

Discussion of the choice of a representative global MOR hydrothermal brine for use in predicting secular variations in seawater chemistry over geologic time.

The use by Spencer and Hardie (1990) and Hardie (1996) of the Reykjanes (Iceland) borehole #8 hydrothermal brine as their model input MOR brine has been criticized by Holland et al. (1996). Although the Reykjanes #8 MOR brine has higher Ca/Cl and K/Cl ratios than most ocean floor vent brines, it was originally selected by Spencer and Hardie (1990) because it was collected directly from a borehole in the host MOR greenstone of known mineralogy and temperature (277°C) at a depth of 1.75 km (Björnsson et al., 1972; Hardie, 1983) and, unlike modern seafloor vent brines, did not require corrections for seawater contamination. Brines collected from modern seafloor vents exhibit a wide range of compositions and salinities. For example, based on 21 analyses of modern MOR brines from vents at sites 21°N, 13°N, Guaymas basin and Southern Juan de Fuca Ridge (Von Damm et al., 1985a, b; Von Damm and Bischoff, 1987; Berndt et al., 1989, Table 7), major ion concentrations (normalized to a seawater Cl value of 547.9 mmol/kg) varied as follows: Na ranged from 401.2 to 489.4, Ca from 12.92 to 51.79, and K from 20.76 to 44.48 mmol/kg. The question of temporal variability in the composition of vent brines has been addressed by Von Damm (1995, p.242). Measurements at the 21°N EPR site (1979 to 1992), the South Cleft of Juan de Fuca Ridge (1984-1994) and Guaymas basin (1982-1993) "all suggest that temporal variability was minor". However, at sites 9-10°N EPR and North Cleft on the Juan de Fuca Ridge, both of which have undergone recent extrusive volcanism, temporal variability in brine chemistry (changes as large as 200%) and brine temperature have been measured. Both sites showed a trend of increasing chloride content. Von Damm (1995, p.242) noted that "it appears that hydrothermal systems undergo an early post-eruptive period during which chemical compositions, fluid volumes, and temperatures may change rapidly". Processes that are likely to have been responsible for variations in MOR brine compositions are (1) variation in host rock composition, (2) variation in P and T, (3) fluid-rock ratios, (4) extent of reaction, which is a function of host rock crystallinity (whether diabase, basalt or hyaloclastite) and permeability, as well as fluid-rock contact time, and (5) whether phase separation (Bischoff and Pitzer, 1989; Bischoff, 1991) has occurred. This last process certainly must be responsible for observed variations in seafloor vent brine chlorinities and salinities. In the system NaCl-H₂O, the fields of liquid and liquid + vapor are P-T dependent, with the two-phase field occurring at a lower pressure for a given temperature. In seawater (3.2 wt. % NaCl) at hydrostatic pressures between about 100 and 600 bars, phase separation (boiling) occurs at temperatures between 300° and 500°C (Bischoff and Pitzer, 1989). The formation of a vapor phase by boiling produces a liquid phase which is more concentrated in NaCl than the parent seawater. The vapor phase, in contrast, is enriched in H₂O and depleted in NaCl compared to seawater.

This phase separation process can explain the significant number of seafloor vent brines that have either lower or higher NaCl concentrations than normal seawater, the former being liquids condensed from the separated vapor phase as it cooled during its upward migration while the latter are the NaCl-enriched liquid separates. Other metal ions in seawater should behave in the same way and may account, for example, for some of the well-established variability in potassium in seafloor vent brines. In laboratory experiments simulating the interaction between hot seawater and oceanic crust rocks (diabases and basalts), Berndt et al. (1989) have shown that the composition of the resulting hydrothermal brines depends upon P and T, host rock type, fluid-rock ratio and reaction time. They found, for example, that at 400°C basalts yielded brines with slightly lower Na but much higher Ca and K concentrations than did diabases. Temperature effects were also significant. For basalts at 400 bars pressure and fluid-rock ratio of 1, they found that reaction yielded fluids with somewhat higher Na (~ 430 vs. ~380 mmol/kg) and considerably higher Ca (~48 vs. ~33 mmol/kg) and K (~30 vs. ~21 mmol/kg) at 350°C than at 425°C.

Overall, it is not clear how representative the sampled vent brines are of the overall, long-term interaction between hot seawater and oceanic crust. As Von Damm (1995, p. 244) notes, up until recently sampling has been focussed mainly on the high temperature "black smokers", which may turn out not to be as important volumetrically or chemically as lower temperature diffuse flow through the oceanic crust. As yet, we do not have a reliable quantitative measure of either the heat or chemical fluxes that exchange between the ocean and the crust and mantle. Without such information we cannot answer the question, posed by Von Damm (1995, p.243), "what was the composition of a 'world average hot spring'?". Nonetheless, the merit of using an "average" ocean floor vent brine composition instead of the Reykjanes brine was explored. After a few iterations in which both the "average" MOR brine and the Spencer-Hardie RW compositions were varied a little, an extremely close fit to modern seawater was obtained using the new mixing model. This procedure yielded the following compositions of the input waters: (1) "average" MOR: Na = 450, K = 30, Ca = 32.5, Mg = 2, SO₄ = 1, HCO₃ = 0, Cl = 547.9 mmol/kg, (2) "average" RW: Na = 0.036, K = -0.045, Ca = 0.75, Mg = 0.237, SO₄ = 0.126, HCO₃ = 0.852, Cl = 0 mmol/kg. Using these values the secular variations in seawater chemistry as a function of MOR/RW flux ratio were calculated. This yielded the same timing of secular variations in Phanerozoic evaporite and non-skeletal carbonate mineralogies as those predicted using the Reykjanes #8 brine (Hardie, 2000). However, the compositions of the paleoseawaters generated with this "average" MOR brine had slightly higher Na, lower Ca and K, and about the same Mg and SO₄ compared to compositions predicted using the Reykjanes #8 brine for a given MOR/RW flux ratio. In view of this finding, together with the foregoing discussion and the first order nature of the simple mixing model, it was decided to retain the Reykjanes #8 brine as the MOR input in the new model.

References

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Time (Ma)	MOR/RW	Mg/Ca	Ca	SO ₄	Mg	K	Na	Ca/SO ₄
550	1.39	2.12	36.3	40.9	76.9	18.7	458.6	0.89
565	1.25	2.71	31.5	45.5	85.6	16.3	461.9	0.69
600	1.10	3.83	25.4	51.6	97.2	13.1	466.2	0.49
750	1.05	4.39	23.6	53.8	101.4	11.85	467.7	0.44
850	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53
900	1.32	2.40	34.2	43.2	81.0	17.6	460.1	0.79
950	1.97	1.10	49.5	29.2	54.9	24.35	451.3	1.70
965	2.38	0.83	54.9	23.9	45.3	26.9	446.7	2.29
985	2.40	0.82	55.1	24.0	45.1	26.95	446.65	2.30
1010	2.38	0.83	54.9	23.9	45.3	26.9	446.7	2.295
1045	1.97	1.10	49.5	29.2	55.0	24.35	451.3	1.70
1085	1.68	1.45	44.2	33.8	63.75	22.15	453.6	1.31
1100	1.53	1.73	40.4	37.2	69.8	20.55	455.9	1.09
1110	1.39	2.12	36.3	40.9	76.9	18.7	458.6	0.89
1130	1.25	2.71	31.6	45.5	85.5	16.3	461.8	0.69
1150	1.21	2.94	30.0	47.1	88.3	15.6	462.9	0.64
1200	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53
1250	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53
1300	1.37	2.19	35.7	41.5	78.1	18.4	459.0	0.86
1350	1.77	1.31	46.0	32.25	60.6	22.95	452.5	1.43
1400	1.61	1.57	42.5	35.6	66.4	21.45	454.65	1.19
1450	1.27	2.62	32.25	44.8	84.3	16.65	461.4	0.72
1500	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53
1550	1.16	3.28	28.0	48.9	92.0	14.5	464.3	0.57
1600	1.30	2.49	33.4	43.75	81.4	17.2	460.6	0.76
1650	1.23	2.83	30.75	46.25	86.9	15.9	462.4	0.66
1700	2.13	0.985	51.8	27.2	51.0	25.3	448.9	1.90
1750	2.13	0.985	51.8	27.2	51.0	25.3	448.9	1.90
1800	2.03	1.06	50.4	28.4	53.3	24.75	449.7	1.78
1850	1.70	1.42	44.6	33.5	63.0	22.35	453.3	1.33
1900	1.33	2.36	34.4	42.75	80.5	17.75	459.9	0.80
1950	1.27	2.62	32.25	44.75	84.3	16.65	461.3	0.72
2000	1.33	2.36	34.4	42.75	80.5	17.75	459.9	0.80
2050	1.68	1.44	44.2	33.8	63.75	22.15	453.6	1.37
2100	1.66	1.49	43.6	34.25	64.4	21.95	453.9	1.27
2150	1.21	2.94	30.0	47.1	88.3	15.6	462.9	0.64
2200	1.14	3.46	27.2	49.75	93.75	14.0	464.9	0.55
2250	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53
2300	1.10	3.84	25.4	51.6	97.2	13.1	466.2	0.49
2350	1.21	2.94	30.0	47.1	88.3	15.6	462.9	0.64
2375	1.43	1.98	37.7	39.75	74.75	19.25	457.8	0.95
2400	1.49	1.82	39.4	38.2	71.7	20.05	456.6	1.03
2450	1.56	1.67	43.8	36.9	68.5	20.9	455.4	1.19
2500	1.88	1.20	47.7	30.4	57.2	23.75	451.2	1.57
2550	2.05	1.045	50.7	28.2	52.9	24.85	449.6	1.80
2600	1.93	1.14	48.8	29.75	55.9	24.1	450.7	1.64
2650	1.37	2.19	35.7	41.5	78.0	18.3	459.0	0.86
2800	1.13	3.55	26.6	50.3	94.6	13.8	465.2	0.53