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High SO₂ flux, sulfur accumulation, and gas fractionation at an erupting submarine

volcano

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Supplementary Methods

Hydrothermal fluids were sampled using the Hydrothermal Fluid and Particle Sampler (HFPS). HFPS pumps fluids through a titanium intake nozzle (Supplementary Figure 5) with an in-line temperature sensor, into a teflon and titanium manifold with 24 ports, then out through a 4-liter/minute pump to an exhaust port. An insulated one-meter extension to the titanium nozzle was used for highly energetic volcanic vent sampling. While the flush pump maintained fluid flow through the manifold, a dedicated sample pump pulled the fluid into selected sample containers, which were either PVC plastic cylinders with Teflon seals, titanium cylinders with Teflon pistons and seals, 0.2 mil Tedlar plastic collapsible bags with Delrin inlet valves, or all-titanium gas-tight samplers with gold seals (Lupton et al., 2008). Free gas bubbles were trapped in a funnel and collected in gas-tight samplers. The sample containers were surrounded by ambient seawater and quickly cooled after collection. Temperature of the fluid flowing into the nozzle and through the manifold during sampling was recorded, allowing calculation of the heat content of the sample. For samples designated with BF or PF in the sample identification number, particles suspended in the flowing water were filtered out and collected on in-line filters. Coarse and heavy particles may have been partially segregated by settling during passage through the manifold. Check valves on container inlets prevented samples from leaking out and pressure relief valves allowed bags and pistons to expand to accommodate excess gas pressure. Standard titanium syringe major samplers (Von Damm 1985) were used on some dives.

Upon arrival on deck, sample containers were removed from the manifold and put into cold storage at 1-5°C. The total gas headspace volume (if present) was measured by removing it into large syringes. An aliquot of gas headspace and fluid was taken for shipboard analysis of H₂ and CH₄ by gas chromatography. Fluid was analyzed on board ship for total dissolved hydrogen sulfide (modified spectrophotometric method of Cline, 1969), pH in closed container with Ross pH electrode, and dissolved silica by spectrophotometry. Sample aliquots were for major ions were filtered through 0.2µm filters and trace metal samples were acidified to pH <2 with ultrapure HCl. Major anions (chloride and sulfate) and cations (Na, K, Mg, Ca) were analyzed by ion chromatography, and in some cases also by titration, ICP-OES, or atomic absorption. Fe, Mn, and Al were analyzed by flame and graphite furnace atomic

absorption on a Perkin Elmer AAnalyst 800. Al was also analyzed by ICP-MS, using matrixmatched standard addition curves and internal standard monitoring on a Perkin Elmer DRC-II or DRC-e. In 2006, sulfite and thiosulfate were analyzed on board ship by preservation/derivitization and liquid chromatography (Vairavamurthy and Mopper, 1990). In 2009, samples were preserved with formaldehyde with minimal air exposure and analyzed on shore for dissolved sulfite (detection limit 20 μ mol/kg) and thiosulfate (detection limit 30 µmol/kg) by ion chromatography (Dionex DX500 with AS11HC column, NaOH eluent, and conductivity detection) after removal of >99% of Cl and SO₄ by precipitation in Dionex On-Guard Ag-Ba-H cartridges (method paper in preparation). Thiosulfate was below detection on all formaldehyde-preserved samples analyzed. Sulfate was analyzed in formaldehydepreserved samples (without removal of Cl/SO₄) to determine the initial sulfate content at the time of preservation. Chromatographic peaks for chloride, sulfite, and sulfate were resolved and samples with millimolar levels of sulfite did not require pre-treatment to remove sulfate. [Sulfate analyzed in non-preserved samples from previous years (Table DR4) gives an approximate measure of the total excess dissolved sulfur species, primarily sulfite and sulfate, after sulfite has oxidized partially or completely to sulfate during sample storage.] Sample J2-401-PF2 collected 4/8/09 with in-situ filtration had a thick pale yellow layer on the filter, assumed to be dominantly elemental sulfur. This material was dried to constant weight (for >two weeks in a dessicator, not under vacuum to avoid sublimation) and weighed on a microbalance to estimate maximum particulate sulfur content assuming that all material was elemental sulfur. Particulate mass was converted to suspended sulfur concentration using the measured fluid volume passed through the filter. This particular sample had small volume due to sulfur clogging the filter, and no formaldehyde preserved cut was taken. Sulfite was analyzed on 5/22/09 in a sample stored in a tightly capped bottle with no headspace after removal of sulfate and chloride, and total sulfate plus sulfite was analyzed 5/27/09 [results in Table DR1].

The 1-sigma precision of the reported results is: pH, 0.02 pH units; dissolved Si, 2%; Fe and Mn, 4%; Al, 8%; K, Mg, Ca, 1.5%; H_2S , 5%; $SO_4^=$, 2%; $SO_2(aq)$, 10%, $S_2O_3^=$, 15%.

Titanium gas-tight samples of fluid and free gas were processed at sea and analyzed on shore, and were previously reported (Lupton et al., 2008). The sulfur gas content was calculated by the difference between manometric total gas and total analyzed gas by chromatography. Because only trace H_2S was present in any of the analyzed samples, and no H_2S smell was present in the extracted gas, the sulfur gas is assumed to be SO_2 .

To estimate a reasonable primary magmatic gas composition for Figure 2, we took the composition predicted for H_2O , CO_2 and SO_2 from Moretti and Papale (2004) and the high-temperature (750-800°C) H_2 concentration from Saito et al (2002). The primary gas

composition in Figure 2 is an estimate, not a direct measurement of gas at magmatic temperatures.

Submarine arc SO₂ flux calculation. To estimate the magnitude of the SO₂ flux from submarine arc volcanoes, we make a simple calculation as follows. Take the product of the global hydrothermal heat flux for the MOR axis (for crust <1Ma, from Stein and Stein, 1994), the proportion of total hydrothermal heat produced by submarine volcanic arcs from Baker et al., 2008 (10% of MOR flux), the proportion of submarine arc heat produced by eruptions (1/4 to ¹/₂ from White et al., 2006), and the average excess sulfur/heat ratio determined from NW Rota volcanic vent fluids. In detail, the numbers are: 3.3×10^{12} J/s x 3600 s/hr x 24 h/d x 365 d/y x 0.1 x 0.25 (or 0.5) x 275 nmol/J x 10^{-9} mol/nmol = 0.7 (to 1.4) x 10^{11} mol of S/y. This is comparable in magnitude to the estimate of 3.15×10^{11} mol SO₂/y for all subaerial arc volcanoes (Fischer, 2008).

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Supplementary video caption:

Windows Media Video file (VideoDR1.wmv) extracted from Jason 2 dive 189, April 25, 2006 at 07:04 UT shows an intense bright yellow plume of fine molten sulfur droplets driven up into a rising volcanic plume during a slow lava eruption. This level of activity persisted for more than one hour. We believe this represents slowly ascending lava driving off elemental sulfur accumulated at the top of the lava conduit. Small lava bombs are seen falling back down into the vent. Abundant gas bubbles indicate active magma degassing from the lava conduit. The nearly continuous churning in middle foreground may be caused by seawater boiling in contact with hot rock or by gas bursts through accumulated tephra in the vent. The two red spots are lasers with 10 cm spacing. For details on NW Rota eruption dynamics, see Chadwick et al. 2008 and Deardorff et al., 2011.

Sample	Average	Heat content	H2S	Sulfite	Initial	Total excess	Excess dissolved
number	temperature °C	relative to	mmol/kg	mmol/kg	sulfate	dissolved sulfur	sulfur to heat
		ambient J/g			mmol/kg	mmol/kg	nmol/J
J2 401-P1	37.7	131.1	n.m.	40.1	37.5	49.9	381
J2 401-PF2	49.8	181.4	n.m.	33.3	34.4	39.7	219
J2 401-P3	35.1	120.4	0.002	24.2	35.6	32.1	267
J2 401-P6	201.3	810.1	0.001	133.6	60.5	166.4	205
J2 405-P6	48.0	173.9	0.001	62.0	40.3	74.6	429
J2 405-PF7	46.4	167.2	< 0.001	54.6	39.3	66.2	396
J2 403-B24	17.3	46.5	< 0.001	2.7	31.7	6.7	144
J2 403-PF4	13.0	28.6	< 0.001	2.5	29.7	4.5	156
Brimstone	50	207	0.001	44	39	55	275
average							
Brimstone	59	250	0.001	42	10	52	113
std. dev.							
MOR high-T	315.6	1547	7.6	0	0	-20.6	-13
vent average							

TABLE DR1. 2009 FLUID SULFUR CHEMISTRY AT BRIMSTONE VENT

Note: All fluid samples in this table except 401-PF2 were preserved with formaldehyde. Initial sulfate is an upper limit for the sulfate concentration at the time of sampling. Total excess dissolved sulfur is the sum of all dissolved sulfur species minus background seawater sulfate. Negative numbers represent a net loss from seawater. We determined 5.15 mmol/kg particulate sulfur in sample J2-401-PF2 by in-situ filtration followed by drying and weighing. This level of particulate sulfur is 60% in excess of what would be produced by reaction 2 based on the excess sulfate relative to seawater in this sample when it was analyzed. n.m. means not measured.

Sample ID	Date collected	Depth m	latitude °N	longitude °E	Sample type
R783-B17	3/30/2004	566	14.5965	144.7777	bag
R783-P20	3/30/2004	549	14.5965	144.7777	piston
R786-B8	4/1/2004	561	14.6008	144.7753	bag
R786-BF11	4/1/2004	561	14.6008	144.7753	filtered bag
R786-P4	4/1/2004	561	14.6008	144.7753	piston
R786-P5	4/1/2004	561	14.6008	144.7753	piston
J2-187-B9	4/23/2006	559.6	14.6009	144.7754	bag
J2-187-PF24	4/23/2006	562	14.6009	144.7754	filtered piston
J2-187MajBlu	4/23/2006	563	14.6010	144.7754	Ti Major
J2-188MajYel	4/24/2006	564	14.6013	144.7764	Ti Major
J2-188MajBlu	4/24/2006	563	14.6009	144.7754	Ti Major
J2-189MajWht	4/25/2006	559	14.5991	144.7778	Ti Major
J2-189MajRed	4/25/2006	560	14.5992	144.7778	Ti Major
J2-191-PF1	4/27/2006	557	14.6010	144.7755	filtered piston
J2-192-BF11	4/28/2006	558.4	14.6009	144.7751	filtered bag
J2-398-PF4	4/5/2009	523.3	14.6008	144.7754	filtered piston
J2-398-P8	4/5/2009	523.3	14.6008	144.7754	piston
J2-398-B24	4/5/2009	523.4	14.6008	144.7754	bag
J2-398-PF2	4/5/2009	524	14.6007	144.7754	filtered piston
J2-401-P1	4/8/2009	523.1	14.6006	144.7753	piston
J2-401-PF2	4/8/2009	523.1	14.6006	144.7753	filtered piston
J2-401-P3	4/8/2009	523.2	14.6006	144.7753	piston
J2-401-P6	4/8/2009	522.8	14.6007	144.7754	piston
J2-403-B24	4/10/2009	519.1	14.6007	144.7753	bag
J2-403-PF4	4/10/2009	519	14.6007	144.7753	filtered piston
J2-403-P1	4/10/2009	519	14.6007	144.7753	piston
J2-405-P3	4/11/2009	521.5	14.6008	144.7754	piston
J2-405-P5	4/11/2009	521.5	14.6008	144.7754	piston
J2-405-PF2	4/11/2009	521.4	14.6008	144.7755	filtered piston
J2-405-B22	4/11/2009	521.5	14.6008	144.7755	bag
J2-405-B21	4/11/2009	521	14.6009	144.7755	bag
J2-405-P6	4/11/2009	521.2	14.6008	144.7755	piston
J2-405-PF7	4/11/2009	521.2	14.6008	144.7754	filtered piston
J2-405-P8	4/11/2009	521.3	14.6008	144.7754	piston
J2-405-PF9	4/11/2009	520.8	14.6008	144.7754	filtered piston
J2-405-BF18	4/11/2009	520.8	14.6008	144.7754	filtered bag

TABLE DR2. BRIMSTONE VENT SAMPLE INFORMATION

Note: in the sample ID prefix, R=ROPOS and J2=Jason 2. An F in the ID suffix means the sample was filtered through a 0.4 micron filter as it was taken.

Sample ID	Vent	Date collected	Tmax	Tavg	рН	dissolved silica	Fe	Mn
			°C	°C	at 22°C	µmol/kg	µmol/kg	µmol/kg
R783b17	Brimstone	3/30/2004	29.8	25.8	2.09	1112	192.5	35.3
R783p20	Brimstone Rim	3/30/2004	16.7	12.8	3.00	388	62.4	11.1
R786p4	Brimstone	4/1/2004	26.1	23.6	2.21	1101	220.4	25.9
R786p5	Brimstone	4/1/2004	29.4	22.6	2.26	838	173.8	20.3
R786b8	Brimstone	4/1/2004	27.1	23.3	2.11	1286	242.8	33.6
R786bf11	Brimstone	4/1/2004	29.5	25.5	1.98	1234	278.2	30.0
J2-187-B9	Brimstone	4/23/2006	28.2	25.4	1.64	n.d.	1616	32.2
J2-187PF24	Brimstone	4/23/2006	95.3	90.2	1.91	550	117	4.66
J2-187MajBlu	Brimstone	4/23/2006	95	n.d.	1.72	3190	2002	35.9
J2-188MajYel	Brimstone	4/24/2006	110	n.d.	1.66	1350	479	9.40
J2-188MajBlu	Brimstone	4/24/2006	95	n.d.	1.05	7060	1873	33.4
J2-189MajWht	Brimstone	4/25/2006	200	n.d.	1.35		808	15.6
J2-189MajRed	Brimstone	4/25/2006	256.6	200	2.11		746	16.7
J2-191-PF1	Brimstone	4/27/2006	41.9	37.6	1.78		473	8.38
J2-407-PF4	Bckgnd SW 581m	4/13/2009	6.4	6.2	7.32	70	<0.09	<0.04
J2-398-PF4	Brimstone	4/5/2009	80.5	53.3	3.80	98	10.9	0.59
J2-398-P8	Brimstone	4/5/2009	31.2	22.5	5.23	94	13.3	0.68
J2-398-PF2	Brimstone	4/5/2009	26.4	22.2	5.86	71	17.9	<0.04
J2-401-P1	Brimstone	4/8/2009	46.9	37.7	1.54	2547	807	16.0
J2-401-PF2	Brimstone	4/8/2009	58.4	49.8	1.62		604	11.6
J2-401-P3	Brimstone	4/8/2009	41.9	35.1	1.66	2581	982	69.9
J2-401-P6	Brimstone	4/8/2009	207.4	201.3	1.06	7032	2737	114
J2-403-B24	Brimstone	4/10/2009	20.5	17.3	3.97	1316	255	21.0
J2-403-PF4	Brimstone	4/10/2009	17.6	13	4.78	577	122	9.33
J2-403-P1	Brimstone	4/10/2009	21.2	18.5	3.65	1431	300	21.7
J2-405-P3	Brimstone	4/11/2009	24.5	20.9	2.27	344	103	2.60
J2-405-P5	Brimstone	4/11/2009	34.7	19	2.25		142	3.48
J2-405-PF2	Brimstone	4/11/2009	44.5	40.6	2.55	273	64.6	1.75
J2-405-B22	Brimstone	4/11/2009	38.7	35.2	1.96	628	188	5.09
J2-405-B21	Brimstone	4/11/2009	21.5	19.2	5.65	257	33.8	7.37
J2-405-P6	Brimstone	4/11/2009	55.7	48	1.49	4280	1108	20.6
J2-405-PF7	Brimstone	4/11/2009	57.9	46.4	1.51	4231	1145	20.9
J2-405-P8	Brimstone	4/11/2009	48.4	41.2	1.43	4037	1043	18.9
J2-405-PF9	Brimstone	4/11/2009	39.5	35.2	1.69	1724	457	10.7
J2-405-BF18	Brimstone	4/11/2009	35.1	28.8	1.96	1295	332	7.19
Brimstone average	59.8		2.4	1819	581	20.5		
MOR Hot Vent Average			315.6		3.5	16000	4600	1190.0
Ratio Volc. Vent:MOR		0.19			0.11	0.13	0.02	

TABLE DR3. VOLCANIC VENT FLUID AND BACKGROUND SEAWATER COMPOSITION (1)

Sample ID	Fe/Mn	Fe/heat	Mn/heat	AI	Al/heat	к	Mg	Са
•		nmol/J	nmol/J	µmol/kg	nmol/J	mmol/kg	mmol/kg	mmol/kg
R783b17	5.5	2.5	0.45	67	0.9	10.32	52.64	10.47
R783p20	5.6	2.5	0.45	19	0.8	10.11	55.85	11.16
R786p4	8.5	3.2	0.37	122	1.7	9.81	50.71	9.77
R786p5	8.5	2.7	0.31	96	1.5	9.99	51.57	10.12
R786b8	7.2	3.6	0.49	154	2.3	10.27	52.87	10.16
R786bf11	9.3	3.6	0.39	141	1.8	10.01	51.58	9.89
J2-187B9	50.17	21.05	0.420	1820	23.6	10.18	54.80	12.51
J2-187PF24	25.15	0.34	0.013	115	0.3	8.99	48.76	9.16
J2-187MajBlu	55.80	5.47	0.098	409	1.1	10.38	54.85	9.20
J2-188MajYel	50.92	1.12	0.022	462	1.1	9.70	49.95	10.07
J2-188MajBlu	56.16	5.12	0.091	2558	7.0	8.26	44.26	11.04
J2-189MajWht	51.84	1.01	0.019	661	0.8	9.66	54.13	11.41
J2-189MajRed	44.58	0.70	0.016	376	0.5	9.33	50.12	9.22
J2-191PF1	56.52	3.72	0.066	814	6.4	9.60	52.19	10.31
J2-407-PF4	n.d.	n.d.	n.d.	<0.01	n.d.	9.99	52.39	10.28
J2-398PF4	18.5	0.06	0.00	14.6	0.1	9.79	50.91	9.87
J2-398-P8	19.6	0.20	0.01	9.9	0.2	9.84	52.50	9.85
J2-398-PF2	n.d.	0.27	n.d.	3.1	0.0	9.93	52.01	10.16
J2-401-P1	50.6	6.15	0.12	1412	11.0	9.68	51.59	11.31
J2-401-PF2	52.1	3.33	0.06	1087	6.1	9.79	51.11	10.79
J2-401-P3	14.1	8.16	0.58	1192	10.1	9.75	51.43	10.75
J2-401-P6	24.0	3.38	0.14	2008	2.5	9.15	46.69	11.94
J2-403-B24	12.1	5.49	0.45	1890	43.4	10.25	52.81	10.45
J2-403-PF4	13.1	4.26	0.33	922	35.8	10.08	52.45	10.37
J2-403-P1	13.8	5.83	0.42	2231	45.9	10.21	52.80	10.62
J2-405-P3	39.6	1.68	0.04	106	1.8	9.94	51.95	10.04
J2-405-P5	40.8	2.65	0.07	242	4.8	9.99	52.03	10.14
J2-405-PF2	36.9	0.45	0.01	351	2.5	9.95	52.17	10.08
J2-405-B22	36.9	1.56	0.04	144	1.2	9.93	51.94	10.06
J2-405-B21	4.6	0.62	0.14	64	1.2	10.01	52.65	10.18
J2-405-P6	53.8	6.37	0.12	2156	12.6	9.54	50.13	11.78
J2-405-PF7	54.9	6.85	0.12	1904	11.6	9.59	50.34	11.62
J2-405-P8	55.2	7.16	0.13	1936	13.6	9.52	50.15	11.31
J2-405-PF9	42.7	3.78	0.09	612	5.2	n.d.	n.d.	n.d.
J2-405-BF18	46.2	3.52	0.08	470	5.1	9.92	52.10	10.37
Brimstone Avg.	32.3	3.8	0.19	781.4	5.7	9.8	51.6	10.5
MOR Avg.	4.3	3.10	0.78	5.5	0.0036	22.6	0.0	31.4
Volc:MOR	7.51	1.22	0.24	142	1603	0.43		0.33

TABLE DR3. VOLCANIC VENT FLUID AND BACKGROUND SEAWATER COMPOSITION (2)

	H2S µM	SO4 mM	S2O3 µm	SO2(aq) mM
R786p5	11.7	33.3	n.m.	n.m.
R783p20	25.0	31.0	n.m.	n.m.
R783b17	64.3	34.0	n.m.	n.m.
R786b8	8.8	35.8	n.m.	n.m.
R786p4	5.2	34.4	n.m.	n.m.
R786bf11	3.4	36.9	n.m.	n.m.
R786b17	20.2	27.7	n.m.	n.m.
J2-187B9	bdl	67.7	n.m.	n.m.
J2-187MajBlu	bdl	57.3	79.1	68.9
J2-187PF24	bdl	47.0	0	14.3
J2-188MajBlu	bdl	164.9	n.m.	163.0
J2-188MajYel	bdl	63.7	n.m	21.3
J2-189MajRed	39.6	29.5	n.m.	n.m.
J2-189MajWht	n.m.	44.2	n.m.	49.4
J2-191PF1	bdl	57.1	n.m.	16.7
.l2-192BE11	bdl	32.5	n m	n m

TABLE DR4. Sulfur Species in 2004/2006 Volcanic Vent Fluids

bdl=below detection limit (0.8µM for H₂S). n.m.=not measured.

Supplementary Figures



Supplementary Figure DR1. Concentrations of major rock components iron, silica and aluminum dissolved in Brimstone volcanic vent fluids. Samples are in chronological order left to right. Samples show high variability due to variable seawater mixing and extent of reaction with rock substrate. Both the Si/Fe and Al/Fe ratios of these fluids average approximately 50% of the rock ratio, indicative of slower uptake of silica and aluminum into solution and/or solubility limitations. Average Al concentration for high-temperature MOR fluids $(5.5\mu M)$ is shown at far right for comparison.



Supplementary Figure DR2. Fe/Mn molar ratio (left axis) and Fe/heat ratio (right axis) in NW Rota volcanic vent fluids. The Fe/Mn ratio (dark blue diamonds) is variable, at times reaching the rock ratio of 55, consistent with congruent dissolution of rock surrounding/covering the eruptive conduit. Lower Fe/Mn ratios indicate solubility limitation and precipitation of secondary iron phases. The average Fe/Mn of all arc volcanic vent samples is 31, considerably higher than the MOR average of 4.3, indicated on the left axis. The Fe/heat ratio is also highly variable, and the overall average of all samples is 3.8, slightly higher than the MOR average of 3.1, shown on the right axis. The near equality of Fe/heat ratios in arc volcanic vents and MOR vents means that they have the same relative importance for global iron flux to the oceans. The flux of Mn from volcanic vents is considerably less than that from MOR vents.



Supplementary Figure DR3. pH (measured shipboard at 22°C) in volcanic vent fluids from Brimstone eruptive vent. Data are in chronological order left to right. 2004 samples are more dilute because they were taken in a buoyant plume within the eruptive pit crater.



Supplementary Figure DR4. NW Rota, Brimstone vent, 2006, Jason-2 dive 188. Gas bubbles, white and yellow sulfur-rich particles venting through volcaniclastic material, including rocks coated with sulfur. Note that yellow smoke is proximal to the volcanic vent, with white smoke and gas bubbles on the distal edges. Temperature probe measurements beneath the white smoke were less than the melting point of sulfur (~115°C). Molten sulfur is present beneath yellow smoke, with temperatures from 120 to 256°C measured.



Supplementary Figure DR5. Sampling fluids with HFPS nozzle in sulfur-rich volcaniclastic material on the edge of Brimstone eruptive vent, dive J2-401, 4/8/2009. In-line fluid temperatures were 25-60°C at this spot beneath white smoke. Minutes later, in a spot beneath yellow smoke approximately 30cm away from this location, fluid temperatures up to 207°C, with pH of 1.05 were measured.



Supplementary Figure DR6. NW Rota 2006, Brimstone vent. Slowly extruding lava plug giving off yellow and white sulfur smoke and gas bubbles, indicative of active magma degassing during extrusion. Temperature measured on the surface of one of these "smoking rocks" reached 256°C, near the seawater boiling point of 265° at 550m depth.



Supplementary Figure DR7. Rock collected near Brimstone vent, NW Rota, 2006. Sample is a lava bomb with one side coated with cemented breccia of sulfur and volcaniclastic basaltic andesite. This is indicative of lava ascending and erupting through a sulfur cap, pushing molten sulfur up through loose material covering the vent. (Field of view is 7x11cm).