



A New Occurrence Model for National Assessment of Undiscovered Volcanogenic Massive Sulfide Deposits

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Introduction

Volcanogenic massive sulfide (VMS) deposits are very significant current and historical resources of Cu-Pb-Zn-Au-Ag, are active exploration targets in several areas of the U.S. and potentially have significant environmental effects. This new USGS VMS deposit model provides a comprehensive review of deposit occurrence and ore genesis, and fully integrates recent advances in the understanding of active seafloor VMS-forming environments, and integrates consideration of geoenvironmental consequences of mining VMS deposits.

Because VMS deposits exhibit a broad range of geological and geochemical characteristics, a suitable classification system is required to incorporate these variations into the mineral deposit model. We classify VMS deposits based on compositional variations in volcanic and sedimentary host rocks. The advantage of the classification method is that it provides a closer linkage between tectonic setting and lithostratigraphic assemblages, and an increased predictive capability during field-based studies. The

lithology-based classification is shown in table 1 and compared to some other schemes that have been used.

Table 1. Classification systems for volcanogenic massive sulfide deposits.

Cox and Singer (1986)	Galley and others (2007)	Mosier and others (2009)	This report
Kuroko	Felsic-siliciclastic	Felsic	Siliciclastic-felsic
	Bimodal-felsic		Bimodal-felsic ¹
	Bimodal-mafic	Bimodal-mafic	Bimodal-mafic
Besshi	Pelitic-mafic	Mafic	Siliciclastic-mafic
Cyprus	Back-Arc mafic		Mafic-ultramafic

¹ Includes hybrid bimodal-felsic group of Galley and others (2007).

Highlights of the VMS deposit model include: (1) the relationship between lithologic deposit classification and tectonic setting, (2) the role of physical volcanology in controlling localization of mineralization, (3) unique characteristics and genesis of exhalites related to modern and ancient seafloor hydrothermal vents, (4) new approaches to using hydrothermal alteration assemblages as vectors to mineralization, (5) current theories of deposit formation, (6) isotope and trace element systematics of mineralizing processes, and (7) new observations on weathering and environmental effects of VMS deposit mining. In addition, a comprehensive examination of igneous, metamorphic, and sedimentary host lithologies, hypogene and supergene mineralization, geophysical characteristics, and guides for resource assessment and exploration are included.

This model is intended primarily to provide the basis for the VMS component of the next national assessment of undiscovered mineral resources in the U.S. using the three-part quantitative assessment strategy (Cunningham and others, 2008; Singer, 2007, 1995, 1993). This methodology includes: (1) delineation of permissive tracts for VMS deposits, (2) selection of grade-tonnage models appropriate for evaluating each tract, and (3) estimation of the number of undiscovered deposits in each tract. Hence, the VMS model must include sufficient data on host lithology, tectonic setting, structure, ore-gangue-alteration mineralogy, geochemical and geophysical signatures, theory of deposit formation, and geoenvironmental features. These data are critical to defining permissive tracts and to determining the appropriate grade-tonnage curves.

The geologic information and quantitative data outlined in this report will be used to identify permissive tracts for VMS deposits and to guide experts in estimating the number of undiscovered deposits in the permissive tracts. In cases where characteristics of felsic, bimodal-mafic, and mafic deposit types differ significantly, we have added subsections to aid in assigning deposits from a tract to a specific deposit model type so that the correct grade-tonnage curve(s) can be used in assessing undiscovered deposits.

Beyond VMS deposit assessment, we believe this model will be useful to exploration geologists, students and teachers of economic geology, and to researchers interested in the origin of this important deposit type and the causes of variations between sub-types.

Deposit Type and Associated Commodities

The VMS deposits are stratabound concentrations of sulfide minerals precipitated from hydrothermal fluids in extensional sea-floor environments. The term volcanogenic

suggests a genetic link between mineralization and volcanic activity, although siliciclastic rocks dominate the stratigraphic assemblage in some settings. The tectonic setting for VMS deposits includes extensional zones within oceanic ridges, volcanic arcs, and volcanic back-arcs. The volcanic rocks hosting individual VMS deposits range from felsic to mafic in composition, but bimodal compositions are not uncommon. The VMS deposits are characterized by abundant Fe sulfides (pyrite or pyrrhotite) and variable, but subordinate amounts of chalcopyrite and sphalerite; galena and barite are concentrated in some deposits. Massive sulfide bodies typically have lensoidal or sheetlike forms. Many deposits, but not all, overlie discordant sulfide-bearing vein systems (stringer or stockwork zones) that represent fluid-flow conduits below the sea floor. Pervasive alteration zones, characterized by secondary quartz and phyllosilicate minerals, also are associated with hydrothermal circulation through footwall volcanic rocks of many deposits. Deposits range in age from Archean (3.4 Ga deposits) on ancient cratons to present-day systems in modern ocean basins.

Worldwide, there are nearly 1,100 recognized VMS deposits, including more than 100 in the United States and 350 in Canada. The VMS deposits are a major global source of Cu, Pb, Zn, Au, and Ag; by-product commodities include Fe, S, Co, Sn, Ba, Se, Mn, Cd, In, Bi, Te, Ga, Ge, and Hg.

Physical Volcanology

Physical volcanology is a highly effective tool for identifying deposit settings in the hydrothermally altered and metamorphosed seafloor volcanic environments in which VMS deposits form. The reconstruction of volcanic history through facies analysis and stratigraphic correlation permits the paleogeographic and geotectonic environment of

volcanic terranes to be unraveled. This provides a framework in which to understand the controls of localization of mineralization. Recognition of distinctive volcanic facies and facies associations is critical to reconstructing the original facies architecture of the system. In general, physical volcanology is used: (1) to identify the products and deposits associated with volcanic eruptions, (2) to understand the complex mechanisms associated with eruptions, (3) to comprehend mechanisms of formation and post-formation processes associated with the deposit, and (4) to recognize volcanic terranes by their geomorphology. The environments for VMS mineralization typically are those of lava flow-dominated lithofacies associations and volcanoclastic-dominated lithofacies associations, which correspond, in general, to deposits that formed in deep-water and shallow-water volcanic environments, respectively.

Regional Environment

The VMS deposits are formed in marine tectonic settings, where a strong spatial and temporal relationship exists between magmatism, seismicity, and high-temperature hydrothermal venting. These settings include extensional seafloor spreading ridges, and volcanic arcs (oceanic and continental margin) and related back-arc basin environments. In addition, extensional environments may form in post-accretion and/or successor-arc settings (for example, rifted continental margins and strike-slip basins). Because plate tectonic processes appear to have operated at least since the Paleoproterozoic and possibly earlier, the geotectonic environments of VMS deposits are described in the framework of modern plate tectonic regimes. In the modern oceans, most known hydrothermal activity is located along mid-ocean ridges (65 percent), with the remainder in back-arc basins (22 percent), along volcanic arcs (12 percent), and on intraplate

volcanoes (1 percent). In contrast, most VMS deposits preserved in the geologic record appear to have formed in extensional, oceanic and continental, volcanic arc and back-arc settings, such as the Miocene Japan arc-back arc system, and the modern Okinawa Trough and Lau and Manus Basins. The general paucity in the geologic record of VMS deposits that formed on mid-ocean ridges probably reflects subduction and recycling of ocean-floor crust since at least the Paleoproterozoic.

The VMS deposits are not uniformly distributed through time, but are concentrated particularly in Late Archean (2.85-2.60 Ga), Paleoproterozoic (2.0-1.7 Ga), Neoproterozoic (900-700 Ma), Cambro-Ordovician (550-450 Ma), Devono-Mississippian (400-320 Ma), and Early Jurassic to Recent (200-0 Ma) subaqueous volcanic sequences. The total tonnage and contained metal content of VMS deposits are concentrated in the same time sequences. Most ancient VMS deposits formed in subduction-related oceanic and continental volcanic arc and back-arc settings, and their temporal distribution corresponds closely with periods of major ocean-closing and terrane accretion following the breakup of large continents. Structural, lithostratigraphic, and geochemical characteristics of these submarine volcanic sequences indicate that they formed during periods of extension. In most arc-related settings, the peak of extension or rifting is short lived and often marked by the occurrence of high silica volcanic rocks (dacite to rhyolite) and their intrusive equivalents. It is during these short-lived periods of extension, typically lasting less than 2 to 3 million years, that VMS deposits are formed.

Many VMS deposits occur in clusters or districts typically about 40 km in diameter that contain about a dozen relatively evenly spaced deposits. One or a few of the deposits typically contain more than half of the district's resources. Controls on the localization of

VMS deposits mainly involve volcanic and synvolcanic features. These features include, but are not limited to, calderas, craters, grabens, domes, faults, fault intersections, and seafloor depressions or local basins. In most cases, localization of sulfide mineralization involved structural preparation of a plumbing system, including the development of permeable conduits for metalliferous hydrothermal fluids.

Studies of modern hydrothermal activity on mid-ocean spreading centers of variable spreading rates demonstrate that high-temperature vent fields are almost universally associated with magmatic heat sources that generate high-temperature hydrothermal activity. In ancient volcanic rock sequences, composite synvolcanic intrusions often are present in the footwall below VMS deposits and represent the heat engine that initiated and sustained the sub-seafloor hydrothermal activity that formed the deposits.

The composition of VMS deposits bear a close relation to the volcanic lithofacies that host them. The VMS deposits that form in mafic flow-dominated successions tend to be Cu-rich, whereas those in felsic successions tend to be Cu-Zn±Pb-rich. In sedimentary rock successions, which are dominated by terrigenous clastic rocks in continental rifts and back-arc basins, the VMS deposits generally contain significant Pb and Ag (for example, Zn-Pb-Cu-Ag deposits). Iron formations and other hydrothermally precipitated chemical sediments (such as, chert, jasper, Fe-Mn-rich sediment) commonly display a spatial and temporal association with VMS deposits, and are particularly well developed and laterally extensive in sedimentary rock-dominated successions that formed in continental rift and back-arc settings (for example, Bathurst camp, Canada).

Physical Description of Deposits

Typical maximum horizontal dimensions of VMS deposits are 100-500 m. Small deposits may only be tens of thousands of square meters in plan view, whereas giant deposits can have dimensions of several square kilometers. Widths or down-dip extents can be as much as 3,500 m. Shapes range widely from stratiform lenses to lenticular mounds to discordant pipes; footwall stockworks (feeders for rising hydrothermal fluids) underlie many deposits. The diversity in shapes reflects a variety of factors including: nature and duration of seafloor and sub-seafloor hydrothermal activity, seafloor topography, permeability of footwall strata, structural or volcanic controls on mineralization; post-ore deformation including shearing, folding, and faulting, extent of erosional preservation, and mining cutoff grades.

Geophysical Characteristics of VMS Deposits

Volcanogenic massive sulfide deposits typically present strong geophysical contrasts with their host rocks because of the substantial differences in physical and chemical properties between the deposits and the rock in which they occur. These properties include density, magnetic susceptibility, gravity, electrical conductivity, and acoustical velocity. For sulfide deposits, contrasts in magnetic, electromagnetic (EM), and gravitational (density) properties can produce exploration vectors. Electrical methods, including resistivity, induced polarization, and EM, can be highly effective in identifying VMS targets by detecting the electrical conductivity of the rocks and minerals, which can range by 20 orders of magnitude. Gamma-ray spectroscopy provides an indirect technique based on chemical contrasts associated with near-surface alteration,

mainly as potassium enrichment or depletion within and surrounding the deposit. Potential field techniques have been highly successful in identifying VMS deposits at depths of as much as 300 m, but high resolution seismic reflection profiling can target much greater depths and has been key in identifying VMS deposits at greater than traditionally mined depths. Successful seismic imaging of a zone of VMS mineralization is a function of the size, shape, orientation/dip of the orebody, and the acquisition parameters used in the seismic survey. As exploration focuses on deeper, concealed base-metal deposits, geophysical techniques are increasingly relied upon to identify areas of VMS mineralization.

Ore Characteristics

In all VMS deposit subtypes, the dominant sulfide mineral is pyrite or pyrrhotite. The next most abundant ore minerals, chalcopyrite and sphalerite, occur in variable amounts, and in a few deposits, one or both are more abundant than Fe sulfides. The only other major sulfide mineral category is galena, which is concentrated in deposits associated with bimodal-felsic and siliciclastic-felsic rocks. Precious metals occur as volumetrically minor minerals, although these can nevertheless be economic concentrations. Visible gold generally is present as inclusions of native gold, electrum, or gold-telluride minerals in major sulfide minerals, whereas silver occurs in Ag sulfides and sulfosalt minerals such as tetrahedrite and freibergite. A deposit-scale zonation pattern is characteristic of VMS deposits— the upper stockwork is dominated by chalcopyrite + pyrite ± magnetite, the basal part of the massive sulfide body is dominated by pyrite + chalcopyrite, and the upper and outer margins of the massive sulfide are dominated by sphalerite ± galena (± barite). This basic pattern is best exhibited in

deposits having bimodal-felsic or bimodal-mafic affinities, and has been attributed to sequential episodes of sulfide deposition and replacement within an intensifying geothermal system.

The VMS deposits span a continuum of physical attributes from massive ores composed of 100 percent sulfide minerals, through semi-massive ores that are mixtures of sulfides, gangue minerals, and host rock (volcanic or sedimentary), and to increasingly sparse sulfide disseminated in wall rocks. At the hand-specimen and thin-section scale, massive sulfides are typically fine-grained (<1 mm), compact aggregates of intergrown sulfide minerals with irregular grain boundaries. More diagnostic primary textures in massive ores include idiomorphic crystals (such as, pyrite, pyrrhotite) projecting into cavities, colloform overgrowths (particularly sphalerite, pyrite, and marcasite), framboidal and botryoidal pyrite, pseudomorphic replacement (for example, sulfate by pyrrhotite), fine-scale replacement relationships (such as, chalcopyrite disease in sphalerite), boxwork intergrowths, and internal mineral growth zoning (particularly in Zn sulfides). Metamorphism causes numerous textural changes, including: (1) recrystallization and increase in grain size, (2) development of porphyroblasts, (3) foliation and alignment of sulfide and gangue crystals, (4) 120° triple junction grain boundaries (annealing textures), (5) remobilization of chalcopyrite, and (6) penetrative deformation (“durchbewegung” texture) of pyrrhotite and wall rock. Breccia and clastic ores are prevalent structural characteristics at the deposit scale. Less common primary structures preserved in some VMS deposits include chimney fragments with fluid channelways, fossils of hydrothermal vent fauna, and traces of microbial life forms.

For deposits that have undergone lower greenschist facies, hypogene gangue minerals may consist of quartz, carbonate, barite, white mica, and or chlorite, together with lesser amounts of magnetite, sodic plagioclase, epidote, tourmaline, analcime, and montmorillonite; fluorite, celsian, greenalite, stilpnomelane, hematite, anhydrite, and gypsum may be present locally. At higher metamorphic grades, the sea floor alteration minerals can be transformed to chloritoid, garnet, amphibole, cordierite, gahnite, staurolite, kyanite, and andalusite gangue, with minor rutile and or titanite occurring in places. Gangue in the cores of sulfide mounds is predominantly quartz, whereas the margins may contain abundant barite and or anhydrite.

Supergene Ore and Gangue Characteristics

In the supergene zone of VMS deposits, copper and other metals are mobilized from primary massive sulfide ore and reprecipitated at depth. This precipitation of Cu sulfides with high Cu/S ratios produces an economically significant copper enrichment at the reactive redox boundary between massive sulfide protore and downward penetrating fluids. The supergene enrichment “blanket” is overlain by an intensely altered and leached Fe oxide-rich gossan (the remains of the original massive sulfide) that extends upward to the paleosurface. Studies of hydrothermal sulfide mounds and chimneys on oceanic spreading axes reveal a second type of gossan formation— oxidation of sulfide minerals by interaction with oxygen-rich ambient seawater. The supergene sulfide mineral assemblages are dominated by a small group of Cu-rich minerals— chalcocite, bornite, covellite, digenite, and enargite. In the supergene blanket, these sulfides may be intergrown with varying amounts of relict hypogene sulfides, such as pyrite, chalcopyrite, and sphalerite. During early stages of alteration, the less resistant primary sulfide

minerals, mainly chalcopyrite, sphalerite, and tetrahedrite, are replaced by chalcocite, digenite, covellite, and other Cu-rich sulfides. Acanthite may form in the supergene zone as silver is released from tetrahedrite. As oxidizing conditions extend to greater depths, covellite and digenite ultimately are replaced by chalcocite. Zonation of supergene minerals is most prominently developed vertically with respect to the weathered paleosurface. A basic weathering profile for VMS deposits contains four zones from the original ground surface downward: (1) a leached capping dominated by Fe oxides, clay minerals, and quartz, (2) an oxidized zone dominated by secondary sulfates, (3) a supergene enrichment zone with abundant chalcocite and other Cu-rich sulfides, and (4) the underlying massive sulfide protore.

Overgrowths and replacement rims of bornite, covellite, or chalcocite on chalcopyrite are frequent indicators of incipient supergene alteration. More advanced alteration of primary sulfides results in partial to complete pseudomorphous replacement textures, first involving Cu sulfides, then various combinations of secondary sulfide, sulfate, and carbonate minerals, and ultimately Fe oxides and oxyhydroxides. A major textural change during supergene processes is the development of secondary porosity. Porous, spongy textures, boxworks, and fragmental zones are typical of the supergene enrichment zone. Fe oxyhydroxides and other secondary minerals typically appear as colloform and botryoidal infillings within void spaces or laminar overgrowths on resistate minerals such as quartz or cassiterite. The residual concentration of precious metals in gossans, in the form of native gold, electrum, and a variety of silver minerals, can be economically important in VMS deposits.

Exhalites

Exhalites are stratiform beds or lenses of chemical sedimentary rock spatially associated with VMS deposits that record the precipitation of amorphous Fe ± Mn ± Si ± S ± Ba ± B minerals from seafloor-hydrothermal vents and plumes. Exhalites characteristically occur in proximal settings within hanging wall strata above the sulfide deposits, and or as marginal aprons at approximately the same stratigraphic level as the sulfide deposits. Distal exhalites, hundreds of meters or more along strike from VMS deposits, also may be present. Major types of exhalites, discriminated on the basis of predominant minerals, are oxide, carbonate, silicate, sulfide, and sulfate facies.

Hydrothermal Alteration

The three-dimensional distribution of hydrothermal alteration, chemical and mineralogical nature of different alteration zones, and the geochemical reactions that produce hydrothermal alteration in host rocks of VMS deposits are important for a number of reasons. Firstly, hydrothermal alteration zones are produced by circulating hydrothermal fluids and thus provide geochemical evidence for physical and chemical conditions of fluid-rock interaction. Hydrothermal alteration zones often are the only direct evidence of fluid circulation patterns related to VMS ore formation. Secondly, systematic arrangement of hydrothermal alteration zones, and recognition of this arrangement, may provide information that is useful in mineral exploration and may in some cases provide vectors to undiscovered mineralization. Thirdly, hydrothermal alteration can provide key information on the origin of metallic elements in VMS deposits. For example, depletion of key elements in altered rocks, combined with

measured or inferred estimates of the volume of altered rock, can constrain possible sources of ore metals. Finally, identification and recognition of hydrothermal alteration assemblages and their zonal relationships in the field may provide important evidence that a tract being studied is favorable for occurrence of VMS deposits.

Weathering Processes

Volcanogenic massive sulfides on the modern seafloor, the presumed precursors of ancient VMS deposits, are unstable in the presence of even small amounts of oxygen. They potentially are subjected to seafloor weathering (halmyrolysis) and other processes that can cause substantial changes in their mineralogy and geochemistry prior to burial and subsequent tectonism (lithification, metamorphism, deformation, subduction or obduction, and erosional unroofing). Weathering is an inevitable consequence of exposure to seawater unless the deposit is rapidly covered by sediment and or volcanic materials that shield sulfides from seawater contact. Microbial degradation of seafloor sulfides plays an important role in seafloor weathering. If a VMS deposit is preserved in the rock record, then it also may be subjected to further degradation if eventually exposed to subaerial oxygenated fluids, atmospheric oxygen, or reactions that involve bacterial activity.

Of the major iron sulfides found in VMS deposits (pyrite, pyrrhotite, and marcasite), pyrrhotite is the most reactive and pyrite the least reactive. This appears to be true for both abiotic and biotic oxidation. Other sulfides also are unstable in ambient, oxygenated seawater. The extent to which these sulfides are destroyed is a function of: (1) their iron content and hence, the extent to which Fe(II) is available for redox reactions; (2) the stability of the crystal lattice, which partly is a function of the degree to

which the lattice can accommodate minor and trace elements; and (3) the metal/sulfur ratio, which determines the extent of weathering and or sulfuric acid production.

Halmyrolic degradation must be the rule rather than the exception during the life cycle of a VMS deposit. The corollary being that exceptional circumstances are required to preserve a VMS deposit in the rock record. The most important consequences of seafloor weathering are initially upgrading of the deposit because of supergene enrichment processes, but eventually there is a substantial loss of metals into the water column and or a physical degradation of the deposit as it loses coherence. At an advanced stage of degradation, insoluble oxides and oxyhydroxides precipitate, which have a high adsorptive capacity. These minerals scavenge elements, particularly transitional metals, from seawater or pore fluids after the metals have been released from sulfides and secondary minerals. The scavenging efficiencies are determined by the rate of accumulation of the oxides and oxyhydroxides. Probably 99 percent or more of the metals are lost during seafloor weathering if gossans are formed.

Subaerial weathering of VMS deposits and, if mined, their mill tailings and spoil heaps, involves processes and products that resemble the processes and products of seafloor weathering. Notable differences involve the presence of gaseous oxygen, oxygen-rich meteoric water, and variable climate and hydrology, all of which affect the processes and products of sulfide oxidation. One consequence of subaerial weathering is the development of surface runoff with high acidity and high metal content, both of which may have deleterious environmental effects. The limitations on acidity are provided by the availability of sulfide minerals to suitable oxidation reactions and or acid

buffering reactions. These latter reactions involve gangue and country rock silicates and carbonates that consume hydrogen ions.

Geochemical Characteristics

All VMS deposits show some degree of geochemical/mineralogical zoning that is a function of the composition and mixing of ore-forming fluids, temperature of mineralization, and porosity/permeability of the host rocks at the time of mineralization. In ancient VMS deposits, the geochemical/mineralogical evolution of deposit growth is difficult to deduce, as the later stages of sulfide precipitation commonly overprint earlier stages. However, studies of modern black smoker chimneys, at 21°N and 9°50'N on the East Pacific Rise, and at the Trans-Atlantic Geotraverse (TAG) active hydrothermal field at the Mid-Atlantic Ridge, provide insights into the evolution of sulfide growth. To some degree, the patterns observed are microcosms of the larger scale zonation observed at the deposit scale because, in both cases, the mineralogic zonation is a function of fluid chemistry (mixing between hydrothermal fluid and seawater) and a steep temperature gradient (hydrothermal fluid as hot as 400°C and ambient seawater at 1-2 °C).

A field of black (and white) smoker chimneys is not, by itself, an economic resource. In addition, the simple accumulation of black smoker debris on the seafloor would not mimic the geochemical/mineralogical zonation that is characteristic of ancient VMS deposits. It would instead represent a spatially random collection of sulfide minerals. The critical unknown link to ancient VMS deposits was found with the 1985 discovery of the TAG active mound at the Mid-Atlantic Ridge, a roughly circular structure with an estimated total massive sulfide resource of 2.7 Mt (2 percent Cu) and 1.2 Mt of mineralized stockwork breccia (1 percent Cu). The TAG mound was

subsequently drilled during Leg 158 of the ocean drilling project, providing a 3-D perspective of the development of a modern VMS deposit. Although the mid-ocean ridge setting of the TAG deposit probably has few equivalents in ancient VMS deposits, the TAG deposit does have general similarities to many mafic-ultramafic type VMS deposits (table 1).

Zonation patterns of base metals in ancient VMS deposits can be interpreted in the framework of zone-refining models that control post-depositional redistribution of minerals and elements in response to ongoing post-depositional hydrothermal fluid flow that may redistribute base metals and sulfide minerals. In association with mafic-ultramafic deposits, stockworks are frequently sub-surface breccia composed of chlorite + pyrite and quartz + pyrite beneath a core of massive pyrite and pyrite + quartz breccia. The latter is sheathed by a marginal facies of sphalerite + chalcopyrite, which is covered with a banded jasper-chert carapace. In bimodal mafic deposits, the stockworks frequently show a complex zoned mineralogy that grades outward from pyrrhotite + pyrite + chalcopyrite, through quartz + chlorite and chlorite + sulfide, and to sericite + chlorite. The main sulfide ores grade outward from massive pyrite + pyrrhotite + chalcopyrite to massive pyrite + sphalerite + chalcopyrite. In bimodal felsic deposits, the massive ore commonly grades outward from chalcopyrite + pyrrhotite + pyrite, through pyrite + sphalerite + chalcopyrite, pyrite + sphalerite + galena, and to pyrite + sphalerite + galena + tetrahedrite + Ag + Au. In siliciclastic-felsic deposits, the stockwork zones are highly siliceous, associated with chlorite + pyrrhotite + pyrite + chalcopyrite, and also may be Au-bearing, as observed at several of the Mount Read (Australia) deposits. The

massive ores commonly are pyrite + pyrrhotite + chalcopyrite, with common Au mineralization, grading outward to layered pyrite + sphalerite + galena + Au + Ag.

Fluid inclusions in gangue and ore minerals provide important information on fluid temperature and composition during periods of mineralization, and the relative involvement of meteoric waters and magmatic fluids. Often the salinity data alone cannot be uniquely interpreted because boiling, fluid mixing, and phase separation can all produce large variations in fluid salinity of an original ore-forming fluid. More constrained interpretations are possible if fluid inclusion data are combined with other information, such as stable isotope composition of gangue minerals. In VMS deposits, stable isotopes also have been used to establish pathways of fluid movement (O), fluid origin (H, O, S), redox variations (C, S), and fluid-phase separation (O, H).

Modern seafloor hydrothermal vent fluids typically have NaCl contents from about 0.1-10 wt.% NaCl, similar to most VMS ore fluid NaCl contents measured in fluid inclusions in gangue minerals. Most modern vent fluids have $\delta^{18}\text{O}$ values from 0-3 permil and δD values from -2 to 3 permil, both of which indicate evolved seawater that is modified because of water-rock reaction or phase separation. Studies of $\delta^{18}\text{O}$ in alteration zones of ancient deposits, for temperature ranges from 200-400 °C indicated by fluid inclusions, give $\delta^{18}\text{O}$ values of fluids generally similar to modern seafloor fluids. Some deposits indicate $\delta^{18}\text{O}$ values as high as 10 permil for altering fluids, perhaps because of very intense water-rock reaction or other affects. Sulfur isotope studies of H_2S in modern deposits and sulfide minerals in ancient deposits indicate sulfur mainly derived from volcanic rocks during hydrothermal interaction, with minor proportions

(~20 percent) derived from seawater sulfate that is reduced to sulfide by water-rock reaction.

Petrology of Igneous Rocks Associated with VMS Deposits

The VMS deposits, by definition, are either hosted within or closely spatially associated with volcanic and sub-volcanic intrusive rocks, which is strong evidence for a genetic connection between magmatism and VMS deposit formation. The lithogeochemistry of volcanic rock associations generally can be applied to specific tectonic settings. In this report, the rock associations are classified as mafic-ultramafic, bimodal-mafic, siliciclastic-mafic, bimodal felsic, and siliciclastic-felsic. The identification of specific tectonic settings for VMS deposits is based on the lithogeochemistry of volcanic rocks in modern tectonic settings. It is common to observe more than one lithologic association in large VMS districts; for example, the giant Bathurst district contains deposits that are associated with bimodal-mafic and siliciclastic-felsic associations. Although these associations form a reasonable descriptive system, gradations between associations are common depending on whether the scale of description is regional or local. Mapping of VMS deposits often reveals felsic lava flows and sub-volcanic felsic intrusions as the local-scale igneous associations. Rock associations are important features of VMS deposits because: (1) at the local scale, they reveal sources of heat that drove hydrothermal circulation, and local sources of magmatic metals and acidity; (2) at the more regional scale, they provide information on sources of metals that may give a VMS deposit its specific metal signature; and (3) they provide a mechanism for the rapid burial of a massive sulfide deposit, such as by the geologically instantaneous emplacement of volcanoclastic turbidites.

Petrology of Sedimentary Rocks Associated with VMS Deposits

The importance and percentage of sedimentary rocks associated with VMS deposits differ among the various deposit types, defined by their lithologic settings. Sedimentary rocks are a negligible component in bimodal-mafic deposit settings, make up a minor component in mafic-ultramafic settings, but are an important component in siliciclastic-mafic, bimodal-felsic, and siliciclastic-felsic settings. Associated sedimentary lithofacies in the majority of all VMS settings are all dominated by terrigenous clastic sedimentary rocks, primarily wacke, sandstone, siltstone, mudstone, and carbonaceous mudstone, with lesser amounts of chert, carbonate, marl, and iron-formation. Volcaniclastic deposits are an important component in most VMS deposits and include both pyroclastic deposits, and reworked and redeposited volcanic material that may be intercalated with terrigenous sediment. Most of the sedimentary rocks were deposited in extensional basins during various stages of rifting associated with intra-arc and back-arc development. However, the VMS deposits themselves generally formed within volcanic centers that were located in smaller grabens within a larger sediment-filled extensional basin. The distribution and thickening of sedimentary strata associated with volcanic and volcaniclastic rocks commonly reveal the presence of synvolcanic growth faults that formed during rifting. These faults are a key tectonic element in the formation of hydrothermal convection systems that discharged metal-bearing fluids onto the seafloor or into permeable strata immediately below the seafloor to form the VMS deposits.

Sedimentary rocks, including redeposited felsic volcaniclastic strata associated with felsic volcanic host rocks, can help elucidate the mode of deposition (subaerial or

submarine) of the felsic volcanic rocks, water depth at the time of submarine volcanic eruptions and VMS formation, and stages of extension and subsidence in a continental-margin incipient rift.

Footwall sedimentary, as well as volcanic, strata can be important source rocks for metals in VMS mineralization. The primary permeability and porosity of footwall lithofacies control the movement of hydrothermal fluids and, thus, the distribution and development of semi-conformable alteration zones. Porosity and grain size of sediments also play an important role in preventing the dissipation of metal-bearing fluids onto the sea floor. Sub-seafloor accumulation and replacement provide an efficient mechanism to trap metals and may be responsible for forming large, tabular VMS deposits. The sub-seafloor VMS deposits form as sulfide minerals are precipitated within the pre-existing pore spaces and fractures in volcanic or sedimentary rocks, or as a result of the replacement of volcanic or sedimentary rock constituents in a chemically reactive host, such as carbonate.

Carbonaceous shale is a common constituent of most VMS deposits and indicates sub-oxic to anoxic, generally deep-water, conditions. Sub-oxic to anoxic, third-order basins in which upwelling sulfur-depleted fluid mix with modified seawater that is rich in biogenically reduced sulfur, can lead to precipitation of massive sulfides on the seafloor. Carbonaceous units within volcanic rock sequences represent hiatuses in volcanism that are typically characterized by hydrothermal activity favorable for the generation of massive sulfides.

Effects of Metamorphism and Deformation on VMS Host Rocks and Deposits

The majority of ancient VMS deposits have been affected by regional metamorphism and deformation. Analysis of metamorphic grades reported by Mosier and others (2009) for 1,090 VMS deposits throughout the world indicates that of the 819 deposits, only 3 percent are unmetamorphosed. The deposits were metamorphosed under conditions of zeolite facies (1.5 percent); sub-greenschist, prehnite-pumpellyite, or pumpellyite-actinolite facies (7 percent); greenschist facies (62 percent); amphibolite facies (11 percent); blueschist- or eclogite-facies (2 percent); granulite facies (0.5 percent); and contact metamorphism (13 percent). Most VMS deposits experienced fold-and-thrust-belt style deformation because the mineral belts formed in short-lived extensional basins near plate margins, which became inverted and deformed during subsequent basin closure. VMS deposits within regionally metamorphosed and deformed sequences commonly are subjected to the following: (1) metamorphic recrystallization increases grain size and purity of the sulfide minerals; (2) ores typically are thicker in the hinge zones of folds, and (3) selective mobilization during metamorphism can result in local enrichment of metal grades.

Metamorphic mineral assemblages formed from recrystallization of older VMS ores and altered host rocks particularly are important in mineral exploration. At low metamorphic grades, the distribution and relationship of chlorite-rich and sericite-rich schists in the wall rocks to VMS deposits can indicate the presence of primary feeder and alteration zones that developed during submarine mineralization. At higher metamorphic

grades, these zones are indicated by coarse-grained suites of distinctive, upper greenschist- to amphibolite-facies minerals, including chloritoid, garnet, staurolite, kyanite, andalusite, phlogopite, and gahnite (zincian spinel); and upper amphibolite- to granulite-facies minerals such as sillimanite, cordierite, orthopyroxene, and orthoamphibole. Determination of metamorphic protoliths is essential to reconstruction of the lithologic associations at the time of mineralization and to deducing the tectonic setting of the deposit. Wall rocks (host rocks) typically contain distinctive lithologies, which may include metachert, magnetite iron-formation, sericite- and chlorite-rich schist, coticule, tourmalinite, albitite, and rarely marble.

Theory of Deposit Formation

The unifying characteristics of the VMS deposit type are association with volcanic rocks and sulfides deposited by hydrothermal solutions at or near the seafloor. Despite thousands of published papers on VMS deposits resulting from intensive study throughout 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. Research on ore genesis of VMS deposits and modern seafloor analogs has focused mostly on hydrothermal water-rock interaction models, with direct magmatic contributions of ore-metals typically relegated to a minor or insignificant role. Experimental studies of basalt-seawater interaction at temperatures of as much as 425 °C have shown that water-rock interaction, in the absence of magmatic volatiles, can account for the observed metal contents of hydrothermal vents that have been studied on the mid-ocean ridges. However, it is well-established that magmatic degassing adds He, CO₂, CH₄, and H₂S or SO₂ to convective hydrothermal systems, and

experimental and fluid inclusion evidence suggest that metal transport by magmatic vapors may be significant, particularly in systems hosted by felsic to intermediate volcanic rocks.

Exploration and Resource Assessment Guides

Useful guides in exploration and resource assessment for VMS deposits include geological, geochemical, isotopic, and geophysical data. Principal geological guides are high-quality geologic maps; identification of favorable ages and volcano-sedimentary rock types; known VMS prospects or occurrences in the study area; presence of exhalites, synvolcanic growth faults or fault intersections, calderas, large subvolcanic and sills and or dikes; and abundant chlorite or white mica and their metamorphosed equivalents in the country rocks. Geochemical guides focus on a variety of media including rocks, minerals, stream sediments and heavy mineral concentrates, glacial till, lake sediments, waters, and soils and soil gases. Rock geochemistry, particularly of host igneous rocks, typically can be used to focus exploration and assessment on favorable volcano-sedimentary belts. Stable and radiogenic isotopic systems may be useful for identifying hidden VMS deposits. A variety of geophysical techniques have been used successfully in VMS exploration, including electromagnetic, magnetic, electrical, and gravimetric methods.

Geoenvironmental Features

Geoenvironmental characteristics of mineral deposits are an important factor in considering undiscovered mineral deposits and are part of the equation in determining what deposits will be future mineral resources. The most important geoenvironmental

affect of all VMS deposit types is their significant acid-generating potential because of the abundance of pyrite, pyrrhotite, or both, and their limited acid-neutralizing potential because of the general absence of carbonate minerals in their mineralization, alteration, and host rock assemblages. Acid generated by the oxidative weathering of either pyrite or pyrrhotite can attack associated ore sulfide minerals and gangue silicate minerals, releasing a variety of potentially toxic elements, including Al, Mn, Cu, Pb, Zn, Cd, Co, Ni, Hg, and As, into solution or onto secondary minerals. The toxicity to aquatic life of elements released to surface water depends on a variety of factors including pH, alkalinity, major and minor element composition, and dissolved organic carbon concentration of the water. Secondary phases may have solubilities that are greater than or less than their precursor sulfide minerals, which determines their potential effects on aquatic ecosystems. Human health risks associated with inhaled or ingested particles also vary depending on the mineralogy of secondary phases. For example, Pb in anglesite (PbSO_4) tends to be less bioavailable than Pb in cerussite (PbCO_3) in the digestive tract of humans.

All types of VMS deposits can have pre-mining geochemical expressions in a variety of media (surface water, ground water, soil, sediment) that exceed regulatory guidelines for selected elements. The presence of elevated concentrations of a variety of elements prior to mining underscores the need for accurate baseline characterization to serve as a basis for establishing closure goals for proposed mines.

Mine drainage from abandoned mines shows a strong link with the underlying geology of the mineral deposits. The pH of drainage can easily reach as low as 2 with total dissolved solids getting as high as 1 to 10 g/L. Sulfate is the dominant anionic

species and Fe and Al are important cations. The underlying geology directly is reflected by the base-metal ratios of mine drainage. The most Zn-rich VMS deposit type, bimodal-felsic deposits, also has the highest Zn:Cu ratio in mine drainage, typically ranging from 1:1 to 10,000:1 on a mass basis. The VMS deposit types with intermediate Zn:Cu ratios in the ores, bimodal-mafic and mafic-siliciclastic deposits, have Zn:Cu ratios in their drainage that typically vary between 1:10 and 100:1. The most Cu-rich VMS deposit type, mafic-ultramafic deposits, typically has Zn:Cu ratios less than 1:1. In contrast, the Zn:Cu mass ratios in mine drainage for all VMS deposit types overlap, which reflects the common source of these elements in mine drainage, which is the mineral sphalerite. These ratios generally vary between 10:1 and 1,000:1.

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