

Web Supplement 19.4.3

19.4.3 Phase Separation: Changing Impact on Ion Speciation

In the hot reaction zone, seawater is heated to temperatures ranging from 340 to 465°C, which is considerably above the boiling point of pure water at 1 atm pressure. Although the high pressures in the deep sea considerably expand the thermal range at which water remains a liquid, the temperatures of the hydrothermal fluids are high enough that some type of phase separation does occur. This phase separation can take three forms listed in order of increasing pressure and temperature requirements: (1) a subcritical form akin to boiling that produces a vapor and a brine, (2) a supercritical form in which a high-chlorinity fluid condenses, and (3) an extreme supercritical form in which halite precipitates.

For the depth range over which most hydrothermal venting occurs (2200 to 2800 m), subcritical phase separation requires a minimum temperature of 375 to 405°C. Subcritical phase separation generates a low-chlorinity vapor phase and a higher chlorinity fluid phase. The degree to which chloride is partitioned between the phases depends on the pressure and temperature at which the phase separation occurred. In Figure W19.1, the solid line defines the minimum pressure and temperature combinations required to support subcritical phase separation for seawater. If the fluid undergoing subcritical phase separation has a chlorinity different from seawater, the minimum pressure and temperature combination will be different. In general, higher pressures and temperatures are required as chlorinity increases.

If the fluid undergoing phase separation has a temperature and pressure combination greater than its critical point (marked CP on Figure W19.1), a high-chlorinity fluid will also condense. This is termed supercritical fluid separation. The critical point for seawater at 3000 m is about 410°C. Both types of phase separation occur in hydrothermal systems. Some evidence also exists for the third type of phase separation in which halite is precipitated. The minimum temperature and pressure conditions required are shown in Figure W19.1 as the region to the right of the dashed line.

Phase separation greatly affects the chemistry of the hydrothermal emissions because it fractionates the volatiles, which are derived from magmatic degassing and water-rock interactions, into a vapor phase. The ionic species, derived from seawater and

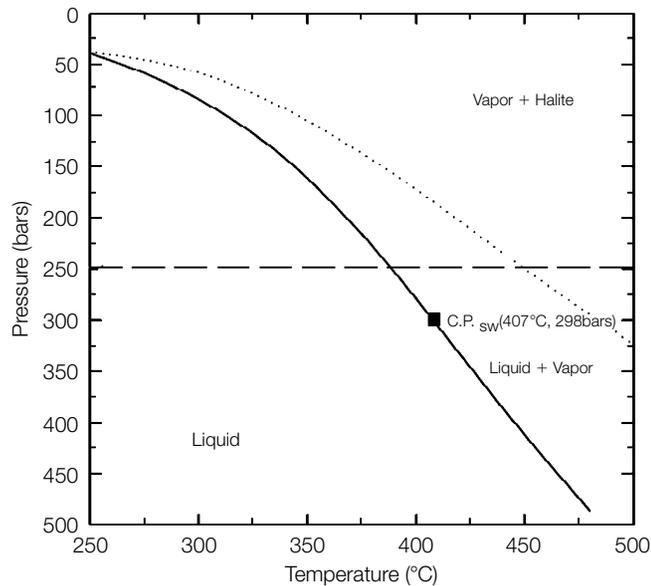


FIGURE W19.1

Phase diagram for water and seawater. Subcritical phase separation (boiling) will occur in seawater at pressure-temperature combinations (x, y points) that lie to the right of the solid line. This separation produces a low-chlorinity vapor phase that coexists with a higher chlorinity liquid phase. Pressure-temperature combinations that lie to the right of the dashed line are predicted to favor the precipitation of halite and formation of a vapor phase. The critical point for seawater is labeled CP. *Source:* From Von Damm, K. L. (2004). Evolution of the hydrothermal system at East Pacific Rise 9°50'N: Geochemical evidence for changes in the upper oceanic crust. In *Mid-Ocean Ridges: Hydrothermal Interactions between the Lithosphere and Oceans*, Geophysical Monograph Series 148, C. R. German, J. Lin, and L. M. Parson, eds, pp. 285–304. American Geophysical Union.

water-rock interactions, are segregated into the fluid phase. The nature of this fractionation is dependent on: (1) the temperature-pressure conditions, (2) which type of phase separation is occurring, and (3) the chemical composition of the fluid undergoing phase separation. Phase separation is critical to determining the chemical composition of the fluids because complexation with chloride determines the solubility of the dissolved metals and other cations and, hence, controls their hydrothermal fluid concentrations.

As noted earlier, seafloor hydrothermal systems evolve over time in response to changes in magma supply. Immediately following a volcanic eruption or magma intrusion, the increased heat flux triggers phase separation. The resulting low-chlorinity gas phase is explosively vented, with the brine phase being temporarily retained around the heat source enabling further water-rock interactions. Over a period of a few years, gas venting transports enough heat to cool the system such that phase separation slows and stops. As the gas phase is depleted, emission of hydrothermal brines commences. As

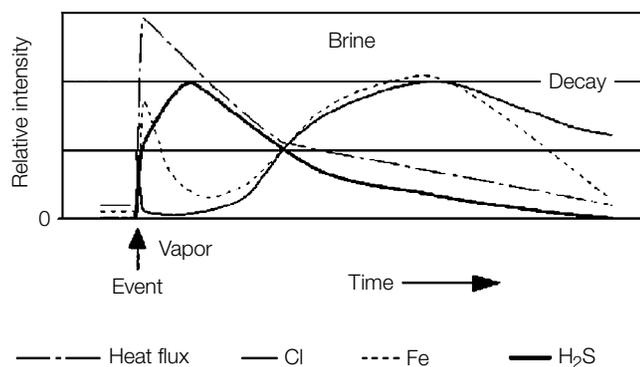


FIGURE W19.2

Response of hydrothermal systems to a volcanic event. Relative intensity of heat flux (dot-dashed line) and vent fluid concentrations of chloride (thin line), iron (dotted line), and hydrogen sulfide (thick line) over time. Systems evolve from a vapor-dominated, high-heat-flux stage accompanied by phase separation through a transition to brine-dominated discharge and eventually decay back toward zero heat flux and seawater composition. High Fe concentrations are present in immediate post-eruptive fluids. *Source:* From Butterfield, D. A., I. R. Jonasson, G. J. Massoth, R. A. Feely, K. K. Roe, R. E. Embley, J. F. Holden, R. E. McDuff, M. D. Lilley, and J. R. Delaney (1997). Seafloor eruptions and evolution of hydrothermal fluid chemistry. *Philosophical Transactions of the Royal Society of London A* 355, 369–386.

shown in Figure W19.2, this phase eventually ends as the magmatic heat source cools. During this stage, the hydrothermal fluid composition becomes progressively similar in composition to seawater. Note that high concentrations of dissolved iron are emitted as part of the initial vapor phase.

