

Sulfide Mineralogy, Textures, and Sulfur Isotope Evidence for the Origin of Subseafloor Replacement-Type Volcanogenic Massive Sulfide Mineralization in the Wolverine Deposit, Yukon, Canada

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Abstract

Preservation of subseafloor replacement-style mineralization in the Wolverine volcanogenic massive sulfide (VMS) deposit illustrates the importance of ambient sedimentary environment and mud replacement in the formation of replacement-style VMS mineralization.

Prior to deposit formation, framboidal pyrite, and likely bacterial sulfate reduction (BSR)-generated H_2S in pore fluids, formed during diagenesis in host sediments in association with BSR of seawater sulfate. Diagenesis was succeeded by the first stage (stage 1) of low-temperature ($<300^\circ\text{C}$) Zn-rich mineralization that utilized the preexisting framboids (and likely water and H_2S in the sedimentary pore fluids) and involved both macro- and microscale replacement of mud and framboids and the deposition of a Zn-Pb-(Ag-Se-Sn)-rich assemblage dominated by sphalerite-galena; colloform, spongy, and euhedral pyrite; tetrahedrite; arsenopyrite; stannite; cassiterite; clausthalite; and naumannite. The stage 1 mineralization was replaced by a Cu-rich assemblage during stage 2 mineralization dominated by chalcopyrite, pyrrhotite, and rounded pyrite. This study interprets that Cu-rich fluids dissolved stage 1 Zn-rich sulfides, which resulted in remobilization of Zn into solution, precipitation of Cu-rich sulfides in their place, and subsequent reprecipitation of Zn at the stratigraphically overlying mud-sulfide interface. It is also interpreted that this zone-refining and Zn-redistribution process was important for the high Zn grades of the Wolverine deposit.

In situ sulfur isotopes from various pyrite textural types, galena, pyrrhotite, and chalcopyrite show extreme variability in the diagenetic and stage 1 mineralization with $\delta^{34}\text{S}$ values ranging from -27.4 to 12.1‰ , whereas stage 2 pyrite, pyrrhotite, and chalcopyrite have restricted $\delta^{34}\text{S}$ values ranging from 10.1 to 14.3‰ . These $\delta^{34}\text{S}$ variations reflect varying contributions of H_2S derived from BSR, inheritance of BSR-derived sulfur from framboids during replacement, and hydrothermal H_2S derived from thermochemical sulfate reduction (TSR) of seawater sulfate.

The process of nucleation and replacement of VMS sulfides on diagenetic framboidal pyrite, mixing of VMS fluids with BSR-derived H_2S in sedimentary pore fluids, and zone refining are likely important in many replacement-style VMS deposits and sediment-rich deposits globally (e.g., mafic-siliciclastic VMS, Irish-type and clastic-dominated Zn-Pb, and sediment-hosted Cu deposits).

Introduction

Volcanogenic massive sulfide (VMS) deposits are important global sources of base, precious, and critical metals (e.g., Galley et al., 2007). These deposits have been interpreted to have formed in extensional geodynamic regimes with hydrothermal fluid circulation driven by magmatic heat, metals derived from the underlying substrate ($\pm$ magmatic fluids), and sulfur derived from diverse sources, including leached substrate, seawater, and in rarer cases biogenic sulfur (Lydon, 1988; Large, 1992; Ohmoto, 1996; Franklin et al., 2005; Galley et al., 2007; Hannington, 2014). Based on comparisons with sea-floor massive sulfides (e.g., Lydon, 1988; Hannington, 2014; Ross and Mercier-Langevin, 2014), many ancient deposits are assumed to have formed from exhalation on the sea floor; however, a subset of deposits shows evidence of having formed below the sea floor via subseafloor replacement (Squires et al., 1991; Galley et al., 1995; Allen et al., 1996; Doyle and Allen, 2003; Piercey et al., 2014; Piercey, 2015; Nozaki et al., 2020, 2021, 2024). The processes governing the formation of exhalative mineralization are generally well understood (Lydon, 1988; Large, 1992; Ohmoto, 1996; Franklin et al., 2005; Galley et al., 2007; Hannington, 2014); however, the formation of re-

placement-style mineralization is less certain. For example, replacement likely involves combinations of void space filling, mixing with seawater in unconsolidated sediments or volcanoclastic material, and dissolution of host rocks and preexisting sulfide and other minerals, as well as reprecipitation of new sulfide minerals in their place (e.g., Doyle and Allen, 2003; Piercey, 2015; Magnall et al., 2020; Nozaki et al., 2020, 2021, 2024).

The Wolverine deposit, Yukon, Canada (6.5 million metric tonnes [Mt] at 12.1% Zn, 1.2% Cu, 1.6% Pb, 363 g/t Ag, and 1.7 g/t Au; Regan et al., 2007), is a high-grade, Zn-enriched VMS deposit (Piercey et al., 2015) and an ideal natural laboratory to study the details of subseafloor replacement processes in a sediment-rich VMS deposit. The deposit is hosted by a mixed sequence of felsic volcanoclastic rocks and variably organic- and sulfide-rich mudstones, with ancillary mafic rocks and felsic porphyritic intrusions (Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2016). The deposit has features that are unequivocally exhalative in origin, including exhalative barite and iron formations, ore textures indicative of hydrothermal fluid-seawater mixing, and metal zoning and hydrothermal alteration patterns common to bona fide exhalative VMS and sea-floor massive sulfides (Peter et al., 2007; Bradshaw et al., 2008). In contrast, extensive hanging-wall alteration, abundant biogenic S signatures in some of the mineral-

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ization, and other ore textural features common to subseafloor replacement deposits are also present in the Wolverine deposit, suggesting that part of the deposit formed by replacement (Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2016). Although the geologic setting and aspects of exhalative mineralization have been discussed (e.g., Peter et al., 2007; Bradshaw et al., 2008), details are incomplete for subseafloor replacement at macro- to microscales, the mineralogical relationships and textures of replacement and their spatial and paragenetic relationships, and texturally controlled S isotope systematics of the mineralization.

In this paper, results are provided that build on previous work in the Wolverine VMS deposit (Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2016). This study is based on a drill hole that contains exceptional preservation of subseafloor replacement sulfides where there are intact relationships between the mudstone sedimentary sequence and associated bed-by-bed replacement of these beds by sulfides, which themselves are underlain by zoned Zn-Pb- to Cu-rich mineralization present in many VMS deposits. Thus, using macro- to microtexture documentation, scanning electron microscopy (SEM), and in situ paragenetically and texturally controlled S isotope geochemistry, it is possible to document the features and evaluate the processes related to subseafloor replacement and zone refining during replacement-style VMS deposit evolution. The work has implications for both VMS deposits and for other sediment-rich deposits globally (e.g., mafic-siliciclastic-hosted VMS, Irish-type, clastic-dominated Zn-Pb, and sediment-hosted Cu deposits).

Regional Geologic Setting

The Wolverine deposit is hosted by rocks of the Yukon-Tanana terrane within the Finlayson Lake district, Yukon (Murphy et al., 2006). The Yukon-Tanana terrane consists of pericontinental arc and back-arc rocks that formed along the western edge of Laurentia in the Devonian through Permian and was accreted to the Laurentian margin in the Mesozoic (Colpron et al., 2006; Mortensen et al., 2006; Nelson et al., 2006, 2013; Piercey et al., 2006; Nelson and Colpron, 2007). The Yukon-Tanana terrane consists of three Paleozoic arc- to back-arc assemblages (Finlayson, Klinkit, and Klondike assemblages) that were constructed atop a metasedimentary-dominated continental assemblage (Snowcap assemblage) interpreted to have western Laurentian affinity (Colpron et al., 2006; Nelson et al., 2006; Piercey and Colpron, 2009; Kroeger et al., 2023). The Finlayson Lake district is dominated by the Finlayson assemblage and consists of three thrust panels (from deepest to shallowest): the Big Campbell, Money Creek, and Cleaver Lake thrust sheets, with all VMS deposits, including the Wolverine deposit, hosted within the Big Campbell thrust sheet (Murphy et al., 2006).

The Big Campbell thrust sheet contains a lower unit, the North River Formation (Fig. 1), which contains mostly quartz-rich metaclastic rocks that were previously correlated with the Snowcap assemblage (Murphy et al., 2006), but new detrital zircon U-Pb and Hf isotope data illustrate that the formation is ~367 to 364 Ma and is the lower part of the Finlayson assemblage in the Finlayson Lake region (Kroeger et al., 2023). These units are overlain by the Kudz Ze Kayah Formation, which consists of predominantly felsic volcanoclastic

rocks, variably carbonaceous mudstones, felsic intrusive rocks, and lesser mafic rocks; the Kudz Ze Kayah Formation hosts the ABM, Krakatoa, and GP4F massive sulfide deposits (Fig. 1; Murphy et al., 2006; Denisová and Piercey, 2022; Manor et al., 2022a, b, 2023). The Kudz Ze Kayah Formation is overlain by the Wind Lake Formation, which is dominated by mafic volcanic and volcanoclastic rocks, carbonaceous mudstones, and lesser carbonate and quartzite (Fig. 1; Murphy et al., 2006; Denisová and Piercey, 2022; Manor et al., 2022a, b, 2023). The Kudz Ze Kayah and Wind Lake Formations have chemical abrasion-thermal ionization mass spectrometry (CA-TIMS) U-Pb zircon ages between ~363.3 and 360.9 Ma and have geochemical and petrological features consistent with formation within a continental back-arc basin with varying contributions from juvenile asthenospheric and lithospheric mantle and evolved continental crust (Piercey et al., 2006; Denisová and Piercey, 2022; Manor et al., 2023).

The Kudz Ze Kayah Formation is overlain by the Wolverine Lake Group. The lowermost unit of the group is the ~357.6 to 356.4 Ma Little Jimmy Formation, which consists of quartzofeldspathic pebble conglomerate, grits, sandstones, and carbonaceous mudstones, which contain varying amounts of felsic volcanic detritus, mudstone clasts, and grains of feldspar like those found in the granitic plutonic rocks (Grass Lakes intrusions) that are coeval with the Kudz Ze Kayah Formation (Fig. 1; Murphy et al., 2006; Manor et al., 2022a, b). The Little Jimmy Formation is overlain by the Little Wolverine Formation, which consists primarily of felsic tuffs and other volcanoclastic rocks, variably carbonaceous mudstones, and feldspar and quartz-feldspar porphyritic intrusions; these rocks comprise the immediate footwall to the Wolverine deposit and felsic tuffaceous rocks and mudstones host mineralization in the deposit (Murphy et al., 2006; Bradshaw et al., 2008; Manor et al., 2022a, b). Overlying the Little Wolverine Formation, and forming the hanging wall to the Wolverine deposit, is the Go Creek Formation (Fig. 1; Manor et al., 2022a, b). The Go Creek Formation consists of carbonate exhalite and iron formation, fine-grained resedimented felsic volcanoclastic rocks (felsic siltstones), felsic siltstone breccias, and carbonaceous mudstones (Fig. 1; Murphy et al., 2006; Bradshaw et al., 2008; Piercey et al., 2016; Manor et al., 2022a, b). The Go Creek Formation is overlain by the Jasper Creek Formation, which consists of massive to pillowed basalts, minor graywacke, and carbonaceous mudstones (Murphy et al., 2006; Piercey et al., 2016; Manor et al., 2022a, b). The Wolverine Lake Group and its contained formations are interpreted to reflect an initial disruption of back-arc magmatism by a ~360.3 to 357.6 Ma deformation event and formation of a rift-drift-related unconformity, along with subsequent reestablishment of magmatism in a continental back-arc basin associated with the Slide Mountain ocean formation (Murphy et al., 2006; Piercey et al., 2006; Manor et al., 2022a, b).

The Finlayson Lake region was subject to multiple episodes of deformation and has experienced regional greenschist facies metamorphism. There was a cryptic ~360.3 to 357.6 Ma deformation event between the formation of the Wind Lake Formation and the overlying Wolverine Lake Group, which is recorded by greater intensity of deformation in units below the Wolverine Lake Group and is marked by ductile fabrics and local isoclinal folding, possibly due to sinistral transpres-

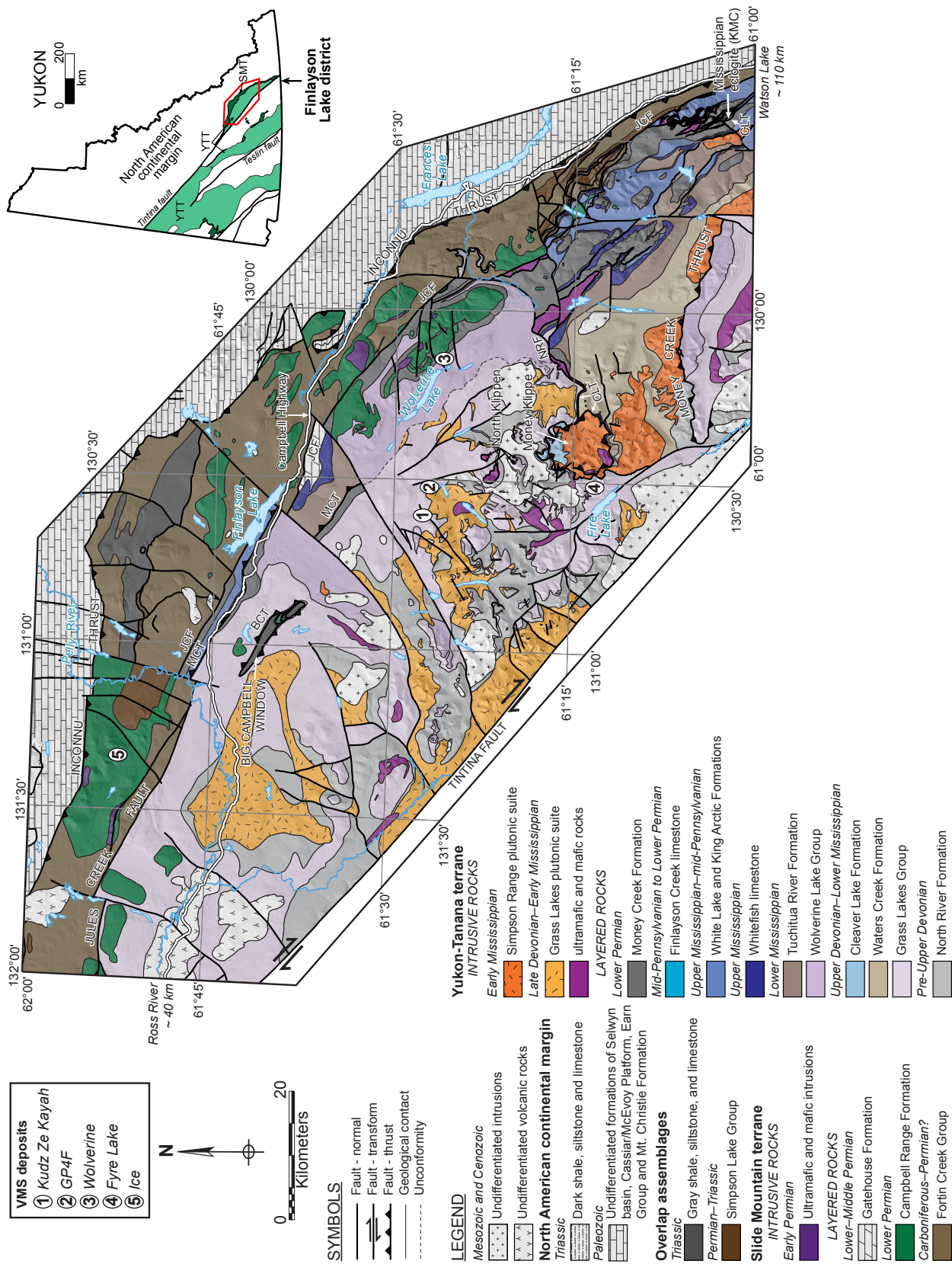


Fig. 1. Regional geologic setting of the Finlayson Lake district, Yukon (modified from Murphy et al., 2006, and Manor et al., 2022a). Inset map illustrates the location of the Finlayson Lake district and distribution of the Yukon-Tanana terrane and Slide Mountain terrane relative to the North American continental margin. Abbreviations: BCT = Big Campbell thrust, CLT = Cleaver Lake thrust, JCF = Jules Creek thrust, MCT = Money Creek fault, NRF = North River fault, VMS = volcanogenic massive sulfide.

sion and Antler deformation along western Laurentia in the Devonian to Early Mississippian (Murphy et al., 2006; Piercey et al., 2006; Manor et al., 2022a). This period of deformation broadly coincides with high-pressure metamorphism recorded in the Klatza metamorphic complex southeast of the Finlayson Lake district (Devine et al., 2006). Thin-skinned, NE-directed thrust faulting recorded by the Big Campbell, Money Creek, and Cleaver Lake thrust sheets and associated foreland-style sedimentation are likely part of a larger-scale Jura-Cretaceous Ikonnu thrust system, which obducted the Yukon-Tanana (and Slide Mountain terrane) onto the western Laurentian (Murphy et al., 2006) and was associated with regional greenschist to amphibolite facies metamorphism (Staples et al., 2014).

Wolverine Deposit Stratigraphy and Mineralization

The Wolverine deposit is a polymetallic felsic-siliciclastic VMS deposit that has exceptional Zn grades (6.5 Mt at 12.1% Zn, 1.2% Cu, 1.6% Pb, 363 g/t Ag, and 1.7 g/t Au; Regan et al., 2007) and is above the 90th percentile for Zn grades in VMS deposit globally (Piercey et al., 2015). The footwall of the deposit consists of rocks from the Little Wolverine Formation and is dominated by 356.4 to 355.2 Ma felsic tuffaceous rocks that contain varying amounts of quartz and feldspar crystals intercalated with carbonaceous mudstones and are intruded by two suites of intrusions, including older quartz-feldspar porphyritic (356.0 Ma) and younger feldspar porphyritic (355.3–355.0 Ma) intrusions (Fig. 2; Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2008, 2016; Manor et al., 2022a, b). The immediate hanging wall to mineralization varies from carbonate exhalite, felsic siltstone, and carbonaceous mudstone, which grades upward into a sequence dominated by carbonaceous mudstone, felsic siltstone, exhalative iron formations, and felsic siltstone breccias, all from the Go Creek Formation, and the uppermost hanging wall consists of graywacke and massive and pillowed basalt of the Jasper Creek Formation (Fig. 2; Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2008, 2016; Manor et al., 2022a, b).

Deposit mineralization is found in three zones: the superficially similar Wolverine and Lynx zones, which are separated from one another by the Hump zone (Peter et al., 2007; Bradshaw et al., 2008). The Wolverine and Lynx zones have thicker central portions that thin toward the Hump zones (Fig. 3) and generally have Zn enrichment throughout, whereas on their edges, downward in drill holes, and within the Hump zone there is more Cu enrichment. Peter et al. (2007) and Bradshaw et al. (2008) interpreted these thickness and grade variations to represent two mounds fed by feeder faults that emanated from a single synvolcanic feeder structure. Peter et al. (2007) also noted that the deposit had both exhalative and replacement-style mineralization.

Alteration in the deposit is typical of many VMS deposits with the associated Cu-rich zones and the interpreted feeder faults having abundant chlorite alteration and grading into sericite alteration outward and toward Zn-rich mineralization; often these alteration patterns are partly semiconformable to stratigraphy like other clastic-rich VMS deposits (Peter et al., 2007; Bradshaw et al., 2008). In contrast to many deposits, however, there is abundant hanging-wall alteration dominated by sericite-quartz-carbonate-magnetite altera-

tion up to 200 to 300 m above mineralization with Fe carbonate enriched closest to mineralization and near carbonate exhalite units (Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2016).

Sulfide Mineralization, Mineralogy, and Textures

Methods

Macroscopic observations were obtained during field work and included in Figures 4 and 5. Samples from drill core for subsequent petrographic and microanalytical work were collected at regular intervals to represent the varying textural and mineralogical assemblages. Standard polished thin sections were created for petrography using a Nikon LV100 polarizing microscope. SEM and energy dispersive spectroscopy (EDS) were undertaken on thin sections and polished mounts utilized for S isotope analysis using an FEI MLA 650 field emission gun SEM equipped with two Bruker silicon drift detectors. The operating conditions included an excitation voltage of 25 kV and a current of ~10 nA. Standard backscattered electron (BSE) images were taken and semiquantitative EDS maps were generated using Bruker Esprit imaging software. All analytical work was undertaken at Memorial University of Newfoundland. Results from field observations and petrographic and SEM results are presented in the following section.

Results

The macroscale features of hole WV05-165 are presented as a graphic log stratigraphic section in Figure 4 and as photographs in Figure 5. The stratigraphy and sulfide facies of this drill hole consist of an immediate hanging wall of variably carbonaceous shale that is underlain by sphalerite-pyrite-galena-(sulfosalt)-rich sulfides with relict laminae and beds of mudstone preserved within it, which in turn are underlain by sphalerite-pyrite-galena-(sulfosalt)-rich sulfides with lesser relict shale. Underlying the sphalerite-rich sulfides are pyritic sulfides that contain pyrite in greater abundance than sphalerite and have increasing chalcopyrite downhole grading into an underlying unit of chalcopyrite-pyrite-pyrrhotite-dominated sulfides, which contain minor clots of chlorite that are interpreted to be relict chlorite-altered felsic tuff. This unit has a conformable lower contact with underlying chlorite-altered felsic tuffs that contain chlorite clots and abundant stringers of chalcopyrite-pyrite-pyrrhotite. The zonation of mineralization is from sphalerite rich at the top to chalcopyrite rich near the base, common to many VMS deposits, and is interpreted to reflect past zone-refining processes during deposit formation (e.g., Eldridge et al., 1983; Large, 1992; Ohmoto, 1996).

The macroscale sulfide textures and relationships are also reflected at the microscale (Figs. 6, 7; Table 1). The uppermost shale-rich unit is dominated by framboidal pyrite, whereas the underlying sphalerite-rich units with relict mudstone beds have abundant framboidal, euhedral, and spongy-textured pyrite, the latter having more diffuse margins and interstitial sphalerite, tetrahedrite, and chalcopyrite (Fig. 6A, B). The framboidal pyrite locally exhibits partial to full replacement by other minerals, including sphalerite and galena, where microcrystals within the framboids are replaced by sphalerite and galena, interstices between pyrite microcrystals in the framboids are replaced by sphalerite and galena, and in

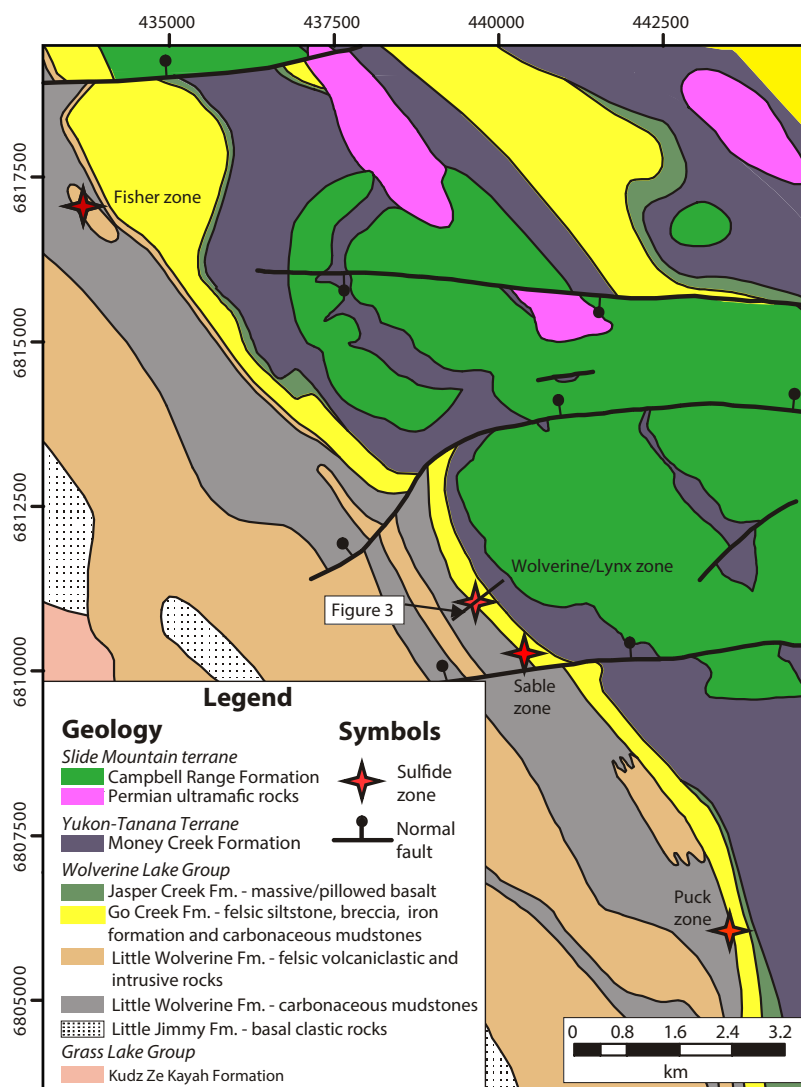


Fig. 2. Geologic map of the Wolverine deposit area along with various prospects outside the main Wolverine deposit. Geologic and unit nomenclature from Murphy et al. (2006) and Manor et al. (2022a). Units on map are Universal Transverse Mercator (UTM) easting and northing values using the North American Datum 1927 (NAD27) in UTM zone 9.

other cases the framboids are completely replaced by sphalerite or galena, having rounded relict features indicative of a previous framboid but which comprise sphalerite and galena (Fig. 6A-G). In these same samples, there is abundant spongy pyrite that has diffuse and subhedral to anhedral morphology that locally grades into coarser euhedral pyrite along its margins; sphalerite, galena, and lesser chalcopyrite also occur in void spaces within the spongy pyrite (Fig. 6E, H). The spongy pyrite and associated euhedral pyrite are associated with anhedral intergrown sphalerite and galena, commonly forming between and surrounding the pyrite masses (Fig. 6D-H). The sphalerite-rich sulfides are also associated with euhedral arsenopyrite (Fig. 6I) and tetrahedrite intergrown with sphalerite, chalcopyrite, and pyrrhotite (Fig. 6I-L). Further downhole, there is an increase in chalcopyrite at the expense of sphalerite and galena, and pyrite is more euhedral (Fig. 6I-L). In the deepest parts of the deposit, the chalcopyrite-pyrrhotite-dominated sulfides are associated with intergrown chalcopy-

rite-pyrrhotite and inclusion-bearing rounded or subrounded pyrite, which locally have embayed margins in contact with chalcopyrite (Fig. 6J-L).

SEM and EDS maps (Figs. 7, 8) supplement the results from reflected-light petrography. The nuance of framboidal replacement is well illustrated where the various pyrite framboid microcrystals are replaced by sphalerite, tetrahedrite, galena, and chalcopyrite (Figs. 7A-D, 8A-D), and in other cases, the framboids are completely replaced by these minerals (Figs. 7A, C, 8A). The framboids are also found as inclusions where they are overgrown by other mineral phases. For example, pyrite framboids occur as inclusions within grains of anhedral sphalerite and tetrahedrite (Fig. 7B, E) and in places appear to coalesce as masses that border the spongy-textured pyrite above (Figs. 7C, 8A, B). Moreover, remnant framboidal pyrite is found intergrown with galena and surrounded by euhedral pyrite (or proximal to euhedral pyrite) in some of the Zn-Pb-rich sulfides (Fig. 7F, G).

SEM also illustrates phases not easily identified by reflected-light microscopy. In the pyrite-sphalerite-rich sulfides, colloform pyrite occurs intergrown with sphalerite and tetrahedrite and has euhedral pyrite and galena along its margins (Fig. 7H). In the same mineralization, euhedral arsenopyrite grains are present and have inclusions of rounded pyrite, which are surrounded by euhedral pyrite and minor chalcopyrite (Fig. 7I). Arsenopyrite is also intergrown with sphalerite, chalcopyrite, and Ag-bearing tetrahedrite (Figs. 7J, 8E-G). The sphalerite- to chalcopyrite-rich assemblages are also associated with cassiterite, stannite, clausthalite, and naumannite (Figs. 7K, L, 8H-N).

The relationships between phases and assemblages show spatial and paragenetic changes downhole (Figs. 6, 9). Further, many of the pyrite textures and associated mineral assemblages are common to zone-refined VMS deposits (e.g., Eldridge et al., 1983). Diagenetic framboidal pyrite (e.g., Wilkin et al., 1996; Raiswell and Canfield, 2012) is found in mudstones hosting sulfides and predates mineralization. The coalescence of framboids to form spongy pyrite with diffuse edges coincides with increased abundance of Zn-Pb mineralization (Fig. 9). Spongy pyrite is locally associated with colloform pyrite and the partial to full replacement of framboidal pyrite by sphalerite, galena, and, to a lesser extent, chalcopyrite (Figs. 6–8). Stage 1 Zn-Pb mineralization also coincides with the formation of abundant galena, sphalerite, and arsenopyrite and trace stannite, cassiterite, clausthalite,

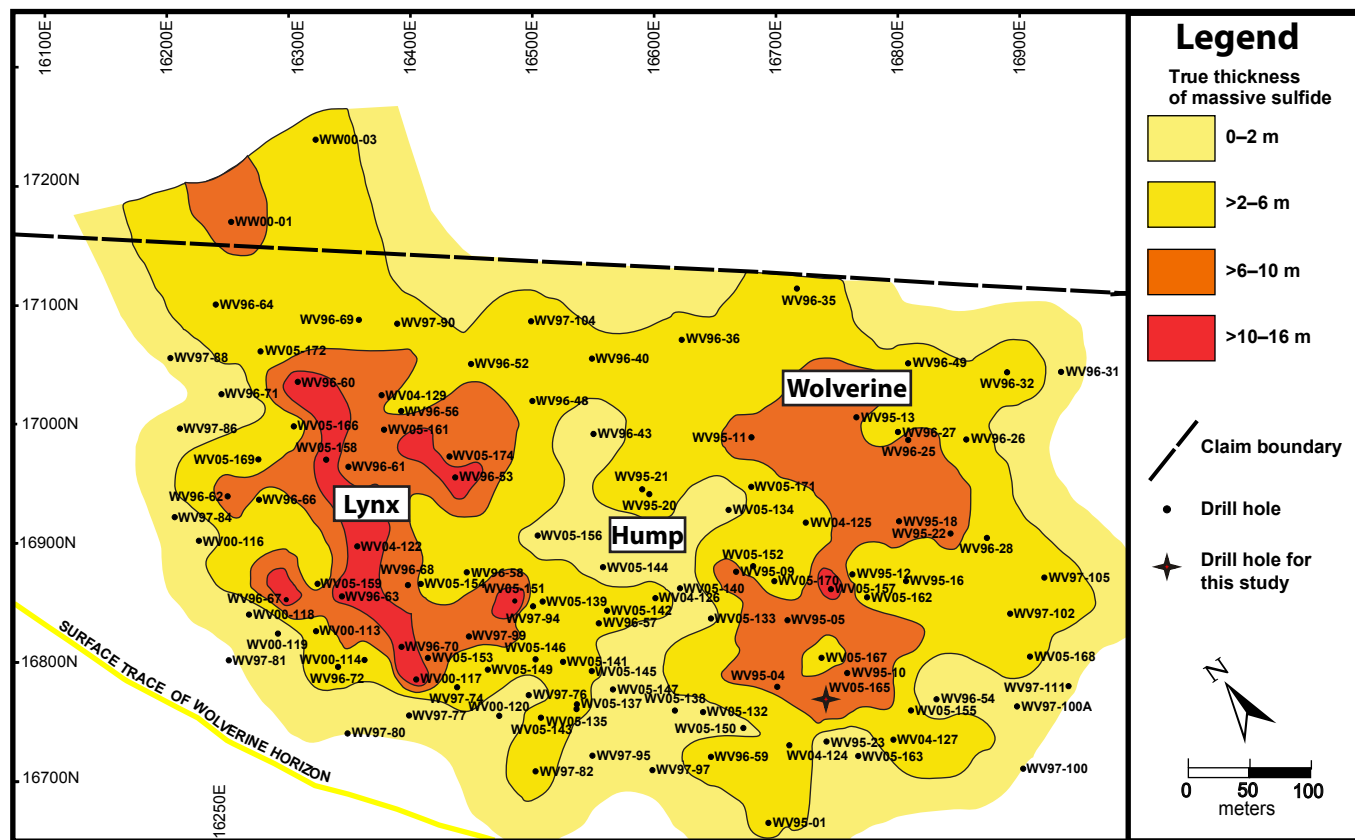
and naumannite (Figs. 6–9). The latter parts of the first stage of VMS mineralization coincide with the formation of euhedral pyrite, often along the edges of spongy pyrite that locally contains inclusions of previously formed phases (Figs. 6–8). The second and final stage of mineralization is dominated by a pyrite-pyrrhotite-chalcopyrite assemblage where there is a transformation of the euhedral pyrite of stage 1 into more rounded and corroded pyrite of stage 2 that is variably inclusion bearing and spatially associated with anhedral sheets of intergrown chalcopyrite and pyrrhotite (Fig. 6). The latter assemblage is found exclusively at the bottom of the mineralized intersection of hole WV-05-165 and generally throughout the deposit associated with Cu-rich mineralization (Peter et al., 2007; Bradshaw et al., 2008).

Sulfur Isotopes

Analytical methods

Sulfur isotopes were collected on six stratigraphically controlled samples from drill hole WV05-165. The samples were collected to reflect the different facies and mineral assemblages above and their downhole relationships. Sulfur isotope analyses were determined on the different textural types of pyrite (framboidal, spongy, euhedral, and rounded), chalcopyrite, galena, and pyrrhotite.

The mineral phases were analyzed in situ using secondary ion mass spectrometry (SIMS), which allowed for the evalu-



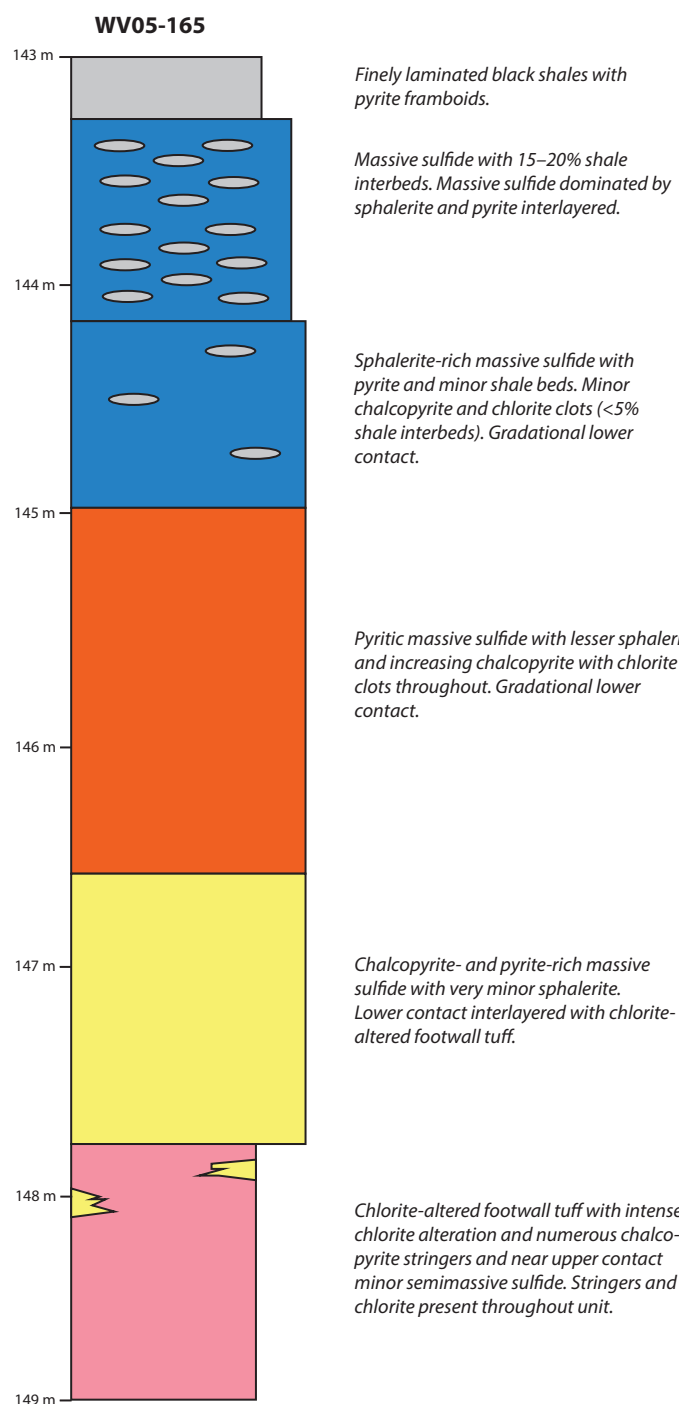


Fig. 4. Graphic log of drill hole WV05-165 with distribution of mineralization facies.

ation of the sulfur isotopes as a function of texture, mineral, and paragenesis, using the methods of Brueckner et al. (2016). Thin-section offcut blocks were cut and mounted in epoxy and hosted in Al rings, polished, and subsequently coated with 300 Å of Au. The Au-coated mounts were then analyzed using a Cameca IMS 4f SIMS at the MAF-IIC Microanalysis Facility of Memorial University. For each sample, determinations of $\delta^{34}\text{S}$ were performed using a primary ion microbeam of 350 to 1,150 pA of Cs^+ , accelerated by a 10-keV potential and fo-

cused into a 5- to 15- μm -diameter spot. The Cs^+ current depended on the analyzed sulfide phase, the size of the analyzed phase, and the matrix surrounding the analyzed grain (sulfides or nonsulfide gangue). To prevent contamination in the polished surface, each spot was first presputtered for 120 to 180 s with a 25- μm -square raster. Depending on the minimum diameter of the critically focused primary beam during each session, a smaller square raster (5–15 μm) was applied to the beam during analysis to improve the homogeneity of primary ion delivery while maintaining lateral resolution at better than 20 μm . Negatively charged sputtered secondary ions were accelerated into the mass spectrometer using a potential of 4.5 keV. The instrument was operated with a medium-contrast aperture (150 μm) and entrance and exit slits paired to give flat-topped peaks at a mass resolving power of 2,975 (10% peak height definition)—sufficient to discriminate $^{33}\text{SH}^-$ (and $^{32}\text{SH}_2^-$) from $^{34}\text{S}^-$. Overall reproducibility, based on replicate standard analyses, is typically better than $\pm 0.5\text{‰}$ (1σ).

Precision and accuracy for each phase was determined via replicate measurements of internal and external reference materials, including (1) UL9 ($\delta^{34}\text{S}$: 15.8‰) and KH87 ($\delta^{34}\text{S}$: 0.2‰) for pyrite; (2) US Geological Survey Norilsk ($\delta^{34}\text{S}$: 8.3‰) for chalcopyrite; (3) PoW1 ($\delta^{34}\text{S}$: 2.3‰) for pyrrhotite; and (4) HT10-4A ($\delta^{34}\text{S}$: 14.2‰) for galena. Precision was determined using the percent relative standard deviation, and accuracy was determined using percent relative difference (see reviews by Piercey, 2014) with results in Appendix 1, Table A1. For all reference materials except KH87, percent relative standard deviation values range from 1.7 to 14.3% with excellent to good precision; some of the higher values are in part due to low total analyses (e.g., the lowest %RSD values are in the materials with the greater total analyses). The percent relative difference values range from –0.83 to –0.06%, with the exception of KH87, demonstrating excellent accuracy.

Results

The locations analyzed for sulfur isotopes within individual samples and minerals were chosen based on petrography, textural features, and paragenetic relationships. Analytical results are provided in Table 2 and Figures 10 and 11; all locations of S isotope spots and associated petrographic images can be found in Appendix 1, item 1. The framboidal pyrite grains have the lowest $\delta^{34}\text{S}$ ranging from –27.4 to 1.7‰ (median = –14.3‰, mean = –15.0‰); spongy pyrite has $\delta^{34}\text{S}$ = –17.6 to 10.9‰ (median = 3.8‰, mean = 0.0‰); euhedral pyrite has $\delta^{34}\text{S}$ = –2.8 to 12.2‰ (median = 9.2‰, mean = 8.1‰); and rounded pyrite has $\delta^{34}\text{S}$ = 10.8 to 13.4‰ (median = 12.1‰, mean = 12.2‰). Galena has positive $\delta^{34}\text{S}$ = 2.8 to 31.6‰ (median = 9.5‰, mean = 13.3‰). Chalcopyrite and pyrrhotite are also uniformly positive with $\delta^{34}\text{S}$ = 3.0 to 14.3‰ (median = 11.4‰, mean = 10.3‰) and $\delta^{34}\text{S}$ = 10.6 to 11.5‰ (median = 11.1‰, mean = 11.1‰), respectively.

There are important spatial and paragenetic variations in the $\delta^{34}\text{S}$ values. Near the top of the drill hole the range of $\delta^{34}\text{S}$ varies greatly with all minerals trending toward lower $\delta^{34}\text{S}$ in the shale-hosted, sphalerite-rich replacement-type sulfides and sphalerite-pyrite-rich sulfides (Fig. 11). In contrast, when pyrite and chalcopyrite become the dominant phases in the pyrite-rich and chalcopyrite-pyrrhotite-pyrite mineralization,

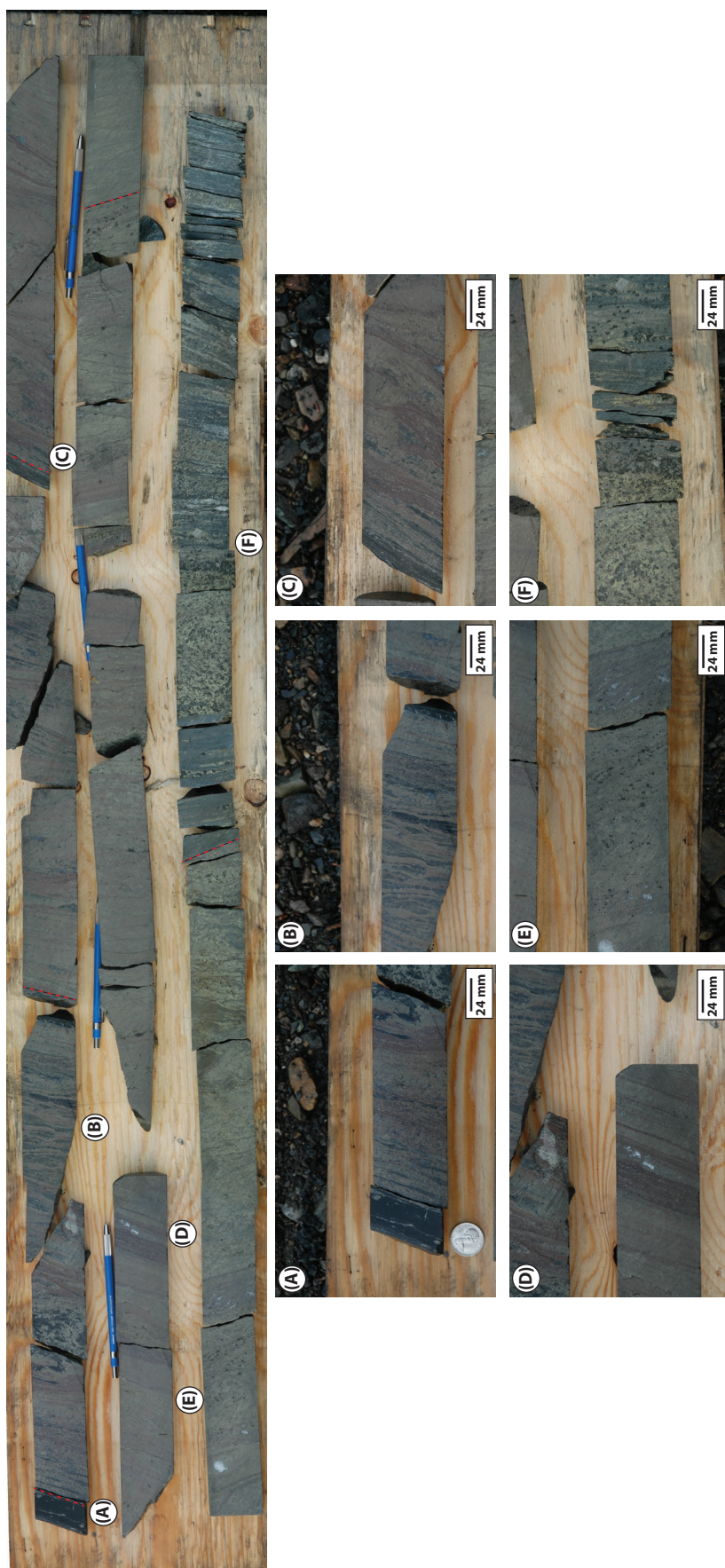


Fig. 5. Photo mosaic of drill hole WV05-165 sulfide intersection graphically shown in Figure 4. (A) Contact between mudstone and underlying sphalerite-rich sulfides with relict mudstone beds. (B) Sphalerite-rich mudstone with relict mudstone beds. (C) Transition between sphalerite-rich sulfides and mudstone beds into sphalerite-rich mineralization. (D) Laminated sphalerite-rich mineralization transitioning into pyrite-rich mineralization. (E) Pyrite-rich mineralization with minor chalcopyrite and clots of chlorite alteration. (F) Chalcopyrite-pyrrhotite-pyrite-chlorite mineralization grading downward into stringer-type chalcopyrite-rich mineralization within chlorite-altered felsic tuff.

the range of $\delta^{34}\text{S}$ is much more restricted (Fig. 11). These variations also are reflected in the proportions of pyrite with mineralization containing more framboidal and spongy textures being found in the upper portion of the shale-, replacement-, and sphalerite-rich sulfides, and having higher $\delta^{34}\text{S}$ variability, whereas in the assemblages with more euhedral to rounded pyrite in the deeper parts of the hole (and paragenetically later), there is a much more restricted range in $\delta^{34}\text{S}$ (Fig. 11).

Discussion

Evidence for replacement and zone refining

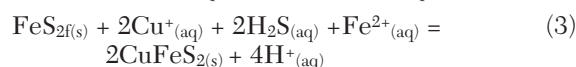
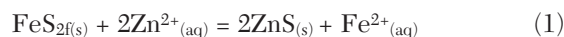
The models for VMS and sea-floor massive sulfides are generally understood, but details about certain processes are still debated. Many exhalative VMS deposits are interpreted to have formed from mixing between VMS fluids and cold seawater, resulting in the deposition of exhalative sulfides and sulfates on the sea floor (e.g., Lydon, 1988; Large, 1992; Ohmoto, 1996; Hannington, 2014). In contrast, a subset of deposits has evidence for formation via subseafloor replacement where sulfide deposition occurred by VMS fluid mixing with water-bearing sediment or volcanoclastic rocks or via dissolution and replacement of existing units by sulfide deposited from the VMS fluid (Doyle and Allen, 2003; Piercey, 2015). Doyle and Allen (2003) outlined numerous criteria for identifying replacement, many of which are preserved in the Wolverine deposit, including rapidly emplaced host facies, relicts of host rocks in the mineralization, replacement fronts between mineralization and host lithofacies, discordance to bedding, and hanging-wall alteration. For example, the deposit is hosted by volcanoclastic rocks in both the hanging wall and footwall that have features indicative of emplacement as submarine, volcanoclastic mass flows (Bradshaw et al., 2008; Piercey et al., 2016). High-precision U-Pb geochronology from these rocks suggests that the entire Wolverine Lake Group was emplaced in less than 1.5 m.y. with accumulation rates of ~800 to 1,400 m/m.y., consistent with the deposit being hosted by rapidly emplaced stratigraphy (Manor et al., 2022b). In addition, relict beds of mudstone are preserved at the interface between the sulfides and enclosing mudstones (Fig. 5), implying potential bed-by-bed replacement during the formation of replacement-style mineralization (e.g., Piercey, 2015). This interface between the sulfides and mudstones where these textures are preserved also constitutes a replacement front where the host stratigraphy was replaced at the macro- to microscale (Figs. 5–8).

The Wolverine deposit is partly semiconformable to host mudstones and footwall rocks, particularly in the replacement zones, but does exhibit evidence for mound-style accumulation and discordant stringer zones underlying it (Fig. 3; Peter et al., 2007; Bradshaw et al., 2008); thus, some mineralization is discordant to host stratigraphy, but of all the replacement criteria of Doyle and Allen (2003) this is the least robust. In contrast, hanging-wall quartz-($\pm$ carbonate-magnetite) alteration is ubiquitous at Wolverine, extending hundreds of meters into the hanging wall of the deposit, and is partly due to replacement-related VMS activity during deposit formation (Peter et al., 2007; Bradshaw et al., 2008; Piercey et al., 2016).

The features above suggest that replacement took place at

Wolverine. Moreover, field and microscopic information provides insights into the details of the replacement processes (Barton, 1978; Barton and Bethke, 1987; Ohmoto, 1996; Putnis, 2009; Piercey, 2015). There appear to be two main loci of replacement in the deposit—along the deposit-mudstone interface and associated with zone refining at depth in the deposit (e.g., Fig. 5; see also Bradshaw et al., 2008 for deposit-scale metal zoning and refining history). At the deposit-mudstone interface there is macroscale evidence of what was likely void space filling in between beds, or dissolution of previous materials and replacement by sulfides (Fig. 5A). Based on comparisons with modern pelagic muds on the sea floor, it is likely that the mudstones were unconsolidated to semiconsolidated at the time of sulfide deposition; thus, it is likely that there was sulfide replacement of the mud (i.e., mineral replacement) and also in pore spaces within the mud where the VMS fluids exploited the permeability within the mud package (e.g., Piercey, 2015). There must have also been mineral replacement by dissolution and reprecipitation coupled with nucleation on preexisting sulfide phases, as evidenced by the presence of framboidal pyrites that are partially to fully replaced by sphalerite, galena, and chalcopyrite, and those that were overgrown and acting as nuclei for paragenetically later spongy and euhedral pyrite (Figs. 6–8).

It is envisioned that this dissolution and replacement of framboidal pyrite occurred as the basal sediments, which likely also had free H_2S and framboids due to bacterial sulfate reduction (BSR) in the sediment column (e.g., Raiswell and Berner, 1986), were infiltrated by low-temperature ($<250^\circ\text{C}$) hydrothermal fluids carrying Zn and Pb (likely as chloride complexes; e.g., Ohmoto et al., 1983; Lydon, 1988; Large, 1992; Ohmoto, 1996), leading to the partial to full replacement of framboidal pyrite ($\text{FeS}_{2\text{f}}$) by sphalerite (ZnS), galena (PbS), and chalcopyrite (CuFeS_2) (e.g., Ohmoto et al., 1983; Ohmoto, 1996):



This initial replacement of framboids by mineralization was also coincident with deposition of paragenetic stage 1 minerals, which are typical of VMS mineralization deposited from low-temperature ($<300^\circ\text{C}$) fluids (e.g., Ohmoto et al., 1983; Lydon, 1988; Large, 1992; Ohmoto, 1996). Stage 1 mineralization involved the deposition of the sulfides, arsenides, sulfoalts, oxides, and selenides (Fig. 9) within centimeters of the sulfide-mudstone interface and also contain relicts of framboid replacement (Fig. 5).

With distance downhole there is a second replacement interface between the Zn-Pb-rich sulfides by chalcopyrite-pyrrhotite mineralization (Fig. 5). This zoning is common to VMS deposits (e.g., Ohmoto et al., 1983; Lydon, 1988; Large, 1992; Ohmoto, 1996) and has been attributed to zone refining and replacement of preexisting lower-temperature Zn-Pb mineralization by higher-temperature ($>300^\circ\text{C}$) Cu-rich mineralization as the VMS hydrothermal system evolves (e.g., Eldridge et al., 1983; Ohmoto et al., 1983; Lydon, 1988; Large, 1992; Ohmoto, 1996). In this case, replacement is less

obvious at a macro level, but there are distinctive microtextural changes in pyrite, from framboidal, spongy, colloform, and lesser euhedral pyrite in the sphalerite-dominated assemblages to almost exclusively rounded pyrite in chalcopyrite-pyrrhotite-pyrite dominated assemblages (Fig. 6). Moreover, when sphalerite is present in the latter assemblage it has evidence for chalcopyrite disease (Barton and Bethke, 1987) and partial replacement by chalcopyrite (Fig. 6), interpreted to have been induced by dissolution of preexisting sphalerite and replacement by chalcopyrite:



These deposit, macro-, and microscale relationships above illustrate that permeability and void space filling and dissolution-reprecipitation were likely important mechanisms for the formation of subseafloor replacement-style mineralization in the Wolverine deposit.

Sulfur sources

The spatially and paragenetically controlled sulfur isotope signatures of the Wolverine deposit provide insight into the sources of sulfur involved in deposit formation and processes related to subseafloor replacement. There are multiple sources of sulfur in VMS deposits, including leached igneous H_2S from footwall rocks, H_2S derived from thermochemical sulfate reduction (TSR) of seawater SO_4 , and more rarely H_2S derived from BSR of seawater SO_4 or from condensation and disproportionation of magmatic-hydrothermal SO_2 (e.g., Ohmoto and Rye, 1979; Ohmoto and Goldhaber, 1997; Seal, 2006; Ono et al., 2007; McDermott et al., 2015; Huston et al., 2023).

It is unlikely that magmatic-hydrothermal SO_2 was a significant source of sulfur in the Wolverine deposit. Magmatic SO_2 disproportionation often leads to distinctive sulfur isotope signatures with sulfides derived from the H_2S having light sulfur and negative $\delta^{34}\text{S}$ signatures and coincident magmatic-hydrothermal sulfates with heavier $\delta^{34}\text{S}$ values (e.g., Rye, 1993, 2005; Huston et al., 2011). There are negative $\delta^{34}\text{S}$ values in sulfides from the Wolverine deposit, but they are spatially restricted to framboidal pyrite in the mudstones or are in sulfides proximal to the mudstone-sulfide contact and containing partially to fully replaced framboid-rich sulfides (Figs. 10, 11). These framboids are interpreted to be formed from BSR of seawater sulfate during diagenesis (e.g., Wilkin et al., 1996); thus, the more negative $\delta^{34}\text{S}$ values are unlikely to have originated from magmatic-hydrothermal fluids.

Even in sulfides that contain evidence for BSR, however, there are higher $\delta^{34}\text{S}$ values that are not consistent with solely BSR-derived sulfur, thus requiring additional sulfur sources. The elevated $\delta^{34}\text{S}$ values are not entirely consistent with derivation from leached igneous sulfur. In general, $\delta^{34}\text{S}$ in MORB-type rocks is restricted to $\delta^{34}\text{S} \sim 0\text{‰}$ (Sakai et al., 1984), whereas in island-arc basalts the values are higher but not as high as those in the Wolverine deposit ($\delta^{34}\text{S} = 4.4 \pm 2.1\text{‰}$) (Ueda and Sakai, 1984). Felsic rocks, like those that would have likely been in the footwall to the Wolverine deposit, can have much greater variability in $\delta^{34}\text{S}$, however. For example, Ishihara and Sasaki (1989) showed that magnetite series granites had $\delta^{34}\text{S} = 1.6$ to 4.0‰ , whereas ilmenite series rocks had lower values ($\delta^{34}\text{S} = -3.7$ to -5.3‰); Seal

(2006) noted that granites globally had $\delta^{34}\text{S} = 1.0 \pm 6.1\text{‰}$. Whereas some of these values overlap the $\delta^{34}\text{S}$ values found at Wolverine, they are still insufficiently high to explain the heavier $\delta^{34}\text{S}$ in some of the Wolverine sulfides, particularly those in the chalcopyrite-pyrite-pyrrhotite-rich sulfides.

In contrast, TSR can potentially explain some of these higher $\delta^{34}\text{S}$ values. To evaluate the role of TSR, modeling of TSR for Early Mississippian seawater sulfate was undertaken using the equations of Ohmoto and Rye (1979) and Ohmoto and Goldhaber (1997) following the methods of Brueckner et al. (2016), McDonald et al. (2018), and Denisová et al. (2024); details are provided in Appendix 2 and results shown in Figure 12. TSR was modeled at 250° and 350°C , the likely range of the temperatures for the assemblages in paragenetic stages 1 and 2, respectively. For the lower-temperature stage 1 assemblage, the higher $\delta^{34}\text{S}$ values in pyrite can be explained by reduction of ~ 0 to 40% seawater sulfate (i.e., $f = 1-0.6$), whereas for sulfides in the stage 2 assemblage it would require at least 20 to 50% reduced seawater sulfate (i.e., $f = 0.8-0.5$) for pyrite, chalcopyrite, and pyrrhotite in these assemblages (Fig. 12). Similar amounts of TSR have been found in other VMS deposits, albeit many toward lower amounts of seawater sulfate reduction (e.g., Solomon et al., 1988; Brueckner et al., 2016; McDonald et al., 2018; Denisová et al., 2024); Ono et al. (2007) noted that ~ 11 to 27% of the sulfur in modern seafloor hydrothermal systems was derived from TSR of seawater sulfate.

The paragenetic trend—from more biogenic influenced early in the history of mineralization, and at the fringes of the deposit, to more TSR dominated with paragenetically later and in deeper chalcopyrite-pyrrhotite-pyrite-rich mineralization—is different from that in some VMS deposits. For example, in both the Hellyer and Ice deposits, there is a shift from early TSR-dominated sulfur sources in low-temperature mineralization to more leached, igneous sulfur isotope signatures in chalcopyrite-rich mineralization (Gemmell and Large, 1992; McDonald et al., 2018). In contrast, in the Trans-Atlantic Geotraverse hydrothermal mound, Gemmell and Sharpe (1998) illustrated that early-stage mineralization was dominated by leached igneous sulfur, whereas higher $\delta^{34}\text{S}$ values preserved in sulfides form later in the paragenetic history and were interpreted to be due to the diminishment of the leached igneous signatures by the ingress of shallow TSR-derived sulfur, resulting in paragenetically late sulfides with $\delta^{34}\text{S} \sim 6$ to 8‰ . This latter signature is similar to the Wolverine sulfur isotope data, and though leached igneous sulfur could have been present in the Wolverine deposit, the lack of any $\delta^{34}\text{S}$ values near 0‰ in any sulfides without biogenic influence makes it challenging to determine whether leached igneous sulfur was important in the sulfur budget of the deposit.

Given the data above, the simplest explanation for the sulfur isotope signatures of the Wolverine sulfides is that they reflect varying contributions from biogenic sulfur derived from BSR or inherited from minerals that contained sulfur derived from BSR and sulfur derived from TSR of seawater sulfate (Figs. 10, 11) (e.g., Bradshaw et al., 2008; Velasco-Acebes et al., 2018; Nozaki et al., 2020). To quantify the varying contributions, a mixing equation has been employed to evaluate the varying proportions of BSR- versus TSR-derived sulfur (modified from Faure, 1986):

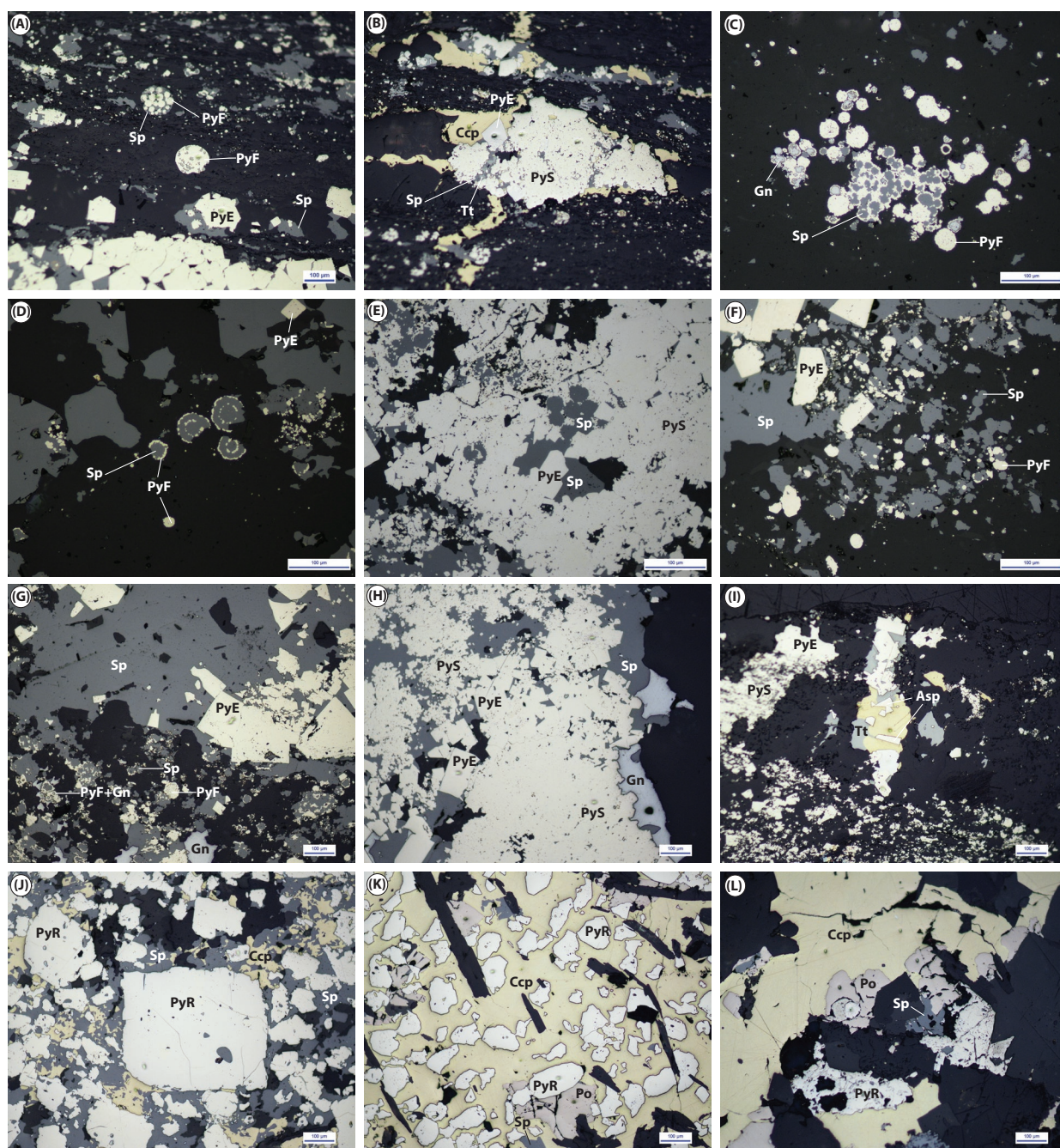


Fig. 6. Photomicrographs of mineralization from the Wolverine deposit. (A) Framboidal pyrite with partial replacement by sphalerite and proximal to euhedral pyrite and anhedral sphalerite (depth 143.24 m). (B) Spongy pyrite with euhedral pyrite nearby, as well as tetrahedrite and sphalerite, and chalcopyrite-sphalerite surrounding mineralization (depth 143.24 m). (C) Framboidal pyrite grains that are partly to fully replaced by sphalerite and galena, often forming the replaced cores with a rim of the remaining framboidal pyrite (depth 143.25 m). (D) Rounded sphalerite with relicts of framboidal (?) pyrite preserved along with sheets of sphalerite and euhedral pyrite (depth 143.25 m). (E) Spongy pyrite with euhedral pyrite nearby. (F) Euhedral pyrite associated with sphalerite as well as rounded grains of sphalerite and pyrite interpreted to have been from the replacement of previous framboidal pyrite (depth 143.25 m). (G) Sphalerite sheets with euhedral pyrite and lesser galena. Also present are framboids that are interpreted to have been partly replaced by sphalerite and galena (depth 144.09 m). (H) Spongy pyrite surrounded by grains of euhedral pyrite, sphalerite, and galena (depth 144.09 m). (I) Euhedral arsenopyrite proximal to chalcopyrite and tetrahedrite. Also present are spongy and euhedral pyrite (depth 144.21 m). (J) Large, rounded pyrite with inclusions of sphalerite and galena and associated with interstitial chalcopyrite and sphalerite (depth 145.58 m). (K) Rounded pyrite grains associated with intergrown chalcopyrite and pyrrhotite (depth 146.61 m). (L) Intergrown chalcopyrite, pyrrhotite, rounded pyrite, and sphalerite (depth 147.08 m). Abbreviations: Asp = arsenopyrite, Ccp = chalcopyrite, Gn = galena, Po = pyrrhotite, PyE = euhedral pyrite, PyF = framboidal pyrite, PyR = rounded pyrite, PyS = spongy pyrite, Sp = sphalerite, Tt = tetrahedrite-tennantite.

$$\delta^{34}\text{S}_{\text{mix}} = X \cdot \delta^{34}\text{S}_{\text{BSR}} + (1 - X) \cdot \delta^{34}\text{S}_{\text{TSR}}, \quad (5)$$

where $\delta^{34}\text{S}_{\text{mix}}$ is the $\delta^{34}\text{S}$ of the sulfide analyzed as part of this study, $\delta^{34}\text{S}_{\text{BSR}}$ is the $\delta^{34}\text{S}$ value of the S derived from BSR, whereas $\delta^{34}\text{S}_{\text{TSR}}$ is the $\delta^{34}\text{S}$ value of the S derived from TSR. The end-member BSR and TSR $\delta^{34}\text{S}$ values present challenges, but we have utilized the average of $\delta^{34}\text{S}$ values of all measured sulfides $<-10\text{‰}$ as being representative of BSR and those $>10\text{‰}$ as being solely from TSR; these $\delta^{34}\text{S}$ values are -18.6‰ and 12.1‰ for BSR and TSR, respectively. The X in the equation above is a proportionality factor that ranges between 1 (100% BSR sulfur) and 0 (0% BSR sulfur), and for samples that had $\delta^{34}\text{S}$ with values less than -18.6‰ or greater than 12.1‰ it was assumed they had 100% BSR- or TSR-derived sulfur, respectively.

Modeling results are shown in Figure 13 and summarized in Table 3; results for individual samples are presented in Appendix 1, Table A2. In general, the percentage of BSR-influenced sulfides is dominant near the upper part of the drill hole, with the highest abundances of BSR found in the framboidal pyrite. There are also BSR-influenced sulfides in shale-hosted, sphalerite-mudstone-hosted, and sphalerite-pyrite-rich sulfide mineralization; the sphalerite-mudstone-hosted and sphalerite-pyrite-rich sulfides, however, tend toward higher $\delta^{34}\text{S}$ values and evidence for TSR contributions (Fig. 13; Table 3). Given the replacement history of framboidal pyrite by later generations of sulfides, it is highly likely that these mixed signatures reflect new TSR-derived hydrothermal sulfur but also inheritance of BSR-derived sulfur from the framboids that were replaced. Further, the influence of BSR reduces dramatically toward the base of the drill hole within the pyrite- and chalcopyrite-rich mineralization, and in paragenetic stage 2 less than 6.5% of the sulfur was derived from BSR and in most cases $>95\%$ of the sulfur was derived from TSR, consistent with mineralization in these areas having less replacement of framboids and greater contributions from Cu-rich hydrothermal fluids and TSR-derived sulfur. Thus, within the Wolverine deposit, sulfur was derived predominantly from BSR during sedimentation and diagenesis, mixtures of BSR inherited from the diagenetic sulfides and TSR during paragenetic stage 1, and almost exclusively from TSR in paragenetic stage 2 (Fig. 12; Table 3).

Importance of ambient sedimentary environment in the formation of seafloor replacement VMS mineralization

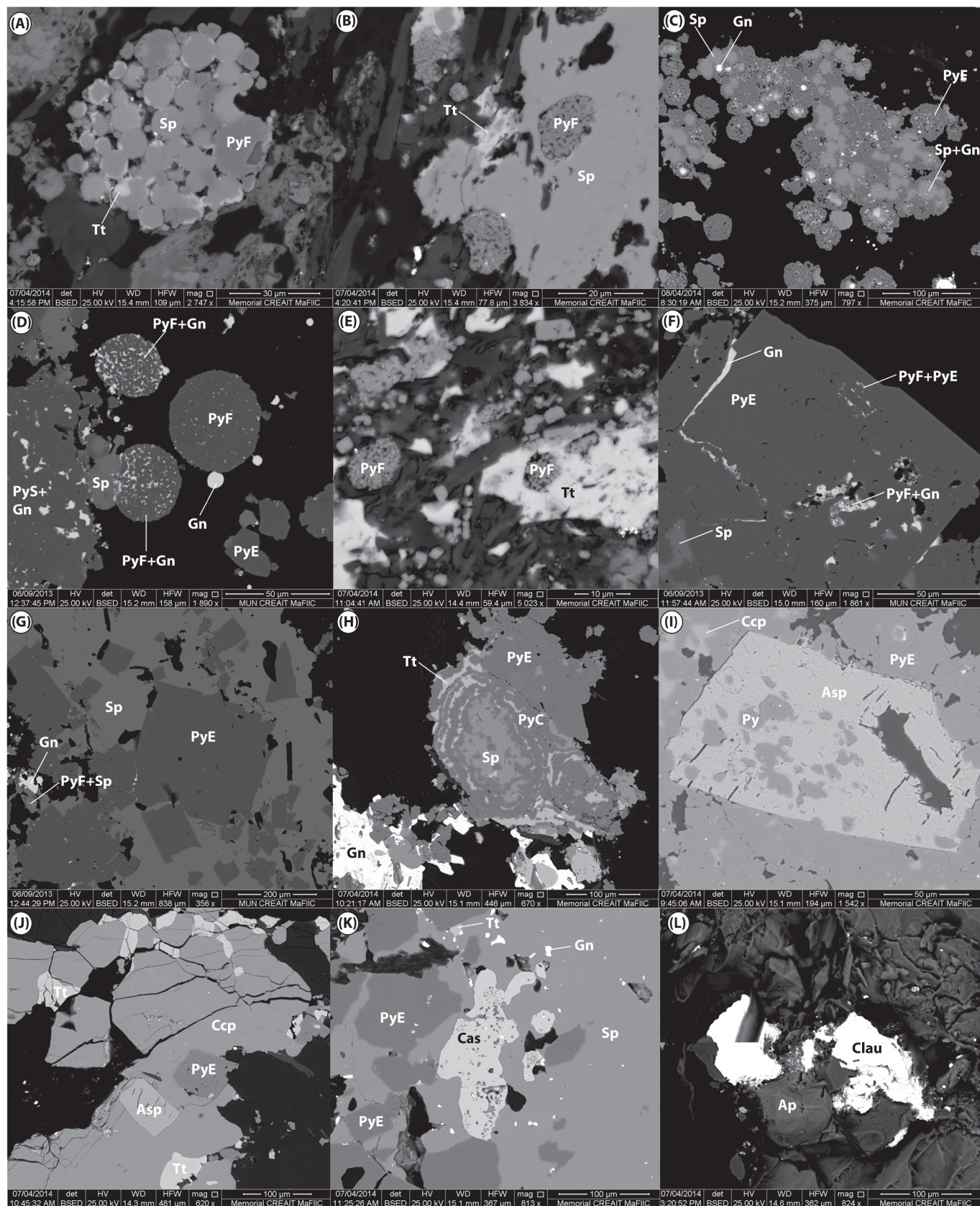
Table 1. Minerals in the Wolverine VMS Deposit and Their Mineral Formulas

Mineral	Mineral formula
Major phases	
Pyrite	FeS_2
Sphalerite	ZnS
Galena	PbS
Chalcopyrite	CuFeS_2
Tetrahedrite	$(\text{Cu}, \text{Fe}, \text{Zn}, \text{Ag})_{12}\text{Sb}_4\text{S}_{13}$
Pyrrhotite	Fe_{1-x}S
Minor phases	
Arsenopyrite	FeAsS
Stannite	$\text{Cu}_2\text{FeSnS}_4$
Cassiterite	SnO_2
Clausthalite	PbSe
Naumannite	Ag_2Se

Abbreviation: VMS = volcanogenic massive sulfide

The Wolverine deposit has strong textural and isotopic relationships, implying that replacement of muds and framboidal pyrite was important in the formation of replacement-style mineralization. These relationships have also been seen globally. For example, Piercey (2015) suggested that seafloor replacement deposits in mud-rich sequences could form from the mixing of VMS-bearing hydrothermal fluids with bacteria-derived H_2S present in pore fluids in the muds and suggested that framboids could have acted as nuclei for new sulfide growth from postframboid VMS-related hydrothermal fluids. Velasco-Acebes et al. (2018) showed that in some Iberian pyrite belt deposits, replacement-style sulfide mineralization formed from mixing between BSR-derived sulfur and that from hydrothermal sources, whether leached igneous or TSR-derived sulfur. They also demonstrated similar variations in sulfur isotope signatures with pyrite texture and mound evolution as observed in this study, demonstrating that diagenetic framboidal pyrite served as nuclei on which new hydrothermal sulfides formed. Nozaki et al. (2024) have found similar isotopic and mineralogical relationships in replacement-type sulfides in the Ezuri Kuroko-type deposit in northeastern Japan, and Nozaki et al. (2020, 2021) have shown similar isotopic and textural relationships in modern sea-floor massive sulfides from the Okinawa trough. In all the deposits above and in our results presented herein, there is a demonstrable relationship between the pre-hydrothermal diagenetic history of the sedimentary rocks proximal to mineralization, including BSR of seawater sulfate and framboid formation, with the framboids serving as nuclei to

Fig. 7. Backscattered electron (BSE) scanning electron microscope (SEM) images of mineralization from the Wolverine deposit. (A) Nanoscale image of framboid with individual buds replaced by sphalerite and tetrahedrite (depth 143.24 m). (B) Framboidal pyrite nuclei surrounded by sheet of sphalerite and tetrahedrite (depth 143.24 m). (C) Framboidal pyrite that is partly replaced by galena and sphalerite (depth 144.09 m). (D) Framboidal pyrite with fine-grained galena found in between framboidal buds and surrounded by spongy pyrite and galena (depth 144.09 m). (E) Pyrite framboids surrounded by tetrahedrite with minor fibrous sericite and chlorite (depth 144.21 m). (F) Euhedral pyrite grain with inclusion of framboidal and euhedral pyrite and inclusions of galena and lesser sphalerite (depth 143.96 m). (G) Euhedral pyrite within sphalerite and galena (depth 144.09 m). (H) Colloform pyrite with interstitial tetrahedrite and sphalerite and surrounded by euhedral pyrite and galena (depth 143.55 m). (I) Euhedral arsenopyrite with inclusions of pyrite, surrounded by euhedral pyrite and lesser chalcopyrite (depth 143.55 m). (J) Intergrown chalcopyrite, euhedral pyrite, euhedral arsenopyrite, and tetrahedrite (depth 144.21 m). (K) Anhedral cassiterite intergrown with euhedral pyrite, sphalerite, and galena (depth 144.85 m). (L) Fine clausenthalite intergrown with apatite (depth 146.85 m). Abbreviations: Ap = apatite, Asp = arsenopyrite, Cas = cassiterite, Ccp = chalcopyrite, Clau = clausenthalite, Gn = galena, Py = pyrite, PyC = colloform pyrite, PyE = euhedral pyrite, PyF = framboidal pyrite, PyS = spongy pyrite, Sp = sphalerite, Tt = tetrahedrite-tennantite.



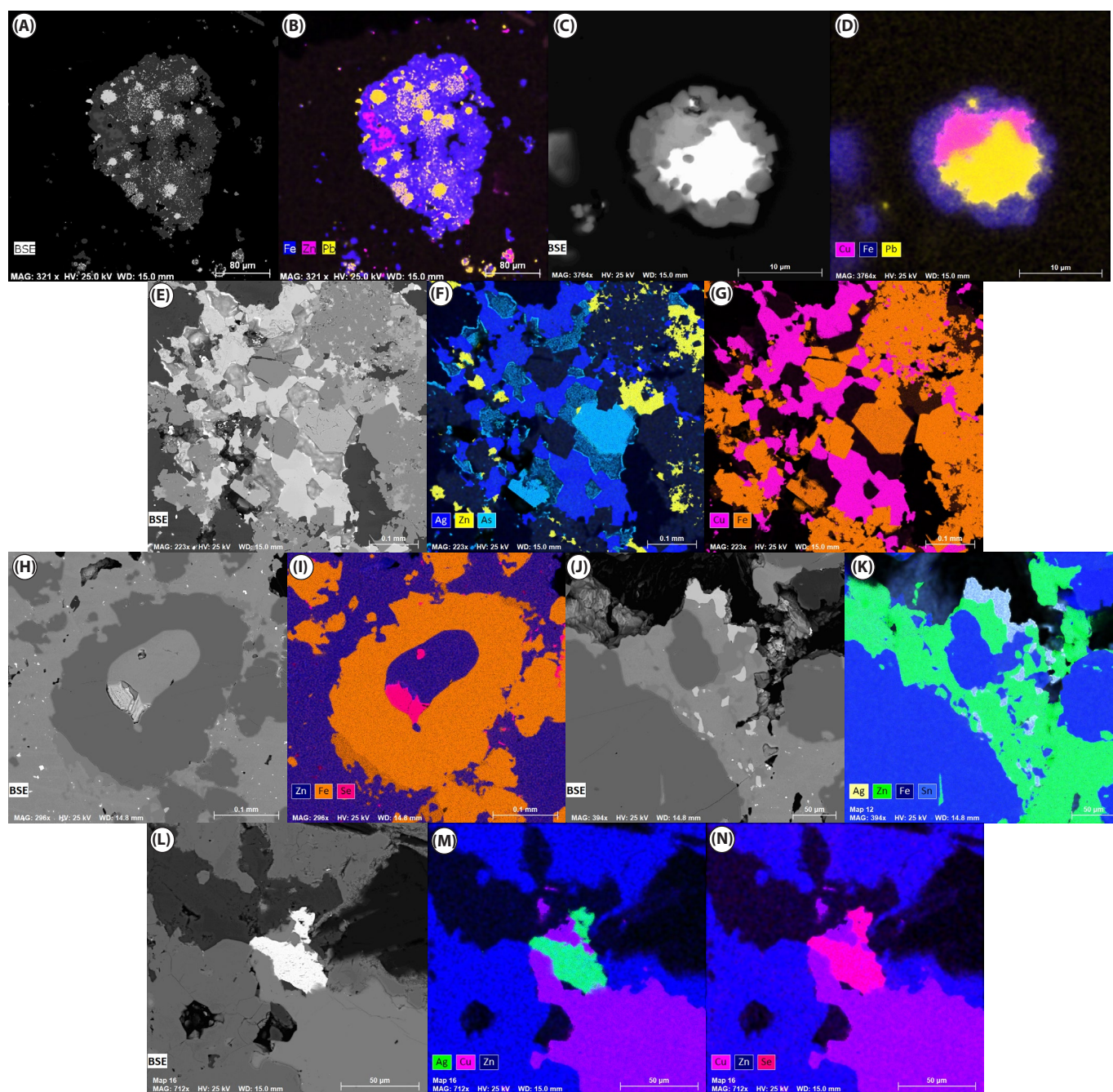


Fig. 8. Semiquantitative scanning electron microscope (SEM)-energy dispersive spectrometry (EDS) maps and backscattered electron (BSE)-SEM images of mineralization from the Wolverine deposit. (A) Coalesced framboidal cluster that is partly replaced by sphalerite and chalcopyrite (depth 143.25 m). (B) SEM-EDS map of (A). (C) Framboid with replacement of its core by chalcopyrite and galena (depth 143.55 m). (D) SEM-EDS map of (C). (E) Intergrown Ag-rich tetrahedrite, arsenopyrite, and sphalerite (depth 143.55 m). (F, G) SEM-EDS maps of (E). (H) Clausthalite intergrown with sphalerite and pyrite (depth 145.58 m). (I) SEM-EDS map of (H). (J) Intergrown pyrite, Ag-bearing tetrahedrite, and cassiterite (depth 145.58 m). (K) SEM-EDS map of (J). (L) Naumannite intergrown with sphalerite and chalcopyrite (depth 146.40 m). (M, N) SEM-EDS maps of (L).

facilitate subsequent replacement-style mineralization.

What is unique about the Wolverine deposit is the textural and isotopic preservation of this initial stage of subseafloor replacement (stage 1) and subsequent evolution via zone refining (stage 2; Fig. 14). Prior to the formation of mineralization in the Wolverine deposit, there was deposition of mudstones,

partial diagenesis, and the formation of framboidal pyrite via BSR of seawater sulfate, coupled with the likely accumulation of H_2S in the sediment pore fluids. This environment was likely water rich given that unconsolidated mud prior to lithification and diagenesis contains appreciable water (e.g., Potter et al., 2005). Thus, the sedimentary package would have been

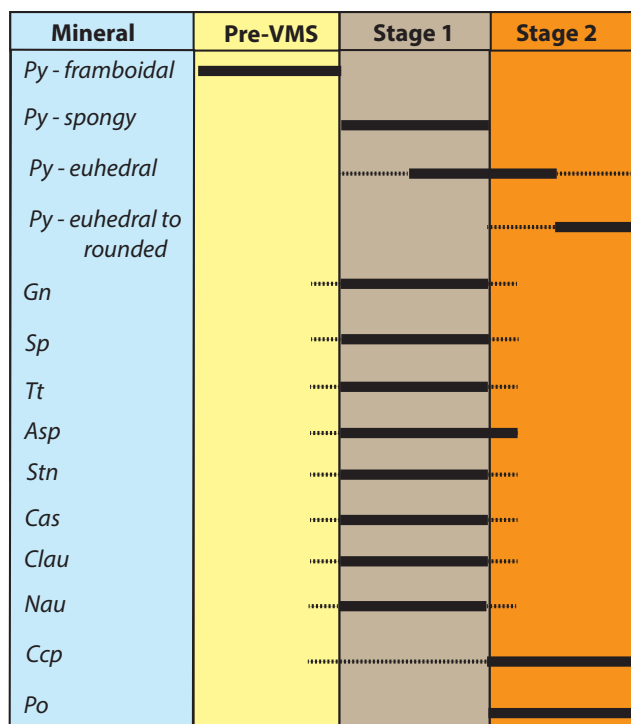


Fig. 9. Paragenetic chart for mineralization stages in the Wolverine deposit. Abbreviations: Asp = arsenopyrite, Cas = cassiterite, Ccp = chalcopyrite, Clau = clausenthalite, Gn = galena, Nau = naumannite, Po = pyrrhotite, Py = pyrite, Sp = sphalerite, Tt = tetrahedrite-tennantite, VMS = volcanogenic massive sulfide.

ideal for precipitating sulfide mineralization below the sea floor, as the mud would have had abundant water to mix with upwelling hydrothermal fluids and potential H_2S to bond with upwelling metal-rich fluids, both of which would have caused sulfide precipitation. The framboidal pyrite in the sediment also served as nuclei for the precipitation and overgrowth of new sulfide minerals via recrystallization and dissolution and replacement of framboids by sphalerite, galena, and chalcopyrite during stage 1 mineralization and, to a lesser extent, during stage 2 mineralization (Fig. 14B).

The downhole textural and paragenetic shifts in pyrite lead to more rounded forms in stage 2 mineralization. The presence of chalcopyrite disease in stage 1 sphalerite and the abundance of chalcopyrite-pyrrhotite-rounded pyrite toward the base of the sulfide mineralization suggest that stage 2 mineralization involved high-temperature, reducing Cu-rich fluids that replaced stage 1 mineralization by dissolution and replacement (e.g., Eldridge et al., 1983; Large, 1992; Ohmoto, 1996). It is envisioned that stage 2 of deposit evolution involved the influx of Cu-rich fluids, dissolution of preexisting Zn-Pb-(Ag-Se-Sn)-rich sulfides, and subsequent reprecipitation of the dissolved Zn and other elements beneath a layer of mud near the sea-floor-subseafloor interface. This process of dissolution, remobilization of Zn, and subsequent reprecipitation beneath the mud-sulfide interface was partly responsible for the high-grade Zn found in the Wolverine deposit. In particular, without this mud-sulfide interface the remobilized Zn would have dissipated into the overlying water column and not reprecipitated; however,

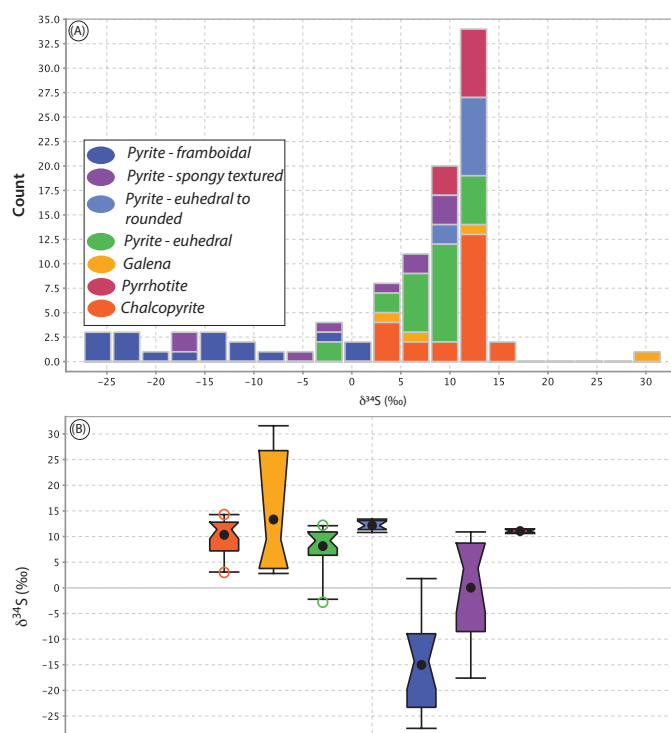


Fig. 10. Sulfur isotope data for the Wolverine deposit. (A) Histogram of sulfur isotope results (bin width = 2.95). (B) Notched box and whisker plot illustrating variations in the population. In this plot for each population, the extents of the boxes reflect the interquartile range of the 1st and 3rd quartiles, the whiskers reflect the minima and maxima, the symbols reflect outliers, the solid dot reflects the mean, and the notch reflects the median.

the mud-sulfide interface had existing sulfides, framboidal pyrite, and potential H_2S in pore waters that ensured the reprecipitation of remobilized Zn resulting in higher Zn grades (e.g., Schardt and Large, 2009; Piercey, 2015; Piercey et al., 2015).

The work herein has demonstrated that replacement of mud rich in framboidal pyrite and likely H_2S was important in initiating subseafloor replacement-style mineralization and enhanced zone refining in the Wolverine deposit, which collectively led to the metal zoning and high-grade mineralization found in this deposit. These processes are likely present in other sediment-rich VMS deposits globally and were likely important in forming both large and high-grade VMS deposits (e.g., Piercey et al., 2015).

Conclusion

The Wolverine deposit has exceptionally well-preserved replacement-style VMS mineralization. Prior to mineralization, in the host sediments framboidal pyrite (and likely H_2S in pore fluids) formed during diagenesis in response to BSR of seawater sulfate. This diagenetic stage was followed by two stages of mineralization. The first stage of mineralization involved a low-temperature hydrothermal stage ($<300^\circ C$) with the deposition of Zn-Pb-(Ag-Se-Sn)-rich mineralization, where there was macroscale replacement of mudstones. In addition, there was microscale partial to full replacement of framboidal pyrite by sphalerite-galena and lesser chalcopyrite, transformation of framboidal pyrite into spongy pyrite, and new growth of

Table 2. Sulfur Isotope Data for Minerals From the Wolverine VMS Deposit

Sample ¹	Depth (m)	Host	Mineral	$\delta^{34}\text{S}$ (‰)
WV14324 Ccp31	143.24	Shale	Chalcopyrite	7.2
WV14324 Ccp51	143.24	Shale	Chalcopyrite	7.2
WV14421 Ccp1	144.21	Sp-py-rich sulfides	Chalcopyrite	4.5
WV14421 Ccp11	144.21	Sp-py-rich sulfides	Chalcopyrite	4.3
WV14421 Ccp21	144.21	Sp-py-rich sulfides	Chalcopyrite	3.0
WV14421 Ccp41	144.21	Sp-py-rich sulfides	Chalcopyrite	3.4
WV14558 Ccp11	145.58	Py-rich sulfides	Chalcopyrite	11.0
WV14558 Ccp12	145.58	Py-rich sulfides	Chalcopyrite	11.0
WV14558 Ccp22	145.58	Py-rich sulfides	Chalcopyrite	12.2
WV14558 Ccp21	145.58	Py-rich sulfides	Chalcopyrite	11.4
WV14558 Ccp22b	145.58	Py-rich sulfides	Chalcopyrite	10.5
WV14558 Ccp23	145.58	Py-rich sulfides	Chalcopyrite	10.1
WV14641 Ccp11	146.41	Ccp-rich sulfides	Chalcopyrite	12.1
WV14641 Ccp12	146.41	Ccp-rich sulfides	Chalcopyrite	11.2
WV14641 Ccp21	146.41	Ccp-rich sulfides	Chalcopyrite	11.9
WV14641 Ccp22	146.41	Ccp-rich sulfides	Chalcopyrite	12.6
WV14708 Ccp11	147.08	Ccp-rich sulfides	Chalcopyrite	12.7
WV14708 Ccp12	147.08	Ccp-rich sulfides	Chalcopyrite	12.8
WV14708 Ccp31	147.08	Ccp-rich sulfides	Chalcopyrite	13.3
WV14708 Ccp32	147.08	Ccp-rich sulfides	Chalcopyrite	14.3
WV14708 Ccp21	147.08	Ccp-rich sulfides	Chalcopyrite	13.7
WV14708 Ccp22	147.08	Ccp-rich sulfides	Chalcopyrite	13.2
WV14708 Ccp23	147.08	Ccp-rich sulfides	Chalcopyrite	14.2
WV14409 Gn11	144.09	Sp-rich replacement sulfides	Galena	31.6
WV14409 Gn12	144.09	Sp-rich replacement sulfides	Galena	12.2
WV14409 Gn21	144.09	Sp-rich replacement sulfides	Galena	6.7
WV14409 Gn31	144.09	Sp-rich replacement sulfides	Galena	2.8
WV14324 Py3E1	143.24	Shale	Pyrite - euhedral	10.9
WV14324 Py5E1	143.24	Shale	Pyrite - euhedral	8.0
WV14324 Py4E1	143.24	Shale	Pyrite - euhedral	11.9
WV14324 Py4E2	143.24	Shale	Pyrite - euhedral	9.8
WV14409 Py4	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	9.2
WV14409 Py1E1	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	6.4
WV14409 Py1E2	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	6.3
WV14409 Py2E1	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	3.9
WV14409 Py2E2	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	7.3
WV14409 Py31	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	9.6
WV14409 Py3E2	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	8.9
WV14409 Py3E2b	144.09	Sp-rich replacement sulfides	Pyrite - euhedral	8.2
WV14421 Py1E1	144.21	Sp-py-rich sulfides	Pyrite - euhedral	-2.8
WV14421 Py1E2	144.21	Sp-py-rich sulfides	Pyrite - euhedral	-0.9
WV14421 Py2E1	144.21	Sp-py-rich sulfides	Pyrite - euhedral	4.9
WV14421 Py3E1	144.21	Sp-py-rich sulfides	Pyrite - euhedral	7.7
WV14421 Py4E1	144.21	Sp-py-rich sulfides	Pyrite - euhedral	5.4
WV14558 Py1E1	145.58	Py-rich sulfides	Pyrite - euhedral	10.7
WV14558 Py1E2	145.58	Py-rich sulfides	Pyrite - euhedral	11.0
WV14558 Py2E1b	145.58	Py-rich sulfides	Pyrite - euhedral	10.7
WV14558 Py2E4	145.58	Py-rich sulfides	Pyrite - euhedral	11.1
WV14558 Py2E5	145.58	Py-rich sulfides	Pyrite - euhedral	10.9
WV14558 Py2E1	145.58	Py-rich sulfides	Pyrite - euhedral	11.2
WV14558 Py2E2	145.58	Py-rich sulfides	Pyrite - euhedral	12.2
WV14558 Py2E3	145.58	Py-rich sulfides	Pyrite - euhedral	10.9
WV14641 Py1E1	146.61	Ccp-rich sulfides	Pyrite - euhedral to rounded	13.4
WV14641 Py1E2	146.61	Ccp-rich sulfides	Pyrite - euhedral to rounded	12.1
WV14641 Py21	146.61	Ccp-rich sulfides	Pyrite - euhedral to rounded	11.5
WV14641 Py22	146.61	Ccp-rich sulfides	Pyrite - euhedral to rounded	11.5
WV14708 Py12	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	10.9
WV14708 Py21	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	12.2
WV14708 Py11	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	10.8
WV14708 Py22	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	13.2
WV14708 Py31	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	12.9
WV14708 Py32	147.08	Ccp-rich sulfides	Pyrite - euhedral to rounded	13.1
WV14324 Py1F1	143.24	Shale	Pyrite - framboidal	-0.8
WV14324 Py1F2	143.24	Shale	Pyrite - framboidal	-7.5

Table 2. (Cont.)

Sample ¹	Depth (m)	Host	Mineral	$\delta^{34}\text{S}$ (‰)
WV14324 Py1F3	143.24	Shale	Pyrite - framboidal	-14.3
WV14324 Py2F1	143.24	Shale	Pyrite - framboidal	-24.5
WV14324 Py2F2	143.24	Shale	Pyrite - framboidal	-27.4
WV14324 Py3F1	143.24	Shale	Pyrite - framboidal	-18.8
WV14324 Py3F2	143.24	Shale	Pyrite - framboidal	1.8
WV14324 Py4F1	143.24	Shale	Pyrite - framboidal	-25.3
WV14324 Py4F2	143.24	Shale	Pyrite - framboidal	-23.0
WV14409 Py3F1	144.09	Sp-rich replacement sulfides	Pyrite - framboidal	-10.6
WV14409 Py4F1	144.09	Sp-rich replacement sulfides	Pyrite - framboidal	-21.7
WV14409 Py4F2	144.09	Sp-rich replacement sulfides	Pyrite - framboidal	-14.2
WV14409 Py3F2	144.09	Sp-rich replacement sulfides	Pyrite - framboidal	-17.6
WV14409 Py3F3	144.09	Sp-rich replacement sulfides	Pyrite - framboidal	-23.6
WV14421 Py2F1	144.21	Sp-py-rich sulfides	Pyrite - framboidal	-10.4
WV14421 Py2F2	144.21	Sp-py-rich sulfides	Pyrite - framboidal	-3.2
WV14421 Py2F3	144.21	Sp-py-rich sulfides	Pyrite - framboidal	-14.3
WV14324 Py3C1	143.24	Shale	Pyrite - spongy textured	10.9
WV14324 Py3C2	143.24	Shale	Pyrite - spongy textured	5.3
WV14409 Py4S1	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	2.3
WV14409 Py4S2	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	-17.6
WV14409 Py4S3	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	-16.1
WV14409 Py1S1	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	6.2
WV14409 Py2S1	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	8.6
WV14409 Py3S1	144.09	Sp-rich replacement sulfides	Pyrite - spongy textured	-6.0
WV14421 Py3S1	144.21	Sp-py-rich sulfides	Pyrite - spongy textured	-2.4
WV14421 Py4S1	144.21	Sp-py-rich sulfides	Pyrite - spongy textured	9.1
WV14641 Po21	146.61	Ccp-rich sulfides	Pyrrhotite	11.0
WV14641 Po22	146.61	Ccp-rich sulfides	Pyrrhotite	10.8
WV14641_Po11	146.61	Ccp-rich sulfides	Pyrrhotite	11.2
WV14641_Po12	146.61	Ccp-rich sulfides	Pyrrhotite	10.6
WV14708 Po11	147.08	Ccp-rich sulfides	Pyrrhotite	11.0
WV14708 Po12	147.08	Ccp-rich sulfides	Pyrrhotite	11.2
WV14708 Po21	147.08	Ccp-rich sulfides	Pyrrhotite	10.6
WV14708 Po22	147.08	Ccp-rich sulfides	Pyrrhotite	11.4
WV14708 Po31	147.08	Ccp-rich sulfides	Pyrrhotite	11.4
WV14708 Po32	147.08	Ccp-rich sulfides	Pyrrhotite	11.5

Abbreviations: Ccp = chalcopyrite, Gn = galena, Po = pyrrhotite, Py = pyrite, Sp = sphalerite

¹All samples come from drill hole WV05-165 at depths given above (location 440018.97E 6810901.47N, UTM Zone 9, NAD27 datum)

Table 3. Results From Sulfur Isotope Modeling

Mineral	Sulfide facies	% BSR -	% BSR -	% BSR -	% BSR -	% TSR -	% TSR -	% TSR -	% TSR -
		Min	Max	Mean	Median	Min	Max	Mean	Median
Chalcopyrite	Chalcopyrite-rich sulfides	0	3	0	0	97	100	100	100
Chalcopyrite	Pyrite-rich sulfides	0	7	4	4	93	100	96	96
Chalcopyrite	Shale-hosted sulfides	16	16	16	16	84	84	84	84
Chalcopyrite	Sphalerite-pyrite-rich sulfides	25	30	27	27	70	75	73	73
Galena	Sphalerite-rich replacement sulfides	0	30	12	9	70	100	88	91
Pyrite - euhedral	Pyrite-rich sulfides	0	4	3	4	96	100	97	96
Pyrite - euhedral	Shale-hosted sulfides	1	13	6	6	87	99	94	94
Pyrite - euhedral	Sphalerite-pyrite-rich sulfides	14	49	30	24	51	86	70	76
Pyrite - euhedral	Sphalerite-rich replacement sulfides	8	27	15	14	73	92	85	86
Pyrite - rounded	Chalcopyrite-rich sulfides	0	4	1	0	96	100	99	100
Pyrite - framboidal	Shale-hosted sulfides	34	100	81	100	0	66	19	0
Pyrite - framboidal	Sphalerite-rich replacement sulfides	74	100	91	97	0	26	9	3
Pyrite - framboidal	Sphalerite-pyrite-rich sulfides	50	86	70	73	14	50	30	27
Pyrite - spongy	Shale-hosted sulfides	4	22	13	13	78	96	87	87
Pyrite - spongy	Sphalerite-rich replacement sulfides	11	97	52	45	3	89	48	55
Pyrite - spongy	Sphalerite-pyrite-rich sulfides	10	47	28	28	53	90	72	72
Pyrrhotite	Chalcopyrite-rich sulfides	2	5	3	3	95	98	97	97

Abbreviations: BSR = bacterial sulfate reduction, TSR = thermochemical sulfate reduction

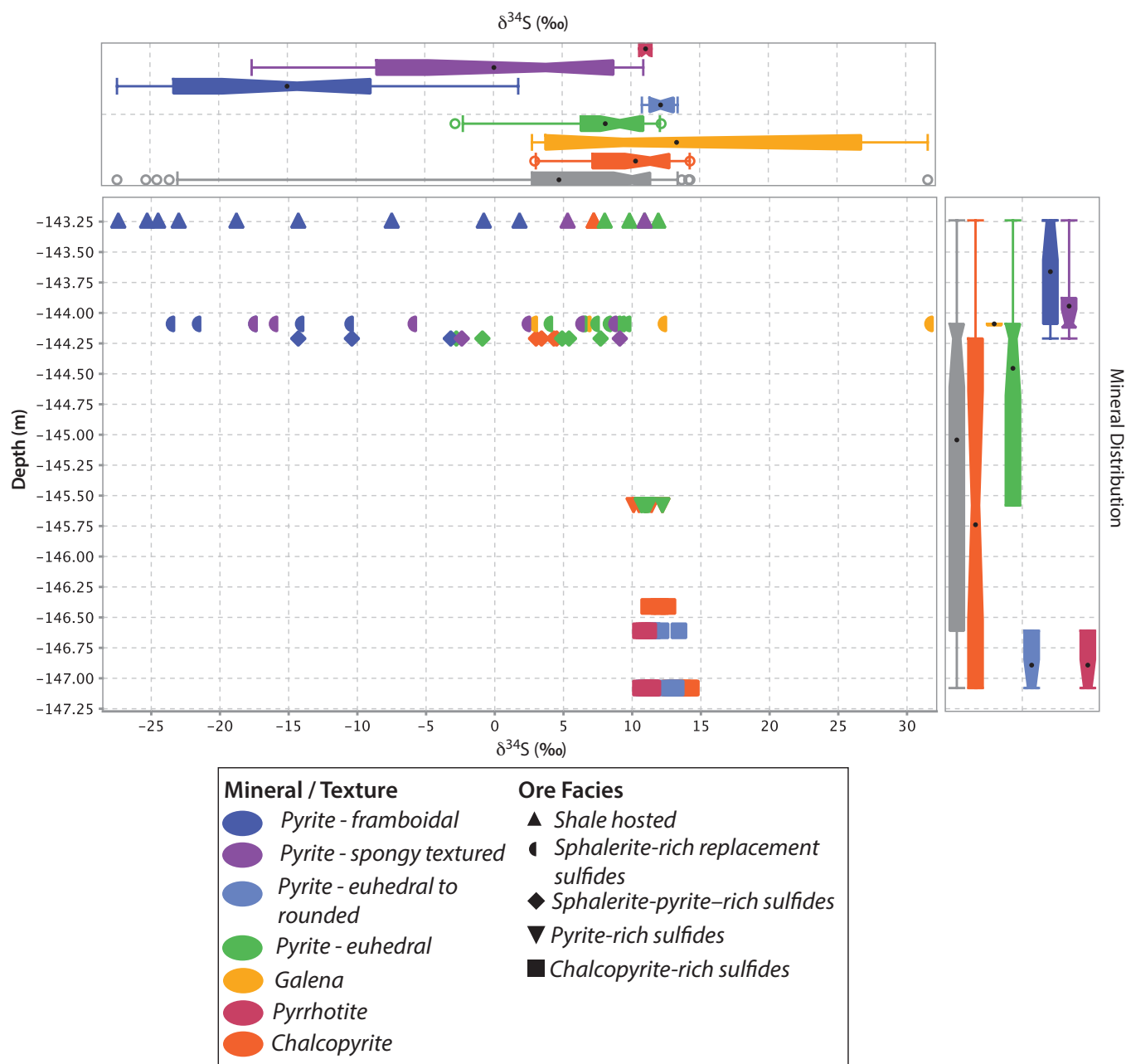
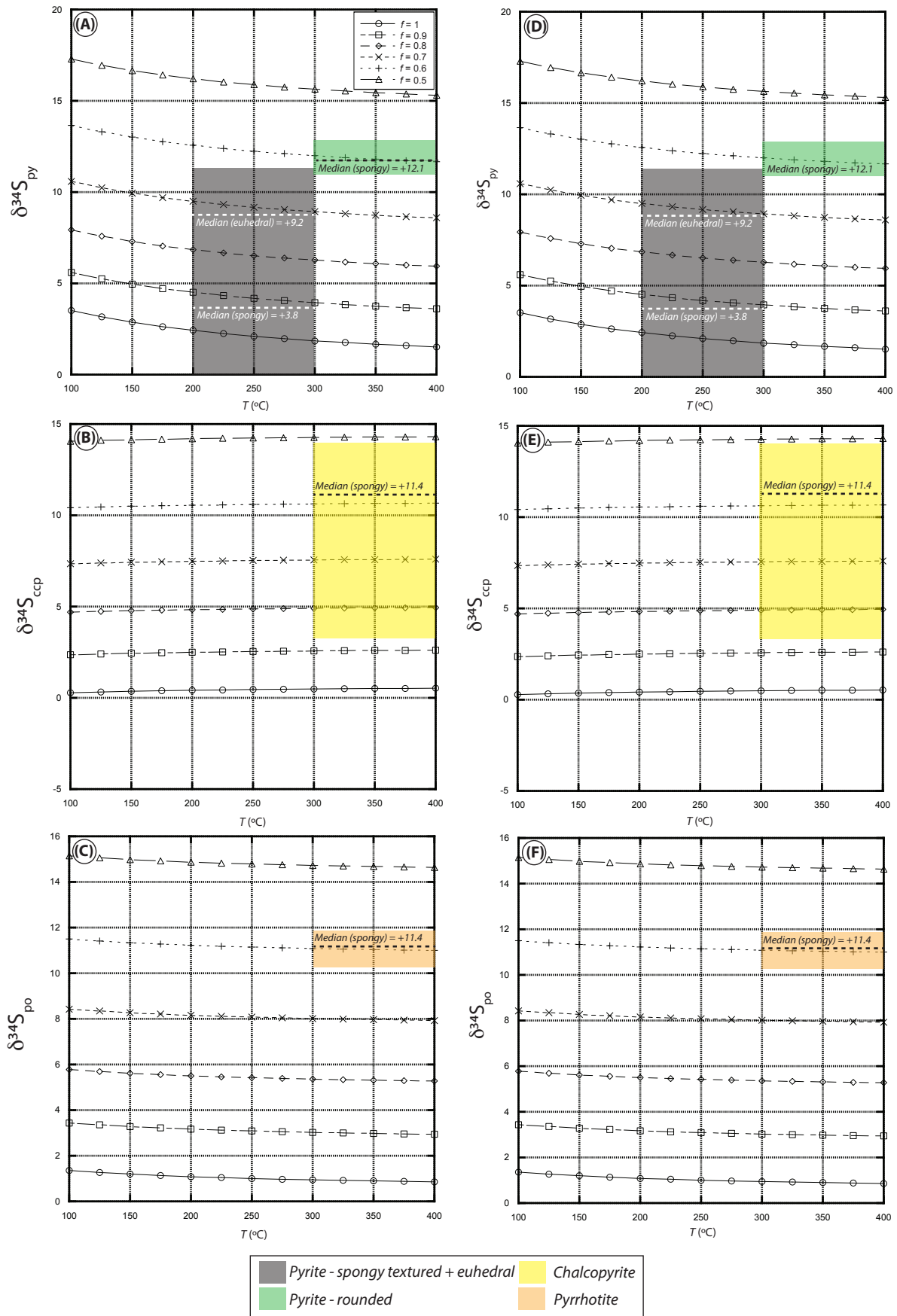


Fig. 11. Downhole profile of sulfur isotope data from the Wolverine deposit showing variation in $\delta^{34}\text{S}$ as a function of depth in drill hole WV05-165. Also shown are the box and whisker plot above the plot and the distribution of sulfide mineral types as a vertical panel. The box plots and symbology are the same as in Figure 10. The gray box reflects the distribution of all data and mineral types in both box and whisker plots that are part of the downhole profile.

Fig. 12. Plots of calculated $\delta^{34}\text{S}$ against temperature for thermochemical sulfate reduction (TSR) of Early Mississippian seawater sulfate ($\sim 20\text{‰}$) at 250°C (A-C) and 350°C (D-F) for pyrite, chalcopyrite, and pyrrhotite, respectively, coupled with cooling pathways for a fluid generated at a given f value. Boxes shown for various mineral textures and types reflect the range of $\delta^{34}\text{S}$ values, coupled with notes for median values for each mineral or mineral texture type, whereas temperatures of deposition are assumed based on assemblage associations and inferences from thermodynamic and modern sea-floor massive sulfide data. Many of the higher $\delta^{34}\text{S}$ values observed in sulfides from Wolverine are consistent with input from TSR of Early Mississippian seawater sulfate. Abbreviations: ccp = chalcopyrite, po = pyrrhotite, py = pyrite.



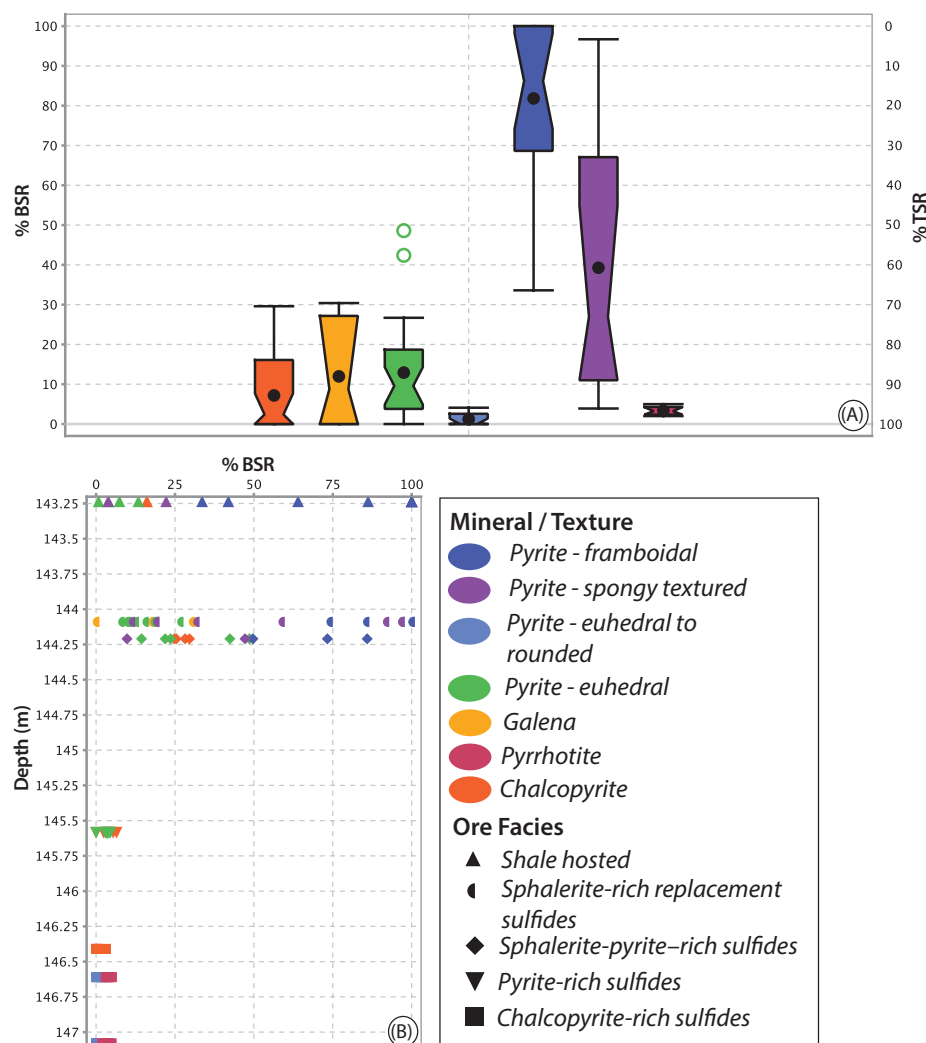


Fig. 13. Results from sulfur isotope mixing models. (A) Box and whisker plots for mixing between bacterial sulfate reduction (BSR)- and thermochemical sulfate reduction (TSR)-derived sulfur. The results illustrate that the framboidal and the spongy-textured pyrite have the greater influence from BSR, whereas pyrrhotite and euhedral to rounded pyrite have the least influence, and galena, chalcopyrite, and euhedral pyrite are mixtures between BSR- and TSR-derived sulfur. In this plot for each population, the extents of the boxes reflect the interquartile range of the 1st and 3rd quartiles, the whiskers reflect the minima and maxima, the symbols reflect outliers, the solid dot reflects the mean, and the notch reflects the median. (B) Downhole profile of the percentage of BSR-derived sulfur in WV05-165. BSR-derived sulfur is restricted to the upper part of the hole and to the shale-hosted, sphalerite-rich replacement, and sphalerite-pyrite-rich sulfides, whereas TSR-derived sulfur dominates in the pyrite- and chalcopyrite-rich sulfides at depth.

euhedral pyrite around existing framboidal and spongy pyrite. This stage of mineralization also involved the deposition of tetrahedrite, arsenopyrite, stannite, cassiterite, clausthalite, and naumannite. The second stage of mineralization (stage 2) involved deposition of chalcopyrite-rounded pyrite-pyrrhotite found predominantly at the base of the deposit, where Cu-rich assemblages crosscut and replaced other phases formed during diagenesis and stage 1 mineralization.

In situ sulfur isotopes from various pyrite textural types, galena, and chalcopyrite from diagenetic and stage 1 mineralization stages have $\delta^{34}\text{S}$ ranging from -27.4 to 12.1‰ , whereas stage 2 pyrite, pyrrhotite, and chalcopyrite have more restricted $\delta^{34}\text{S}$ ranging from 10.1 to 14.3‰ . These variations reflect varying contributions from H_2S derived from BSR, inheritance of BSR-derived sulfur from framboids during replacement, and

hydrothermal H_2S derived from TSR of seawater sulfate.

A model for replacement-style mineralization in the Wolverine deposit is provided. The formation of the deposit was preceded by diagenesis of water-rich muds at the seawater-subseafloor interface, which resulted in the formation of framboidal pyrite and likely H_2S in sedimentary pore fluids, both in response to BSR of seawater sulfate. The first stage of mineralization involved low-temperature, $<300^\circ\text{C}$ Zn-Pb-(Ag-Se-Sn)-rich fluids that mixed with water ($\pm$ BSR-derived H_2S) in the mud, dissolved and partly to fully replaced the framboidal pyrite, and utilized framboidal pyrite to nucleate new sulfide mineralization, resulting in the deposition of a sphalerite-rich sulfide assemblage. The final stage of mineralization involved zone refining by hot ($>300^\circ\text{C}$) Cu-rich fluids and involved dissolution and replacement of preexisting Zn-Pb

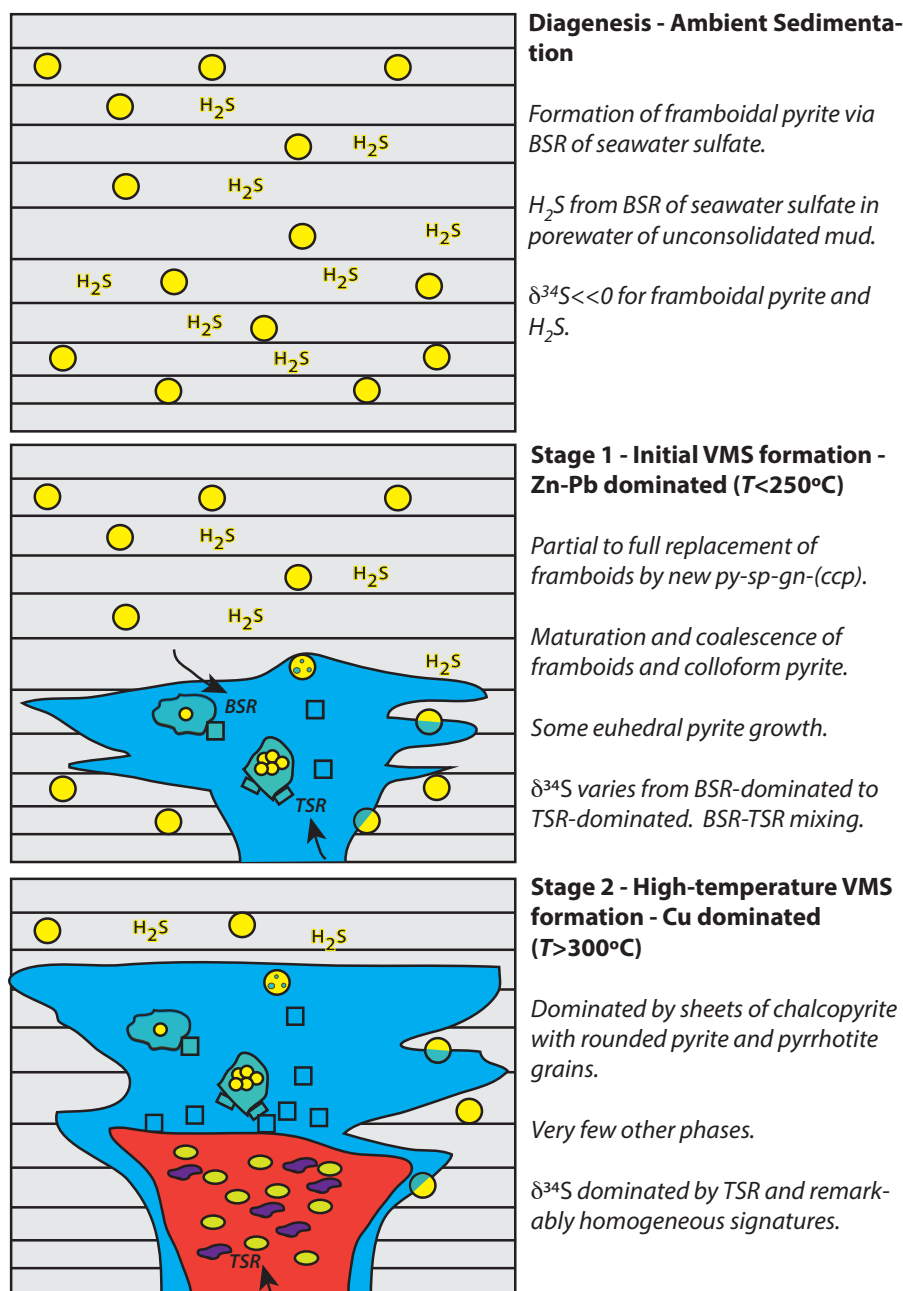


Fig. 14. Model for the evolution of mineralization and sulfur sources within the Wolverine volcanogenic massive sulfide (VMS) deposit. Abbreviations: BSR = bacterial sulfate reduction, ccp = chalcopyrite, gn = galena, py = pyrite, sp = sphalerite, TSR = thermochemical sulfate reduction.

mineralization and deposition of a chalcopyrite-rounded pyrite-pyrrhotite-rich assemblage at the base of the deposit. This stage of mineralization was also marked by a redistribution of the dissolved material and reprecipitation of Zn-rich material beneath a mud or mud-sulfide-rich layer, which is interpreted to have led to Zn grade increases in the mineralization.

This process of hydrothermal sulfide replacement of mud and diagenetic framboidal pyrite, and potential mixing of hydrothermal fluids with bacterial H_2S in sedimentary pore waters, is likely important in many replacement-style VMS deposits and may be important in other sediment-rich hy-

drothermal deposits (e.g., felsic and mafic-siliciclastic VMS, Irish-type, clastic-dominated Zn-Pb, and sediment-hosted Cu deposits).

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