GSA DATA REPOSITORY 2014260

"Effects of temperature, sulfur, and oxygen fugacity on the composition of sphalerite from submarine hydrothermal vents"

Manuel Keith, Karsten M. Haase, Ulrich Schwarz-Schampera, Reiner Klemd, Sven Petersen, and Wolfgang Bach

Methods

A total of 12 polished sections and thin sections were petrographically examined prior to the geochemical analysis in order to identify the different mineral phases and to avoid effects of mineral inclusions. For this purpose the back-scattered electron mode of the electron probe microanalyzer has also been used. A total amount of 200 representative analyses were carried out by the electron microprobe analysis (Table DR2). The major and minor element composition of sphalerite was determined by electron microprobe analysis using a JEOL JXA-8200 Superprobe at the GeoZentrum Nordbayern. The quantitative analysis was carried out in an evacuated chamber (<4.3 x 10^{-6} mbar) with a focused beam, an acceleration voltage of 20 kV, and a beam current of 20 nA. The detected elements in sphalerite are Cu, Fe, S, and Zn calibrated using the following standards: $CuFeS_2$ (Cu), FeS_2 (Fe, S), and ZnS (Zn).

We used previously published fluid data for H_2S and H_2 of the examined vent sites (Table 1) to calculate f_{S_2} and f_{O_2} of emanating fluids (Table DR3) in order to compare these results with the chemical composition of sphalerite. Our calculations are based on fluid temperatures and H_2(aq) and H_2S(aq) concentrations, as shown by the following reactions:

(1) $H_2S(aq) = H_2(aq) + 0.5S_2(g)$
(2) $H_2(aq) + 0.5\ O_2(g) = H_2O$

The equilibrium constants for these reactions were computed using SUPCRT92 (Johnson et al., 1992) for the specific temperatures of the individual vents and a constant pressure of 50MPa.

Table DR1. Compilation of samples processed in this study, including the tectonic setting, the sample localities, the water depth, the wall rock composition, and the detected fluid temperatures.

Tectonic setting			Location	Wall rock	*T* [°C]	Ref.
MOR	MAR	TAG	26°08'N/44°49'W	basaltic	n.a.	1,2
		5°S (Turtle Pits)	04°48'S/12°22'W	basaltic	407	3, 4, 5
		5°S (Sisters Peak)		basaltic	400	3, 4, 5
	CIR	Kairei	25°19'S/70°2'E	ultramafic-basaltic	365	6, 7
		MESO zone	23°23'S/69°14'E	basaltic	n.a.	8
BA	Okinawa	Jade	27°16'N/127°04'E	basaltic-rhyolitic (sediments)	220	9
	PACManus	Roman Ruins	3°43'S/151°40'E	dacitic-rhyodacitic	329	10
IA	Tonga	Volcano 19	24°48'S/177°01'W	basaltic-basaltic andesitic	265	11

Abbreviations: MOR = mid-ocean ridge, BA = back-arc, IA = island arc, MAR = Mid-Atlantic Ridge, CIR = Central Indian Ridge, TAG = Trans-Atlantic Geotraverse, PACManus = PacificAustraliaCanadaManus

References: [1]Smith an Humphris (1998), [2]Hannington et al. (1998), [3]Koschinsky et al. (2006), [4]Koschinsky et al. (2008), [5]Hoernle et al. (2011), [6]Nakamura et al. (2009), [7]Gallant and Von Damm (2006), [8]Münch et al. (1999), [9]Halbach et al. (1993), [10]Bach et al. (2011), [11]Stoffers et al. (2006)

Table DR2. Compilation of the electron microprobe analysis of sphalerite, including the standard deviation (SD) and the average value of the detected elements in sphalerite, concentrations in wt%. The complete sphalerite data set can be found in Table DR4. (n = number of measurements)

Locality	sample#		Cu	Fe	S	Zn	Fe/Zn
TAG	ALV2189-5-1	av.	0.40	2.32	32.4	64.2	0.04
	n=14	SD	0.36	1.03	0.20	1.23	0.02
5°S	M64/1-139GTV-2F4	av.	0.51	13.6	33.2	51.5	0.26
Turtle Pits	n=50	SD	0.44	6.03	0.44	6.84	0.04
5°S	M68/1-20ROV-3A	av.	0.31	4.60	32.6	60.8	0.08
Comfortless Cove	n=17	SD	0.23	1.42	0.27	1.61	0.03
Kairei	105-4-S4	av.	1.19	8.78	32.7	55.7	0.16
	n=8	SD	0.48	1.94	0.37	2.41	0.04
	106-3-S1b	av.	0.44	9.23	32.9	55.8	0.17
	n=14	SD	0.22	1.80	0.21	1.95	0.05
MESO zone	AS9895f	av.	0.56	0.72	33.0	65.4	0.01
	n=6	SD	0.16	0.33	0.15	0.56	0.00
	102GTVA	av.	0.44	1.68	32.2	63.3	0.03
	n=5	SD	0.37	0.58	0.37	0.71	0.01
Okinawa Trough	102GTVA-No.1	av.	0.26	14.5	33.2	50.4	0.29
Jade	n=11	SD	0.49	1.68	0.22	2.19	0.05
	114GTVA	av.	0.32	14.3	34.1	51.7	0.28
	n=46	SD	0.49	2.15	0.21	2.63	0.06
PACManus	SO218-53ROV-06	av.	0.85	6.68	32.9	57.3	0.12
Roman Ruins	n=15	SD	0.48	1.34	0.32	1.59	0.03
Volcano 19	SO192-49TVG-01	av.	0.63	5.00	33.3	59.7	0.08
	n=14	SD	0.24	0.96	0.21	1.29	0.03

Table DR3. Compilation of fluid data used for f_{S_2} and f_{O_2} recalculation,

Literature data					**calc. f_{O_2}**		**calc. f_{S_2}**	
Vent Site	***T*** **[°C]**	**H_2(aq) [mmol/kg]**	**H_2S(aq) [mmol/kg]**	**Ref.**	**min.**	**max.**	**min.**	**max.**
TAG	360-366	0.05-0.23	2.5-4	1,2	-27.6	-26,2	-8.7	-7.4
5°S (Turtle Pits)	407	0.664	4.2	3, 4	-25.2		-8.4	
5°S (Sisters Peak)	400	0.061	8.3	3, 4	-23.6		-5.9	
Kairei	315-365	2.48-8.15	3.93-6.4	5-7	-34.9	-30.0	-13.2	-10.6
Okinawa	320	0.05	12.4	8	-30.0		-7.6	
PACManus	241-358	0.004-0.325	1.5-19.3	9	-36.1	-27.4	-10.7	-6.4
Middle Valley	202-281	1.9-8.2	2.4-7.9	10	-48.4	-37.3	-17.0	-13.2
21°N	273-355	0.2-1.7	6.6-8.4	8	-35.9	-30.0	-10.9	-10.0

References: [1]Edmond et al. (1995), [2]Douville et al. (2002), [3]Haase et al. (2007), [4]Koschinsky et al. (2008), [5]Kumagai et al. (2008), [6]Gallant and Von Damm (2006), [7]Gamo et al. (2001), [8]Gamo (1995), [9]Reeves et al. (2011), [10]Cruse (2003).

Table DR4. Electron microprobe analyses of sphalerite from the described vent sites (Table DR1), concentrations in wt%.

Locality/sample #	Cu (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Mid-Atlantic Ridge	0.33	1.35	32.39	65.70
TAG	0.22	0.82	32.02	65.72
ALV2189-5-1	0.81	1.82	32.35	64.77
	0.75	3.10	32.41	63.14
	0.14	2.24	32.25	64.52
	1.41	3.11	32.57	62.29
	0.24	3.61	32.81	62.83
	0.24	4.72	32.41	61.88
	0.18	1.41	32.57	65.81
	0.33	1.65	32.29	65.08
	0.66	1.18	32.04	65.02
	0.13	2.50	32.50	64.35
	0.06	2.38	32.31	64.27
	0.18	2.66	32.44	64.11
Mid-Atlantic Ridge	11.02	12.57	32.90	41.53
5°S	6.39	10.50	32.63	48.62
Turtle Pits	9.79	11.53	33.31	45.22
M64/1-139GTV-2F4	2.48	6.85	32.19	57.38
	4.08	7.55	32.30	55.22
	5.47	10.79	32.17	50.19
	6.74	9.86	33.35	50.38
	6.10	9.14	32.69	51.40
	14.21	15.00	34.17	36.93
	5.73	9.54	33.17	51.62
	11.06	12.76	33.25	42.86
	3.93	7.48	32.81	55.20
	12.35	13.63	33.11	40.63
	9.87	12.05	33.09	45.34
	9.12	11.09	33.10	46.53
	, do	11.55	32.99	45.47
	12.54	13.58	32.86	40.75
	14.56	14.63	33.29	36.72
	0.40	6.77	32.64	59.86
	1.08	14.08	33.28	50.92
	3.22	12.11	33.02	50.97
	3.67	9.62	33.15	53.45
	0.91	8.12	32.57	57.37
	0.94	6.28	32.78	60.00
	0.60	13.43	33.44	51.74
	0.86	10.20	33.08	54.81
	0.30	24.50	33.74	39.90

Locality/sample #	Cu (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Mid-Atlantic Ridge	0.19	22.45	34.01	41.92
5°S	0.36	8.08	32.99	57.49
Turtle Pits	0.03	14.86	33.71	50.85
M64/1-139GTV-2F4	0.16	7.27	32.40	58.60
continued	0.10	7.09	33.09	58.91
	0.05	11.25	32.89	54.87
	0.30	21.23	33.94	43.20
	0.93	17.97	33.29	46.11
	0.03	9.61	32.75	56.05
	0.27	14.56	33.33	50.01
	0.26	5.82	32.73	59.70
	1.04	23.44	33.82	40.18
	1.36	23.38	34.01	40.01
	2.46	19.96	33.48	42.70
	0.59	9.99	33.39	55.22
	0.41	6.77	33.28	59.24
	1.40	22.24	33.16	40.92
	0.04	7.70	32.79	58.19
	0.10	16.51	33.45	48.91
	0.09	12.82	33.37	53.06
	0.00	9.85	33.06	56.32
	1.08	18.90	33.22	45.13
	1.03	18.95	33.81	45.29
Mid-Atlantic Ridge	0.06	3.95	32.26	61.87
5°S	0.10	4.33	32.44	61.17
Comfortless Cove	0.74	4.22	32.71	60.61
Sisters Peak	0.70	2.75	32.50	62.54
M68/1-20ROV-3A	0.20	5.61	32.59	59.74
	0.04	2.79	32.33	63.13
	0.36	3.22	32.53	62.23
	0.19	3.93	32.57	61.84
	0.31	2.97	32.48	62.38
	0.30	5.33	32.39	60.19
	0.24	4.26	32.58	61.61
	0.08	3.26	32.67	62.46
	0.37	5.49	32.84	59.78
	0.75	5.58	32.63	59.23
	0.12	6.42	33.27	59.21
	0.47	6.15	33.07	58.57
	0.22	7.94	33.08	57.22
Central Indian Ridge	0.57	4.20	31.88	61.37
Kairei	1.49	10.59	32.86	53.62
105-4-S4	1.61	9.49	33.07	54.65
	2.83	11.03	32.88	52.25

Locality/sample #	Cu (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Central Indian Ridge	1.91	9.20	32.62	54.37
Kairei	0.82	9.10	32.58	55.48
105-4-S4	1.32	8.98	32.56	55.54
continued	0.64	9.94	33.01	54.56
Central Indian Ridge	0.27	7.98	33.36	57.53
Kairei	0.58	7.36	33.08	57.43
106-3-S1b	0.26	9.98	32.92	55.08
	0.58	5.49	32.94	60.11
	0.15	11.94	33.16	52.92
	5.88	12.57	33.20	46.71
	0.12	12.56	33.14	52.44
	0.32	9.26	32.66	55.94
	0.34	9.92	32.91	55.36
	0.41	9.08	32.78	55.93
	0.60	9.10	32.67	55.73
	0.99	10.63	32.77	53.75
	0.52	8.39	32.68	56.37
	0.52	8.37	32.80	56.45
Central Indian Ridge	0.87	0.99	33.06	64.89
MESO zone	0.45	0.40	32.72	66.11
AS9895f	0.53	0.45	33.19	64.43
	0.36	1.27	33.03	65.78
	0.54	0.76	32.96	65.50
	0.63	0.42	33.08	65.57
Central Okinawa Trough	0.06	1.18	32.68	63.95
Jade	0.14	1.19	32.48	64.12
102GTVA	0.23	2.09	32.29	62.33
	0.90	1.31	31.78	63.62
	0.87	2.62	31.77	62.69
Central Okinawa Trough	0.07	14.45	33.61	51.23
Jade	0.17	16.18	33.29	48.90
102GTVA-No1	0.36	16.90	33.42	47.82
	0.01	13.05	33.02	52.39
	0.03	13.53	33.17	51.79
	0.02	12.47	32.94	52.78
	0.02	14.09	33.34	50.73
	0.04	13.51	32.97	51.73
	0.01	12.37	32.88	52.50
	0.39	16.48	33.07	48.00
	1.75	16.89	33.29	45.98
Central Okinawa Trough	0.03	12.64	33.87	53.80
Jade	0.02	13.22	33.65	53.36
114GTVA	0.16	15.55	34.04	50.70
	0.02	11.97	34.15	54.55
	0.04	14.09	34.17	52.03

Locality/sample #	Cu (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Central Okinawa Trough	0.30	15.71	33.98	50.03
Jade	1.85	17.23	34.20	47.17
114GTVA	3.00	16.51	34.30	46.63
continued	0.01	12.28	33.90	54.03
	0.11	15.14	34.16	50.53
	0.05	13.66	33.52	52.71
	0.05	12.99	34.00	53.33
	0.08	14.02	34.20	51.94
	0.00	11.49	34.25	54.56
	0.03	12.55	33.86	54.08
	0.09	16.05	34.15	50.25
	0.06	12.67	34.06	54.07
	0.04	14.30	34.00	51.89
	1.12	15.18	34.45	49.95
	0.03	12.67	33.94	53.53
	1.08	15.39	34.12	49.49
	3.91	17.94	34.29	44.03
	0.16	13.71	34.14	52.30
	0.05	11.59	33.88	55.06
	1.22	16.31	34.48	48.41
	0.60	14.76	34.27	50.86
	2.78	16.71	34.22	46.81
	0.07	13.66	34.24	52.60
	1.59	17.86	34.36	46.19
	0.05	18.17	34.42	47.78
	2.90	17.96	34.38	45.33
	0.19	18.43	34.07	47.47
	0.11	15.64	34.50	50.30
	0.11	11.26	33.88	55.23
	0.59	18.04	34.22	47.41
	0.00	11.75	34.18	54.79
	0.04	12.37	34.29	53.53
	0.00	12.58	33.84	53.50
	0.03	12.45	34.23	53.65
	0.00	11.92	34.29	54.31
	3.60	17.55	34.39	45.00
	0.18	15.43	34.03	50.88
	1.20	18.33	33.95	46.66
	0.15	16.04	34.24	49.68
	0.04	11.12	34.05	55.72
	2.21	17.78	34.36	45.52
Manus Basin	1.00	5.12	32.75	59.36
PACManus	1.70	5.90	32.63	57.78
Roman Ruins	0.59	5.97	32.82	58.44
SO216-53ROV-06(1,2)	7.34	7.77	32.77	49.01

Locality/sample #	Cu (wt%)	Fe (wt%)	S (wt%)	Zn (wt%)
Manus Basin	7.56	7.16	31.98	49.19
PACManus	0.33	8.81	32.79	55.14
Roman Ruins	0.61	7.63	33.53	55.84
SO216-53ROV-06(1,2)	0.24	1.29	32.18	64.02
continued	0.31	1.92	32.19	63.95
	0.10	1.16	32.29	64.18
	0.30	0.58	32.14	63.97
	0.71	3.46	32.78	60.60
	0.23	1.90	31.98	64.13
	0.37	1.13	32.76	63.83
	0.38	2.21	32.28	62.57
Tonga arc	0.91	5.82	33.19	58.85
Volcano 19	0.50	3.82	33.83	61.45
SO192-49TVG-01	0.82	5.62	33.24	59.48
	0.61	5.32	33.20	59.60
	0.40	4.07	33.16	61.25
	0.49	4.96	33.42	59.87
	0.39	5.32	33.21	59.62
	0.46	3.91	33.50	61.30
	0.52	4.03	33.04	60.62
	0.48	3.85	33.15	60.62
	0.55	5.58	33.28	58.70
	2.87	8.42	33.14	54.02
	0.91	5.63	32.98	58.68
	1.19	7.07	33.39	56.70

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