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Targeted Geoscience Initiative 4: Contributions to the Understanding of Volcanogenic Massive Sulphide Deposit Genesis and Exploration Methods Development

Precious metal enrichment processes in volcanogenic massive sulphide deposits — A summary of key features, with an emphasis on TGI-4 research contributions

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ABSTRACT

Volcanogenic massive sulphide deposits contain precious metals (Au, Ag) that can be present in high to low grades and total amounts; depending on tonnage and/or precious metal grade, such deposits can represent desirable exploration targets. Globally, deposits with >3.46 g/t Au are considered "auriferous", those with ≥31 t of contained Au are "anomalous", and those with both large tonnage (≥31 t Au) and high gold grade (>3.46 g/t Au) are considered "Au-rich". There are still no clear statistical criteria to determine thresholds that would define "anomalous" Ag grades and/or total amount of Ag in volcanogenic massive sulphide deposits, as grades vary widely depending on the nature of the host succession.

Two general requisites may explain anomalous primary precious metal budgets in volcanogenic massive sulphide deposits: 1) inherently Au- and/or Ag-enriched source rocks and fluids due to a specific geodynamic setting or heritage and/or to magmatic input, and 2) efficient transport (favourable ligands) and precipitation (e.g. boiling/phase separation, zone refining). These two requisites, which are of different scales, may or may not be mutually exclusive. Late or "secondary" Au- and/or Ag-enrichment in volcanogenic massive sulphide deposits can be due to the superposition of mineralizing systems of a different style (e.g. epithermal, intrusion-related, orogenic, etc.). Weathering processes (e.g. supergene enrichment) on the seafloor or on land can also significantly modify the distributions of precious metals in a volcanogenic massive sulphide deposit.

Volcanogenic massive sulphide deposits in volcanic belts that formed in pericratonic settings or on older crust basement in the early stages of rifting are commonly slightly better endowed in precious metals than those formed in belts or settings with no or limited basement influence. Gold-rich and auriferous VMS are preferentially associated with calc-alkaline or transitional magmatic successions, with andesite-dacite-rhyodacite-rhyolite magmatic suites and with thick (10s to 100s of m) felsic volcanic packages. Evidence for a magmatic input and of deposition in response to boiling/phase separation include the presence of complex mineral assemblages comprising sulphosalts, sulphides, native elements, and anomalous trace element signatures (e.g. enrichment in the "epithermal suite" of elements Au-As-Sb-Ag-Hg and/or in felsic magma-associated elements Bi-W-Te-In-Sn). A laterally extensive sericitic (phyllic) ±siliceous alteration halo, a zone of intense aluminous (argillic to advanced argillic-style) alteration, and heterogeneous Au and Ag distributions and mineralogical residence sites within or near the sulphide bodies are also indicators of a possible magmatic contribution of Au, Ag, and other metals, such as Te and Bi, or metal deposition due to boiling in VMS systems.

INTRODUCTION

Volcanogenic massive sulphide (VMS) deposits contain variable amounts of precious metals, both in average grade and total contained metals. Gold and/or Ag-rich VMS deposits are attractive exploration targets as their precious metal content contributes significantly to their total value and their polymetallic nature makes them less vulnerable to metal price fluctuations. In order to objectively identify truly anomalous Au grades and contents in VMS deposits and help identify the geological parameters that may be responsible for atypical Au enrichments in VMS systems, Mercier-Langevin et al. (2011a) completed a statistical analysis of the global VMS grades and tonnages, resulting in several findings. 1) VMS deposits that contain more than 3.46 g/t Au are auriferous, regardless of their base

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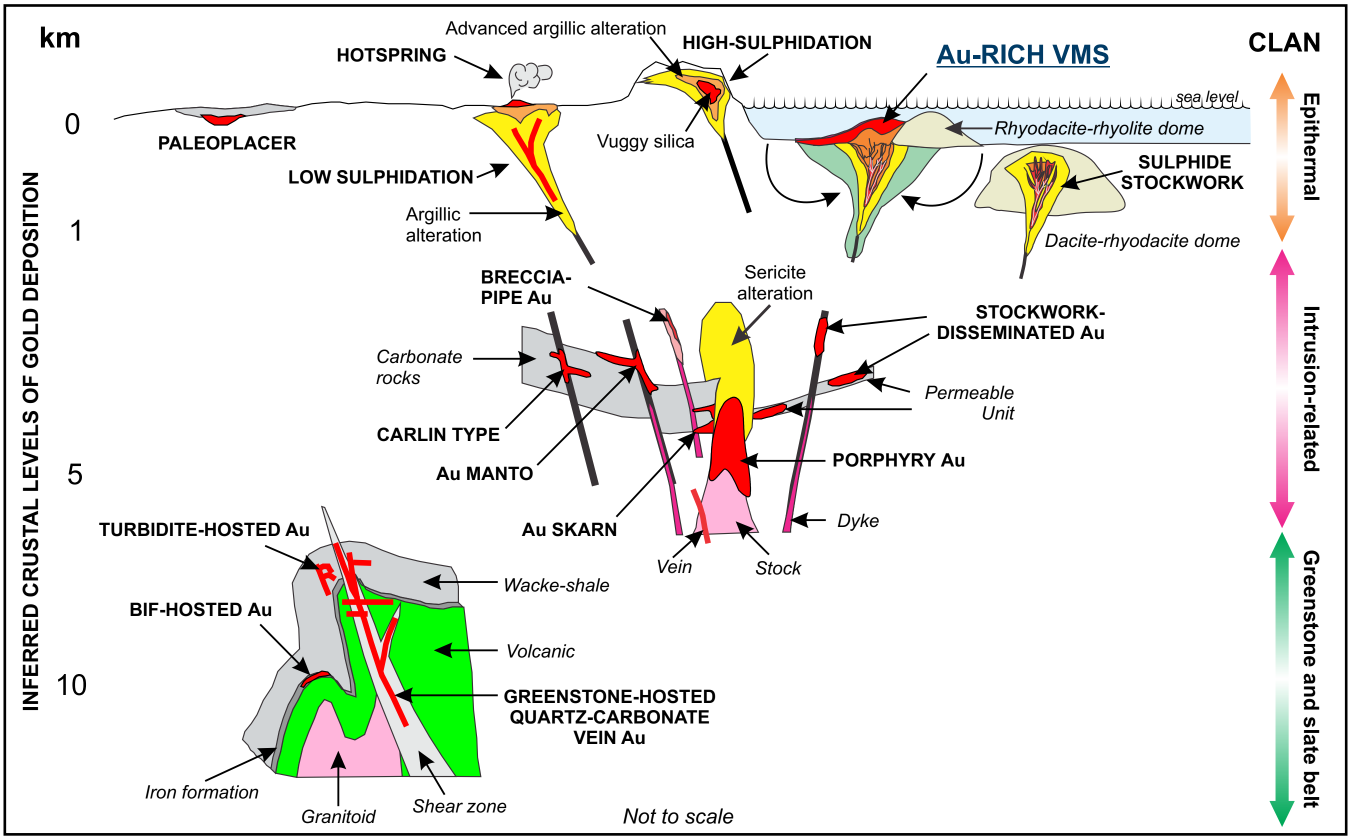


Figure 1. Schematic illustration of the various types of gold deposits, including Au-rich volcanogenic massive sulphide, shown at their inferred crustal level of formation (modified from Hannington et al. (1999), Poulsen et al. (2000), and Dubé et al. (2007a)).

metal content. Many of these deposits have gold grades (in g/t) higher than the combined content of base metals in weight percent, as previously noted by Poulsen and Hannington (1995), and are also considered to be auriferous. 2) Deposits with 31 t of Au or more (~1 Moz) exceed the geometric mean plus one geometric standard deviation and are clearly anomalous. 3) Deposits with a grade of more than 3.46 g/t Au and 31 t Au or more are considered Au-rich. Consideration of the geometric mean for smaller populations, such as VMS deposits in individual districts or mining camps, can also help to identify those deposits with statistically significant Au enrichments, even if they have Au grades that are far below the global mean value. There are still no clear statistical criteria to determine thresholds that would define "anomalous" Ag grades and/or total amount of Ag in volcanogenic massive sulphide deposits, as Ag grades vary significantly depending on the nature of the host succession. Deposits hosted in felsic-dominated successions are significantly richer in Ag than VMS deposits hosted in bimodal-mafic and mafic-dominated successions (25 g/t vs. 9.5 and 6.3 g/t, respectively, at the 50th percentile: Mosier et al. (2009); 93 g/t vs. 37 and 20 g/t, respectively, on average: Barrie and Hannington (1999); 56 g/t vs. 21 and 11 g/t, respectively, geometric mean: Franklin et al. (2005)). Globally, Canadian VMS deposits are characterized by average and median Ag grades of 63 and 37 g/t, respectively (Galley et al., 2007), indicating a right-skewed grade distribution due to a small number of very high-grade deposits. Therefore, in the absence of objective criteria, deposits with Ag grades above the average grade of their inferred group (e.g. felsic-dominated vs. mafic-dominated) or of the other deposits of their host district are considered to be Ag-rich.

Gold-rich and auriferous VMS deposits are considered to be subtypes of both VMS and lode gold deposits (Fig. 1), with some VMS deposits hosting world-class Au mines (Poulsen et al., 2000; Dubé et al., 2007a) and some considered to be hybrids of VMS and epithermal systems (e.g. Sillitoe et al., 1996; Galley et al., 2007). Although Au and Ag are commonly co-sited at the mineral-grain scale, and with only a few exceptions (e.g. Greens Creek, Alaska and Eskay Creek, British Columbia), Au-rich VMS deposits are not Ag-rich, and Ag-rich deposits are not Au-rich. This suggests distinct enrichment/transport mechanisms and/or variably endowed source rocks.

The geological characteristics, mechanisms of Au concentration, and genetic models for auriferous VMS deposits have been previously reviewed for both

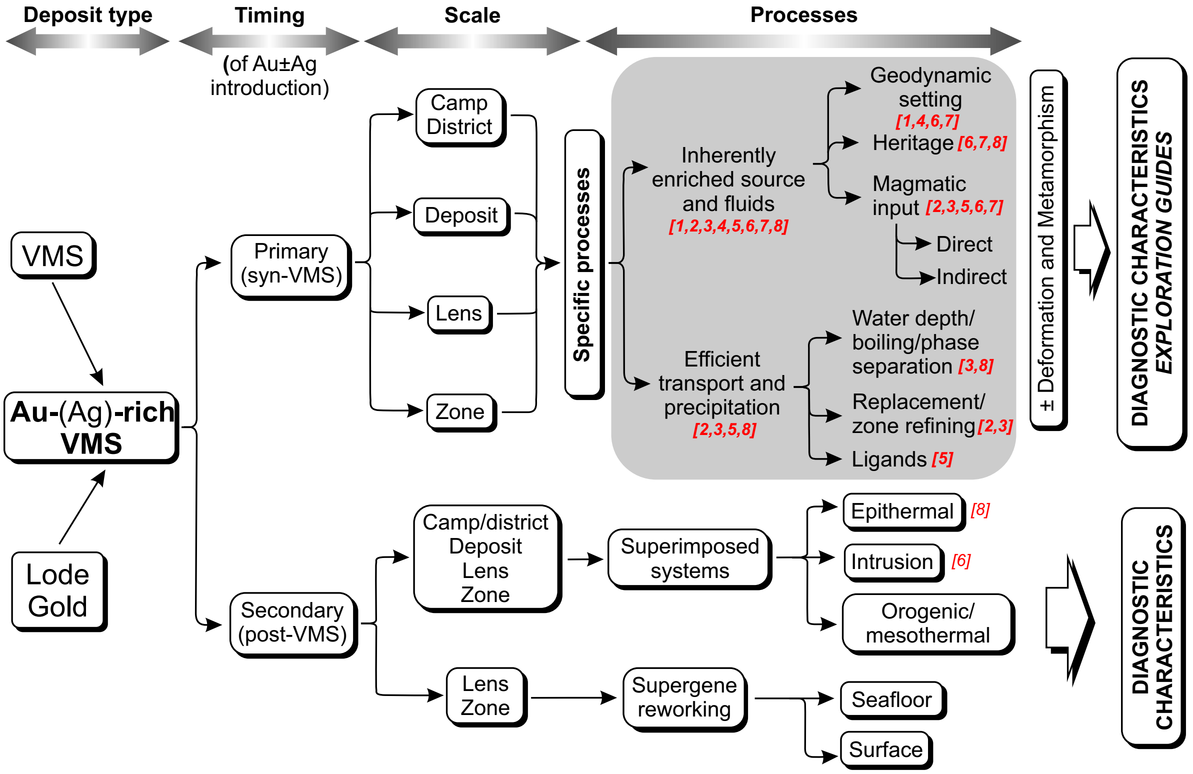


Figure 2. Graphic summary of the many different possible controls on Au- and Ag-enrichment in volcanogenic massive sulphide systems that operate on different spatial and temporal scales. The numbers in brackets refer to the deposits studied through the TGI-4 program and whether the specific mechanisms were documented or inferred. 1 = Lalor (Manitoba), 2 = Ming (Newfoundland), 3 = Lemarchant (Newfoundland), 4 = Boliden (Sweden), 5 = Lemoine (Quebec), 6 = Westwood (Quebec), 7 = Bousquet 2-Dumagami and LaRonde Penna (Quebec), 8 = Nurukawa (Japan).

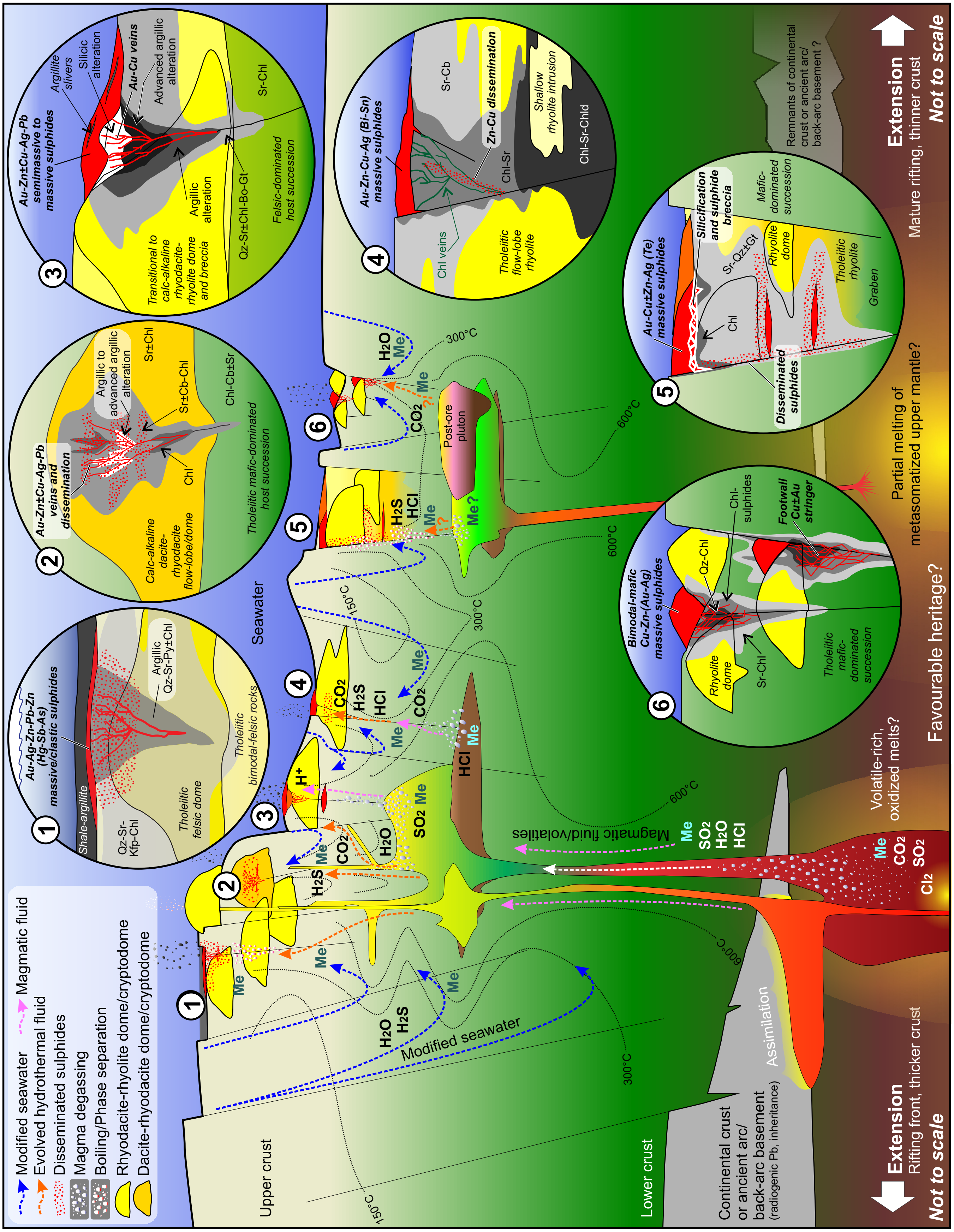
ancient and modern settings (e.g. Hannington et al., 1986, 1999; Hannington and Scott, 1989; Huston and Large, 1989; Large et al., 1989; Large, 1992; Poulsen and Hannington, 1995; Sillitoe et al., 1996; Huston, 2000; Dubé et al., 2007a; Mercier-Langevin et al., 2011a), but controversies remain, especially concerning the source(s) of the precious metals. Ongoing research on ancient precious metal-rich deposits, including studies conducted under the auspices of the Targeted Geoscience Initiative 4 (TGI-4) Program VMS Ore System led by the Geological Survey of Canada, and those on modern seafloor hydrothermal systems (e.g. Hannington et al., 2005; de Ronde et al., 2011, 2012, 2014 and references therein) brings a wealth of new information that can be used to formulate and refine genetic and exploration models for such deposits and define exploration criteria.

Several different Au- and Ag-rich VMS deposits and districts were studied under the VMS (Peter and Mercier-Langevin, 2015) and Lode Gold Ore Systems projects of the TGI-4 program, building on work initiated during previous programs at Natural Resources Canada. The aim is to better understand precious metal-enrichment processes in VMS deposits and apply this information to improve genetic and exploration models. The deposits studied range from Archean to Miocene and from small (<1 Mt) to very large (50–100 Mt) in size. Furthermore, they occur as isolated deposits or parts of clusters, perfectly preserved to intensely deformed and metamorphosed, and vary markedly in Au and/or Ag grade. Only some examples are discussed here, with the aim of highlighting specific processes that are thought to play a critical role in precious metal enrichment of VMS, with an emphasis on Au. Readers are referred to Boulerice et al. (2015), Caté et al. (2015), Duff et al. (2015), Gill et al. (2015), Pilote et al. (2015) and Yergeau et al. (2015) for TGI-4 site-specific studies.

PRECIOUS METAL-RICH VMS SYSTEMS

Timing and Scale of Precious Metal Enrichment

Precious metals, and more particularly Au, can be introduced in VMS deposits during the lifetime of the VMS-forming hydrothermal system (so-called “primary” enrichment; Fig. 2) or they can be introduced and/or redistributed after the cessation of hydrothermal activity (so-called “secondary” enrichment; Fig. 2). The siting and scale of the enrichment processes can vary significantly. Some districts (or mining camps) are characterized by numerous Au-rich VMS deposits (e.g. Doyon-Bousquet-LaRonde mining camp,


Modified seawater
Evolved hydrothermal fluid
Disseminated sulphides
Magma degassing
Boiling/Phase separation
Rhyodacite-rhyolite dome/cryptodome
Dacite-rhyodacite dome/cryptodome
Magmatic fluid
1
Au-Ag-Zn-Pb-Zn (Hg-Sb-As) massive/clastic sulphides
Shale-argillite
Qz-Sr-Kfp-Chl
Tholeiitic felsic dome
Argillic Qz-Sr-Py±Chl
Tholeiitic bimodal-felsic rocks
2
Au-Zn±Cu-Ag-Pb veins and dissemination
Argillic to advanced argillic alteration
Sr±Chl
Sr±Cb-Chl
Chl
Chl-Cb±Sr
Calc-alkaline dacite-rhyodacite flow-lobe/dome
Tholeiitic mafic-dominated host succession
3
Au-Zn±Cu-Ag-Pb semimassive to massive sulphides
Argillite slivers
Silicic alteration
Au-Cu veins
Advanced argillic alteration
Argillic alteration
Qz-Sr±Chl-Bo-Gt
Sr-Chl
Transitional to calc-alkaline rhyodacite-rhyolite dome and breccia
Felsic-dominated host succession
4
Au-Zn-Cu-Ag (Bi-Sn) massive sulphides
Sr-Cb
Zn-Cu dissemination
Shallow rhyolite intrusion
Chl-Sr
Chl-Sr-Chld
Chl veins
Tholeiitic flow-lobe rhyolite
5
Au-Cu±Zn-Ag (Te) massive sulphides
Silicification and sulphide breccia
Sr-Qz±Gt
Chl
Rhyolite dome
Mafic-dominated succession
Tholeiitic rhyolite
Graben
Disseminated sulphides
6
Bimodal-mafic Cu-Zn-(Au-Ag) massive sulphides
Qz-Chl
Chl-sulphides
Footwall Cu±Au stringer
Rhyolite dome
Sr-Chl
Tholeiitic mafic-dominated succession
Seawater
Upper crust
Lower crust
Modified seawater
H2O
H2S
Me
CO2
SO2 Me
HCl
H+
Me?
150°C
300°C
600°C
Post-ore pluton
Magmatic fluid/volatiles
Me
SO2
H2O
HCl
Me
CO2
SO2
Cl2
Assimilation
Volatile-rich, oxidized melts?
Favourable heritage?
Partial melting of metasomatized upper mantle?
Continental crust or ancient arc/back-arc basement (radiogenic Pb, inheritance)
Remnants of continental crust or ancient arc/back-arc basement ?
Extension
Rifting front, thicker crust
Not to scale
Extension
Mature rifting, thinner crust
Not to scale

Quebec: Dubé et al., 2007a, 2014; Mercier-Langevin et al., 2007a, 2011b) or by consistently anomalous high background Au (e.g. Mount Read Volcanics, Tasmania: Corbett, 1992). This illustrates the provinciality of some Au- and/or Ag-rich VMS deposits (Hannington et al., 1999; Huston, 2000) and strongly suggests large-scale geological controls on the enrichment of precious metals. Other districts might contain only one or two isolated auriferous VMS deposits (e.g. Nurukawa deposit, Hokuroku district, Japan: Yamada et al., 1987) or significantly "above district average" deposits (e.g. Caribou and Louvicourt deposits, Bathurst Mining Camp, New Brunswick: McClenaghan et al., 2003; Mercier-Langevin et al., 2011a). Many VMS deposits are characterized by lenses or zones that are significantly enriched in Au relative to the entire deposit (e.g. 1806 Zone, Ming deposit, Newfoundland: Pilote et al. (2014a, b, 2015), Brueckner et al. (2014); Brunswick 12 North End Zone: McClenaghan et al. (2009)). These different scales of Au (and Ag) enrichment indicate that local primary or secondary processes also play a major role in the precious metal budget of VMS systems.

Precious Metal Enrichment Processes

Anomalous primary precious metals budgets of VMS deposits can result from (1) inherently enriched source rocks and deep-seated fluids, and/or (2) efficient transport (in aqueous fluid and/or vapour) and precipitation. These two conditions are not necessarily mutually exclusive, and different processes can be active at the same time and/or at the same site but at different scales (Figs. 2 and 3). Secondary enrichment can be due to the superposition of younger mineralizing systems and weathering can significantly modify the distribution of precious metals.

In ancient, deformed and metamorphosed terranes and/or belts, it may be difficult to establish the absolute timing of the precious metal enrichment in a VMS deposit. For example, in the 1980s Au was first thought to be synvolcanic in the Au-rich VMS deposits of the Doyon-Bousquet-LaRonde mining camp, then in the 1990s a syntectonic overprint was proposed, and more recently the Au has been confirmed to be part of the VMS-forming systems (Dubé et al., 2007b, 2014; Mercier-Langevin et al., 2007a, b, 2009, 2011b, c; Wright-Holfeld, 2011; Yergeau, 2015; Yergeau et al., 2013, 2015, and references therein).

Among the more robust indications of a synvolcanic timing for Au are (1) the presence of auriferous sulphide clast-bearing units associated with the ore; (2) spatial correlation between Au and base metals, at the scale of the deposit or lens; (3) spatial association of Au with a VMS-associated alteration halo; (4) the presence of auriferous mineralization that is cut by synvolcanic dykes; (5) stacking of auriferous sulphide lenses in the volcanic sequence; and (6) gold-bearing late structural features that are devoid of Au outside the limits of the VMS orebody. The absence of isotopic (e.g. O, S, Pb) disturbance due to overprinting metasomatism associated with deformation and/or metamorphism is considered indirect evidence for syngenetic Au introduction, especially when supported by field evidence.

Primary (syn-VMS) Enrichment Processes

Inherently enriched source and fluids: An inherently enriched source (magma or host sequence) and/or fluids, as suggested by the strong provinciality of Au- and Ag-rich VMS deposits, can explain why some VMS deposits are enriched in precious metals. Enrichment in the source can be related to a specific geodynamic setting or heritage, as explained below, and is commonly thought to be associated with a direct magmatic input of Au- and/or Ag-bearing (and other metals) fluids and/or vapour into the ore-forming system (Figs. 2 and 3).

The geodynamic setting strongly influences not only the type of VMS deposits (and other deposit types, such as orogenic Au) that will be formed but also the metal budget of the deposits. For example, the Paleoproterozoic deposits of the Flin Flon-Snow Lake belt (Manitoba) and Skellefte District (Sweden) are, on average, slightly richer in Au than deposits in most major VMS-bearing belts, and include both Au-rich

Figure 3 (opposite page). Schematic diagram illustrating various settings and styles of precious metal-rich volcanogenic massive sulphide (VMS) deposits. Note that the diagram is not to scale, and some systems are much larger than others. The (relative) water depth as depicted may not be representative of the water depth at the time the deposits were formed. Metamorphic grade is not taken into account. Inset 1 depicts a system having features similar to those at Eskay Creek, with which Lemarchant may share some similarities. Inset 2 depicts a sub-seafloor mineralization similar to the Rainy River synvolcanic Au deposit. Inset 3 depicts Au-rich VMS-type systems such as Bousquet 2-Dumagami or LaRonde Penna. The Boliden and Nurukawa deposits are largely similar to this type of Au-rich VMS deposit. The Ming deposit also has some features common to this type of deposit. Inset 4 represents systems such as Lemoine. The Lalor deposit may have shared similarities with this type of system prior to intense deformation and metamorphism. Inset 5 depicts Horne- and Quemont-style Au-rich VMS systems. Inset 6 shows a typical Noranda-type VMS deposit in which Au typically occurs in the footwall stringer veins. This may have been the case at Lalor prior to deformation and metamorphism. See text for discussion. Based on Poulsen and Hannington (1995), Hannington et al. (1999), Huston (2000), Dubé et al. (2007a, 2014), Galley et al. (2007), Mercier-Langevin et al. (2007c, 2014b). Abbreviations: Bo= biotite, Cb= carbonate, Chl= chlorite, Chld= chloritoid, Gt= manganese garnet, Kfp= potassium feldspar, Me= metals, Py= pyrite, Qz= quartz, Sr= sericite.

(e.g. Skellefte: Boliden, Holmtjarn, and Petiknas North) and auriferous (e.g. Flin Flon-Snow Lake belt: Lalor) deposits. Although a number of processes active at various scales have been shown to be responsible for Au enrichment in these deposits, their particular setting (i.e. mature submarine arc and arc–back-arc rift systems constructed on older crust) appears to have influenced the overall Au budget of the deposits (Mercier-Langevin and Pehrsson, 2014; Fig. 3). This probably applies to some Archean and Phanerozoic VMS districts formed in similar settings. The crustal setting may be important for Ag enrichment, as suggested by the provinciality of "Ag-rich" versus "conventional" VMS deposits in the Slave Province, which may correlate with a tectonic setting ("arc-like environment" versus "bimodal rift" classification: Bleeker and Hall, 2007). Many of the VMS deposits enriched in Ag occur in "arc-like environments", and sulphides from these deposits display a larger range of $\Delta^{33}S$ compared to deposits from bimodal rift environments with a smaller range and primarily negative values of $\Delta^{33}S$; these characteristics suggest the incorporation of crustal sulphur (and, by inference, Ag and other metals) in the former group of deposits (Taylor et al., 2015). A common feature of belts such as Skellefte and Flin Flon-Snow Lake that host Au-enriched deposits is their crustally contaminated Pb-isotope signature and their association with felsic rocks showing evidence of contamination (e.g. inherited zircons, evolved Nd-isotope signature).

Another common characteristic of these Au-rich VMS-bearing belts and districts is a preferential association of Au-rich VMS deposits with rifted arc and back-arc settings characterized by transitional to calc-alkaline andesite-dacite-rhyodacite-rhyolite suites, comprising thick (10s to 100s of m) sequences of felsic volcanic rocks (Hannington et al., 1999; Dubé et al., 2007a; Mercier-Langevin et al., 2007c, d, 2011a; Fig. 3). Early rifting and extension-subsidence in an arc–back-arc-style environment is considered to be an important prerequisite in the genesis of the Au-rich VMS deposits of the Blake River Group in the southern Abitibi, where 6 of 11 of the richest and largest Au-rich VMS deposits are located (Mercier-Langevin et al., 2011a). The Au-rich VMS deposits of the Blake River Group occur in distinctly different volcanic and structural settings from other "conventional" VMS deposits in the district. The Horne and Quemont Au-rich deposits are separated in time and space from the Noranda Mine Sequence bimodal-mafic Cu-Zn VMS deposits; both of these former deposits are located in the southern part of the Noranda camp in fault-bounded structural blocks separated from the slightly younger Cu-Zn deposits (Mercier-Langevin et al., 2011a, b, c; McNicoll et al., 2014). The Bousquet Formation, which hosts the Au-rich VMS deposits of the Doyon-Bousquet-LaRonde mining camp, is coeval with the volcanic rocks that host the Cu-Zn VMS of the Noranda Mine Sequence, but is distinguished from them by its transitional to calc-alkaline affinity and dominantly felsic composition. The Bousquet Formation and its deposits were formed in a volcanic complex at the periphery of the central part of the Blake River Group, possibly in an area characterized by thicker basement, and therefore it is postulated to have been spatially more proximal to an arc (immature or early arc-rift stage). Recent dating in the Noranda and Doyon-Bousquet-LaRonde mining camps indicates that Horne and Quemont also formed during an episode of early extension-subsidence and thick transitional to felsic volcanism at Noranda (Monecke et al., 2008) at 2702–2701 Ma (McNicoll et al., 2014). Extension, VMS-related hydrothermal activity and transitional to calc-alkaline volcanism had migrated eastward to the Doyon-Bousquet-LaRonde mining camp by 2698–2697 Ma, at which time Horne and Quemont had already formed and the Cu-Zn deposits of the Noranda Mine Sequence were being deposited in the more mature, tholeiitic to transitional, mafic-dominated extensional setting (Monecke et al. 2008; Mercier-Langevin et al., 2011a, c).

A favourable heritage, or predisposition of certain areas of the upper mantle and lower crust to preconcentrate Au, has been proposed for Phanerozoic belts where ore-forming processes tap the same enriched lithospheric mantle source for a prolonged period of time with the recurrent generation of Au deposits, perhaps related to favourable geodynamic conditions that fertilize the upper mantle and lower crust and link them to the upper crust (Sillitoe, 2008; Hronsky et al., 2012; Fig. 3). Such favourable predisposition in the lower crust and/or upper mantle has been proposed to explain the strong provinciality of Au-rich VMS and orogenic Au deposits in the southern Abitibi belt (Dubé et al., 2007a; Mercier-Langevin et al., 2012). This uniquely endowed portion of the greenstone belt contains more than 85% of the Au in the entire belt (all deposit types) and more than 90% of the VMS-hosted Au (Mercier-Langevin et al., 2011a, 2014a).

A magmatic input of Au, either directly through degassing and/or fluid exsolution or indirectly through leaching of crystallized magma bodies at depth, is a plausible mechanism to explain precious metal-enrichment in some VMS deposits and districts, as indicated by research on active systems (e.g. Hannington et al., 1999; de Ronde et al., 2005; Fig. 3) and some ancient deposits (e.g. the Doyon-Bousquet-LaRonde mining camp: Dubé et al. (2007a, b, 2014), Mercier-Langevin et al. (2007a, c, d), Yergeau et al. (2015); the Lemoine deposit, northeastern Abitibi: Mercier-Langevin et al.

(2014b), and the Ming deposit, Newfoundland: Brueckner et al. (2014), Pilote et al. (2015)). The evidence for a direct magmatic input of Au can be circumstantial, but the involvement of magmatic fluids can be readily inferred in many ancient Au-rich VMS systems. The presence of extensive zones of aluminous alteration (metamorphosed advanced argillic alteration) at Bousquet 2-Dumagami and LaRonde Penna, for example, has been interpreted as evidence for a magmatic input into the hydrothermal system (Dubé et al., 2007b, 2014), and similar inferences have been made for Lemoine (Mercier-Langevin et al., 2014b), Boliden (Mercier-Langevin et al., 2013) and Nurukawa (Ishiyama et al., 2001). Such aluminous alteration zones develop in response to condensation of H_2S vapour or disproportionation of magmatically derived SO_2 that produce very low-pH, acidic, and oxidizing fluids, which leach most elements in the rock except for Al and Si. Although not diagnostic evidence for a magmatic input (e.g. Huston et al., 2011), the presence of a synvolcanic intrusion near the deposits is thought to be a prognostic indicator of this process. At the Westwood Mine, Au-rich VMS lenses are located above a synvolcanic intrusion that hosts part of the 5 Moz Au Doyon intrusion-related deposit, the latter being associated with local zones of aluminous alteration (Mercier-Langevin et al., 2009; Wright-Holfeld et al., 2010, 2011; Yergeau et al., 2013, 2015; Galley and Lafrance, 2014). The Horne (53.7 Mt at 6.06 g/t Au) and Quemont (13.8 Mt at 5.49 g/t Au: Mercier-Langevin et al., 2011b) deposits, located in the central Blake River Group, lack aluminous alteration, but, based on O isotopic evidence, are thought to have formed from long-lived hydrothermal systems that were related to synvolcanic magmatism (Taylor et al., 2014). According to Beaudoin et al. (2014), a heavy (6.5–22‰) $\delta^{18}O$ whole-rock composition also supports a magmatic input in the LaRonde Penna ore-forming hydrothermal system. Moreover, at both Horne and LaRonde Penna, there is no isotopic evidence for later magmatic activity or hydrothermal overprint, which supports synvolcanic Au introduction and is in agreement with field evidence.

At Lemoine, intense leaching of light rare earth elements in the high-temperature footwall alteration zones is considered to indicate acidic conditions in the presence of both CO_2 and HCl-bearing fluids sourced from the underlying Doré Lake synvolcanic intrusive complex. The presence of high Bi contents in the Au-rich ore is also considered to be evidence of a magmatic input (Mercier-Langevin et al., 2014b), which may have been facilitated by the relative abundance of shallow felsic intrusive rocks in the deposit host succession (Boulerice et al., 2015).

Specific element suites, such as In, Te, and Bi in high-temperature Cu-rich ores and As, Sb, Hg, and Ag (the "epithermal suite") and complex sulphosalt assemblages in low-temperature Zn-rich ore, also have been linked to a direct magmatic contribution of metals into the ore-forming hydrothermal system (Hannington et al., 1999; Huston et al., 2011); both associations have been documented at Ming (Brueckner et al., 2014; Pilote et al., 2015) and at Lemarchant in central Newfoundland (Gill et al., 2013, 2015).

Efficient transport and precipitation mechanisms: Whereas some districts contain VMS deposits that are uniformly enriched in Au and/or Ag, some districts/camps contain VMS deposits that are much more enriched than others in the same district (e.g. Horne and Quemont, Noranda district). This implies that local processes were involved in precious metal enrichment, including boiling/phase separation, optimal zone refining, availability of favourable ligands for aqueous- or vapour-phase transport, and the presence of elements acting as sinks for precious metals (e.g. Bi at Lemoine: Mercier-Langevin et al., 2014b) (Fig. 2). These processes govern which metals (including precious metals) were transported and deposited, and where in the system this occurred. The role of boiling/phase separation, which is largely controlled by the water depth, but also by the initial composition of the fluids, and the role of different ligands has been discussed in detail by Hannington et al. (1999), Huston (2000), and others, and readers are referred to these papers for in-depth discussions. Boiling is considered to have been a major factor for precious and other trace metal enrichment at Lemarchant in central Newfoundland (Gill et al., 2013, 2015; Gill and Piercey, 2014; Piercey et al., 2014; Gill, 2015). At the same time, evolving conditions in a VMS-forming hydrothermal system can have caused major redistribution of metals through zone refining (see Ohmoto, 1996), for example, concentrating precious metals in some specific areas, lenses, or zones in a VMS deposit (e.g. Large et al., 1989; Huston, 2000). This process is considered to be a key element in controlling the Au endowment of the 1806 zone at Ming relative to the other lenses of the deposit (Brueckner et al., 2014; Pilote et al., 2015).

Secondary (Post-Magmatic) Enrichment Processes

Secondary enrichment processes have affected the precious metal content and distribution in many deposits, and although not discussed in detail here, they include (1) superimposed mineralization of a different style; and (2) later reworking (Fig. 2). Supergene reworking can have occurred on the seafloor as the deposit was being formed or soon thereafter (e.g. Herzig et al., 1991; Galley and Koski, 1999; Maslennikov et al., 2012), or much later, as the deposits were exposed to weathering on land (e.g. Boyle, 1979). Although supergene modification can have locally increased the grade of metals in near-surface gossans (e.g. Boyle, 2003), this mechanism most likely did not provide a significant new input of base and precious metals in VMS deposits, in contrast to overprinting systems (Fig. 2). A VMS deposit also can have been overprinted by a younger hydrothermal system (e.g. epithermal, intrusion-related, and orogenic) that added metals and/or influenced precious and base metal distribution. It is interesting to note however that VMS systems, which formed at or very near the seafloor, can have overprinted other styles of mineralization, commonly in response to major subsidence (e.g. VMS overprinting epithermal-style mineralization; Nurukawa deposit, Japan: Mercier-Langevin et al., unpubl. data).

In high-grade metamorphic belts, Au in VMS deposits is commonly preferentially located in structural sites (folds, high-strain zones, etc.) but in many cases this spatial relationship has been interpreted to reflect local remobilization of synvolcanic Au during deformation and metamorphism (e.g. Lalor, Snow Lake, Manitoba: Caté et al., 2013a, b, 2014a, b, 2015; Duff et al., 2015). Small-scale, local Au-Ag remobilization is documented in most deformed and metamorphosed VMS deposits, where Au-Ag is restricted to the immediate ore zones or deposit area, but does not extend into the structures outside the deposit; this indicates that there was no input of metals from an external source. At Lalor, for example, where (synvolcanic) Au, Ag, and Pb were remobilized and overprinted the footwall VMS-related alteration assemblages, the lead isotopic compositions of galena in the ore and whole-rock oxygen isotopic compositions of altered rocks show no evidence of post-magmatic disturbance, which would be expected if Au had been introduced during metamorphism (e.g. as in the nearby orogenic gold deposits: Mercier-Langevin et al., 2014c; Duff et al., 2015).

IMPLICATIONS FOR EXPLORATION

The TGI-4 program has made a number of key contributions to the current understanding of the mechanisms for precious metals enrichment in VMS deposits. However, evidence of the causative processes commonly is not observable in the field; therefore, exploration must focus on the visual evidence of the enrichment process(es) (or diagnostic features) that can be mapped at a range of different scales, as summarized in Figure 3. VMS deposits in mature and rifted arc sequences formed on older crust or ancient arc–back-arc basement in the early stages of rifting, which may be evidenced by tracer isotopes (e.g. Pb-Pb, Nd-Sm), high-resolution U-Pb geochronology (e.g. presence of inherited zircons), and whole-rock lithogeochemistry, appear to be slightly better endowed in precious metals, and Au-rich and auriferous VMS deposits tend to occur in clusters within those belts (provinciality). Gold-rich deposits are preferentially associated with calc-alkaline or transitional magmatic successions with andesite-dacite-rhyodacite-rhyolite magmatic suites and with thick (10s of 100s of metres) felsic volcanic rock packages or centres. A direct magmatic contribution (fluids and metals including Au and Ag) can be inferred in some Au-rich and auriferous VMS deposits, as evidenced by a spatial and temporal association with felsic synvolcanic intrusions, enrichment in the “epithermal suite” of elements (As-Sb-Ag-Bi-Hg-Te) and associated complex mineral assemblages, atypically extensive areas of sericitic (phyllic), siliceous, and especially metamorphosed argillic- to advanced argillic-style alteration.

A number of the characteristics enumerated above and their associated processes are also common to some magmatic-hydrothermal deposits, such as high-sulphidation deposits formed in subaerial to shallow submarine volcanic arc settings, supporting the inferred magmatic contribution of Au and/or Ag to precious metal-rich VMS systems (e.g. Lydon, 1996; Sillitoe et al., 1996; Hannington et al., 1999). Some Au deposits thought to have formed in the VMS environment at or near the seafloor from a magmatic-hydrothermal system may be hybrid (Hannington et al., 1999; Large et al., 2001; Galley et al., 2007), or they may lack some of the diagnostic characteristics of their deposit type, which may hinder a complete understanding of their genesis, and consequently decrease the effectiveness of exploration models. The Boliden deposit was originally considered to be an epithermal deposit (e.g. Bergman-Weihed et al., 1996) prior to the current interpretation that it is a VMS deposit (e.g. Allen et al., 1996; Mercier-Langevin et al., 2013, unpubl. data). The Archean Rainy River Au deposit in the Wabigoon Subprovince of northwestern Ontario may also be a good example of such a synvolcanic Au deposit that cannot readily be classified as a typical VMS or as an epithermal deposit; Wartman (2011) interprets the Rainy River deposit as having low-sulphidation-style mineralization, whereas Pelletier et al. (2014, 2015) recognize a number of diagnostic features typical of VMS deposits in their study of this deposit. Although the exact relationship between VMS, shallow-water hydrothermal systems, and epithermal deposits continues to be debated, exploration models for precious metal-rich VMS may have to take into account both the VMS and epithermal models.

On a more local scale, boiling/phase separation, zone refining, and the availability and/or stability of favourable ligands also can explain higher than average precious metals contents in some deposits or parts thereof. Deposits in which this occurred may possess features such as bladed minerals, and complex or irregular Au and Ag distribution and mineralogical associations (e.g. Monecke et al., 2014).

In summary, from our work at Bousquet 2-Dumagami, LaRonde Penna, Westwood and Lemoine (Québec), Lalor (Manitoba), Ming and Lemarchant (Newfoundland), Boliden (Sweden), Nurukawa (Japan), Slave Province (Nunavut), and Rainy River (Ontario), TGI-4 research contributions to precious metal enrichment processes in VMS deposits indicate that primary enrichment in precious metals, and more particularly Au, can occur in deposits of all ages, and that a number of conditions and mechanisms are active at the same time and/or at the same site, but at different scales.

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