

**GEOCHEMICAL MODELS OF REACTIONS OF SEAWATER AND METEORIC WATER WITH BASALT AND PERIDOTITE.** Mark H. Reed, and James Palandri, Department of Geological Sciences, University of Oregon, Eugene, Oregon 97403-1272, [mhreed@uoregon.edu](mailto:mhreed@uoregon.edu), [palandri@uoregon.edu](mailto:palandri@uoregon.edu).

**Introduction:** Reaction of seawater with basalt produces the most common hydrothermal fluid on Earth—a fluid that is characteristic of hot springs along the entire mid-ocean ridge system and in most submarine springs of island arc volcanoes. Such reaction dramatically changes the original seawater and strictly controls fluid composition, providing an excellent example of the critical role of rock reaction in fixing fluid composition, most notably pH and redox state. Seawater-basalt-derived fluids transport large quantities of copper, zinc and iron to sulfide

mound and chimney deposits on the sea floor and to scales that clog geothermal power plant pipes with chalcopyrite, bornite, covellite, sphalerite and pyrite as in Kyushu [1] and Iceland [2].

Reaction of seawater with submarine peridotite produces fluids that are quite alkaline [3] relative to those from basalt reaction, and which provide an instructive comparison to basalt-derived fluids. Reactions of basalt and peridotite with meteoric waters in subaerial geothermal systems yield fluids that are quite distinct in pH and redox conditions from those originating from seawater.

Using calculations of multiphase equilibria with program CHILLER [4] or its new offspring CHIM-XPT, we explore basalt and peridotite reactions from moderate temperature to little-explored temperatures up to 500°C as a basis for understanding hydrothermal fluids from deep ocean hot springs and subaerial volcanic settings where meteoric waters dominate. For both the seawater and meteoric water reactions, a focus on temperatures exceeding 350°C is of direct value in modeling the likely fluids to be encountered in the ongoing Icelandic Deep Drilling Project, where one goal is the examination of *in situ* supercritical fluids and their rock environment.

**Seawater and fresh water reaction with basalt:** We computed seawater-basalt reaction at nine temperatures between 100°C and 500°C and a range of water/rock ratios (w/r) from  $>10^4$  to 1. In seawater-basalt reaction, the dominant effect at  $T \geq 400^\circ\text{C}$ , as at lower T, is the production of acid ( $\text{H}^+$ ) by precipitation of chlorite, driven by reaction of seawater  $\text{Mg}^{2+}$  with Al and Si from the basalt, yielding minimum pH's of 3.8 at 400° and 500°C. As at lower T, the acidic conditions enable dissolution and transport of Fe, Cu and Zn, but the higher temperatures enable more than an order of magnitude larger concentrations of the metals than at  $T \leq 300^\circ$ . At every temperature, aqueous Cu and Zn concentrations are limited by precipitation of sulfides, which form from sulfide produced by reduction of seawater sulfate as ferric

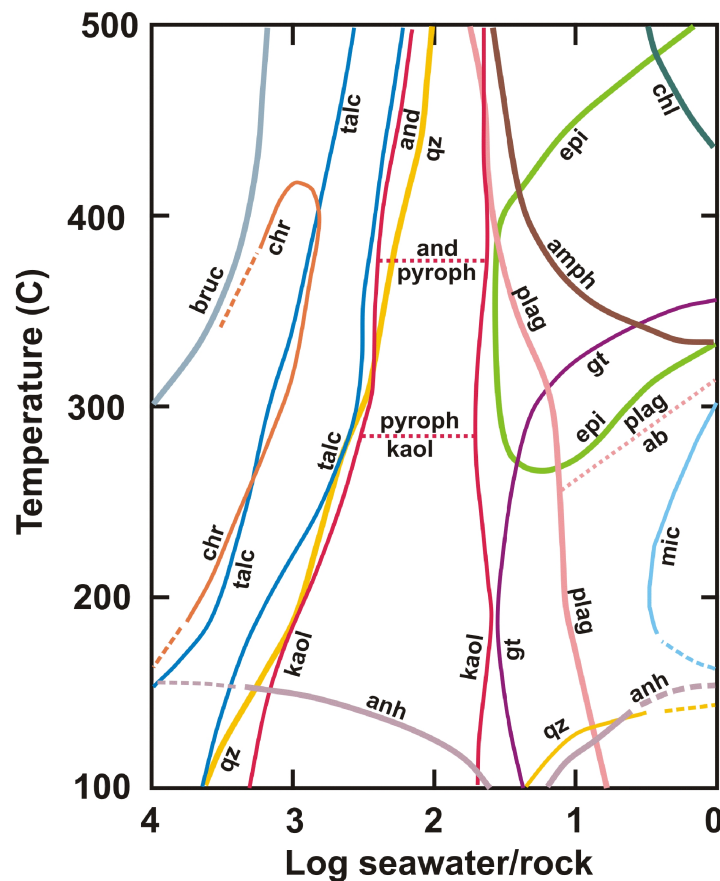


Figure 1. Mineral distribution from reaction of seawater with an Icelandic basalt. Each curve shows a boundary wherein the mineral is present on the side of the curve where the mineral name is given, but absent on the other side. Mineral abbreviations are given in the text. The graph summarizes separate model runs at nine temperatures, each of which was run at w/r ranging from  $>10^4$  to 1. The phase boundary geometries are approximate where curves for several phases with components in common intersect in a small area.

iron minerals precipitate. Although a modest amount of  $H_2$  forms,  $H_2S$  is the dominant reduced aqueous species at low  $w/r$ , in contrast to other systems described below. With decreasing  $w/r$ , the pH increases to the neutral range after  $Mg^{2+}$ -based buffers fail causing feldspars, epidote and amphiboles join the mineral assemblage. The reaction produces the characteristic mineral assemblages known from metabasalts and meta-andesites world wide, including combinations of chlorite, epidote, quartz, albite, calcite, garnet, actinolite and clinopyroxene, among others, e.g. [5]. The computed mineral assemblages are depicted in Figure 1, which is a summary of results from the nine individual model runs. The general pattern of brucite and Mg-silicates (chl, chr, talc), at high  $w/r$  yielding to Ca-silicates with decreasing  $w/r$  reflects the pH trend from acidic to neutral as described above.

In meteoric water reaction with basalt at  $T \geq 300^\circ C$ , the small initial concentration of  $Mg^{2+}$  precludes the acidic pH's of the seawater reaction and pH climbs from 5.5 to 7.5 with decreasing  $w/r$ . Metal concentrations remain relatively small, but substantial  $H_2$  forms, although much less  $H_2$  than in peridotite reaction.

**Seawater and fresh water reaction with peridotite:** In contrast to the seawater-basalt reaction, seawater-peridotite reaction yields no acidic pH's at any temperature explored up to  $500^\circ C$  (e.g. pH ranges from 5.2 to 8.1 at  $500^\circ C$  and 5.2 to 7.8 at  $300^\circ C$ ) because brucite and Mg-silicates buffer pH at neutral values at the elevated  $Mg^{2+}$  concentrations of seawater. Reduction of seawater sulfate yields sulfide which precipitates Cu and Co in sulfide minerals, holding aqueous metal concentrations very small at the alkaline pH's of the system. At every T, coupled reduction of  $H_2O$  and oxidation of ferrous iron where magnetite precipitates yields abundant  $H_2$ —two orders of magnitude more than in seawater-basalt reaction at  $500^\circ C$ , and far more  $H_2$  than  $H_2S$ .

Fresh water-peridotite reaction yields a typical serpentinite assemblage, as for the seawater reaction, but pH is much higher, ranging up to pH 11 ( $300^\circ C$ ).  $H_2$  concentration is similar to that in the seawater reaction.

**Boiling and cooling:** Hydrothermal fluids cool or boil as they rise to the surface, resulting in pH changes as shown in Figure 2. In general, pH decreases with decreasing temperature in the seawater systems, but remains relatively constant and about 4 units higher in the fresh water systems.

**Mineral Abbreviations:** ab, albite; amph, amphibole (actinolite, riebeckite); and, andalusite; anh,

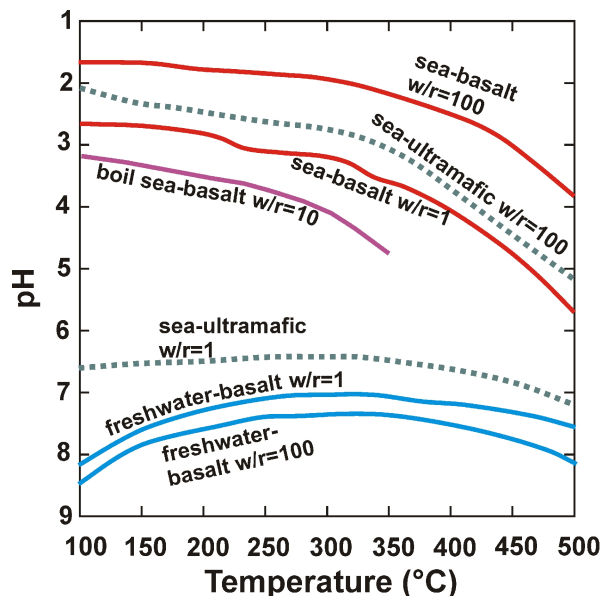


Figure 2. pH vs temperature for cooling of fluids derived from reactions of basalt and peridotite. Boiling of a seawater-basalt-derived fluid is also shown. The pH path for boiling of a freshwater basalt fluid at  $w/r=10$  is quite close to the curve shown above for simple cooling of the  $w/r=100$  freshwater-basalt fluid.

anhydrite; bruc, brucite; chl, chlorite (Fe-Mg solid solution); chr, chrysotile; epi, epidote; gt, garnet (grossular, andradite); kaol, kaolinite; mic, microcline; mt, magnetite; plag, An(30); pyroph, pyrophyllite; qz, quartz.

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