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A NEW SUBSEAFLOOR REPLACEMENT MODEL FOR THE MACMILLAN PASS CLASTIC-DOMINANT Zn-Pb ± Ba DEPOSITS (YUKON, CANADA)

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Abstract

Sedimentary exhalative (SEDEX) deposits are a subset of sediment-hosted massive sulfide deposits and provide our dominant resource of Zn. In the SEDEX model, base metals (Zn, Pb, Fe) are hydrothermally vented into sulfidic (euxinic) seawater and deposited coevally with the organic-rich mudstone host rock, resulting in laterally extensive layered mineralization. In the Selwyn Basin (Canada) at Macmillan Pass, two deposits (Tom, Jason) are well preserved in a succession of Upper Devonian mudstones and are considered type-characteristic examples of the SEDEX deposit model. As with a number of SEDEX deposits, at Macmillan Pass barite is abundant in the succession hosting hydrothermal mineralization. Early work presented a hydrothermal model for barite formation, in which barite coprecipitated with base metal sulfides in a redox-stratified water column. Recently, however, studies have both proposed an alternative diagenetic model for barite formation and provided more precise constraints on the chemistry of the hydrothermal fluid that entered the vent complexes. Here, we present a new model for Macmillan Pass in which sulfide mineralization occurred entirely within the subsurface. The introduction of hot (300°C) hydrothermal fluids into the shallow subsurface (<1-km depth) resulted in the thermal degradation of organic matter and generated CO_2; this promoted barite dissolution, which both provided a source of sulfate for thermochemical sulfate reduction and increased the porosity and permeability within the system. Importantly, there was clear potential for the development of positive feedbacks and self-organization between diagenetic and hydrothermal processes, resulting in highly efficient ore-forming systems. In contrast to the SEDEX model, alteration footprints will be controlled by the mass transfer involved in (barite) replacement reactions rather than hydrothermal venting, and exploration criteria at a district scale should strongly favor highly productive continental margins.

Introduction

Sediment-hosted massive sulfide (SHMS) deposits represent the anomalous enrichment of base metals and sulfur within marine sedimentary rocks (Leach et al., 2005). A subtype of SHMS deposits is hosted by carbonaceous mudstone and has been traditionally referred to as *sedimentary exhalative* (SEDEX; Goodfellow et al., 1993) or, more recently, as *clastic-dominant* (CD) type (Leach et al., 2010). The location of major CD-type deposits is restricted to a limited number of sedimentary basins in the geologic record, and the geologic factors that ultimately control basin fertility remain poorly constrained (Wilkinson, 2013). In the Selwyn Basin (Fig. 1A), CD-type mineralization is in three lower Paleozoic stratigraphic intervals, and the total known Pb and Zn reserves comprise 55 Mt in 17 different deposits (Goodfellow, 2007); only the Paleoproterozoic Mt. Isa-McArthur Basin (Australia; Large et al., 2005) and Paleozoic Kuna Basin (USA; Kelley and Jennings, 2004) contain a greater tonnage of base metals.

In many CD-type systems, the conformable relationship between sulfides (± barite) and the host rock has led to the general acceptance that exhalative processes are an important feature of hydrothermal mineralization (Goodfellow et al., 1993; Goodfellow and Lydon, 2007). In the SEDEX model, cotransportation of barium and base metals occurs in hydrothermal fluids that are exhaled from a vent complex, which is associated with an active fault. A sulfidic (i.e., euxinic; $H_2S > Fe^{2+}$) water column provides the chemical trap, and sulfides and barite precipitate when the hydrothermal fluids are ex-

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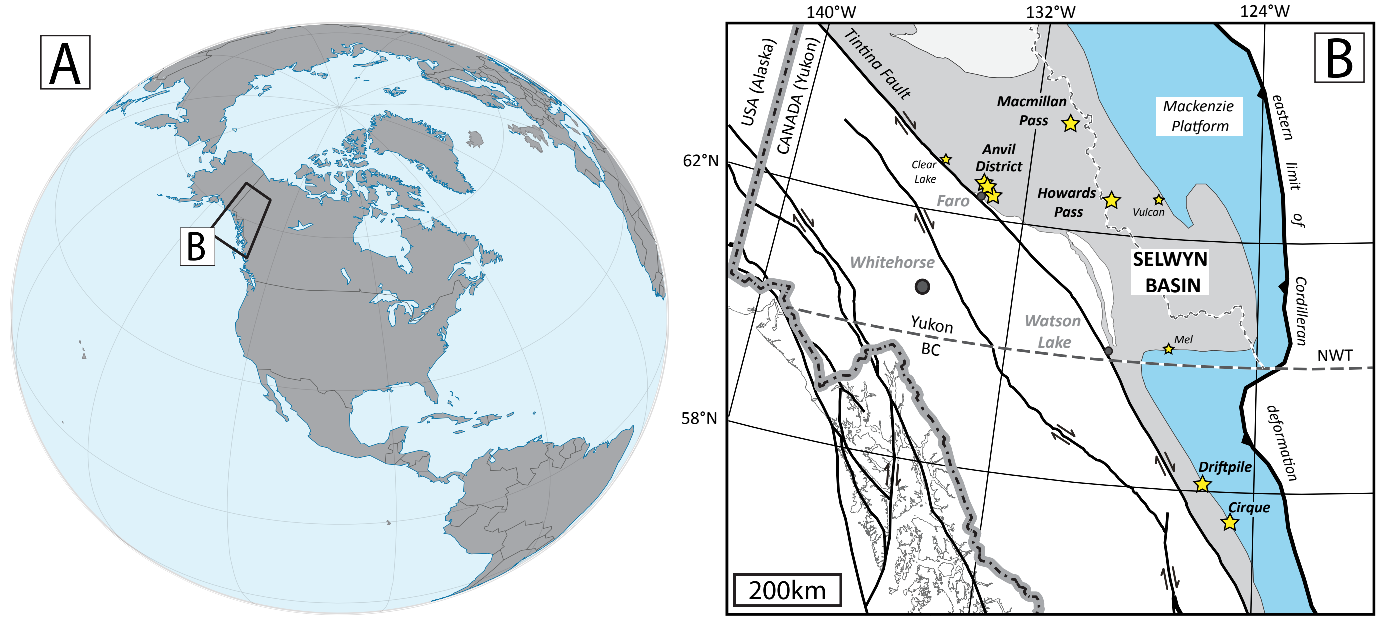

Fig. 1. A. The location of the Selwyn Basin in western North America. B. The regional extent of the Selwyn Basin (gray) and adjoining carbonate platform, with major structural features denoted by thick black lines (modified after Nelson and Colpron, 2007). Stars represent the locations of known shale-hosted massive sulfide deposits.

haled above the sediment water interface (SWI) as either a buoyant plume or dense brine that accumulates in topographic depressions on the paleoseafloor (Sangster, 2002). As vent complexes are rarely well preserved in the geologic record, the brine pool model has frequently been used to invoke migration of metal-bearing brines away from the site of venting (e.g., Sangster, 2018). Implicit within all SEDEX models is the link between euxinic conditions and metallogenesis, which is used to explain the fertility of particular basins in the geologic record (Goodfellow, 1987). Consequently, the absence of active CD-type systems on the modern seafloor has been linked to the pervasive oxygenation of the modern oceans (e.g., Turner, 1992).

In the Macmillan Pass district, Yukon Territory (Canada), two CD-type deposits, Jason and Tom, are hosted in Upper Devonian strata of the Selwyn Basin. The complete deposit architecture (layered mineralization and underlying vent complex) is well preserved at both Jason and Tom (Fig. 2), and these systems have previously been considered type-characteristic examples of ancient SEDEX hydrothermal systems (Gardner and Hutcheon, 1985; Ansdell et al., 1989; Goodfellow et al., 1993). Recently, a series of studies investigated different components of the CD-type systems at Macmillan Pass to improve our understanding of the following: (1) the depositional environment and seawater paleoredox (Magnall et al., 2015, 2018); (2) pathways of sulfate reduction during diagenesis (Magnall et al., 2016a); (3) vent fluid chemistry and base metal solubility (Magnall et al., 2016b); (4) and the paragenesis and mineralogical evolution of the layered mineralization (Magnall et al., 2020). In this contribution, we review the key aspects of these recent studies and propose a new, internally consistent subseafloor replacement model for CD-type mineralization at Macmillan Pass. Rather than coeval formation of barite and sulfides, we describe how diagenetic barite is overprinted by hydrothermal activity beneath the paleoseafloor (Fig. 3). The implications of this new model are then discussed within the broad context of CD-type mineralization in the geologic record and the potential for modern analogues.

A New Model for Subseafloor Replacement at Macmillan Pass

Depositional environment

The organic-rich mudstones that host the mineralization at Macmillan Pass were originally interpreted to have been deposited via pelagic processes in a deep-water, anoxic environment of a restricted basin (Goodfellow, 1987). This depositional model was based on a series of assumptions: (1) the stratiform relationship between sulfide minerals and host rock developed via synsedimentary processes; (2) sulfide precipitation required stratified euxinic conditions, for which the suggested modern analogue was the restricted Black Sea Basin; and (3) accumulation and preservation of sulfides and organic matter were enhanced by anoxic conditions and slow sedimentation rates.

The observations, however, of erosional basal surfaces, graded beds, and lenticular laminations at Tom and Jason (Magnall et al., 2020) are consistent with more energetic depositional conditions (Schieber et al., 2010), rather than truly pelagic sedimentation. Furthermore, since the SEDEX model was developed, depositional models for carbonaceous mudstones have been greatly refined beyond the Black Sea restricted, euxinic basin analogue (Arthur and Sageman, 1994; Smith et al., 2019). Indeed, at Macmillan Pass and in samples from correlative Upper Devonian sections, there is no geochemical evidence to support the Black Sea analogue: for example, Mo-U covariation both at Macmillan Pass (Magnall et al., 2018) and in correlative mudstones from the Mackenzie platform (Kabanov, 2018) preserves no evidence of water mass restriction. This is further supported by δ^{98}Mo values (0.6–1.0‰) and low levels of authigenic Mo enrichment (<30 ppm) preserved in unaltered mudstones surrounding the mineralization at Macmillan Pass, which are consistent with a noneuxinic depositional environment (Magnall et al., 2018). Instead, the high total organic carbon (<5 wt %) and biosiliceous nature of the host rock provide evidence of a highly productive depositional environment, perhaps more analogous to an oxygen minimum zone in a region of nutrient upwelling (Magnall et al., 2015, 2018).

Host-rock diagenetic environment

Diagenetic processes are largely overlooked in the SEDEX model, where sulfide mineralization takes place above the sediment water interface (SWI) and, by definition, predates diagenesis. One of the characteristic features of CD-type deposits is the preservation of highly positive δ^{34}S values in sulfide minerals (Farquhar et al., 2010). In the Selwyn Basin, previous workers have argued that the coupled preservation of positive δ^{34}S values in barite and pyrite represents Rayleigh fractionation effects developed in a euxinic water column (Goodfellow and Jonasson, 1984). The key assumption of Goodfellow and Jonasson (1984) is that both barium and iron were hydrothermally exhaled, and coeval precipitation occurred from seawater that was undergoing progressive sulfate depletion during microbial sulfate reduction (MSR).

More recently, however, Magnall et al. (2016a) proposed that barite and two distinct generations of pyrite formed in a pre-ore, diagenetic environment. The role of two pathways of sulfate reduction during diagenesis was constrained following in situ analyses of δ^{34}S values in both barite and pyrite: negative values preserved by framboidal pyrite are consistent with MSR in open-system conditions (i.e., unlimited sulfate supply); in contrast, the preservation of positive δ^{34}S values is restricted to euhedral pyrite formed during later stages of diagenesis, when sulfate depletion occurred within pore fluids during sulfate-driven anaerobic oxidation of methane (SD-AOM). In modern environments, SD-AOM occurs at the sulfate methane transition zone (SMTZ), where opposing diffusional fluxes of sulfate and methane produce a sharp redox gradient (Jørgensen and Kasten, 2006).

The SMTZ is increasingly being recognized as the location of diagenetic barite formation in organic-rich mudstones from a number of geologic time periods (e.g., Torres et al., 2003). In the diagenetic model for barite formation, barite precipitation occurs initially within microenvironments associated with primary producers (e.g., radiolarians) in the water column (e.g., Dehairs et al., 1980; Martinez-Ruiz et al., 2019). During anoxic diagenesis, however, consumption of sulfate during MSR can result in the development of highly reducing, methane-rich pore fluids that increase barium solubility (Torres et al., 1996; Jørgensen and Kasten, 2006). Reprecipitation of barite then occurs at the SMTZ, when the barium-bearing, methane-rich fluids mix with sulfate within shallower diagenetic pore fluids. At Macmillan Pass, a number of observations support this model for diagenetic barite formation: (1) barite is associated with the pre-ore diagenetic pyrite assemblage (Magnall et al., 2016a) and clearly predates hydrothermal sulfide mineralization (Magnall et al., 2020); and (2) similar occurrences of barite are located in correlative unmin-

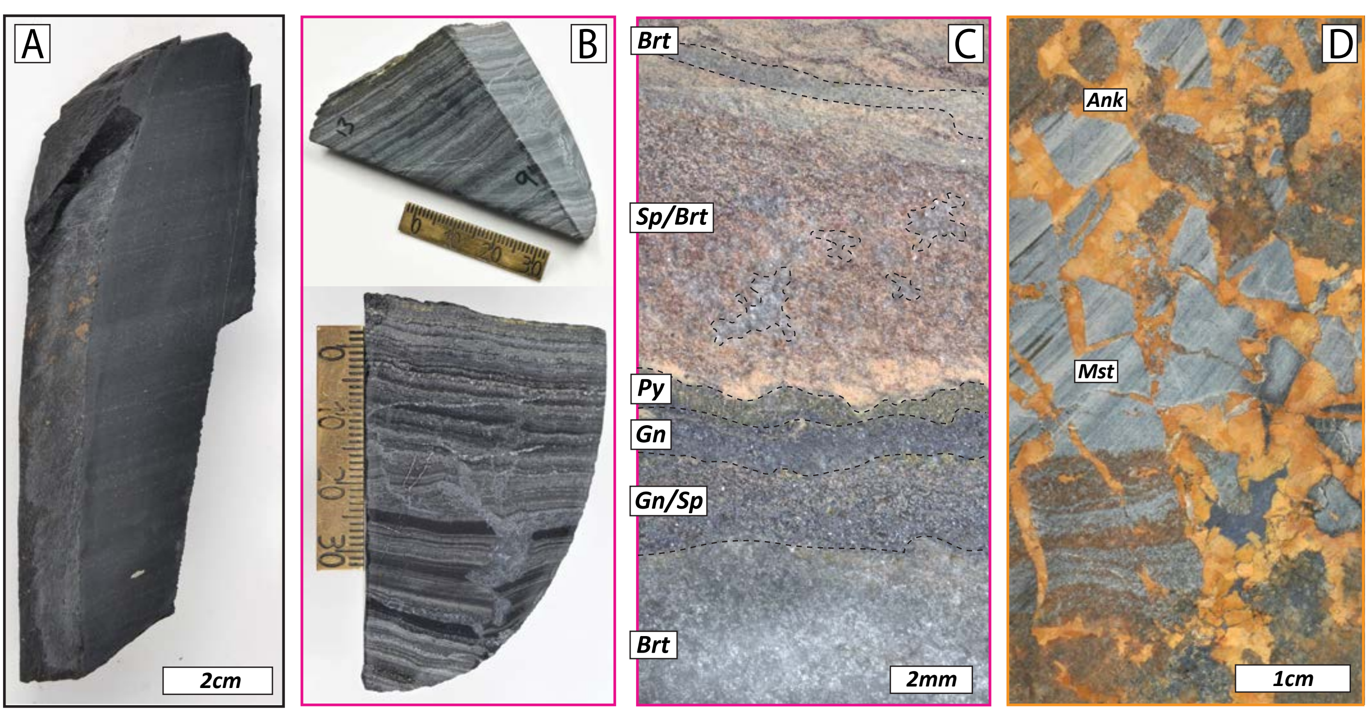

Fig. 2. Photographs of representative samples from the different components of the deposit architecture at Macmillan Pass. A. Carbonaceous mudstone that is the host rock to mineralization. B. Weak layered mineralization, showing an irregular sulfide veinlet crosscutting planar bedding. C. Strong layered mineralization, containing layers of barite (brt), mixed barite and sphalerite (sp), pyrite (py), and galena (gn) mineralization. D. Ankerite (ank) alteration and veining within the vent complex. Mst = mudstone.

eralized stratigraphic units in the Selwyn Basin (Fernandes et al., 2017). Furthermore, the geochemical record of this process is now recognized in the host rocks of a number of CD-type deposits (e.g., Red Dog, Johnson et al., 2009; Howards Pass, Johnson et al., 2018).

Hydrothermal fluid input

Macmillan Pass is one of the few localities where the vent complexes of CD-type deposits are well preserved. Early fluid inclusion studies provided a range of temperature (157°–335°C) and salinity (2.6–18 wt % NaCl equiv) constraints (Gardner and Hutcheon, 1985; Ansdell et al., 1989); however, the cotransportation of barium and base metals implied by the SEDEX model placed restrictive constraints on the modeling of fluid chemistry, as barite and sulfides are soluble under contrasting redox conditions (e.g., Cooke et al., 2000). In separating barite formation from ore-stage mineralization (previous section), the model for base metal solubility is simplified. Recently, a suite of geochemical data was generated on vent complex samples (e.g., Fig. 2D) to provide revised constraints on base metal solubility in the vent complexes (Magnall et al., 2016b). In combining new, paragenetically constrained fluid inclusion data, isotopic modeling ($\delta^{13}C$ and $\delta^{18}O$), and carbonate rare earth element chemistry, it has been shown that the fluids entering the vent complex were hot (≤300°C) but rapidly cooled (<125°C) upon mixing with diagenetic fluids (Magnall et al., 2016b). Furthermore, the fluids entering the vent complex were sulfur poor ($aH_2S = 10^{-3}$), acidic (pH ≤4.5), and only moderately saline (<7 wt % NaCl) but had a substantial capacity to transport base metals (1,000–3,000 ppm Zn, 300–1,000 ppm Cu, and 80–200 ppm Pb) due to the high temperatures and low availability of reduced sulfur (Magnall et al., 2016b).

In addition to fluid chemistry, the preservation of vent complexes at Macmillan Pass provides the opportunity to consider certain hydrological aspects of these systems. For example, in siliciclastic sequences, such as at Macmillan Pass, faults are unlikely to have acted as fluid-flow conduits at shallow depths (Barnicoat et al., 2009). Rather than fluids exhaling above the SWI, therefore, it is more likely that greater sediment permeability resulted in complex flow networks developing away from the fault. A lower constraint on the depth at which subseafloor replacement occurred can be inferred on the basis that the skeletal structure of radiolarians is preserved by sulfides in the layered mineralization overlying the vent complex (Magnall et al., 2015). The opaline silica of radiolarian tests is unstable on diagenetic timescales (Davies et al., 2008) and undergoes a two-step mineralogical transformation to quartz (opal-A–opal-CT–quartz) that is dependent primarily on the initial sediment clay content and ambient temperature (2°–55°C; Bohrmann et al., 1994). The preservation of radiolarian tests by hydrothermal sulfides, therefore, constrains mineralization to the upper 1 km beneath the Late Devonian seafloor. Moreover, prior to the transformation of opaline silica to quartz, biosiliceous sediments retain extremely high porosities (>70% at 500-m depth; Isaacs, 1982). The volume preservation provided by opaline silica represents an important parameter of the metal trap and the capacity for subseafloor replacement. Indeed, how vent complex fluids interacted with the biosiliceous host rock and overlying diagenetic barite is an important consideration for the genetic model for mineralization at Macmillan Pass.

Metal deposition

In a subseafloor replacement system, the formation of high-grade mineralization will depend upon sufficient porosity combined with an abundance of reduced sulfur. At Macmillan Pass, multiple pathways of sulfate reduction contributed to the reduced sulfur budget of the host rock, including microbial and methane-driven sulfate reduction (Magnall et al., 2016b) together with thermochemical sulfate reduction (TSR; Magnall et al., 2016a). There is also evidence that a greater proportion of diagenetic sulfur was reduced via AOM-sulfate reduction in the mudstones surrounding the layered mineralization at Macmillan Pass (Magnall et al., 2016b, 2018) and elsewhere in the Selwyn Basin (Howards Pass; Johnson et al., 2018), providing evidence that diagenesis may have been hydrothermally accelerated.

It is likely, therefore, that during the onset of hydrothermal activity at Macmillan Pass, there was accelerated circulation of H_2S, CH_4, and other hydrocarbons in diagenetic fluids. Within the vent complexes at Macmillan Pass, the interaction of the hydrothermal fluid with the organic-rich host rock resulted in the thermal degradation of organic matter coupled with the release of volatile components (CO_2, CH_4, C_1-C_4 hydrocarbons, N_2). Such dynamic interactions could be analogous to modern settings, such as the Guaymas Basin (Gulf of California), where shallow magma emplaced within carbonaceous sediments results in destabilization of gas hydrates and seepage of H_2S, CH_4, and other hydrocarbons (Einsele et al., 1980; Berndt et al., 2016). This seepage promotes authigenic barite and carbonate mineralization (Núñez-Useche et al., 2018) and provides an excellent modern analogue for how diagenetic processes can be accelerated by hydrothermal processes.

At Macmillan Pass, an effective metal trap resulted from interactions between diagenetic and hydrothermal processes. This began with diagenetic barite formation, which provided a mechanism by which to concentrate sulfur into the host rock. For example, the enrichment of barite in the host rock at Macmillan Pass (>15 wt %) represents a sulfate concentration factor in excess of 100, relative to Late Devonian seawater (7 mM; Horita et al., 2002). Through equations 1 to 4, it is possible to see how a positive feedback may have developed between TSR (1), sulfide precipitation and acid generation (2), and barite dissolution (3, 4) as the vent fluids were discharged into the shallow subsurface:

$$2CH_2O + SO_4^{2-} = 2HCO_3^- + H_2S, \quad (1)$$

$$Zn^{2+} + H_2S = ZnS + 2H^+, \quad (2)$$

$$2HCO_3^- = 2H^+ + 2CO_3^{2-}, \quad (3)$$

and

$$2BaSO_4 + 2CO_3^{2-} = 2BaCO_3 + 2SO_4^{2-}. \quad (4)$$

Beyond serving as a direct source of sulfur, barite dissolution would lead to the development of secondary porosity and the enhanced circulation of diagenetic fluids into the vent complex. Notably, there is direct evidence of mixing between diagenetic and hydrothermal fluids preserved in the trace element composition of the carbonates from the vent complex (Magnall et al., 2016b).

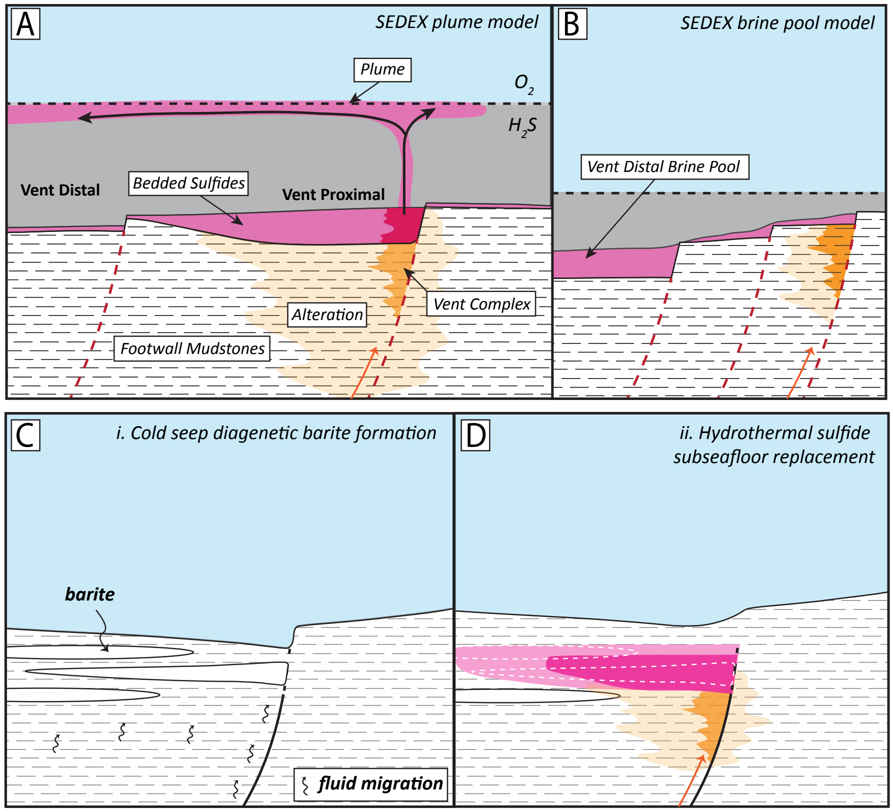

Fig. 3. The contrasting models for CD-type mineralization in the Selwyn Basin. A. The SEDEX model, modified from Goodfellow et al. (1993). B. The brine pool model, modified from Sangster (2002). C and D. A two-stage model for diagenetic barite formation (C) followed by subseafloor hydrothermal replacement (D).

In the Macmillan Pass deposits, abundant barite remains in the layered sulfide mineralization, which represents oxidized sulfur that has not been recycled by the hydrothermal system. It is tempting to conclude, therefore, that a smaller fluid flux limited the extent of zone refining at Macmillan Pass and may be the reason why the vent complexes are so well preserved relative to many larger deposits. Irrespective of relative size, however, it is likely that, contrary to the SEDEX model in which layered sulfide mineralization requires long-lived (>1 m.y.) hydrothermal activity (e.g., Turner, 1992), subseafloor replacement could take place on much shorter timescales.

Implications and Outlook

The new model for subseafloor replacement at Macmillan Pass (Fig. 3C, D) has been developed following a number of studies that combined high-resolution petrographic and geochemical data from different parts of the deposit architecture (e.g., Fig. 2). This approach has benefited from techniques that were unavailable to earlier workers (e.g., laser ablation-inductively coupled plasma-mass spectrometry, secondary-ion mass spectrometry), but which are essential for understanding systems where diagenetic and hydrothermal assemblages are inherently fine grained and intergrown. At Macmillan Pass, barite replacement resulted in barium mobility, and establishing the mineral phases where barium ultimately resides will be a necessary consideration for constraining the deposit footprint; clearly, therefore, it is critical to develop comprehensive petrographic models that not only focus on the relative timing of ore mineral phases (pyrite, sphalerite, galena), but that also consider the fine-grained gangue assemblages (e.g., Magnall et al., 2020). Barite is an important component of a number of other Paleozoic deposits, so many aspects of the subseafloor barite replacement model should be relevant to other localities (e.g., Red Dog, Alaska; Gataga district, Canada; Rammelsberg, Germany; Yangtze block, China).

Up to this point, research and exploration in the modern oceans have been heavily focused toward hydrothermally active vent sites at active spreading centers, which provides us with a direct modern analogue to volcanogenic massive sulfide (VMS) deposits in the geologic record (Hannington et al., 2005). In contrast, there are no modern equivalents of CD-type mineralization, which in the SEDEX model has been attributed to the lack of suitable euxinic basins (e.g., Turner, 1992). In a subseafloor replacement model, however, there is no direct causal relationship between depositional redox conditions and mineralizing processes (Magnall et al., 2018).

As more sites are drilled, it is becoming apparent that replacement-style sulfide mineralization is an important component of VMS deposits (e.g., Zierenberg et al., 1998). Indeed, the largest deposits actually form where sediment prevents fluid exhalation and the resulting loss of the hydrothermal metal budget to seawater (Hannington et al., 2005). There is a very real possibility, therefore, that there could be actively forming, undiscovered CD-type deposits beneath the modern seafloor. One suggestion is to explore the modern continental margins associated with the breakup of Pangaea

(Hannington et al., 2017) where there is also cold seep activity and barite formation (e.g., Gulf of Mexico; Fu et al., 1994; Feng and Roberts, 2011). Notably, in terms of reduced sulfur and a metal trap, the highest rates of carbon burial and rates of sulfate reduction occur along continental margins, and not in deep ocean settings (Turchyn and Schrag, 2006; Kallmeyer et al., 2012).

Yet our predictive capacity looks set to be inhibited by some critical unknowns, such as what ultimately controls basin fertility during particular periods of CD-type metallogenesis. For example, whereas the Late Devonian was a time of major carbon burial in a number of sedimentary basins, CD-type deposits are restricted to a select few (e.g., Selwyn Basin; Magnall et al., 2018). Future work should focus on determining precisely where metals came from, how they were extracted, and the hydrological constraints on metal transportation at deeper levels of the system.

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