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SAMPLING AND ANALYTICAL METHODS, PLUS COMPILATION OF DISCHARGE COMPOSITION OF SEAFLOOR BLACK SMOKERS

The deep liquid at Reykjanes was sampled in May, 2007, from the only three wells that were available that were also vertical; deviated wells have the potential for the down-hole sampler tool, unique in the world (Simmons and Brown, 2006, 2007), to become stuck. Two wells are fitted with slotted liners, open to the reservoir through the slots, that extend below the solid production casing (from depths of 763 and 611 m in RN19 and 21, respectively), whereas the third well (RN-12) has no slotted liner, just an open hole below the solid production casing (base at 854 m). Bottom depths of the wells are 2506 m (RN12), 2235 m (RN19), and 1664 m (RN21). All three wells were sampled during a short period of power station maintenance, with the wells discharging at a very low rate, 3-5 kg/s, to prevent non-condensable gases from accumulating; normal production flow rates are $\sim 110 \text{ kg/sec}$. The pressure and temperature in the wells were logged using a Kuster K-10 tool, less than 4 hours prior to sampling. In each case the depth of sampling was at least 150 m below the boiling level in the well, as defined by the change in slope of the measured pressure (Fig. 2). This change in slope is due to the transition from liquid to a boiling, two-phase mixture at \sim 1300 m depth, above which the vapor phase controls the pressure profile.

A titanium down-hole sampler, designed specifically to provide reservoir liquid samples for trace element analysis (particularly metals), was used to collect the deep liquid, as previously

described by Brown and Simmons (2003) and Simmons and Brown (2006, 2007). After lowering the sampler to the sample depth, it was opened by an inertial trigger; the internal volume of the sampler is 800 ml. Although the deep liquid samples were collected below the boiling zone, contamination by previously precipitated metal sulfide, either well bore scale or particulate (colloidal) sulfide suspended in the boiling zone, cannot be totally ruled out (although the narrow range of trace element concentrations from the three separate wells argue again ingestion of foreign particles; Fig. 3). Simmons and Brown (2007) showed that blanks using this down-hole sampler indicate little or no contamination when samples are being collected; in addition, because the samples were collected below the boiling level (Fig. 2), the presence of scales at this depth is not likely. All components of the sample vessel in contact with the liquid are titanium. Copper seals in the sampler are isolated from the liquid sample by viton O-rings. These O-rings are replaced before each sampling.

The sealed container prevents the liquid from boiling on ascent to the surface, by the use of a non-return valve so the sample maintains the same pressure as that collected; there was no evidence of leakage during recovery of the samples. At the surface the sampler was cooled below atmospheric boiling point by pouring cold water on its exterior, after which the sampler was opened and the solution collected (425-625 ml). All liquid samples were greyish in color due to the suspension of fine precipitates, assumed to have formed after sampling, due to mineral saturation (largely sulfides) on cooling. The sampler was then rinsed with 40 ml aqua regia to dissolve any precipitate that may have adhered to the internal titanium wall of the vessel, followed by rinsing with 40 ml of distilled water; this was repeated again with acid and distilled water. The total diluent (160 ml) was added to the original sample, and this dilution was later corrected for in the final reported analyses (Table 1).

Samples were analyzed at CSIRO Australia, Lucas Heights. Analytical methods include: CSIRO; Ag, Au, Be, Bi, Br, Cd, Co, Cr, Cu, I, Mo, Ni, Pb, Sb, Sn, Te, Tl, V, W by ICP-MS (Inductively coupled plasma-Mass spectrometry), B, Ba, Ca, Cu, Fe, K, Na, Li, Mg, Mn, Na, S, Si, Sr, Zn by ICP-OES (Inductively coupled plasma-Optical emission), As and Se by Hydride-AAS (Atomic absorption spectrometric) analysis, Hg by AFS (Atomic fluorescence spectroscopy). The pH, CO₂, H₂S and SO₄ were not measured in the downhole samples due to acid addition upon sample retrieval. Surface-collected fluids have pH measured in the field, and are then analyzed by the Iceland GeoSurvey (B, Br, Cl, K, Mg, Na, SiO₂, CO₂, H₂S and SO₄ by spectrophotometer, ion chromatography, AAS) and at ALS Scandinavia AB Sweden (Al, Ba, Sr, Li, I and trace elements by ICP-SFMS, ICP-AES, ICP-SMS).

Surface samples are collected 2–3 m downstream of the wellhead, at pressures of 28–32.5 bar absolute (i.e., equivalent to 230–238°C, respectively) from the production wells at regular intervals for production monitoring purposes by the Iceland GeoSurvey. These samples consist of liquid and vapor phases of known proportion, determined from sample pressure and discharge enthalpy (Henley et al., 1984), with volatile species largely fractionated into the vapor sample. After analysis of all major components, including gases, from both samples they are recombined to provide the composition of the reservoir liquid, prior to boiling, using standard methods (Henley et al., 1984); a typical H₂S concentration in the reservoir liquid is 0.8 mM (sample collected at the surface from RN19). The surface samples of liquid are also analyzed for their trace element composition (a typical composition from RN19 is given in Table 1, corrected for concentration due to vapor loss at the sample point, i.e., equivalent to reservoir concentrations except for elemental changes due to precipitation on ascent prior to sampling).

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TABLE DR1. MAJOR AND TRACE ELEMENT CONCENTRATIONS FROM
SELECTED SEAFLOOR BLACK SMOKER VENTS

	Axial Seamount [*]	Lucky Strike Effel ^{†,§}	Lucky Strike Crystal ^{†,§}	Rainbow [§]	Logatchev [§]	Menez Gwen [§]	Broken Spur [§]	Snakepit [§]	TAG [#]	Red Lion"	Turtle Pits 2005**	Turtle Pits 2006**	Sisters Peak**	Brandon brine ^{††}	Brandon vapor ^{††}	Kairei 4 Kairei 6 ^{§§}		Edmond 2 ^{§§}	Edmond 10 ^{§§}
Sampling depth, m	1540	1007		0000	0050	050	0000	0.400	3650	0000		0000	3000	0001	0004	0.450	0.450	0000	
•	1540	1687	1726	2300	2950	850	3090	3480		3000	3000	3000		2834	2834	2452	2452	3300	3303
T°C	328	325	281	365	353	271	360	341	366	349	405	407	400	376	405	315	365	273	293
pН	3.5	4.1	4.2	2.8	3.3	4.4	N.D.	3.7	3.4	N.D.	N.D.	N.D.	N.D.	3.3	<3.7	3.35	3.62	<3.02	≤2.97
CI (mM)	624	438	535	750	515	400	469	550	636	552	291	271	224	557	338	571	620	929	926
Na (mM)	499	386	431	553	438	313	420	515	557	480	230	237	209	441	303	492	528	698	718
K (mM)	27	21	29	20	22	24	19	23	17	20	8	9	7	14	9	13	15	45	45
Ca (mM)	47	30	35	67	28	33	12	11	31	19	8-11	9	12-17	33	21	29	31	58	65
SiO ₂ (mM)	15	16	15	7	8	11	N.D.	20	21	22	11 0 ^{##}	12	14	13	9	17	17	20	19 0 ^{##}
Mg (mM)	0##	0##	0##	0##	0##	0##	0##	0##	0##	0##		0##	0##	0##	0##	0##	0##	0##	
Al (µM)	N.D.	(4-11)	N.D.	2	4	6	N.D.	12	10	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	4.35	5.29	7.28	19.1
Ba (µM)	26	(>8)	N.D.	>67	>4.5	>12	>21	>4	19	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sr (µM)	192	77	91	200	138	108	45	54	99	63	28	25	35-52	94	63	70	80	165	182
Β (μΜ)	590	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	520	536	547	591	465	431	N.D.	N.D.	N.D.	N.D.
Li (µM)	636	303	356	340	245	280	1030	835	850	1217	416	427	343	488	335	553	545	1080	1070
Br (µM)	956	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	873	494	482	392	890	680	920	970	1440	1390
I (μM)		N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Fe (µM)	1065	623	56	24000	2500	18	1970	2400	5590	803	3120	3940	3380	12300	8680	3540	6010	10500	13100
Cu (µM)	10	(<2-30)	N.D.	140	27	<2	43	35	140	5	111	9-76	110-374	105	51	276	118	146	403
Zn (µM)	111	(<2-40)	N.D.	160	29	<2	72	53	46	60	55	28-69	50-155	121	81	67	85	122	149
Mn (µM)	1150	267	73	2250	330	68	254	400	680	730	454	473	704	1300	790	811	857	1450	1430
Ni (µM)	N.D.	(<2)	N.D.	3	<2	<2	N.D.	<2	<2	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
As (µM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Pb (µM)	0.3	(0.035-0.130)	N.D.	0.1	0.1	0.1	N.D.	0.3	0.1	0.4	0.2	0.1-0.2	0.1-0.4	N.D.	N.D.	0.3	0.3	0.8	1.3
Cd (µM)	N.D.	(0.018-0.079)	N.D.	0.13	0.063	0.01	N.D.	0.44	0.07	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.07	0.11	0.22	0.28
Cr (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Ag (nM)	N.D.	(5-25)	N.D.	47	11	17	N.D.	31	51	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
V (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sb (nM)	N.D.	(<3-6)	N.D.	3	<3	5	N.D.	11	4	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Mo (nM)	N.D.	(3-84)	N.D.	2	1	10	N.D.	3	5	16	101	15-57	80-270	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Te (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Se (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<400	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
TI (nM)	N.D.	(7-16)	N.D.	9	7	11	N.D.	25	13	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
W (nM)	N.D.	(/-10) N.D.	N.D.	N.D.	, N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Au (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sn (nM)	N.D.																		N.D. N.D.
Hg (nM)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	Ν

Note: H_2S concentrations for these fluids range from 0.8 to 11.2 mM, averaging ~4.7 mM. N.D. No data. * Butterfield et al., 1990. [†] Von Damm et al., 1998.

[§] Douville et al., 2002.
 [#] Douville et al., 2002; Hannington et al., 2005.
 ^{*} Koschinsky et al., 2008
 ^{††} Von Damm et al., 2003.
 ^{§§} Gallant and Von Damm, 2006.
 ^{##} Assumed by authors to be 0 for calculation.