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A SEMIPERMEABLE INTERFACE MODEL FOR THE GENESIS OF SUBSEAFLOOR REPLACEMENT-TYPE VOLCANOGENIC MASSIVE SULFIDE (VMS) DEPOSITS

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Abstract

Subseafloor replacement-style volcanogenic massive sulfide (VMS) deposits are a subset of VMS deposits where sulfides have replaced unconsolidated volcanic, volcano-sedimentary, and sedimentary material. These deposits are anomalously large and are important global sources of metals. They have distinct textures at the sulfide-ore interface, including bed-by-bed replacement of sedimentary layers, and typically fill void space between unconsolidated volcaniclastic detritus or fractures in flows or intrusions. At the microscale, metal-bearing sulfides have partially to fully replaced frambooidal (bacteriogenic) sulfides, or the frambooidal sulfides have acted as nuclei upon which additional metalliferous massive sulfide is deposited.

The textures presented are reconciled within a semipermeable interface model for replacement. In this model unconsolidated sediment, volcaniclastic rocks, or fractured coherent volcanic rocks provide a permeable to semipermeable interface that allowed ingress of cold seawater into the pore spaces of the stratigraphic sequence prior to and during lulls in hydrothermal activity. Seawater sulfate in the pore water is partially reduced by bacteria to provide reduced sulfur (H_2S) as well as frambooidal pyrite in the host sequence(s). The reduced sulfur and frambooidal pyrite, as well as the cool pore water, provided a thermal, redox, and chemical gradient in which upwelling hydrothermal fluids interact. In such an environment rising hydrothermal fluids mix with cold water, not only at the seawater interface leading to exhalative sulfide deposition, but also in the subseafloor leading to sulfide precipitation via replacement. The upwelling hydrothermal fluids can also interact with bacterial H_2S in the pore spaces of the unconsolidated material, resulting in additional subseafloor precipitation of metal sulfides. The fluids also result in replacement of frambooidal pyrite nuclei pseudomorphous after the original frambooidal masses. This semipermeable interface also favors enhanced zone refining, assuming the hydrothermal system is sufficiently long lived, leading to upgrading of the tenor of the sulfides with well-developed metal zoning, as observed in many ancient replacement-type deposits. Furthermore, the precipitation of a significant subseafloor sulfide mineralization results in greater trapping of metals from upwelling fluids and larger tonnage deposits with greater contained metal.

This model may also be applicable to other replacement-type deposits in broadly similar geologic and hydrothermal environments (e.g., sediment-hosted and Irish-type Zn-Pb deposits). Additional, critical tests are required to validate and refute the model and potential tests are presented herein.

Introduction

Volcanogenic massive sulfide (VMS) deposits are critical sources of base and precious metals (e.g., Franklin et al., 2005). Current models for both modern seafloor massive sulfides and ancient VMS suggest that sulfide mineralization forms via the mixing of hydrothermal fluids with ambient seawater (Lydon, 1988; Galley, 1993; Humphris and Tivey, 2000; German and Von Damm, 2003; Franklin et al., 2005; Hannington et al., 2005). However, this mixing process is very inefficient and in some cases >95% of the metals are lost to the overlying water column with only a minor amount precipitated in the sulfide

deposits (Converse et al., 1984). Correspondingly, modern seafloor massive sulfides are smaller and constitute a fraction of the resources currently identified on land (Hannington et al., 2011). In contrast, ancient VMS have much larger median tonnages and greater contained metals (Franklin et al., 2005). Part of this bias resides in the status of exploration of seafloor deposits (e.g., Jamieson et al., 2014), particularly our inability to explore in the third dimension on the seafloor, something commonplace for deposits on land. A second factor is the style of formation of ancient deposits. Many ancient VMS deposits are interpreted to have formed similar to modern seafloor hydrothermal deposits via exhalation of fluids on the seafloor (i.e., exhalative VMS deposits). Other ancient deposits,

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however, have formed fully to partially beneath the seafloor via the replacement of subseafloor strata (subseafloor replacement-type deposits, e.g., Large, 1992; Zaw and Large, 1992; Galley et al., 1993; Doyle and Huston, 1999; Hannington et al., 1999; Large et al., 2001; Doyle and Allen, 2003; Piercy et al., 2014). Ancient subseafloor replacement-type deposits are commonly much larger and have greater contained metals than exhalative deposits (Doyle and Allen, 2003; Franklin et al., 2005).

Despite their economic and scientific significance, understanding of ore-forming processes and genesis of subseafloor replacement-type deposits is incomplete. In this paper, macro- and microscale observations are documented and a semipermeable interface model is proposed that provides insight into the processes that form subseafloor replacement-type VMS deposits. The results have implications into how VMS deposits form but are also relevant to other exhalative-to replacement-type ore systems (e.g., sediment-hosted and Irish-type Zn-Pb deposits).

Textural Observations for Subseafloor Replacement

The macro- to microscale textural preservation of subseafloor replacement sulfides and relationships to bounding

rocks has been documented but can be difficult to reconcile in ancient deposits due to deformation and metamorphism. Correspondingly, exceptionally well preserved examples are required to document replacement and provide insight into replacement process. Three examples are provided below where the relationships between mineralization and host rocks are very well preserved at various scales, particularly on the sulfide deposit-host rock replacement interface. The deposits include the ~347 Ma shale- and volcanic-rich Wolverine deposit (Yukon-Tanana terrane, Yukon, Canada; Bradshaw et al., 2008), and the Cambrian (~509 Ma) Boundary (volcanic-clastic-dominated) and Duck Pond (flow-dominated) deposits (Tally Pond belt, Newfoundland, Canada; Squires and Moore, 2004; McNicoll et al., 2010; Piercy et al., 2014; Fig. 1). In the Wolverine deposit, parts of the deposit contain massive sphalerite-galena-pyrite-rich sulfides that have bed-by-bed replacement textures with surrounding carbonaceous shales (Fig. 1a). In the Boundary VMS deposit, pyrite-chalcopyrite-sphalerite-rich sulfides show replacement textures with rounded lapilli tuff units at the contact with more coherent rhyolite flows; they also contain chlorite-sericite-quartz-altered fragments within the sulfides common to replacement-type sulfides (Fig. 1b, d; Piercy et al., 2014). The Duck Pond deposit is hosted

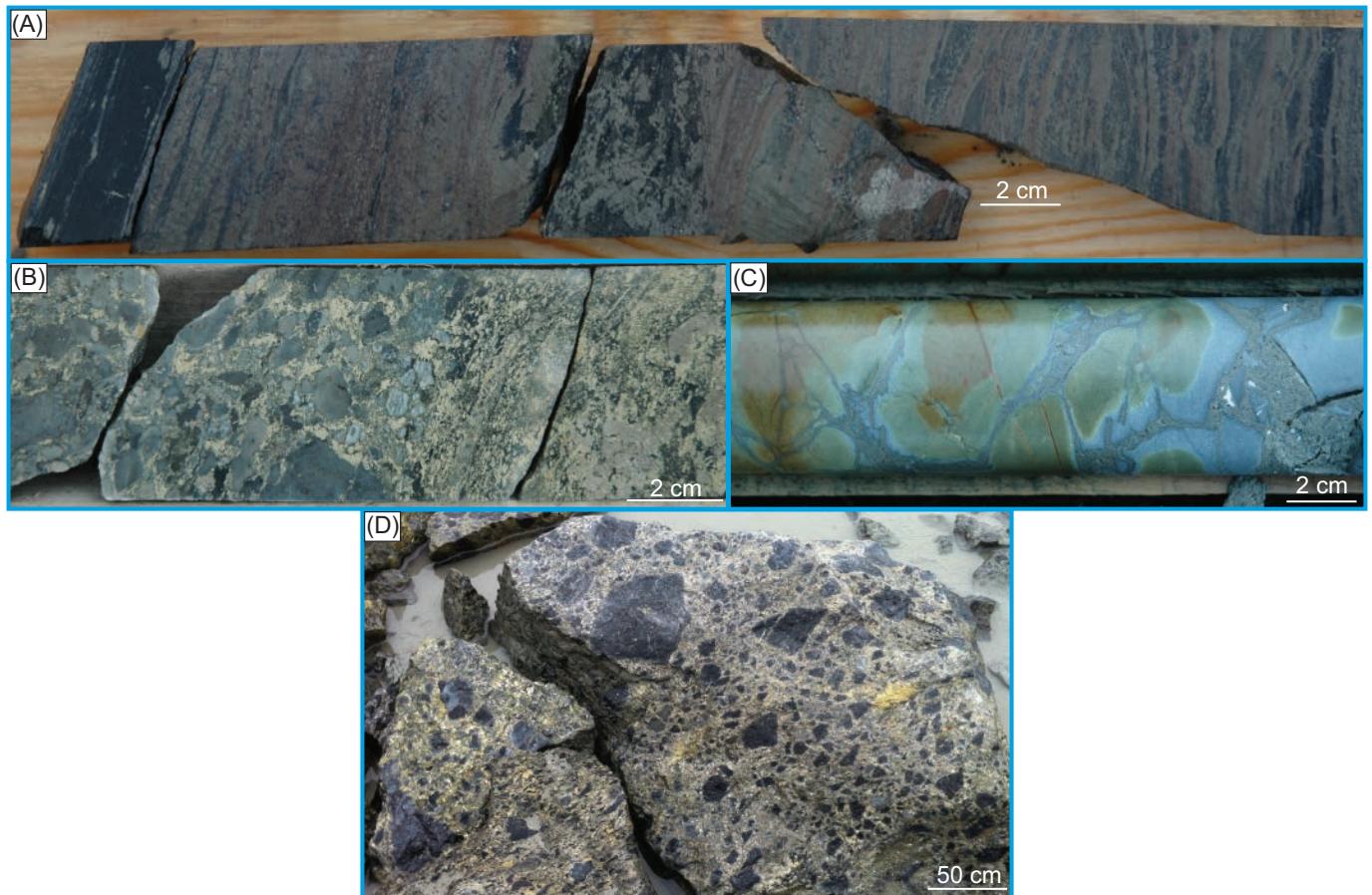


FIG. 1. Macroscale to microscale textures associated with subseafloor replacement. A. Replacement of shales by sphalerite-pyrite-rich massive sulfide. Massive sulfide has relict beds preserved within the sulfide (Wolverine deposit). B. Drill core with sulfides in between sericite-chlorite-altered rhyolite clasts (Boundary deposit). C. Polygonally jointed rhyolite flow with joints replaced by pyrite (Duck Pond deposit). D. Massive pyrite-chalcopyrite with chlorite-altered rhyolite clasts of host volcanic rocks (Boundary deposit).

primarily within rhyolite flows and a flow-dome complex with volcaniclastic rocks proximal to carbonaceous shales that are variably faulted (Squires et al., 2001; McNicoll et al., 2010). The massive sulfide at Duck Pond is found in between polygonally jointed rhyolite breccia and locally interingers with surrounding volcaniclastic units similar to Boundary (Fig. 1c; McNicoll et al., 2010). The macrotextural features preserved in all of these deposits suggest replacement of unconsolidated and permeable/semipermeable sediment and volcanic/volcaniclastic material.

Microtextural features provide further evidence for replacement processes. In both the Duck Pond and Boundary deposits framboidal pyrite of likely biogenic origin (e.g., Piercey et al., 2013) are found as cores or islands within larger euhedral pyrite grains, sheets of pyrite, or sheets of chalcopyrite, sphalerite, and galena, implying that the framboids served as nuclei for additional crystal growth (Fig. 2a-d). In Wolverine and Duck Pond, there is partial bud-by-bud replacement of framboids, and in some cases complete replacement of pre-existing framboids, by sphalerite, galena, and chalcopyrite

during zone refining of the deposits (Fig. 2e-p; e.g., Eldridge et al., 1983).

Semipermeable Interface Model

The textures above illustrate that replacement is an important process in some ancient VMS deposits. Any model for replacement-type VMS deposits must account for both the requirement of partial or complete permeability of host stratigraphy (Doyle and Allen, 2003) and a mechanism to induce precipitation (e.g., cooling, mixing, etc.). The textures outlined above provide some insight into the possible processes that may have been important in forming replacement-type VMS systems and are encompassed within a semipermeable interface model.

In this model the footwall stratigraphic succession consists of permeable to semipermeable strata (e.g., volcaniclastic rocks, fracture coherent rocks, and/or sedimentary rocks) that are unconsolidated. Unconsolidated units allow ingress of seawater into the pore spaces of the stratigraphic succession prior to and during lulls in hydrothermal activity, providing

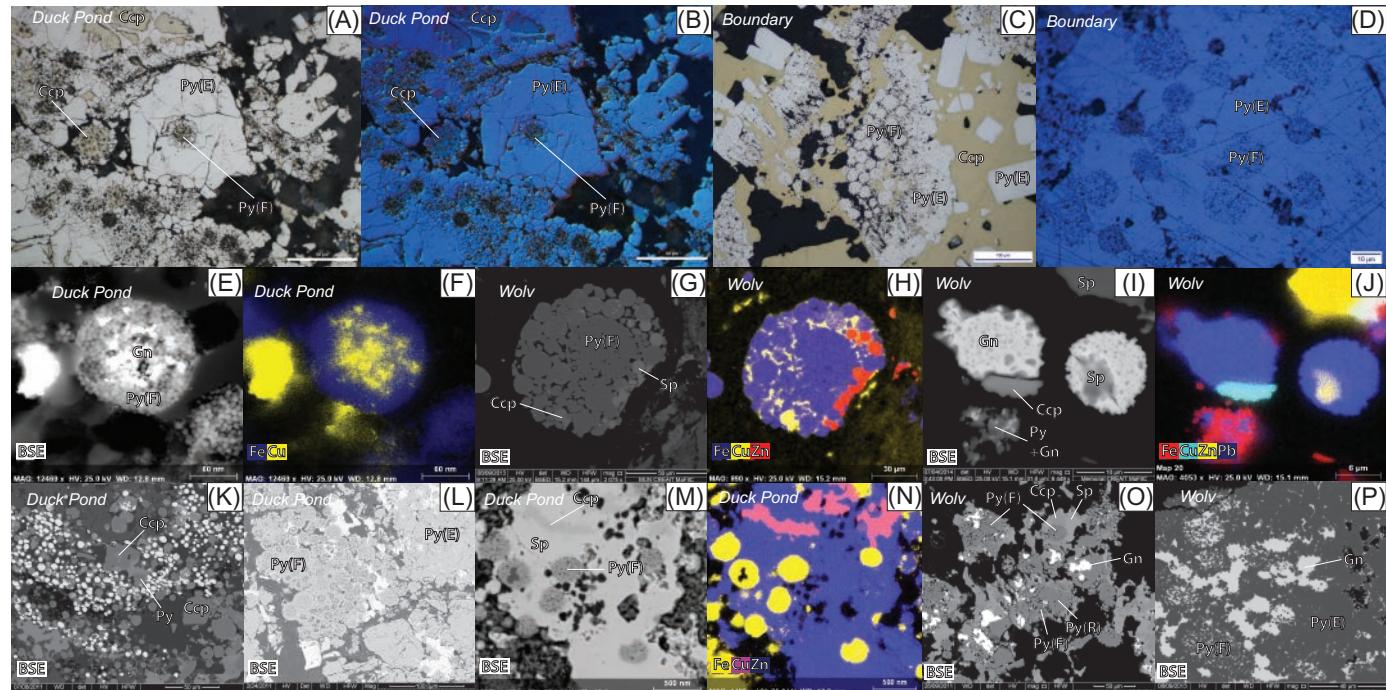


Fig. 2. Microscale textures associated with subseafloor replacement. A. Photomicrograph of framboidal pyrite surrounded by zoned euhedral pyrite and both partially replaced by chalcopyrite. B. Differential interference contrast image of (A), illustrating zoning and textural relationships between mineral types (Duck Pond deposit). C. Coalesced framboids surrounded by euhedral pyrite within a sea of chalcopyrite, suggesting that the framboids were nuclei for growth of new phases (Boundary deposit). D. Differential interference contrast image of framboidal pyrite as nuclei for massive euhedral pyrite sheets (Boundary deposit). E. Scanning electron microscope-backscatter electron (SEM-BSE) image of framboidal pyrite partially replaced by galena. F. Scanning electron microscopy-energy dispersive energy X-ray (SEM-EDS) semiquantitative elemental map of Duck Pond deposit (E). G. Framboids partially to fully replaced by sphalerite and chalcopyrite. H. SEM-EDS semiquantitative elemental map of Wolverine deposit (G). I. SEM-BSE image of full replacement of framboids by galena, sphalerite, and chalcopyrite. J. SEM-EDS semiquantitative elemental map of Wolverine deposit (I). K. SEM-BSE image of partially to replaced pyrite framboids by galena (white), along with subhedral pyrite and chalcopyrite (Duck Pond deposit). L. SEM-BSE image of coalesced pyrite framboids surrounded by galena (white) near euhedral pyrite (Duck Pond deposit). M. SEM-BSE image of sheet of sphalerite with chalcopyrite surrounding framboidal pyrite nuclei. N. SEM-EDS semiquantitative elemental map of Duck Pond deposit (M). O. SEM-BSE image of pyrite framboids forming nuclei for surrounding recrystallized, subhedral pyrite, chalcopyrite, sphalerite and being partly to fully replaced by galena (Duck Pond deposit). P. SEM-BSE image of relict pyrite framboids partly replaced by galena surrounded by sheets of euhedral pyrite (Wolverine deposit). Abbreviations: Ccp = chalcopyrite, Gn = galena, Py = pyrite, Py(E) = euhedral pyrite, Py(F) = framboidal pyrite, Py(R) = recrystallized, Sp = sphalerite, Wolv = Wolverine.

environments for bacterial reduction of seawater sulfate and generation of H_2S , and loci for frambooidal pyrite (Fig. 3; e.g., Ohmoto and Goldhaber, 1997; Seal and Wandless, 2003; Seal, 2006). Furthermore, the abundance of cool seawater in the stratigraphic pile creates a semipermeable interface with

temperature, redox, and chemical gradients with which hotter, rising hydrothermal fluids could interact (Fig. 3).

In normal VMS hydrothermal systems sulfides precipitate due to hydrothermal fluid-seawater mixing at the vent-seawater interface, but with only a minority of the metal

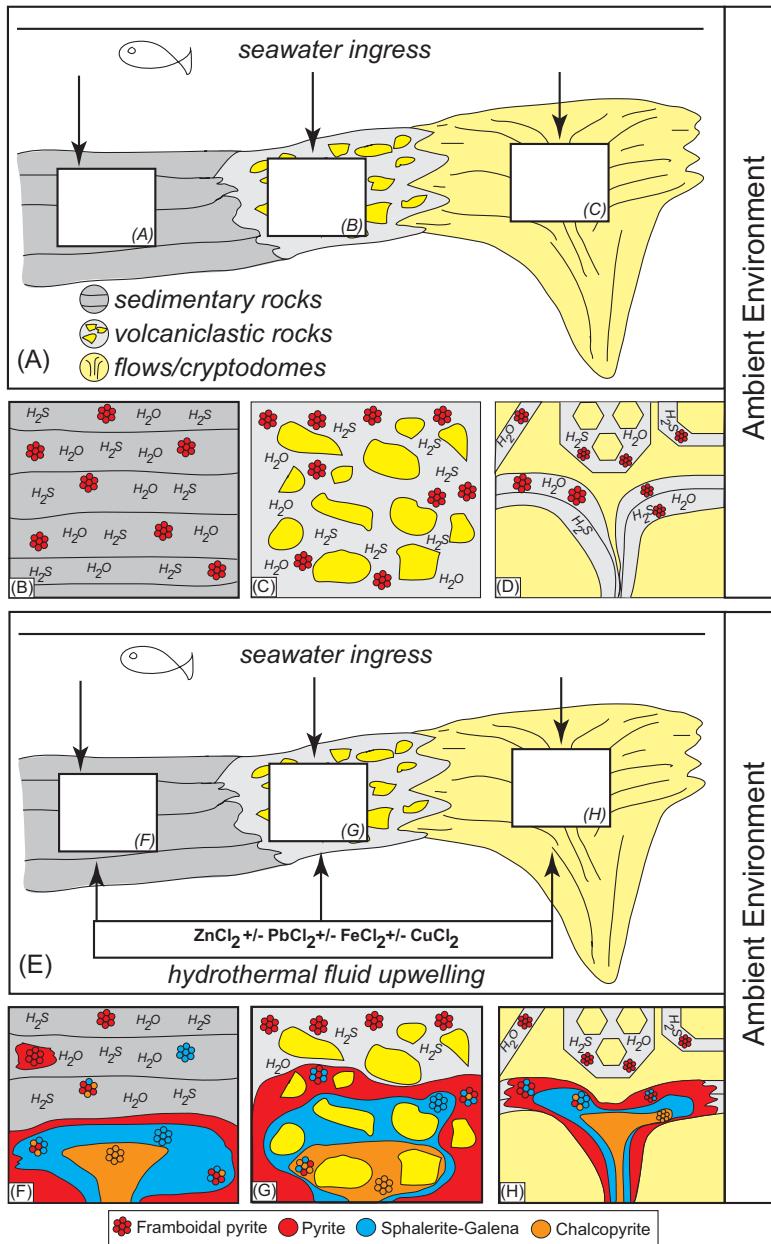


FIG. 3. A. Ambient environment for massive sulfides with sedimentary- (B), volcaniclastic- (C) and flow-dominated (D) sub-settings. In these environments primary porosity and permeability allow the ingress of seawater into the volcanic to sedimentary pile. Seawater sulfate in the primary pile is partly reduced to H_2S by sulfate-reducing bacteria leading to an environment dominated by sediment and volcanic particles with abundant, relative low temperature ($<25^\circ C$) pore water and reduced sulfur. In addition, bacterial derived H_2S forms frambooidal pyrite by reacting with iron in the volcanic and sediment pile. E. Influx of VMS hydrothermal fluid below results in the mixing between the upwelling hydrothermal fluids and the porewater and H_2S – sedimentary- (F), volcaniclastic- (G) and flow-dominated (H) environments. The mixing with pore-water results in deposition of sulfide due to cooling, and additional sulfide is precipitated by reacting with H_2S . Furthermore, existing frambooidal pyrite provide nuclei which new sulfides can replace or overgrow. This shallow subseafloor interface was likely to be partially to fully connected to overlying seawater (i.e., semipermeable interface) and the process of replacement coincided with and was succeeded by zone refining and replacement of lower temperature, earlier formed Zn-Pb-Fe-rich assemblages by higher temperature Cu-rich assemblages leading to the metal and mineralogical zoning found in many replacement-type VMS deposits.

precipitating from the fluid (e.g., Converse et al., 1984). The presence of a semipermeable interface would greatly enhance the probability and abundance of metal precipitation. First, cold seawater in the subseafloor strata would create a thermal gradient and increase the amount of hydrothermal fluid-seawater mixing, leading to greater metal precipitation at both the seawater-vent interface and in the subseafloor stratigraphic pile (Fig. 3; Gibson et al., 1999; Doyle and Allen, 2003). The unconsolidated nature of the subseafloor materials also allow lateral transport of the hydrothermal fluids and precipitation of additional mineralization distal from the main synvolcanic structures that control hydrothermal fluid flow (e.g., Piercey et al., 2014). Precipitation would also be enhanced by the presence of bacterial H_2S in the pore spaces of the unconsolidated material, resulting in greater metal precipitation than dissipation into the water column (Fig. 3), similar to sediment-hosted Zn-Pb or Irish-type deposits (e.g., Goodfellow, 1987; Fallick et al., 2001). Framboidal pyrite associated with the bacterial activity also contributes to sulfide precipitation acting as nuclei for the precipitation of sulfide from the subsequent hydrothermal fluids, either through partial or full replacement of the original framboid, or as framboidal nuclei around which sulfide sheets grow (Figs. 2, 3).

The semipermeable interface also favors enhanced zone refining of the sulfides, assuming that that hydrothermal system is long lived. Early formed Zn-Pb-Fe replacement-type sulfides can act as a semipermeable cap, allowing for successively higher temperature Cu-rich fluids to refine the mound (Figs. 2, 3; Eldridge et al., 1983; Large, 1992; Ohmoto, 1996; Schardt and Large, 2009). This would allow for the dissolution of earlier formed Zn-Pb mineralization and subsequent reprecipitation of the Zn-Pb material closer to the seawater-vent interface, coupled with precipitation of Cu-(Fe)-rich sulfides at the base of the sulfide zone, leading to increases in both zonation and metal tenor (Fig. 3; Eldridge et al., 1983; Large, 1992; Ohmoto, 1996; Schardt and Large, 2009).

Implications and Testable Consequences

There are implications and testable consequences of the semipermeable interface model for subseafloor replacement-style VMS deposits. The thermal, redox, and chemical interface between the seawater and impermeable seafloor provides an ideal environment to enhance and increase the amount of metal precipitated during hydrothermal venting and partly explains why many large ancient VMS deposits are associated with subseafloor replacement (e.g., Doyle and Allen, 2003). Replacement processes also lead to creation of a semipermeable cap, which enhances zone refining of the sulfide deposit, leading to upgrading of existing mineral assemblages and their grades, which can increase the contained metal of a deposit (Eldridge et al., 1983; Ohmoto, 1996; Schardt and Large, 2009). Replacement is also important in other mineral deposit types, including sediment-hosted Zn-Pb deposits (e.g., Kelley et al., 2004; Gleeson et al., 2013) and Irish-type Zn-Pb deposits (e.g., Wilkinson et al., 2005). These deposits are also large and the mixing between upwelling hydrothermal fluids with H_2S -bearing seawater in the shallow subsurface is well documented (Fallick et al., 2001; Kelley et al., 2004; Wilkinson et al., 2005), suggesting that a semipermeable interface model may also be applicable to these giant deposit types as well.

Critical tests of this model are also required to test its validity. The examples shown are from Phanerozoic deposits with varying substrates and provide macro- and microtextural evidence for replacement. While macrotextural evidence has been proposed for numerous deposits globally (e.g., Galley et al., 1995; Doyle and Allen, 2003), microtextural evidence is lacking for many deposits, including those from Precambrian environments. It is anticipated that other replacement-type deposits should exhibit similar microtextures, including framboids acting as nuclei and partial to complete replacement of framboids by other sulfide phases (Fig. 2); this information may be partially to fully obscured, however, in highly metamorphosed and deformed VMS deposits (e.g., Huston et al., 1995). In addition, replacement-type sulfides should have gangue barite, which would form due to mixing between Ba from the VMS fluids and porewater sulfate. This would be fundamentally different from the bedded barite common to many exhalative VMS deposits (e.g., Ohmoto, 1996). Furthermore, the presence of bacterial H_2S within the semipermeable zone, coupled with zone refining during ore formation, should result in a distinctive sulfur isotope zonation in replacement-type systems. The outer margins in the semipermeable replacement zone should exhibit $\delta^{34}S$ values that are generally more negative and mixtures between sulfur derived from bacterial reduction of seawater sulfate (i.e., $\delta^{34}S < 0$) and hydrothermal or igneous sulfur from the upwelling hydrothermal fluid ($\delta^{34}S \geq 0$). In contrast, with depth in the sulfide body and distance from the semipermeable replacement zone the sulfur isotope values should become more positive, indicative of sulfur derived from thermochemical sulfate reduction of seawater sulfate or igneous sulfur leached from basement rocks (e.g., Bradshaw et al., 2008). It is important to note that the low $\delta^{34}S$ associated with bacterial sulfur influence can be obscured and difficult to determine in deposits that have had magmatic fluids involved in their genesis (e.g., Rye, 1993; Gemmell et al., 2004; Huston et al., 2011); however, the combination of textural relationships (e.g., preserved framboids) and alteration assemblages (e.g., normal VMS assemblages vs. acidic alteration assemblages) may help in delineating bacterial versus magmatic sulfur influences in subseafloor replacement-type VMS deposits.

While replacement is acknowledged as an important process in VMS deposits, it is likely that most deposits exhibit both exhalation and replacement processes (Doyle and Allen, 2003). It is likely the balance between the two processes that will likely determine the size and potential metal budgets of VMS and similar deposits. It is the identification of these replacement processes in ancient environments that may provide insight into which deposits have the greatest potential to provide significant resources.

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