa, 60 s duration					
V9	V9-trav1-1	CaO-normal	18	-12.1	1.0
V9	V9-trav1-2	CaO-normal	18	-12.9	1.0
V9	V9-trav1-3	CaO-normal	16	-14.3	1.1
V9	V9-trav1-4	CaO-normal	16	-10.5	1.1
V9	V9-trav1-5	CaO-normal	15	-12.4	1.1
V9	V9-trav1-6	CaO-normal	15	-11.5	1.2
V9	V9-trav1-7	CaO-normal	15	-10.0	1.2
V9	V9-trav1-8	CaO-normal	16	-11.6	1.1
V9	V9-trav1-9	CaO-normal	15	-12.0	1.1
V9	V9-trav1-11	CaO-normal	15	-10.9	1.1
V9	V9-trav1-12	CaO-normal	14	-11.4	1.1
V9	V9-trav1-13	CaO-normal	14	-9.3	1.1
V9	V9-trav1-14	CaO-normal	14	-10.9	1.2
V9	V9-trav1-15	CaO-normal	14	-8.2	1.1
V9	V9-trav1-16	CaO-normal	13	-13.0	1.2
V9	V9-trav1-17	CaO-normal	12	-10.6	1.3
V9	V9-trav1-18	CaO-normal	12	-14.4	1.2
V9	V9-trav1-19	CaO-normal	9	-14.7	1.4
V9	V9-trav1-20	CaO-normal	11	-12.3	1.3
V9	V9-trav1-21	CaO-rich	2	-37.1	2.6
V9	V9-trav1-22	CaO-rich	3	-40.5	2.9
V9	V9-trav1-23	CaO-rich	5	-24.3	1.9
V9	V9-trav1-24	CaO-rich	3	-32.6	2.2
V9	V9-trav1-25	CaO-rich	3	-37.8	2.4
V9	V9-trav1-26	CaO-rich	4	-25.8	1.9
V9	V9-trav1-27	CaO-rich	4	-29.7	2.0
V9	V9-trav1-29	CaO-rich	4	-24.9	2.1
V9	V9-trav1-30	CaO-rich	2	-39.6	2.6
V9	V9-trav1-31	CaO-rich	3	-31.8	2.2
V9	V9-trav1-32	CaO-rich	3	-35.5	2.4
V9	V9-trav1-33	CaO-rich	3	-37.8	2.4
V9	V9-trav1-35	CaO-rich	3	-33.8	2.3
V9	V9-trav1-36	CaO-rich	4	-26.3	2.0
V9	V9-trav1-37	CaO-rich	3	-24.2	2.2
V9	V9-trav1-38	CaO-rich	4	-25.9	2.0
V9	V9-trav1-39	CaO-rich	4	-28.4	2.1
V9	V9-trav1-41	CaO-rich	7	-17.1	1.6

Table S4 continued.

Experiment I.D.	SIMS I.D.	Glass type	B ppm	$\delta^{11}B$ ‰	± ‰
V1, limestone reactant, 1200°C, 0.5 GPa, 90 s duration					
V1	V1-trav1-1	CaO-normal	161	-6.3	0.8
V1	V1-trav1-2	CaO-normal	163	-5.6	0.6
V1	V1-trav1-3	CaO-normal	166	-6.6	0.6
V1	V1-trav1-6	CaO-normal	237	-6.2	0.6
V1	V1-trav1-7	CaO-normal	240	-7.5	0.6
V1	V1-trav1-8	CaO-normal	141	-11.7	0.6
V1	V1-trav1-9	CaO-normal	177	-8.5	0.6
V1	V1-trav1-10	CaO-normal	195	-8.8	0.6
V1	V1-trav1-12	CaO-normal	133	-10.1	0.6
V1	V1-trav1-13	CaO-rich	70.8	-24.9	0.6
V1	V1-trav1-14	CaO-rich	85	-22.3	0.7
V1	V1-trav1-15	CaO-rich	64	-25.5	0.7
V1	V1-trav1-16	CaO-rich	60	-21.8	0.7
V1	V1-trav1-18	CaO-rich	46	-29.6	0.8
V1	V1-trav1-19	CaO-rich	66	-23.2	0.7
V1	V1-trav1-20	CaO-normal	241	-10.1	0.6
V1	V1-trav1-21	CaO-normal	166	-9.2	0.6
V1	V1-trav1-22	CaO-normal	163	-9.6	0.7
V1	V1-trav2-2	CaO-normal	226	-7.6	0.6
V1	V1-trav2-3	CaO-normal	128	-9.8	0.7
V1	V1-trav2-4	CaO-rich	51	-22.2	0.8
V1	V1-trav2-5	CaO-rich	51	-20.2	0.8
V1	V1-trav2-6	CaO-rich	38	-27.9	0.9
V1	V1-trav2-8	CaO-rich	52	-25.1	0.8
V1	V1-trav2-9	CaO-rich	43	-27.2	0.7
V1	V1-trav2-10	CaO-rich	54	-23.7	0.7
V1	V1-trav2-11	CaO-rich	56	-21.6	0.7
V1	V1-trav2-12	CaO-rich	80	-19.8	0.7
V1	V1-trav2-14	CaO-normal	155	-9.1	0.6
V1	V1-trav2-15	CaO-normal	144	-8.1	0.6
V1	V1-trav2-16	CaO-normal	160	-6.9	0.6
V1	V1-trav2-17	CaO-normal	180	-6.3	0.6
V1	V1-trav2-18	CaO-normal	154	-7.1	0.6
V1	V1-trav3-1	CaO-normal	163	-7.2	0.6
V1	V1-trav3-2	CaO-normal	181	-6.4	0.6
V1	V1-trav3-3	CaO-normal	268	-4.9	0.6
V1	V1-trav3-4	CaO-normal	189	-5.8	0.6
V1	V1-trav3-6	CaO-normal	160	-6.3	0.6
Merapi series					
375-7, limestone reactant, 1200°C, 0.5 GPa, 150 s duration					
375-7	375-7trav2-2	CaO-rich	6	-17.1	1.7
375-7	375-7trav2-3	CaO-rich	5	-14.3	1.9
375-7	375-7trav2-4	CaO-rich	5	-20.9	1.8
375-7	375-7trav2-5	CaO-rich	5	-15.9	1.8
375-7	375-7trav2-6	CaO-rich	6	-14.0	1.7
375-7	375-7trav2-7	CaO-rich	7	-9.9	1.7

Table S4 continued.

Experiment I.D.	SIMS I.D.	Glass type	B ppm	$\delta^{11}B$ ‰	± ‰
375-7	375-7trav2-8	CaO-rich	5	-17.4	1.9
375-7	375-7trav2-9	CaO-rich	4	-17.4	1.9
375-7	375-7trav2-10	CaO-rich	4	-21.9	2.5
375-7	375-7trav2-11	CaO-rich	4	-19.0	2.0
375-7	375-7trav2-12	CaO-rich	4	-20.4	2.3
375-7	375-7trav2-13	CaO-rich	4	-19.4	2.0
375-7	375-7trav2-14	CaO-rich	5	-18.1	1.9
375-7	375-7trav2-15	CaO-rich	4	-18.3	2.0
375-7	375-7trav2-16	CaO-rich	5	-18.2	1.9
375-7	375-7trav2-17	CaO-rich	5	-17.9	2.0
375-7	375-7trav2-18	CaO-rich	7	-11.0	1.8
375-7	375-7trav2-19	CaO-normal	13	-2.2	1.2
375-7	375-7trav2-20	CaO-normal	14	-0.9	1.2
375-7	375-7trav2-21	CaO-normal	14	+0.1	1.2
375-7	375-7trav2-22	CaO-normal	14	-2.8	1.1
375-7	375-7trav2-23	CaO-normal	14	-4.0	1.3
375-7	375-7trav2-24	CaO-normal	14	-2.3	1.2
375-7	375-7trav2-25	CaO-normal	14	-3.3	1.2
375-7	375-7trav2-26	CaO-normal	14	-2.8	1.1
375-7	375-7trav3-1	CaO-rich	7	-9.8	1.5
375-7	375-7trav3-2	CaO-rich	4	-22.2	2.1
375-7	375-7trav3-3	CaO-rich	4	-18.8	2.2
375-7	375-7trav3-4	CaO-rich	4	-20.9	2.0
375-7	375-7trav3-5	CaO-rich	4	-21.6	2.0
375-7	375-7trav3-6	CaO-normal	10	-5.3	1.3
375-7	375-7trav3-7	CaO-normal	13	-3.3	1.4
375-7	375-7trav3-8	CaO-normal	13	-3.1	1.2
375-7	375-7trav3-9	CaO-normal	14	-2.8	1.2
375-7	375-7trav3-10	CaO-normal	13	-1.8	1.2
375-7	375-7trav3-11	CaO-normal	14	-3.7	1.2
375-7	375-7trav3-12	CaO-normal	14	-3.7	1.2
375-7	375-7trav3-13	CaO-normal	13	-3.6	1.2
375-7	375-7trav3-14	CaO-normal	13	-3.0	1.2
375-7	375-7trav3-15	CaO-normal	13	-3.9	1.3
374-5, limestone reactant, 1200°C, 0.5 GPa, 300s duration					
374-5	374-5trav1-1	CaO-normal	12	-3.1	1.3
374-5	374-5trav1-3	CaO-rich	9	-9.5	1.4
374-5	374-5trav1-4	CaO-rich	10	-10.0	1.6
374-5	374-5trav1-5	CaO-rich	10	-9.7	1.4
374-5	374-5trav1-6	CaO-rich	7	-10.6	2.4
374-5	374-5trav1-7	CaO-rich	6	-16.2	1.7
374-5	374-5trav1-8	CaO-rich	10	-10.4	1.4
374-5	374-5trav1-9	CaO-rich	6	-16.5	1.8
374-5	374-5trav1-10	CaO-rich	6	-16.6	1.7
374-5	374-5trav1-11	CaO-rich	6	-9.8	1.7
374-5	374-5trav1-12	CaO-rich	6	-13.7	1.9
374-5	374-5trav1-13	CaO-rich	6	-16.9	1.8

Table S4 continued.

Experiment I.D.	SIMS I.D.	Glass type	B ppm	$\delta^{11}B$ ‰	± ‰
374-5	374-5trav1-14	CaO-rich	7	-11.1	1.7
374-5	374-5trav1-15	CaO-normal	12	-2.8	1.3
374-5	374-5trav1-16	CaO-rich	6	-12.5	1.7
374-5	374-5trav1-17	CaO-rich	7	-14.0	1.6
374-5	374-5trav1-18	CaO-rich	7	-13.7	1.7
374-5	374-5trav1-19	CaO-normal	13	-4.4	1.2
374-5	374-5trav1-20	CaO-normal	13	-1.0	1.2
374-5	374-5trav1-21	CaO-normal	13	-0.6	1.2
374-5	374-5trav1-22	CaO-normal	13	-2.2	1.2
374-5	374-5trav1-23	CaO-normal	13	0.0	1.2
374-5	374-5trav1-24	CaO-normal	13	-0.8	1.2
374-5	374-5trav1-25	CaO-normal	13	+1.2	1.3

All data obtained using a CAMECA IMS 1280 SIMS instrument at the Swedish Museum of Natural History in Stockholm (Nordsim).

Table S5. Boron concentration and isotope data for selected geochemical reservoirs from the literature (plotted in Figure 1)

	B ppm range	$\delta^{11}B$ ‰ range	Reference
Surface, slab, mantle, and arc-related reservoirs			
Seawater	4 to 5	+39.3 to +40.2	Spivack and Edmond, 1987; Hemming and Hanson, 1992; Foster *et al*., 2010
Carbonates (sediments, biogenic skeletons, corals, foraminifera, calcite)	4 to 58	+8.9 to +39.8	Hemming and Hanson, 1992; Vengosh *et al*., 1991; Spivack *et al*., 1993; Gaillardet and Allègre, 1995; Deyhle *et al*., 2001
Lime- and dolostone	2 to 18	+1.5 to +8.4	Vengosh *et al*., 1991; Gonfiantini *et al*., 2003
Altered ocean crust (AOC)	1 to 104	-4.3 to +24.9	Smith *et al*., 1995
Marine sediment	13 to 163	-17.0 to +10.5	Ishikawa and Nakamura, 1993; Moriguti and Nakamura, 1998; Tonarini *et al*., 2011
Mid Ocean Ridge Basalt (MORB)	0.3 to 3.6	-10.8 to -1.2	Spivack and Edmond, 1987; Chaussidon and Jambon, 1994; Moriguti and Nakamura, 1998; le Roux *et al*., 2004; Ganoun *et al*., 2007; Shaw *et al*., 2012; Marschall and Monteleone, 2014
Ocean Island Basalt (OIB)	0.3 to 7.8	-16.9 to +7.8	Chaussidon and Jambon, 1994; Chaussidon and Marty, 1995; Gurenko and Chaussidon, 1997; Kobayashi *et al*., 2004; Turner *et al*., 2007; Brounce *et al*., 2012
Arc metamorphic rocks and minerals	0.4 to 59	-15.6 to +7.9	Peacock and Hervig, 1999; Nakano and Nakamura, 2001; Pabst *et al*., 2012
Island arcs			
Halmahera	2 to 32	-2.3 to +3.6	Palmer, 1991
Izu	3 to 65	-6.8 to +12.0	Ishikawa and Nakamura, 1994; Straub and Layne, 2002
Kurile	5 to 48	-3.8 to +5.9	Ishikawa and Tera, 1997
Lesser Antilles	2 to 102	-25.6 to +12.9	Smith *et al*., 1997; Bouvier *et al*., 2008; Bouvier *et al*., 2010
Manus		-0.6 to +5.8	Shaw *et al*., 2012
Marianas	9 to 28	+2.9 to +6.2	Ishikawa and Tera, 1999
NE Japan	3 to 15	-4.7 to +3.4	Moriguti *et al*., 2004
S. Sandwich	3 to 20	+12.1 to +17.6	Tonarini *et al*., 2011
Aeolian Islands	5 to 60	-13.7 to +2.3	Tonarini *et al*., 2001a; Schiavi *et al*., 2012

	B ppm range	$\delta^{11}B$ ‰ range	Reference
Continental arcs and volcanoes			
Anatolia	7 to 66	-15.1 to -0.2	Tonarini *et al.*, 2005
Andes	10 to 60	-7.2 to +4.2	Rosner *et al.*, 2003
Cascades	1 to 18	-21.3 to +4.4	Rose *et al.*, 2001; Leeman *et al.*, 2004; Le Voyer et al., 2010
Ecuadorian Andes	6 to 12	-17.9 to +3.5	Le Voyer *et al.*, 2008
El Salvador	5 to 36	-2.7 to +6.3	Tonarini *et al.*, 2007
Kamchatka	11 to 36	-3.7 to +5.6	Ishikawa *et al.*, 2001
Phlegrean province	5 to 118	-10.6 to -2.8	Tonarini *et al.*, 2004; 2009
Vesuvius and Etna	7 to 36	-7.6 to -3.5	Tonarini *et al.*, 2001b; Di Renzo *et al.*, 2007

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