18. Theory of Deposit Formation

By W.C. Pat Shanks III

Volcanogenic Massive Sulfide Occurrence Model

Scientific Investigations Report 2010–5070–C

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

Contents

Figures

18. Theory of Deposit Formation

By W.C. Pat Shanks III

Ore Deposit Types

The unifying characteristics of the volcanogenic massive sulfide deposit type are (1) association with volcanics, and (2) mineralization by hydrothermal solutions at or near the seafloor. Early papers referred to these deposits as stratiform and stratabound deposits, or exhalative deposits. Deposits in volcanic, clastic sedimentary, marine carbonate, and metamorphic terranes were lumped together. This meant that all massive sulfide deposits, including those strictly in volcanic terranes (VMS), those in shale basins (SEDEX), and those in carbonate strata (MVT), were grouped based on some gross similarities (base-metal deposits, massive sulfide ores, low-to-moderate temperature hydrothermal processes).

These early attempts at classification indicate that there is a more or less continuous spectrum of massive sulfide deposit types, and that classifications are sometimes difficult to apply even today because of the gradational nature of the deposit characteristics. The key distinction among VMS deposits is that they formed as seafloor massive sulfides from hydrothermal fluids that are driven by magmatic heat. This mineralizing process may involve convecting seawater that evolves by water/rock interaction into a slightly acidic metalliferous fluid, which may contain a significant component of magmatic volatiles. In some settings, volcanic or intrusive rocks are only present in the footwall sequence or are peripheral to the actual sulfide deposit, and in these cases a genetic link must be established using geology and geochemistry.

Volcanogenic massive sulfide deposits have clear system affinities to, and are transitional to, sedimentary-exhalative (SEDEX) deposits. Most SEDEX deposits occur in shale basins with little or no exposure of igneous rocks. In contrast to most (but not all) VMS deposits, they tend to be Zn-rich, commonly display fluid-inclusion evidence for formation from concentrated (basinal) brines, form at low to moderate temperatures (50–200 °C), and typically show evidence of sulfide derivation from local sources at the site of deposition (bacterial sulfide in pore-waters or dissolved H_2S in an anoxic water column).

However, there is accumulating fluid inclusion evidence that some VMS deposits, especially those in felsic-siliciclastic settings like the Tasmanian deposits in the Mt. Reed volcanics, the Bathurst deposits (New Brunswick), and the Iberian Pyrite Belt deposits in Spain and Portugal (Solomon and others, 2004; Solomon, 2008; Tornos and others, 2008), formed from saline fluids in brine pools on the seafloor. These deposits consist of sheet-like massive sulfide bodies due to deposition in areally extensive brine pools, similar to those of the modern Red Sea deposits (6×14 km, 20 m thick; fig. 3–2). Mafic-siliciclastic deposits like the Besshi deposits probably also formed from dense brine pools, but fluid inclusion evidence is not attainable from most Besshi deposits because of significant postore deformation. The Windy Craggy deposit, British Columbia, has well-preserved fluid inclusions that indicate formation from moderately saline fluids (9–17 wt% NaCl equivalent; Peter and Scott, 1999) that could have formed negatively buoyant brine-pools on the seafloor.

Finally, VMS deposits have some system affinities with high-sulfidation epithermal precious-metal deposits in marine volcanic rocks, volcanogenic manganese deposits, and Algoma-type iron-formations.

Sources of Metals and Other Ore Components

Despite thousands of published papers on VMS deposits resulting from intensive study over the past 50 years, and despite the incredible opportunities to observe and sample actively-forming deposits on the seafloor, there is continued debate about the fluids that form economic VMS ore deposits. In fact, the argument has not evolved much. For example, the debate in the 1850s about what we now know to be VMS deposits (Stanton, 1984, p. 1432–1433) can be distilled as follows:

> ….the Norwegians considered the replacing ore materials to have come from intrusive granitoid masses, whereas the Americans saw them as derived from the surrounding country, and segregated into the favorable beds by lateral secretion.

This debate was renewed in the 1960s with the discovery of widespread metalliferous sediment deposits on the seafloor (Bostrom and others, 1969) spatially associated (fig. 3–1) with the mid-ocean ridges (MORs). Corliss (1971) focused attention on the possibility of leaching incompatible elements from basaltic pillow interiors as seawater penetrates through cracks in the lavas. The discovery that heat flow on the flanks of

divergent plate boundaries is not nearly as high as expected for conductive heat loss (Anderson and others, 1977) implicated convective heat loss due to seawater circulation. Muehlenbachs and Clayton (1971, 1972, 1976) used $\delta^{18}O$ studies of greenstones and other metamorphosed volcanic rocks dredged from the seafloor to demonstrate that subseafloor metamorphism was due to high-temperature reactions of seawater with oceanic crust, which suggested convective seawater circulation could be a common process that significantly alters the oceanic crust. Hydrothermal experiments between seawater and basalt at 200–500 °C (Bischoff and Dickson, 1975; Seyfried and Bischoff, 1977; Mottl and Holland, 1978) showed strong Mg-removal due to the formation of secondary sheet silicates, producing acidic solutions capable of transporting ore-forming metals (Fe, Cu, Zn, Pb). Thus, the "lateral secretion" model of the past has become the water/rock interaction model of the present.

Research on ore genesis in VMS deposits and modern seafloor analogs over the last 30 years has focused mostly on water/rock interaction models, with direct magmatic contributions usually relegated to a minor or insignificant role (Bischoff and Dickson, 1975; Large, 1977; Ohmoto and others, 1983; Shanks, 2001; Seyfried and Shanks, 2004). Experimental studies of basalt/seawater interaction at temperatures up to 425 °C have shown that water/rock interaction, without the presence of magmatic volatiles, can account for the complete spectrum of observed metal contents of hydrothermal vent fluids that have been analyzed from the mid-ocean ridges (Seyfried and others, 2002, 2004; Seyfried and Shanks, 2004).

However, it is well established that magmatic degassing adds He (helium), CO_2, CH_4, and H_2S or SO_2 to convective hydrothermal systems (Lilley and others, 1982; Kadko and others, 1995; Glasby and others, 2008). A few researchers have consistently advocated for an important, perhaps pivotal, role for metal supply by magmatic fluids (Sawkins and Kowalik, 1981; Urabe and Marumo, 1991; de Ronde, 1995; Lydon, 1996; Yang and Scott, 1996, 2002, 2003, 2006). In particular, Yang and Scott (2002) have shown that in Manus Basin the compositions of metallic precipitates found in vesicles of melt inclusions and matrix glass progressively change from Ni + Cu + Zn + Fe in basalt and basaltic andesite, to Cu+ Zn + Fe in andesite, to Cu + Fe in dacite, to Fe in rhyodacite, and to Fe + Zn (+ Pb?) in rhyolite. Williams-Jones and Heinrich (2005) provided further evidence from experimental studies and laser ICP-MS analyses of individual vapor-rich fluid inclusions that Cu and Au, together with As and Sb, are preferentially concentrated in magmatic vapor at concentrations that are much higher than those in Cl-rich brines. These observations, combined with studies that show the Cu, Au, As, and Sb enrichments in the seafloor massive sulfide deposits from rhyolitic and rhyodacitic settings in the eastern Manus Basin, suggest that pulses of magmatic fluids injected into seawater convective systems may be important metal contributors in

felsic environments, and that water/rock interaction may dominate metal supply in mafic settings. An alternative view is that magmatic volatile-rich fluids add acid to convective hydrothermal systems and the resulting very acidic fluids (pH <1) are able to leach additional metals (Craddock and others, 2007).

Sources of Ligands Involved in Ore Component Transport

The principal anion in seawater is Cl, with a remarkably constant concentration of 543 millimoles per liter (mM/L) or 19,277 milligrams per liter (mg/L). The next most important anion is SO_4 at 2,600 mg/L or 27 mM/L, followed by HCO_3 (140 mg/L), Br (65 mg/L), and H_3BO_4 (24 mg/L). Knowledge of the Cl content of fluids involved in the formation of VMS deposits comes from studies of fluid inclusions and from direct sampling of active hydrothermal systems on the modern seafloor. Fluid inclusion compositional variations are summarized in Chapter 14 of this report; fluid inclusions from most ancient VMS deposits have Cl concentrations close to that of seawater (3–6 wt% NaCl), but many have much higher Cl contents. Studies of active systems (Von Damm, 1995; Von Damm and others, 1995, 1997, 2003) have shown that the principal cause of salinity variation at mid-oceanic ridges is phase separation into low- and high-chloride fluid phases. Chlorine values in sampled vent fluids display a smaller range than in VMS fluid inclusions, ranging from 10 to 200 percent of seawater values (0.3–7 wt% NaCl). The Red Sea brine pools represent a unique modern case where convective seawater has reacted with subsurface evaporate minerals to achieve Cl contents about 8 times that of seawater (25 wt% NaCl), close to NaCl saturation (Zierenberg and Shanks, 1986).

Hydrogen sulfide is the other anion that can be an important metal complexing agent, participating in reactions such as:

$$Au(s) + H_2S(aq) = AuHS(aq) + 0.5H_2(g)$$

or

$$Cu^+ + 2HS^- = Cu(HS)_2^-.$$
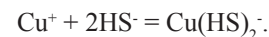
Hydrogen sulfide can be supplied to circulating hydrothermal fluids by (1) hydrothermal or bacterial reduction of seawater sulfate, (2) hydrolysis reactions with volcanic glass or sulfide phases in host rocks, or (3) direct injection of magmatic volatiles. Sulfur dioxide is unstable in aqueous environments and disproportionates to SO_4 and H_2S, or to SO_4 and native S (Holland, 1965; Symonds and others, 2001) by the following reactions:

$$4SO_2(g) + 4H_2O(aq) = H_2S(aq) + 3H_2SO_4(aq)$$
$$3SO_2(g) + 2H_2O(aq) = S(s) + 2H_2SO_4(aq)$$
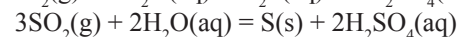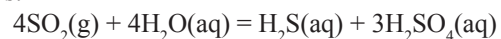
Thus, SO_2 disproportionation reactions also strongly contribute to the acidity of hydrothermal fluids.

Sources of Fluids Involved in Ore Component Transport

The vast majority of chemical and isotopic studies of fluid compositions in modern and ancient VMS deposits indicate that seawater or evolved seawater is the dominant mineralizing fluid (see Chapter 14, this report). Seawater circulation in VMS deposits is driven by magmatic heat. The resulting convection system produces compositionally evolved seawater following reactions with host rocks along the flow path and fluid temperatures up to about 400 °C in the upflow zone and the hydrothermal vent site on the seafloor.

Other potentially important contributors to the ore-transport process are magmatic water and related volatiles. Typically, magmatic gases are about 90 mol percent H_2O, with 5–10 mol percent CO_2, 1–2 mol percent sulfur species such as SO_2 and (or) H_2S, and lesser amounts of H_2, HCl, and HF. HCl is an especially important magmatic volatile in island-arc and back-arc settings (Taran and others, 1995). All of these gas species can be directly absorbed into convecting seawater hydrothermal systems, and a substantial addition of the magmatic component would result in dilution of Cl by addition of H_2O, CO_2, S, and F (fluorine) and a decrease in pH.

The magmatic fluid may contribute significant amounts of carbon and sulfur components, and potentially appreciable metallic components. Some fluid-inclusion and experimental evidence indicates that magmatic vapors can carry exceptionally high metal contents (Williams-Jones and Heinrich, 2005), thus raising the possibility that a short-term, limited-volume, magmatic flux could be very important in providing metals to the system.

Magmatic water from a variety of igneous environments has δD of -40 to -80 per mil and $\delta^{18}O$ of 6 to 8 per mil (Rye, 1993), and these values can be applied to MOR systems. Arc and back-arc systems are somewhat different because of water contributed by dehydration of the descending slab; arc-related magmatic waters are estimated to have δD values of about -25 per mil (Giggenbach, 1992; Shaw and others, 2008). Thus, even small contributions of magmatic water should be distinguishable by negative δD values in hydrothermal fluids.

Shanks and others (1995) discovered vent fluids from the 1991 MOR volcanic eruption area at 9°45-52'N EPR with δD values as low as -2 per mil. These values, which are the only negative δD values found for vent fluids from MOR sites, could result from either a small component of magmatic water or an open system, isobaric phase-separation process (Berndt and others, 1996). Seawater convection is the process that cools axial magma chambers and mines heat from the oceanic crust. Seawater cannot quench magma without experiencing phase separation. Magmatic water mixing, together with fluid-basalt reactions that shift $\delta^{18}O_{H2O}$ to higher values, could explain the isotope systematics of the D-depleted vents at 9–10°N. However, mid-ocean ridge basalts (MORBs) tend to be quite "dry," with only about 0.2 wt% water (Dixon and others, 1988); studies of Hawaiian glasses have shown that they never reach saturation with respect to water at eruption depths of more than a few hundred meters (Dixon and others, 1991). That is, seafloor basaltic lavas do not exsolve water at depths greater than a few hundred meters simply by freezing to form glass. However, complete crystallization of a MOR basalt dike containing only anhydrous phases could release magmatic water. In summary, the negative δD values from the 9–10°N EPR site do not provide conclusive proof of magmatic water in the convectively venting system there. Similarly, stable isotope and fluid inclusion evidence from VMS deposits for a magmatic water component is generally equivocal (Huston, 1999).

In a back-arc tectonic setting, vent fluids with negative δD values (-8.1 per mil) have been analyzed from the DESMOS vent field in Manus Basin (Gamo and others, 1997). This hydrothermal field is hosted by andesitic to rhyodacitic rocks, and the magmas that produce them are significantly more water-rich than MORB. Recent work (Craddock and others, 2007; Bach and others, 2007; Reeves and others, 2011) indicates that vent fluids from the eastern Manus Basin sites have fluid chemistries consistent with a mixture of two-thirds seawater and one-third magmatic water-rich volatiles.

Hydrogen sulfide also may be added to hydrothermal systems by magmatic degassing, but evidence of this process is ambiguous for MOR systems because H_2S is produced in abundance by leaching of igneous sulfides from basaltic rocks during water/rock interactions (Seyfried and Bischoff, 1981). Studies of $\delta^{34}S_{H2S}$ in MOR black smoker vent fluids has indicated consistently that some seawater-derived sulfate is incorporated via sulfate-reduction reactions (Shanks, 2001; Ono and others, 2007), which produces the slightly positive $\delta^{34}S$ values observed in samples of vent fluid H_2S and massive sulfide.

Felsic magmas tend to be more oxidizing, relative to mafic magmas, so SO_2 is expected to be the dominant magmatic sulfur gas. Various investigators have invoked SO_2 disproportionation reactions (to H_2S and SO_4) to explain negative $\delta^{34}S$ values (-3 to -18 per mil) of H_2S and sulfide minerals and lower-than-seawater $\delta^{34}S_{SO4}$ values (10–17 per mil) in associated SO_4 or sulfate minerals (McMurtry and others, 1993; Gamo and others, 1997; Alt and others, 1998; Herzig and others, 1998; Resing and others, 2007). The chemical and sulfur isotopic data provide an explanation for the negative $\delta^{34}S$ values of sulfides related to arc and back-arc volcanic-hosted VMS systems and strongly suggest derivation of the sulfur species from magmatic SO_2 vapor.

Chemical Transport and Transfer Processes

The ligands of most importance in ore-forming metallic element transport are Cl and HS, based on the current state of knowledge of aqueous complexes in hydrothermal solutions as summarized in databases like SUPCRT (Johnson and others,

1992) and SOLTHERM (Reed and Palandri, 2006). It has been known for many years, thanks to the seminal work of Harold Helgeson, that Cl is an important complexing agent that significantly increases the solubility of base metals (Fe, Cu, Pb, Zn) in hydrothermal solutions (Helgeson, 1969). Recent studies have suggested that sulfide complexing (MeHS) is important in increasing solubility of some metals (Me), especially Cu and Au (Mountain and Seward, 2003; Stefannson and Seward, 2004).

Geochemical reaction calculations that consider all possible aqueous species and their affect on mineral solubilities (Shanks and Bischoff, 1977; Reed, 1982; Janecky and Seyfried, 1984; Bowers and Taylor, 1985; Janecky and Shanks, 1988; Reed and Palandri, 2006) have clearly shown that fluids having seawater or higher salinity are capable of transporting metals and sulfide at temperatures above 200°C, and that deposition from VMS ore fluids is mainly due to temperature change as the hydrothermal fluids mix with cold, ambient bottom waters. Janecky and Seyfried (1984) predicted the sequence of sulfide, sulfate, and silicate minerals (fig. 18–1) that form as a result of mixing of 350°C fluid from 21°N EPR with cold, ambient, bottom seawater and showed that cooling is the most important factor.

Fluid Drive Including Thermal, Pressure, and Geodynamic Mechanisms

Fluid circulation in subseafloor hydrothermal systems is driven by buoyancy forces related to the heat of subvolcanic

intrusives (see Lowell and others, 2008). Inferred convective hydrothermal flow paths are shown in figures 4–2, 4–6, and 4–7 for fast and slow spreading ridges and submarine caldera settings, respectively. However, these relatively simple inferred pathways for hydrothermal circulation are difficult to constrain with any degree of certainty. Active seafloor systems provide only limited exposure, and technical difficulties have limited the amount of drilling into the roots of modern hydrothermal systems. For deposits exposed on the continents, there is generally better exposure of faults and alteration zones (see Chapters 4 and 11) that allow reconstruction of the hydrothermal systems, but unraveling long, complicated histories is difficult because of limited exposure and later tectonic and metamorphic events.
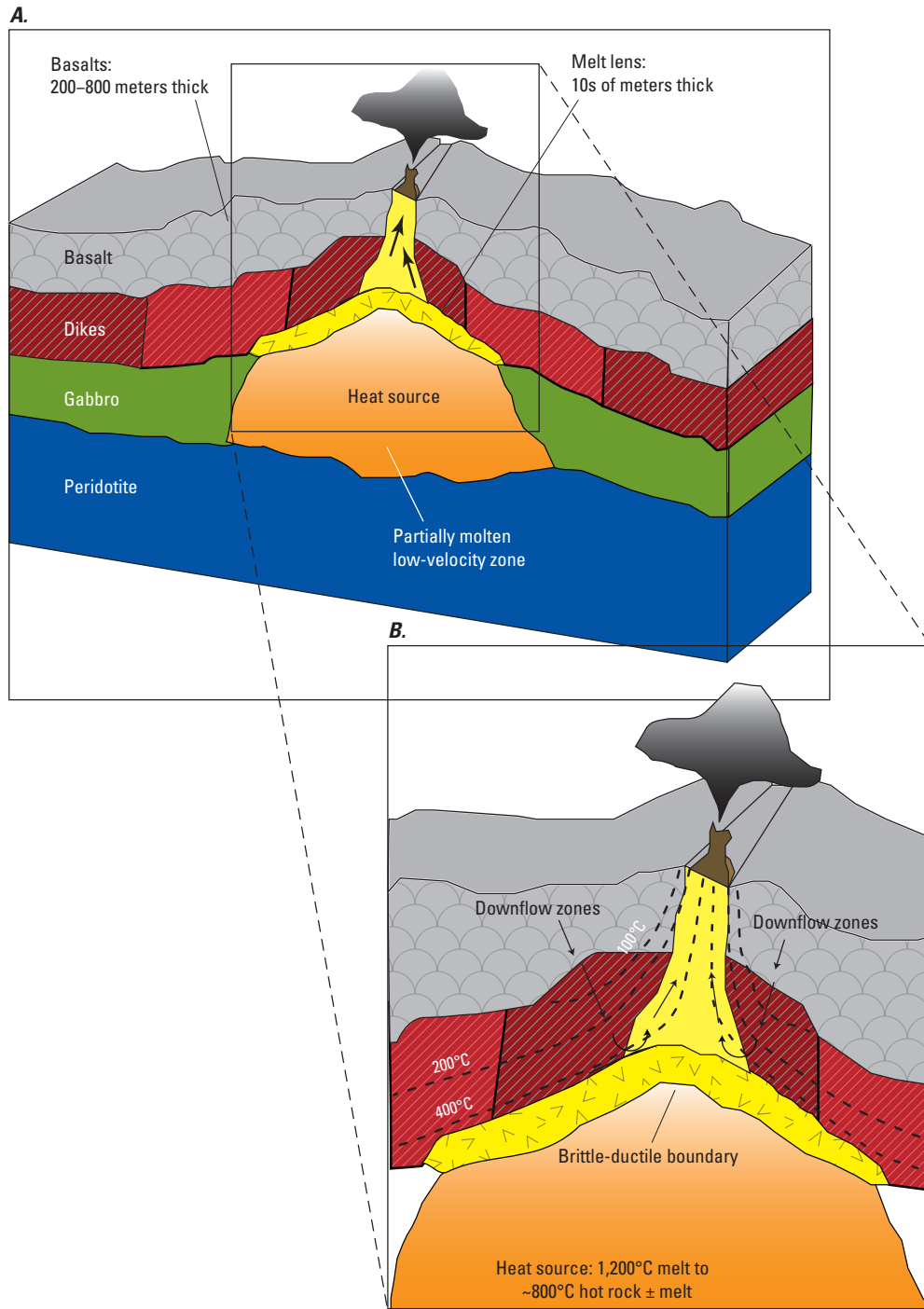
Fluid flow models have been used since the earliest studies of VMS deposits and MOR hydrothermal systems (Spooner, 1977; Turner and Gustafson, 1978; Fehn and Cathles, 1979; Lowell and Rona, 1985) and are very helpful in placing constraints on the overall nature of hydrothermal systems. In general, fluid flow models are limited by insufficient knowledge of lithologies and associated porosity/permeability, faulting and fracturing, and depth and nature of the heat source. In addition, flow models with capability for incorporating multi-phase fluid flow, phase-separation, magmatic volatile degassing, and permeability change due to mineral precipitation/dissolution are still being developed and improved.

The current state of VMS fluid flow models is summarized nicely by Lowell and others (2008) and Schardt and Large (2009). In principle, the nature of fluid and mass transport in subseafloor hydrothermal systems (Kelley and others, 2002) can be conceptualized as a simple problem (fig. 18–2). Convection is driven by magmatic heat, so there is
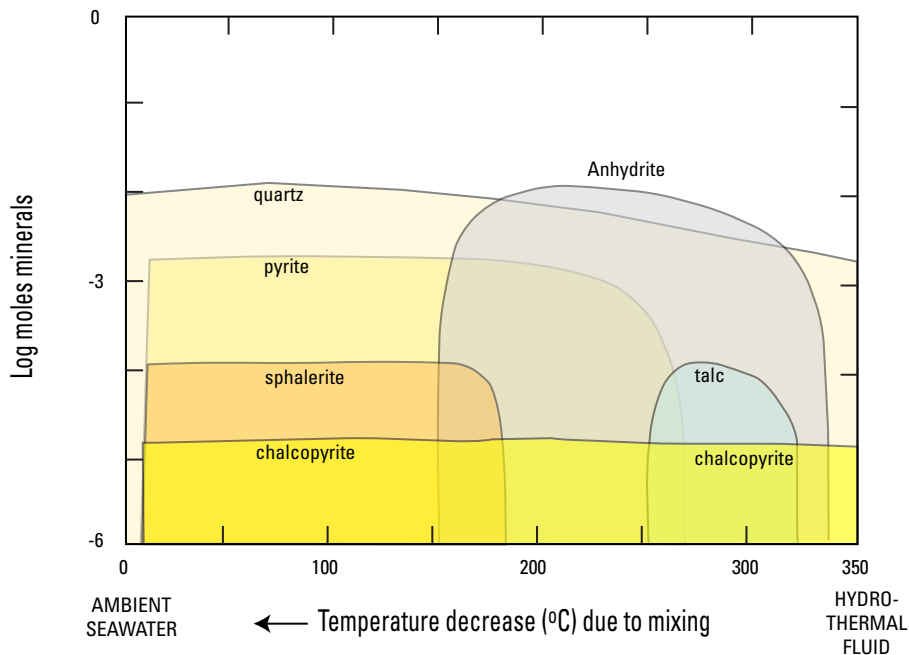
Figure 18–1. Reaction progress diagram showing mineral stabilities and amounts formed as 350°C East Pacific Rise hot spring water (right side) mixes progressively with cold (2°C) bottom seawater (toward the left side of the diagram). Abundant mineral precipitation occurs despite the dilution of the hydrothermal fluid, and cooling is the cause of pyrite, chalcopyrite, sphalerite, and quartz precipitation. Anhydrite, talc, and barite precipitate because of mixing and addition of sulfate and magnesium from seawater. The predicted sequence of minerals, especially chalcopyrite→anhydrite→pyrite-sphalerite agrees well with the sequence in some massive sulfide deposits and seafloor chimneys. Modified from Janecky and Seyfried (1984).

A.

Basalts:
200–800 meters thick

Melt lens:
10s of meters thick

Basalt

Dikes

Gabbro

Heat source

Peridotite

Partially molten
low-velocity zone

B.

Downflow zones

100°C

Downflow zones

200°C

400°C

Brittle-ductile boundary

Heat source: 1,200°C melt to
~800°C hot rock ± melt

Figure 18–2. Schematic cross section of typical mid-ocean ridge crustal architecture. *A,* Cross section showing pillow lavas and pillow ridges, sheeted dikes, gabbros (including a convecting axial magma chamber), and ultramafic rocks. *B,* Closer view showing the magmatic heat source, brittle-ductile transition zone, and inferred hydrothermal fluid circulation patterns, including multiple downflow zones and a focused upflow zone beneath the ridge axis and black smoker vents on the seafloor within the axial rift zone. Modified from Kelley and others (2002).

a symmetrical down-flow zone where cold seawater recharges the system and a more focused upflow zone where heated fluid ascends buoyantly and rapidly to the seafloor. The systems of interest are typically dominated by one or two rock types and a single fluid, seawater. In practice, though, the process is very complicated. Lowell and others (2008) described recent modeling advances that consider dynamics related to dike injection, heat transfer from the magma chamber to the hydrothermal system, and convection and magma replenishment within the chamber. Lowell and others (2008) also presented new modeling approaches that allow realistic approximation of two-phase flow in the $NaCl–H_2O$ system. This modeling allows simulation of different chemical and physical and transport processes in low-salinity vapor and high-salinity brine phases. These models are leading to a better understanding of the temporal evolution of seafloor hydrothermal systems and of the fate of brines produced in the subsurface by phase separation.

Schardt and Large (2009) summarized many fluid flow modeling studies of ancient and modern VMS systems and used coupled reactive transport models and fracture permeability models to gain understanding of the conditions necessary to form a large VMS deposit. They concluded that average-size VMS deposits (approx. 1.2 Mt total Zn and Cu) require 5,000 yrs to form and that supergiant deposits (>12 Mt Zn or 24 Mt Cu total metal; Singer, 1995) either require much longer (>35,000 yrs) or much higher metal contents in the fluid (>100 ppm).

Character of Conduits/Pathways that Focus Ore-Forming Fluids

Numerous studies of active hydrothermal vents on the seafloor show that focused, high-velocity flow (1–2 m/s) typically occurs in the highest temperature black smoker fluids. These flow rates require open fluid conduits, but there is little direct information on these in modern systems. However, stringer or feeder zones are observed in a number of cases on the modern seafloor or in drilling beneath seafloor massive sulfide deposits (Ridley and others, 1994; Humphris and others, 1995; Zierenberg and others, 1998). By analogy, stockwork zones, which are common in ancient VMS deposits, represent feeder zones below massive sulfide bodies.

Deeper portions of the upflow systems are even less well known. One area of proposed deep vigorous upflow is in the Solea graben, Cyprus, where massive epidote-quartz alteration developed in Cretaceous lavas reflects high water/rock reactions caused by high-temperature hydrothermal fluids (Bettison-Varga and others, 1992). Similar fossil upflow zones have been observed above subvolcanic intrusions in other ophiolitic VMS systems (Galley and Koski, 1999).

Recharge zones are more difficult to characterize because these flow systems are more diffuse and the resulting alteration is less intense. Footwall alteration is extensive and in some cases semiconformable, suggesting low to moderate temperatures over a broad recharge zone. However, promising studies are underway on the seafloor, using microearthquakes to track near-surface fluid flow. These studies have shown predominantly along-axis fluid flow at 9°50'N on the EPR (Tolstoy and others, 2008), but much more work needs to be done in order to understand such recharge systems.

Nature of Traps and Wallrock Interaction that Trigger Ore Precipitation

In VMS systems, cooling at the seafloor is regarded as the principal cause of sulfide precipitation, and wall rock alteration is largely considered less significant to ore precipitation. However, observations of rapid oxidation of sulfides on the seafloor have led to suggestions of various mechanisms that preserved ancient deposits. These include anoxic (including sulfidic) bottom waters, capping lava flows, or chemical precipitates of silica or sulfate minerals that cap and isolate the system from oxidizing bottom waters (Barriga and Fyfe, 1988; Hannington and others, 2005; Schardt and Large, 2009).

Structure and Composition of Residual Fluid Outflow Zones

Hanging wall alteration is common in VMS deposits (Galley and others, 2007) and provides the best evidence of residual fluid outflow, probably because of continued fluid convection due to continued cooling of underlying plutons following the ore forming period.

References Cited

Alt, J.C., Teagle, D.A.H., Brewer, T.S., Shanks, W.C., III, and Halliday, A.N., 1998, Alteration and mineralization of an oceanic forearc and the ophiolite-ocean crust analogy: Journal of Geophysical Research—Solid Earth, v. 103, no. B6, p. 12365–12380.

Anderson, R.N., Langseth, M.G., and Sclater, J.G., 1977, Mechanisms of heat transfer through the floor of the Indian Ocean: Journal of Geophysical Research, v. 82, p. 3391–3409.

Bach, W., Seewald, J.S., Tivey, M.A., Tivey, M.K., Yoerger, D., and Craddock, P.R., 2007, Hydrothermal systems in the eastern Manus Basin—Effects of phase separation and fluid mixing: Geochimica et Cosmochimica Acta, v. 71, p. A48.

Barriga, F.J.A.S., and Fyfe, W.S., 1988, Giant pyritic base-metal deposits—The example of Feitais (Aljustrel, Portugal): Chemical Geology, v. 69, p. 331–343.

Berndt, M.E., Seal, R.R., II, Shanks, W.C., III, and Seyfried, W.E., Jr., 1996, Hydrogen isotope systematics of phase separation in submarine hydrothermal systems—Experimental calibration and theoretical models: Geochimica et Cosmochimica Acta, v. 60, p. 1595–1604.

Bettison-Varga, L., Varga, R.J., and Schiffman, P., 1992, Relation between ore-forming hydrothermal systems and extensional deformation in the Solea Graben spreading center, Troodos Ophiolite, Cyprus: Geology, v. 20, no. 11, p. 987–990.

Bischoff, J.L., and Dickson, F.W., 1975, Sea water-basalt interaction at 200°C and 500 bars—Implications for origin of sea-floor heavy-metal deposits and regulation of sea water chemistry: Earth and Planetary Science Letters, v. 25, no. 3, p. 385–397

Boström, K., Peterson, M.N.A., Joensuu, O., and Fisher, D.E., 1969, Aluminum-poor ferromanganoan sediments on active ocean ridges: Journal of Geophysical Research, v. 74, p. 3261–3270.

Bowers, T.S., and Taylor, H.P., Jr., 1985, An integrated chemical and stable-isotope model of the origin of midocean ridge hot spring systems: Journal of Geophysical Research, v. 90, p. 12583–12606.

Corliss, J.B., 1971, The origin of metal-bearing submarine hydrothermal solutions: Journal of Geophysical Research, v. 76, p. 8128–8138.

Craddock, P.R., Tivey, M.K., Seewald, J.S., Rouxel, O., and Bach, W., 2007, The role of magmatic volatile input, near-surface seawater entrainment and sulfide deposition in regulating metal concentrations within Manus Basin hydrothermal systems [abs.]: EOS, Transactions, American Geophysical Union, v. 88, no. 52, Fall meeting supplement, abstract V34B-05.

de Ronde, C.E.J., 1995, Fluid chemistry and isotopic characteristics of seafloor hydrothermal systems and associated VMS deposits—Potential for magmatic contributions, in Thompson, J.F.H., ed., Magmas, fluids and ore deposits: Ottawa, Ontario, Mineralogical Association of Canada Short Course Series, v. 23, p. 479–510.

Dixon, J.E., Clague, D.A., and Stolper, E.M., 1991, Degassing history of water, sulfur, and carbon in submarine lavas from Kilauea Volcano, Hawaii: Journal of Geology, v. 99, p. 371–394.

Dixon, J.E., Stolper, E., and Delaney, J.R., 1988, Infrared spectroscopic measurements of CO_2 and H_2O in Juan de Fuca Ridge basaltic glasses: Earth and Planetary Science Letters, v. 90, p. 87–104.

Fehn, U., and Cathles, L.M., 1979, Hydrothermal convection at slow-spreading mid-ocean ridges, in Francheteau, J., ed., Tectonophysics: Amsterdam, Elsevier, p. 239–260.

Galley, A.G., Hannington, M.D., and Jonasson, I.R., 2007, Volcanogenic massive sulphide deposits, in Goodfellow, W.D., ed., Mineral deposits of Canada—A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, Special Publication 5, p. 141–161.

Galley, A.G., and Koski, R.A., 1999, Setting and characteristics of ophiolite-hosted volcanogenic massive sulfide deposits, in Barrie, C.T., and Hannington, M.D., Volcanic-associated massive sulfide deposits—Processes and examples in modern and ancient settings: Reviews in Economic Geology, v. 8, p. 221–246.

Gamo, T., Okamura, K., Charlou, J.-L., Urabe, T., Auzende, J.-M., Ishibashi, J., Shitashima, K., and Chiba, H., 1997, Acidic and sulfate-rich hydrothermal fluids from the Manus back-arc basin, Papua New Guinea: Geology, v. 25, no. 2, p. 139–142.

Giggenbach, W.F., 1992, Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin: Earth and Planetary Science Letters, v. 113, p. 495–510.

Glasby, G.P., Iizasa, K., Hannington, M., Kubota, H., and Notsu, K., 2008, Mineralogy and composition of Kuroko deposits from northeastern Honshu and their possible modern analogues from the Izu-Ogasawara (Bonin) Arc south of Japan—Implications for mode of formation: Ore Geology Reviews, v. 34, no. 4, p. 547–560.

Hannington, M.D., de Ronde, C.E.J., and Petersen, S., 2005, Sea-floor tectonics and submarine hydrothermal systems, in Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., and Richards, J.P., eds., Economic Geology 100th anniversary volume 1905–2005: Littleton, Colo., Society of Economic Geologists, p. 111–141.

Helgeson, H.C., 1969, Thermodynamics of hydrothermal systems at elevated temperatures and pressures: American Journal of Science, v. 267, p. 729–804.

Herzig, P.M., Hannington, M.D., and Arribas, A., Jr, 1998, Sulfur isotopic composition of hydrothermal precipitates from the Lau back-arc—Implications for magmatic contributions to seafloor hydrothermal systems: Mineralium Deposita, v. 33, p. 226–237.

Holland, H.D., 1965, Some applications of thermochemical data to problems of ore deposits—Part 2. Mineral assemblages and the composition of ore forming fluids: Economic Geology, v. 60, p. 1101–1166.

Humphris, S.E., Herzig, P.M., Miller, D.J., Alt, J.C., Becker, K., Brown, D., Brugmann, G., Chiba, H., Fouquet, Y., Gemmell, J.B., Guerin, G., Hannington, M.D., Holm, N.G., Honnorez, J.J., Iturrino, G.J., Knott, R., Ludwig, R., Nakamura, K., Petersen, S., Reysenbach, A.L., Rona, P.A., Smith, S., Sturz, A.A., Tivey, M.K., and Zhao, X., 1995, The internal structure of an active sea-floor massive sulphide deposit: Nature, v. 377, no. 6551, p. 713–716.

Huston, D.L., 1999, Stable isotopes and their significance for understanding the genesis of volcanic-hosted massive sulfide deposits—A review, in Barrie, C.T., and Hannington, M.D., eds., Volcanic-associated massive sulfide deposits—Processes and examples in modern and ancient settings: Reviews in Economic Geology, v. 8, p.157–179.

Janecky, D.R., and Seyfried, W.E., Jr., 1984, Formation of massive sulfide deposits on oceanic ridge crests—Incremental reaction models for mixing between hydrothermal solutions and seawater: Geochimica et Cosmochimica Acta, v. 48, p. 2723–2738.

Janecky, D.R., and Shanks, W.C., III, 1988, Computational modeling of chemical and sulfur isotopic reaction processes in seafloor hydrothermal systems—Chimneys, mounds, and subjacent alteration zones: Canadian Mineralogist, v. 26, p. 805–825.

Johnson, J.W., Oelkers, E.H., and Helgeson, H.C., 1992, SUPCRT92—A software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1-bar to 5000-bar and 0°C to 1000°C: Computers and Geosciences, v. 18, no. 7, p. 899–947.

Kadko, D., Baross, J., and Alt, J.C., 1995, The magnitude and global implications of hydrothermal flux, in Humphris, S.E., Zierenberg, R.A., Mullineaux, L.S., and Thomson, R.E., eds., Seafloor hydrothermal systems—Physical, chemical, biological, and geological interactions: Washington, D.C., American Geophysical Union, p. 446–466.

Kelley, D.S., Baross, J.A., and Delaney, J.R., 2002, Volcanoes, fluids, and life at mid-ocean ridge spreading centers: Annual Review of Earth and Planetary Sciences, v. 30, p. 385–491.

Large, R.R., 1977, Chemical evolution and zonation of massive sulfide deposits in volcanic terrains: Economic Geology, v. 72, p. 549–572.

Lilley, M.D., De Angelis, M.A., and Gordon, L.I., 1982, CH_4, H_2, CO and N_2O in submarine hydrothermal vent waters: Nature, v. 300, p. 48–50.

Lowell, R.P., Crowell, B.W., Lewis, K.C., and Liu, L., 2008, Modeling multiphase, multicomponent processes at oceanic spreading centers, in Lowell, R.P., Seewald, J.S., Matexas, A., and Perfit, M.R., eds., Magma to microbe—Modeling hydrothermal processes at ocean spreading centers: American Geophysical Union, Geophysical Monograph Series 178, p. 15–44.

Lowell, R.P., and Rona, P.A., 1985, Hydrothermal models for the generation of massive sulfide ore deposits: Journal of Geophysical Research, v. 90, p. 8769–8783.

Lydon, J.W., 1996, Characteristics of volcanogenic massive sulfide deposits—Interpretations in terms of hydrothermal convection systems and magmatic hydrothermal systems: Instituto Tecnologico Geominero de Espana, Boletin Geologico y Minero, v. 107, no. 3–4, p. 15–64.

Mottl, M., and Holland, H.D., 1978, Chemical exchange during hydrothermal alteration of basalt by seawater—Part I. Experimental results for major and minor components of seawater: Geochimica et Cosmochimica Acta, v. 42, p. 1103–1115.

Mountain, B.W., and Seward, T.M., 2003, Hydrosulfide/sulfide complexes of copper(I)—Experimental confirmation of the stoichiometry and stability of $Cu(HS)_2$ to elevated temperatures: Geochimica et Cosmochimica Acta, v. 67, p. 3005–3014.

Muehlenbachs, K., and Clayton, R.N., 1971, Oxygen isotope ratios of submarine diorites and their constituent minerals: Canadian Journal of Earth Sciences, v. 8, no. 12, p. 1591–1595.

Muehlenbachs, K., and Clayton, R.N., 1972, Oxygen isotope geochemistry of submarine greenstones: Canadian Journal of Earth Sciences, v. 9, no. 5, p. 471–478.

Muehlenbachs, K., and Clayton, R.N., 1976, Oxygen isotope composition of the oceanic crust and its bearing on seawater: Journal of Geophysical Research, v. 81, p. 4365–4369.

Ohmoto, H., Mizukamis, M., Drummond, E., Eldridge, C.S., Pisutha-Arnonda, V., and Lenagh, T.C., 1983, Chemical processes of Kuroko formation, in Ohmoto, H., and Skinner, B., eds., The Kuroko and related volcanogenic massive sulfide deposits: Economic Geology Monograph 5, p. 570–604.

Ono, S., Shanks, W.C., III, Rouxel, O.J., and Rumble, D., 2007, S-33 constraints on the seawater sulfate contribution in modern seafloor hydrothermal vent sulfides: Geochimica et Cosmochimica Acta, v. 71, p. 1170–1182.

Peter, J.M., and Scott, S.D., 1999, Windy Craggy, northwestern British Columbia—The world's largest Besshitype deposit, in Barrie, C.T., and Hannington, M.D., eds., Volcanic-associated massive sulfide deposits—Processes and examples in modern and ancient settings: Reviews in Economic Geology, v. 8, p. 261–295.

Reed, M.H., 1982, Calculation of multicomponent chemical equilibria and reaction processes involving minerals, gases and an aqueous phase: Geochimica et Cosmochimica Acta, v. 46, p. 513–528.

Reed, M.H., and Palandri, J., 2006, Sulfide mineral precipitation from hydrothermal fluids, in Vaughan, D.J., ed., Sulfide mineralogy and geochemistry: Mineralogical Society of America, Reviews in Mineralogy and Geochemistry 61, p. 609–631.

Reeves, E.P., Seewald, J.S., Saccocia, P., Bach, W., Craddock, P.R., Shanks, W.C., Sylva, S.P., Walsh, E., Pichler, T., and Rosner, M., 2011, Geochemistry of hydrothermal fluids from the PACMANUS, Northeast Pual and Vienna Woods hydrothermal fields, Manus Basin, Papua New Guinea: Geochimica et Cosmochimica Acta, v. 75, p. 1088–1123.

Resing, J.A., Lebon, G., Baker, E.T., Lupton, J.E., Embley, R.W., Massoth, G.J., Chadwick, W.W., Jr., and de Ronde, C.E.J., 2007, Venting of acid-sulfate fluids in a high-sulfidation setting at NW Rota-1 submarine volcano on the Mariana Arc: Economic Geology, v. 102, no. 6, p. 1047–1061.

Ridley, W.I., Perfit, M.R., Jonasson, I.R., and Smith, M.F., 1994, Hydrothermal alteration in oceanic ridge volcanics—A detailed study at the Galapagos fossil hydrothermal field: Geochimica et Cosmochimica Acta, v. 58, p. 2477–2494.

Rye, R.O., 1993, The evolution of magmatic fluids in the epithermal environment—The stable isotope perspective: Economic Geology, v. 88, p. 733–753.

Sawkins, F.J., and Kowalik, J., 1981, The source of ore metals at Buchans—Magmatic versus leaching models, in Swanson, E.A., Strong, D.F., and Thurlow, J.G., eds., The Buchans Orebodies—Fifty years of geology and mining: Geological Association of Canada, Special Paper 22, p. 255–267.

Schardt, C., and Large, R.R., 2009, New insights into the genesis of volcanic-hosted massive sulfide deposits on the seafloor from numerical modeling studies: Ore Geology Reviews, v. 35, p. 333–351.

Seyfried, W.E., Jr., and Bischoff, J.L., 1977, Hydrothermal transport of heavy metals by seawater—The role of seawater/basalt ratio: Earth and Planetary Science Letters, v. 34, no. 1, p. 71–77

Seyfried, W.E., Jr., and Bischoff, J.L., 1981, Experimental seawater-basalt interaction at 300°C, 500 bars, chemical exchange, secondary mineral formation and implications for the transport of heavy metals: Geochimica et Cosmochimica Acta, v. 45, p. 135–149.

Seyfried, W.E., Jr., Ding, K., and Rao, B., 2002, Experimental calibration of metastable plagioclase-epidote-fluid equilibria at elevated temperatures and pressures—Applications to the chemistry of hydrothermal fluids at mid-ocean ridges, in Hellman, R., and Wood, S.A., eds., Water-rock interactions, ore deposits and environmental geochemistry—A tribute to David A. Crerar: San Antonio, Tex., The Geochemical Society Special Publication no. 7, p. 258–278.

Seyfried, W.E., Jr., Foustoukos, D.I., and Allen, D.E., 2004, Ultramafic-hosted hydrothermal systems at mid-ocean ridges—Chemical and physical controls on pH, redox carbon reduction reactions: American Geophyscial Union, Geophysical Monograph 148, p. 267–284.

Seyfried, W.E., Jr., and Shanks, W.C., III, 2004, Alteration and mass transport in mid-ocean ridge hydrothermal systems—Controls on the chemical and isotopic evolution of high-temperature crustal fluids, in Davis, E.E., and Elderfield, H., eds., Hydrogeology of the oceanic lithosphere: Cambridge, Cambridge University Press, p. 451–494.

Shanks, W.C., III, 2001, Stable isotopes in seafloor hydrothermal systems—Vent fluids, hydrothermal deposits, hydrothermal alteration, and microbial processes, in Valley, J.W., and Cole, D.R., eds., Stable isotope geochemistry: Reviews in Mineralogy and Geochemistry, v. 43, p. 469–525.

Shanks, W.C., III, and Bischoff, J.L., 1980, Geochemistry, sulfur isotope composition, and accumulation rates of Red Sea geothermal deposits: Economic Geology, v. 75, p. 445–459.

Shanks, W.C., III, Böhlke, J.K., and Seal, R.R., 1995, Stable isotopes in mid-ocean ridge hydrothermal systems—Interactions between fluids, minerals and organisms, in Humphris, S.E., Zierenberg, R.A., Mullineaux, L.S., and Thompson, R.E., eds., Seafloor hydrothermal systems—Physical, chemical, biological, and geological interactions: American Geophysical Union, Geophysical Monograph 91, p. 194–221.

Shaw, A.M., Hauri, E.H., Fischer, T.P., Hilton, D.R., and Kelley, K.A., 2008, Hydrogen isotopes in Mariana arc melt inclusions—Implications for subduction dehydration and the deep-Earth water cycle: Earth and Planetary Science Letters, v. 275, p. 138–145.

Singer, D.A., 1995, World-class base and precious metal deposits—A quantitative analysis: Economic Geology, v. 90, p. 88–104.

Solomon, M., 2008, Brine pool deposition for the Zn-Pb-Cu massive sulphide deposits of the Bathurst mining camp, New Brunswick, Canada—Part I. Comparisons with the Iberian pyrite belt: Ore Geology Reviews, v. 33, p. 329–351.

Solomon, M., Gemmel, J.B., and Zaw, K., 2004, Nature and origin of the fluids responsible for forming the Hellyer Zn-Pb-Cu, volcanic-hosted massive sulfide deposit, Tasmania, using fluid inclusions, and stable and radiogenic isotopes: Ore Geology Reviews, v. 25, p. 89–124.

Spooner, E.T.C., 1977, Hydrodynamic model for the origin of the ophiolite cupriferous pyrite ore deposits of Cyprus, in Volcanic Processes in Ore Genesis, London, 21–22 January 1976, Proceedings: Geological Society of London–Volcanic Studies Group, Institution of Mining and Metallurgy, Geological Society of London Special Publication, p. 58–71.

Stanton, R.L., 1984, Investigations of the Appalachian-Caledonide ore province and their influence on the development of stratiform ore genesis theory—A short historical review: Economic Geology, v. 79, p. 1428–1441.

Stefannson, A., and Seward, T.M., 2004, Gold(I) complexing in aqueous sulphide solutions to 500°C at 500 bar: Geochimica et Cosmochimica Acta, v. 68, p. 4121–4143.

Symonds, R., Gerlach, T., and Reed, M., 2001, Magmatic gas scrubbing—Implications for volcano monitoring: Journal of Volcanology and Geothermal Research, v. 108, p. 303–341.

Taran, Y.A., Hedenquist, J.W., Korzhinsky, M.A., Tkachenko, S.I., and Shmulovich, K.I., 1995, Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands: Geochimica et Cosmochimica Acta, v. 59, p. 1749–1761.

Tolstoy, M., Waldhauser, F., Bohnenstiehl, D.R., Weekly, R.T., and Kim, W.-Y., 2008, Seismic identification of along-axis hydrothermal flow on the East Pacific Rise: Nature, v. 451, p. 181–185.

Tornos, F., Solomon, M., Conde, C., and Spiro, B.F., 2008, Formation of the Tharsis massive sulfide deposit, Iberian Pyrite Belt—Geological, lithogeochemical, and stable isotope evidence for deposition in a brine pool: Economic Geology, v. 103, p. 185–214.

Turner, J.S., and Gustafson, L.B., 1978, The flow of hot saline solutions from vents in the seafloor—Some implications for exhalative massive sulfide and other ore deposits: Economic Geology, v. 73, p. 1082–1100.

Urabe, T., and Marumo, K., 1991, A new model for Kuroko-type deposits of Japan: Episodes, v. 14, p. 246–268.

Von Damm, K.L., 1995, Temporal and compositional diversity in seafloor hydrothermal fluids: Reviews of Geophysics, v. 33, Supplement Part 2, p. 1297–1305.

Von Damm, K.L., Buttermore, L.G., Oosting, S.E., Bray, A.M., Fornari, D.J., Lilley, M.D., and Shanks, W.C., III, 1997, Direct observation of the evolution of a seafloor "black smoker" from vapor to brine: Earth and Planetary Science Letters, v. 149, no. 1–4, p. 101–111.

Von Damm, K.L., Lilley, M.D., Shanks, W.C., III, Brockington, M., Bray, A.M., O'Grady, K.M., Olson, E., Graham, A., Proskurowski, G., Collier, R., Cowen, J., Haymon, R., Tivey, M.K., Fornari, D., Nakamura, K., McLaughlin-West, E., Shank, T., Kaye, J., Hobson, J., Sarrazin, J., Sparrow, M., Hubbard, D., McGee, D., Brinson, S., and Cushman, B., 2003, Extraordinary phase separation and segregation in vent fluids from the southern East Pacific Rise: Earth and Planetary Science Letters, v. 206, no. 3–4, p. 365–378.

Von Damm, K.L., Oosting, S.E., Kozlowski, R., Buttermore, L.G., Colodner, D.C., Edmonds, H.N., Edmond, J.M., and Grebmeier, J.M., 1995, Evolution of east pacific rise hydrothermal vent fluids following a volcanic eruption: Nature, v. 375, no. 6526, p. 47–50.

Williams-Jones, A.E., and Heinrich, C.A., 2005, Vapor transport of metals and the formation of magmatic-hydrothermal ore deposits: Economic Geology, v. 100, p. 1287–1312.

Yang, K., and Scott, S.D., 1996, Possible contribution of a metal-rich magmatic fluid to a seafloor hydrothermal system: Nature, v. 383, p. 420–423.

Yang, K., and Scott, S.D., 2002, Magmatic degassing of volatiles and ore metals into a hydrothermal system on the modern sea floor of the Eastern Manus Back-Arc Basin, Western Pacific: Economic Geology, v. 97, p. 1079–1100.

Yang, K., and Scott, S.D., 2003, Geochemical relationships of felsic magmas to ore metals in massive sulfide deposits of the Bathurst mining camp, Iberian Pyrite Belt, Hokuroko district and the Abitibi Belt, in Goodfellow, W.D., McCutcheon, S.R., and Peter, J.M., eds., Massive sulfide deposits of the Bathurst mining camp, New Brunswick, and northern Maine: Economic Geology Monograph 11, p. 457–478.

Yang, K., and Scott, S.D., 2006, Magmatic fluids as a source of metals in seafloor hydrothermal systems, in Christie, D.M., ed., Back-arc spreading systems—Geological, biological, chemical, and physical interactions: American Geophysical Union, Geophysical Monograph Series 166, p. 163–184.

Zierenberg, R.A., Fouquet, Y., Miller, D.J., Bahr, J.M., Baker, P.A., Bjerkgarden, T., Brunner, C.A., Duckworth, R.C., Gable, R., Gieskes, J.M., Goodfellow, W.D., Groeschel-Becker, H.M., Guerin, G., Ishibashi, J., Iturrino, G.J., James, R.H., Lackschewitz, K.S., Marquez, L.L., Nehlig, P., Peter, J.M., Rigsby, C.A., Schultheiss, P.J., Shanks, W.C., III, Simoneit, B.R.T., Summit, M., Teagle, D.A.H., Urbat, M., and Zuffa, G.G., 1998, The deep structure of a sea-floor hydrothermal deposit: Nature, v. 392, no. 6675, p. 485–488.

Zierenberg, R.A., and Shanks, W.C., III, 1986, Isotopic constraints on the origin of the Atlantis II, Suakin and Valdivia brines, Red Sea: Geochimica et Cosmochimica Acta, v. 50, p. 2205–2214.