

# The Iceland Deep Drilling Project (IDDP): (IV) Interpretations of black smoker fluid compositions

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**What can we determine about how deep black smoker fluids circulate and the temperature in the hydrothermal reservoir, from compositional data obtained at the vent?**

## Purpose

One goal of the IDDP is to understand high-temperature reaction zones such as those that feed hydrothermal fluids to active mid-ocean ridge black smoker vents. These fluids emerge from a reservoir of composition, temperature and pressure resembling those expected in a supercritical IDDP well in the Reykjanes geothermal system. We have reconstructed black smoker fluid compositions based on published analyses, and then computed mineral saturation indices,  $\log(Q/K)$ , for a wide range of P-T conditions, from which we identify a pressure and temperature where a group of probable alteration minerals equilibrated with the fluid.

## Previous Work

### Geobarometry method

The composition of hydrothermal fluids depends on the T and P at which the fluid equilibrated with the alteration mineral assemblage in its host rocks. Earlier studies show that hydrothermal waters *do* equilibrate with their mineral environment (e.g. Reed and Spycher, 1984). We must determine which minerals equilibrate under what conditions and whether any processes changed fluid composition between the deep fluid-rock reservoir and the analytical laboratory.

In earlier work, Karen Von Damm and others (e.g. Von Damm, et al, 1985, 1990, 1995, 1998) estimated pressure on the basis of quartz solubility by determining the pressure at which quartz equilibrates with measured smoker silica concentrations at a temperature estimated from an adiabatic decompression correction to the measured vent temperature.

Here we extend the mineral equilibrium approach to include feldspar, mica, zeolites, amphibole, pyroxene, epidote, garnet and chlorite, using the assemblage to *determine simultaneously the T and P* of equilibration. This approach extends into the pressure regime the methods we previously developed for estimating temperature in geothermal and sedimentary fluids (Reed and Spycher, 1984; Pang and Reed, 1998; Palandri and Reed, 2001) by computing and plotting mineral saturation indices ( $\log Q/K$ ) as a function of temperature. We apply computer program SOLVEQ (Reed, 1998) with a new data base that enables calculation at arbitrary choices of pressure, data for which are derived from the recent compilations by Shock, et al (1997) and Holland and Powell (1998).

### Potential problems

Mixing of black smoker fluids with variable amounts of seawater before and during sampling is unavoidable. Since the Mg content in black smoker fluids is negligible, it is assumed that Mg in the analysis is due to entrained seawater, and the true composition of the black smoker fluid is obtained by removing seawater from the analysis and extrapolating the Mg content to 0.0 ppm (Von Damm, 1990).

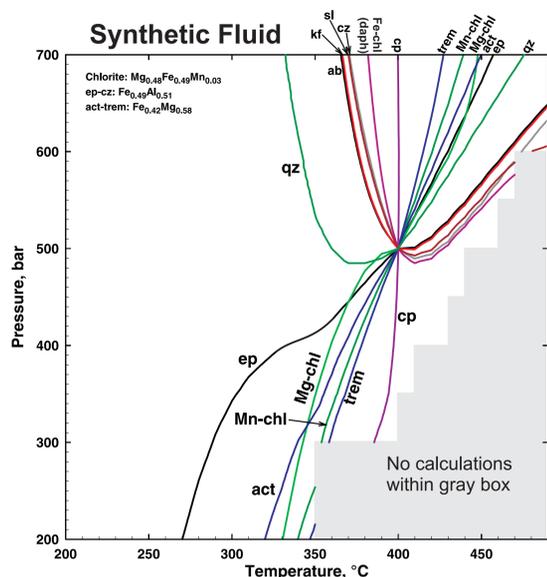
As black smoker fluid ascends from the reservoir and its T and P decrease, its composition may change as minerals precipitate or dissolve, depending on rates of re-equilibration and of fluid movement.

Mixing with seawater might also cause minerals to precipitate that would not otherwise. e.g. anhydrite precipitation where Ca is supplied by the reservoir fluid and sulfate is supplied by seawater. Mixing and re-equilibration both obscure the true composition of the fluid in the reservoir.

### Mineral abbreviations

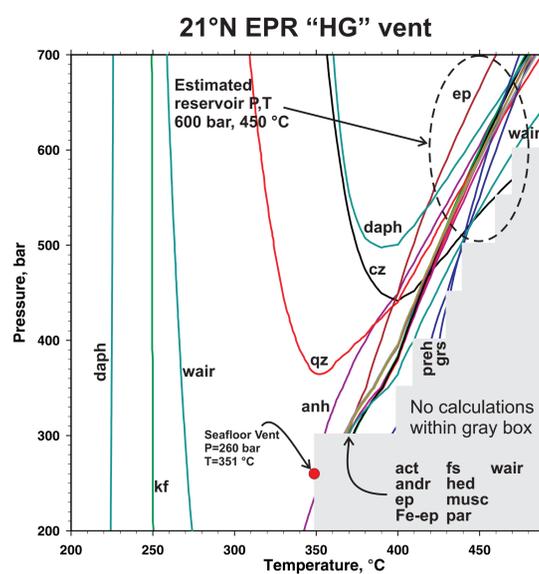
ab, albite; act, actinolite; andr, andradite; anh, anhydrite; cz, clinozoisite; chl, chlorite; cp, chalcophyrite; daph, daphnite; ep, epidote ( $\text{Ca}_2\text{Al}_2\text{Fe}(\text{SiO}_4)_3(\text{OH})$ ); Fe-ep, Fe-epidote ( $\text{Ca}_2\text{AlFe}_2(\text{SiO}_4)_3(\text{OH})$ ); fs, ferrosillite; grs, grossular; kf, microcline; musc, muscovite; par, paragonite; preh, prehnite; qz, quartz; sl, sphalerite; po, pyrrhotite; wair, wairakite.

Black smoker vent "HG" composition from VonDamm et al. (1985)



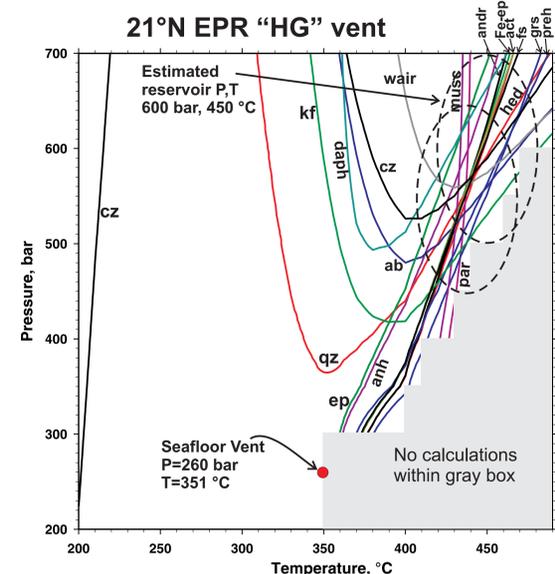
### Synthetic fluid example

Simultaneous determination of pressure and temperature requires that we find the point in P-T- $\log Q/K$  space where the 3-D surfaces representing mineral  $\log Q/K$  intersect each other and  $\log Q/K=0$ . Since we know that the intersection of interest is at  $\log Q/K=0$ , we can simply graph the  $\log Q/K=0$  curves in P-T space to seek the point of intersection, if it exists. To illustrate the concept, we synthesized a test fluid by computing the reaction of seawater with basalt at 400°C and 500 bar. Concentrations of some important components are quite low, i.e. Mg is 0.13 ppm and Al is 1.77 ppm.



### Reconstruction of aluminum concentration

Graph of  $\log Q/K = 0$  contours for fluid from HG vent (Von Damm et al., 1985) 21°N. EPR. The aluminum concentration is reconstructed by forcing equilibrium with an appropriate aluminous mineral, in this case albite, at all conditions by automatically adjusting Al concentration, aka the "FixAl" method. T and P are estimated to be where the curves form a knot and are in agreement. In this case we estimate approximately 600 bar and 450°C, where the tight bundle of curves intersect the quartz curve. The aluminum concentration at these conditions is 2.40 ppm.

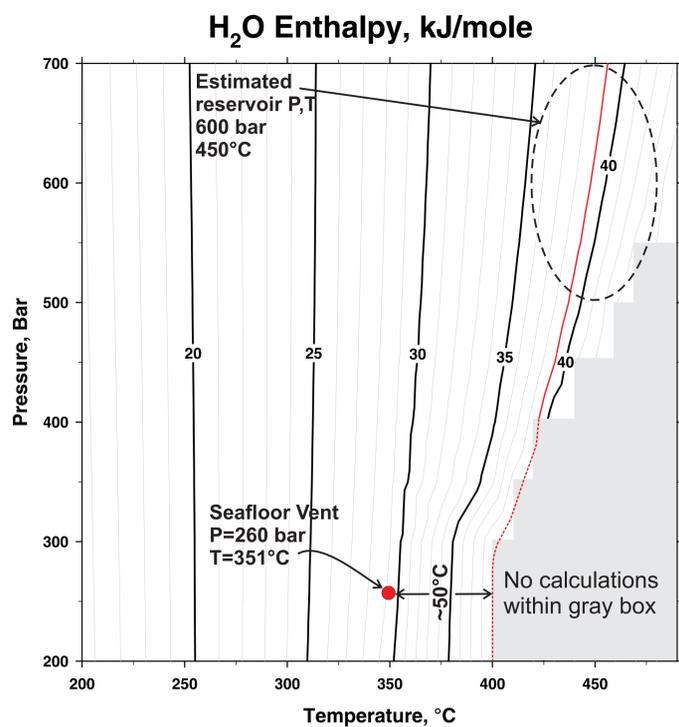


### Reconstructed aluminum

Graph of  $\log Q/K = 0$  contours for HG vent, 21°N. EPR, using the aluminum concentration obtained at 600 bar and 450°C in the FixAl method. The knot of curves appears more diffuse, and appears to indicate about 50 bar lower pressure and 20° lower temperature than the FixAl method.

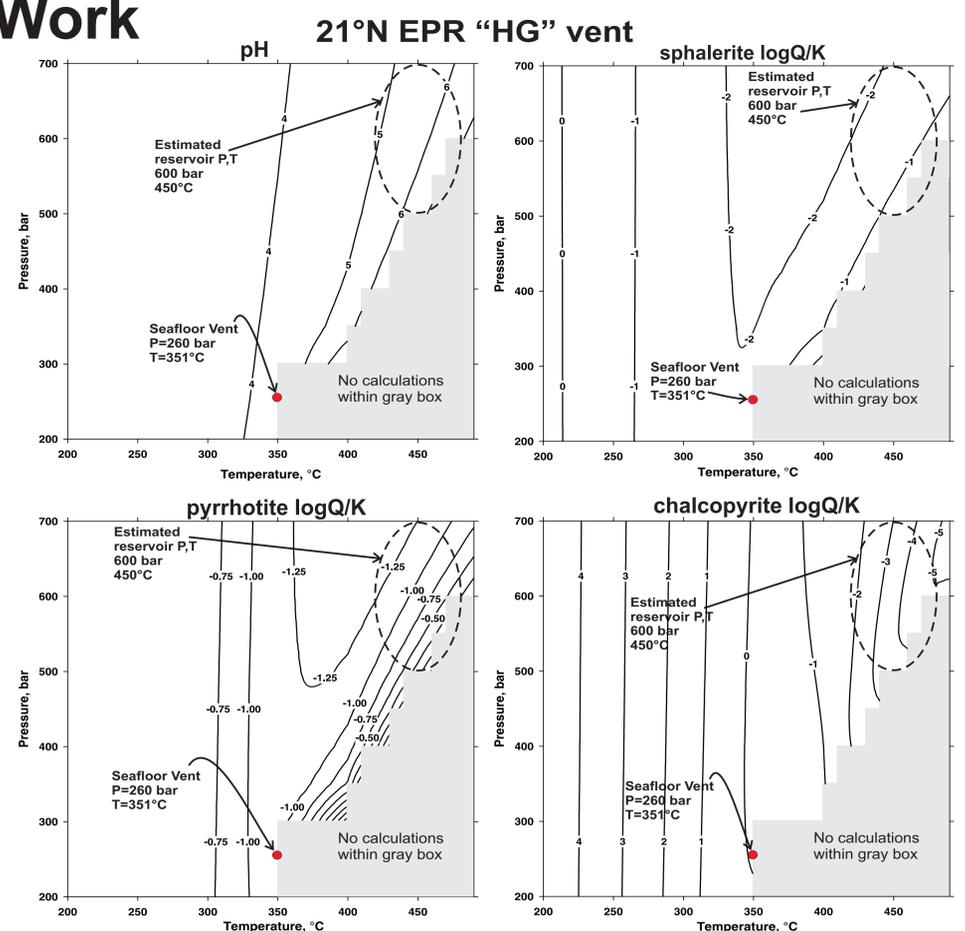
Quartz, feldspars, wairakite, Fe-chlorite (daphnite), and clinozoisite have stronger pressure dependence than the other minerals; the quartz contour indicates a pressure at *least* 100 bar greater than at the vent, and where in agreement with the other minerals, ~350 bar.

# Current Work

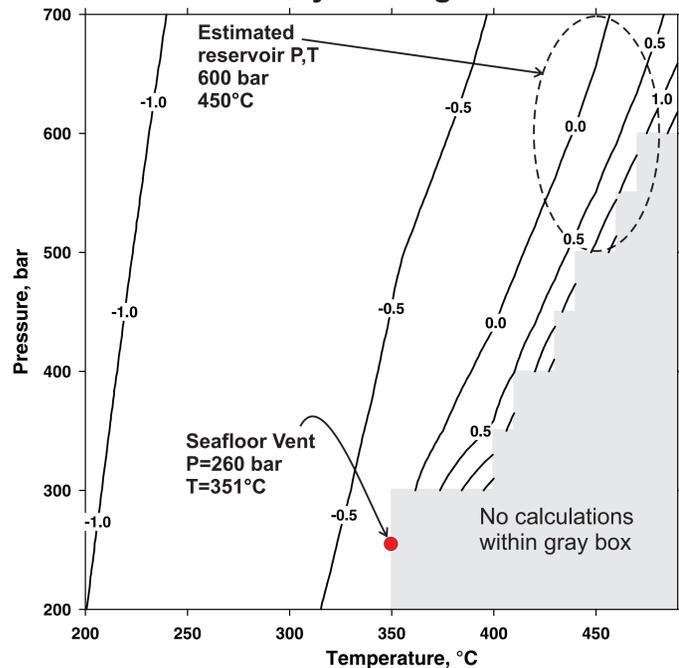


## Isoenthalpic cooling

Adiabatic decompression from reservoir conditions would result in cooling from 450 to 400°C. The observed temperature indicates about 50°C of additional cooling most likely due to mixing with seawater and conductive cooling along the fluid ascent path.



## 21°N EPR "HG" vent anhydrite logQ/K



## Effects of anhydrite precipitation

Anhydrite is essentially saturated at the vent, and due to its retrograde solubility, it is apparently slightly supersaturated in the reservoir. Given that Ca and sulfate were subtracted from the vent analysis in the seawater subtraction, anhydrite was probably supersaturated in the fluid-seawater mixture at the vent, and actively precipitating because its precipitation kinetics are fast. Further it is highly unlikely that anhydrite is truly supersaturated in the reservoir, also because of precipitation kinetics, thus anhydrite saturation in the vent fluid reflects newly added Ca and/or sulfate despite the removal of seawater. It is possible that the pre-sea-mixed fluid was anhydrite saturated (possibly owing to admixed seawater in the sub-vent zone, but where Mg precipitated in a silicate). These results suggest that the reported value for Ca concentration is not representative of fluid in the reservoir, which in turn affects our computed saturation indices for Ca-bearing minerals.

## References

- Holland TJB, Powell R (1998) An internally consistent thermodynamic data set for phases of petrological interest. *J Metamorph Geol* 16:309-343
- Palandri, J. and Reed, M.H., 2001, Reconstruction of in situ composition of sedimentary formation waters, *Geochimica et Cosmochimica Acta*, Vol. 65 (11), 1741-1767.
- Pang, Z.H. and Reed, M.H., 1998, Theoretical chemical thermometry on geothermal waters: Problems and methods. *Geochimica et Cosmochimica Acta*, 62, 1083-1091.
- Reed, M.H., 1998, Calculation of simultaneous chemical equilibria in aqueous-mineral-gas systems and its application to modeling hydrothermal processes, Chapter 5, in J. Richards, and P. Larson, eds., *Techniques in Hydrothermal Ore Deposits Geology*, Reviews in Economic Geology, Volume 10, p. 109-124.
- Reed, M.H., and N. Spycher, 1984, Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution. *Geochim. Cosmochim. Acta*, v. 48, p. 1479-1492.
- Shock E. L., Sassini D. C., Willis M., and Sverjensky D. A. (1997) Inorganic species in geologic fluids: Correlations among standard molal thermodynamic properties of aqueous ions and hydroxide complexes. *Geochim. Cosmochim. Acta* 61, 907-950.
- Von Damm, K.L., Bray, A.M., Buttermore, L.G., and Oosting, S.E., 1998, The geochemical controls on vent fluids from the Lucky Strike vent field, Mid-Atlantic Ridge. *EPSL*, 160, 521-536.
- Von Damm K. L., Edmond J. M., Grant B., Measures C. I., Walden B., and Weiss R. F. (1985a) Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim. Acta* 49, 2197-2220.
- Von Damm K. L. (1990) Seafloor hydrothermal activity: black smoker chemistry and chimneys. *Annual Reviews of Earth and Planetary Science* 18, 173-204.
- Von Damm K. L. (1995) Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In *Seafloor hydrothermal systems: physical, chemical, biological, and geological interactions* (eds. S. E. Humphris, R. A. Zierenberg, L. S. Mullineaux, and R. E. Thomson). American Geophysical Union, monograph 91, Washington, DC. pp. 222-247.

## Sulfide mineral precipitation effect on pH

An accurate reconstructed *in situ* pH is essential. The reported pH for HG vent samples is 3.3 (Von Damm, 1985), which, assuming pH was measured at 25°C, leads to a calculated pH of 4.3 at the vent T and P, and 5.7 in the reservoir. Aside from temperature effects, the pH in such samples is elevated by mixing with cold seawater, and lowered by precipitation of sulfides at the vent.

Chalcopyrite, pyrrhotite and sphalerite are common vent sulfides, and logQ/K contours shown above indicate at the vent approximate saturation of chalcopyrite, moderate undersaturation (-1 to -2) of sphalerite and pyrrhotite, and in the reservoir moderate undersaturation of all three. Since all three are known to precipitate at the vents, it is difficult to see how any could be moderately undersaturated, as opposed to saturated or supersaturated, unless analytical errors are large for metal or sulfide, which seems unlikely, or the measured pH is low owing to sulfide and silicate precipitation. Fe measured in vent fluids are likely depressed by sulfide precipitation, thereby decreasing logQ/K's for Fe-bearing minerals such as epidote, andradite and daphnite. A depressed pH affects saturation indices of all minerals except quartz.

An accurate estimate of the reservoir fluid composition therefore requires a "re-dissolution" of metals and sulfide into the fluid, limited by saturation at the reservoir P and T with chalcopyrite, pyrrhotite and sphalerite. Re-dissolution is problematic because these minerals share sulfide, thus precluding a straightforward determination of the relative quantities of each to re-dissolve.

## Conclusions

In reported analyses for black smoker vent fluid compositions, the following are likely not truly representative of the fluid in the reservoir. 1) pH: Mixing with seawater and precipitation of sulfide minerals changes pH. 2) Fe: Pyrrhotite precipitation removes Fe. 3) Ca: Mixing with seawater, and anhydrite precipitation modify Ca concentration. 4) Mg = 0 ppm: The fluid was likely in equilibrium with chlorite, resulting in a small Mg concentration (Although Mg should be present, its concentration is likely too low to be measured accurately.) 5) Cu and Zn: Mixing with seawater and cooling cause chalcopyrite and sphalerite (among others) to precipitate, removing Cu and Zn from the fluid.

Given that the aluminum concentration was estimated assuming equilibrium with albite, thereby establishing a dependence of aqueous Al on Na<sup>+</sup> concentration, the sole remaining independent concentrations are those of SiO<sub>2</sub> and K<sup>+</sup>. The K<sup>+</sup> can be applied with microcline or muscovite to estimate conditions, however, this too is compromised by the uncertainty in the pH. Thus, we arrive again at the need to assess the meaning of the measured pH and the magnitude of the effect on pH of precipitation of vent sulfide minerals.