

Effect of conductive cooling on chemistry of mid-ocean ridge hydrothermal fluids: experimental and theoretical constraints

K. Ding
W.E. Seyfried Jr.

Department of Geology and Geophysics, University of
Minnesota, Minneapolis, MN 55455, USA.

Introduction

Hot spring fluids issuing from the vents have been sampled at numerous sites on actively spreading mid-ocean ridges. The chemistry of these fluids has been extensively studied to provide insights on the processes occurring at depth in the ocean crust, and to constrain the hydrothermal flux of elements into and out of seawater. Although measured temperatures of vent fluids are generally around 350°C or less, these fluids have experienced much higher temperatures as evidenced by a number of chemical geothermometers. The discrepancy between measured temperatures and temperatures inferred from the dissolved concentrations of temperature dependent species can be largely attributed to conductive cooling of high temperature fluids in up-flow zones. However, before one can use the chemistry of hot spring fluids to access unambiguously conditions and processes in subseafloor reaction zone, it is important to understand the role of heat loss on vent fluid chemistry. Based on recent results of mineral solubility experiments designed to determine and retrieve thermodynamic data for H₂, H₂S, and Fe-, and Cu-bearing species, we can now constrain the effect of heat loss by conduction on the chemistry of hot spring fluids.

Methods

To better illustrate the role of cooling on dissolved metals and gases in up-flow zone hydrothermal

fluids, we performed a series of computer based simulations using a Newton-Raphson iterative technique to solve appropriate mass balance, charge balance and mass action equations as a function of temperature. In the simulations, a 0.5M NaCl fluid and a pH_(in-situ) of 5.0 was allowed to equilibrate with hematite-magnetite-pyrite-chalcopyrite at 400°C, and then cooled isobarically to 300°C. Different paths in terms of pressure and chlorinity, which range from 500 to 300 bars, and 0.3 to 1.0 M respectively, were explicitly examined. Since hydrothermal up-flow zones at mid-ocean ridges are likely characterized by very high time-integrated fluid/rock ratios, it is assumed here that fluids after having equilibrated at depth in the subseafloor reaction zone are largely unaltered by chemical exchange and wall-rock reaction on ascent to seafloor. Thermodynamic data for aqueous Fe, Cu species, and salting-out effects on dissolved H₂ and H₂S are taken from results of our previous experiments, while all other thermodynamic data are from 'SUPCRT92' (Johnson *et al*, 1992 and references therein). An extended form of the Debye-Huckel equation was used to determine activity coefficients for aqueous species at different temperatures and bulk fluid chemistry.

Results and discussion

Table 1 shows results for cooling from 400°C to 300°C, at 500 bars and 0.5M NaCl. As indicated, dissolved concentrations of H₂S, Fe, and Cu are

TABLE 1. Predicted change in concentrations of dissolved species resulting from conductive cooling in up-flow zones at 500 bars, and seawater chlorinity

T°C	H ₂ S(mM)	H ₂ (μM)	Fe(mM)Cu(μM)	pH _(in-situ)	pH _(25°C)	Redox	
400	9.47	57	1.93	81	5.00	3.60	HMPy
375	9.46	58	1.92	55	4.59	3.56	Py
350	9.37	85	1.87	27	4.23	3.44	Py
300	9.23	142	1.76	3.5	3.92	3.28	Py

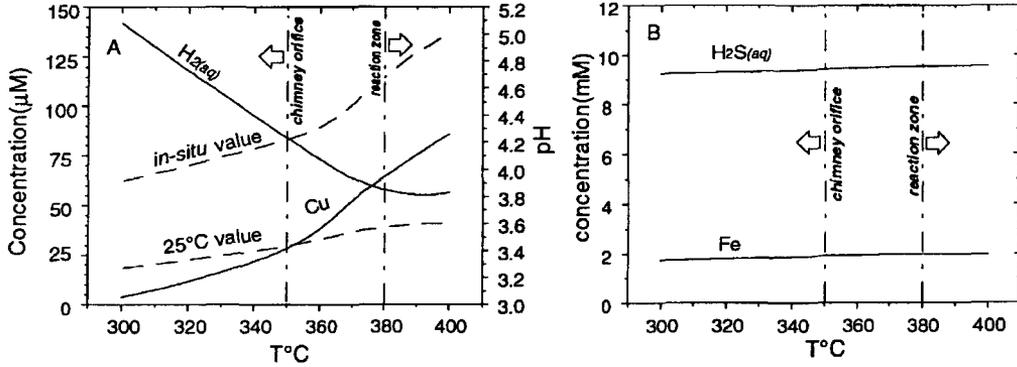


FIG. 1. Predicted changes for the effect of conductive cooling on dissolved concentrations of Cu, H₂(aq), (in A), and Fe, H₂S(aq) (in B) for mid-ocean ridge hot spring fluids at 500 bars, and seawater chlorinity. Both pH_(in-situ) and pH_(25°C) values are shown in A (dash line). Reaction zone and vent temperatures are indicated by dot-dash lines.

systematically decreased with decrease in temperature, while H₂ shows a strong increase in concentration with cooling. Both pH_(in-situ) and pH_(25°C) values are also observed to decrease substantially. Clearly, it can be demonstrated that a fluid evolves towards becoming increasingly reducing and acidic as a result of conductive cooling. As a consequence of this, the fluid maintains virtually all dissolved Fe, while losing Cu owing to the effects of temperature, redox, and pH on the relative solubilities of chalcopyrite and pyrite. In effect, slight, but significant precipitation of pyrite generates more H₂ and lowers fluid pH, which prevents further precipitation of Fe. Reducing conditions, in contrast, constrain the solubility of Cu-bearing minerals and cause dissolved Cu to be removed from the fluid.

As demonstrated by Fig. 1B, species such as Fe, and H₂S, which are abundant in source fluid, are relatively insensitive to the cooling, while trace components, H₂, and Cu show large departures from their original concentrations, even by cooling just to 350°C (see Fig. 1A). Owing to temperature

dependent precipitation of chalcopyrite and pyrite, the fluid becomes increasingly acidic, which may contribute to dissolution of previously precipitated sulfide phases (i.e. sphalarite), especially at relatively low temperatures. That Fe and H₂S, are not greatly affected by cooling indicates that these species can be relied on with confidence to infer reaction zone conditions (e.g. Fe pH-indicator and H₂S-geothermometer (Ding and Seyfried, 1992)). Since H₂ and Cu concentrations are predicted to change significantly during cooling, these species must be used with caution to predict condition in subsurface reaction zones. These species, however, can be still used to constrain lower limits of log f_{O_2} , or/and minimum temperatures.

Reference

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 Johnson J. W., Oelkers E. H., and Helgeson H. C. (1992) *Computers Geosci.*, **18**, 899–947.