DR2008149

Appendix Table DR1: Measured composition of individual hydrothermal fluid samples at 5°S, MAR

		T	pH	H2S	Mg	Cl	Br	Na	K	Ca	Si	Li	Sr	Fe	Mn	Cu	Co	Zn	Pb	Mo	B
Year	Sample ID	°C	25°C	µM	mM	mM	µM	mM	mM	mM	mM	µM	µM	µM	µM	µM	µM	µM	nM	nM	µM
TURTLE PITS - Two Boats																					
2005	141 ROV-12	-	5.19	-	34.3	459	653	388	9.6	10.6	3.3	172	67.8	788	170	52.1	0.70	25.8	101	82	468
	141 ROV-13	-	5.1	-	31.3	446	645	376	9.4	10.3	4.9	192	62.5	1146	192	-	-	-	-	-	478
	141 ROV-14	-	4.9	-	30.7	445	632	375	9.6	10.1	4.3	203	62.0	1218	205	-	-	-	-	-	488
	141 ROV-15	-	3.8	-	24.1	396	612	334	8.9	9.0	6.7	234	53.6	1961	245	-	-	-	-	-	476
2006	3 ROV-10	395	3.2	-	8.3	317	-	273	8.8	9.3	9.8	356	34.9	3345	411	64.8	0.75	25.4	93	66	-
	12 ROV-8	407	3.1	3990	2.8	283	495	249	8.8	8.8	11.0	410	28.4	3733	443	8.8	0.48	27.0	53	20	541
	12 ROV-B7	-	6.2	-	49.5	-	-	460	10.3	10.5	0.8	52	81.4	253	31	1.0	0.04	2.6	8	124	430
	12 ROV-B8	-	5.6	-	44.2	503	792	435	10.1	10.3	1.8	90	77.1	588	71	2.7	0.12	8.8	23	105	436
	12 ROV-5	405	3.4	-	13.2	339	573	296	9.1	9.2	8.7	333	40.4	2952	351	14.9	0.64	52.7	139	53	518
COMFORTLESS COVE- Sisters Peak																					
2006	20 ROV-5	350	4.9	-	38.1	459	720	401	9.5	12.5	4.3	114	76.7	1000	193	90.6	0.43	40.7	110	160	469
	20 ROV-6	380	3.1	7200	7.4	269	450	245	7.8	11.5	12.6	300	42.0	2913	609	94.2	0.38	42.4	108	84	569
RED LION - Sugarhead																					
2005	146 ROV-2	-	7.9	-	54.2	559	839	479	10.4	10.6	0.06	28	90.2	0.57	0.69	-	-	-	-	-	436
	146 ROV-7	-	4.9	-	19.1	553	897	481	16.4	15.8	12.1	785	72.2	-	467	-	-	-	-	-	493
	146 ROV-8	-	4.5	-	11.1	547	897	478	17.7	16.9	17.8	963	69.1	-	573	-	-	-	-	-	496
	146 ROV-9	-	4.2	-	5.3	550	840	485	19.0	17.9	20.6	1115	65.5	724	668	-	-	-	-	-	514
	146 ROV-11	-	6.1	-	43.1	553	896	482	12.3	11.8	4.1	252	83.9	-	133	-	-	-	-	-	454
	146 ROV-12	-	6.2	-	44.9	553	851	476	12.0	11.8	3.6	222	84.3	-	119	-	-	-	-	-	448
	146 ROV-9/10				20.5											3.5	0.02	40.1	264	53	
RED LION - Tannenbaum																					
2006	7 ROV-4	345	5.5	-	38.4	551	845	467	12.7	11.8	4.6	310	77.9	164	161	-	-	-	-	-	439
RED LION - Mephisto																					
2006	7 ROV-13	346	5.9	-	45.4	558	856	461	11.3	11.0	2.2	162	80.9	114	113	-	-	-	-	-	421

TABLE DR2. DIFFERENT ENDMEMBER FRACTIONS
OF Fe, Cu, AND Zn IN THREE INDIVIDUAL SAMPLES
FROM THE VENT TWO BOATS AT SITE TP

Element	Fraction	12 ROV-8	12 ROV-5	3 ROV-10
	Sampling T (°C)	407	405	395
Fe (µM)	total	4055	4290	4053
	filtered	4007	3833	3965
	free and labile	4000	3900	3880
Cu (µM)	total	9	18	76
	filtered	<3	<3	<3
	free and labile	0.0003	0.01	1.9
Zn (µM)	total	28	64	29
	filtered	<3	<3	<3
	free and labile	0.48	0.93	1.1

Note: The total fraction comprises the unfiltered sample, the filtered fraction is the <0.2 µm fraction (both analysed by ICP-MS), and the free and labile fraction has been analysed onboard in filtered samples by voltammetry after 1 hour UV digestion.

Methods:

In-situ temperature measurements of the hydrothermal fluids were performed using an on-line temperature probe based on a hi-temperature NTC resistor, which was integrated into the KIPS fluid sampling system. The NTC is embedded in a soda glass bead and was aged at high temperatures. This assembly is mounted in the tip of a stainless steel tube with a resulting temperature constant of 5.2 s. The characteristic function of the individual sensor was determined by a calibration at 23 temperatures between 0°C and 450°C with an uncertainty of +/- 0.05°C at each point, which was carried out by a licensed calibration laboratory. The sensor was operated at an external port of a Sea&Sun Technologies CTD, Germany, with real-time data transmission through the ROV serial port.

For the chemical analyses, different aliquots were collected: a non-filtered, non-acidified aliquot for onboard determination of pH, Eh, and sulfide concentration, a filtered, non-acifided aliquot for the determination of dissolved Fe (free and labile fraction), one filtered and acidified aliquot for the determination of dissolved major, minor, and trace metals, and one non-filtered, acidified aliquot for the total concentration of major, minor, and trace metals. Undissolved particles (mainly sulfides) were separately dissolved with pressure digestion, using 3ml HCl, 1ml HNO_3 and 1ml HF.

Dissolved Cu and Zn (free and labile fraction) were also analysed onboard directly after sampling by voltammetry using a Metrohm system with a 757 VA Computrace. Filtered fluid aliquots were submitted to a digestion for 1 hour in a UV Digestor (Model 705, Metrohm), buffered at pH 4.6 with 1 M acetate buffer solution and measured by anodic stripping voltammetry.

Sulfide concentrations were measured on-board via spectrophotometry at 660 nm wave length (Biochrom Libra S 12 spectrophotometer) applying the methylene blue method of Cline (1969). For this, dissolved sulfide was stabilized in a colloidal form as zinc sulfide using zinc acetate gelatine solution (100 µl for 1 ml of hydrothermal fluid).

Dissolved Fe concentrations in filtered samples of hydrothermal fluids were measured on-board via spectrophotometry at 511 nm wave length, based on the determination of an orange-red ferroin complex, which is formed by Fe(II) ions in the fluid sample with 1,10-phenantroline in a pH range of 3-5

Ref.: Cline, J.D. (1969) Spectrophotometric Determination of Hydrogen Sulfide in Natural Waters. Limnology and Oceanography, 14: 454-458.

Calculation of the depth of the reaction zone and the depth of phase separation:
Quartz solubility constraints can be used to infer P-T conditions of the reaction zone below TP, based on experimental data from Foustoukos and Seyfried (2007). Assuming equilibrium between the low-chlorinity fluid and the host rock, a shallow reaction zone at ~430°C/350 bars is indicated. Calculating the depth of initial phase separation, based on the measured maximum temperature and the chlorinity of the emanating fluid (Bischoff and Pitzer, 1989; Tanger and Pitzer, 1989) yielded comparable results of 425°C/350 bars for TP and about 430°C/360 bars for SP (Fig. 3). However, both approaches are confined to closed system conditions. Hence, uncertainties may result from possible re-equilibrium between vapor phase and rock at lower pressures, from continuing phase separation during ascent, and from heat loss.