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Sediment-Hosted Lead-Zinc Deposits in Earth History

David. L. Leach,[1,5,†] Dwight C. Bradley,[2] David Huston,[3] Sergei A. Pisarevsky,[4] Ryan D. Taylor,[1] and Steven J. Gardoll[5]

[1]*U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225*

[2]*U.S. Geological Survey, 4200 University Drive, Anchorage, Alaska 99508*

[3]*Geoscience Australia, GPO Box 378, Canberra, ACT 2601, Australia*

[4]*School of Geosciences, University of Edinburgh, Grant Institute, West Mains Road, Edinburgh EH9 3JW, Scotland*

[5]*Centre for Exploration Targeting, M006, University of Western Australia, 35 Stirling Highway,Crawley,WA 6009, Australia*

Abstract

Sediment-hosted Pb-Zn deposits can be divided into two major subtypes. The first subtype is clastic-dominated lead-zinc (CD Pb-Zn) ores, which are hosted in shale, sandstone, siltstone, or mixed clastic rocks, or occur as carbonate replacement, within a CD sedimentary rock sequence. This subtype includes deposits that have been traditionally referred to as sedimentary exhalative (SEDEX) deposits. The CD Pb-Zn deposits occur in passive margins, back-arcs and continental rifts, and sag basins, which are tectonic settings that, in some cases, are transitional into one another. The second subtype of sediment-hosted Pb-Zn deposits is the Mississippi Valley-type (MVT Pb-Zn) that occurs in platform carbonate sequences, typically in passive-margin tectonic settings.

Considering that the redox state of sulfur is one of the major controls on the extraction, transport, and deposition of Pb and Zn at shallow crustal sites, sediment-hosted Pb-Zn ores can be considered a special rock type that recorded the oxygenation of Earth's hydrosphere. The emergence of CD and MVT deposits in the rock record between 2.02 Ga, the age of the earliest known deposit of these ores, and 1.85 to 1.58 Ga, a major period of CD Pb-Zn mineralization in Australia and India, corresponds to a time after the Great Oxygenation Event that occurred at ca 2.4 to 1.8 Ga. Contributing to the abundance of CD deposits at ca 1.85 to 1.58 Ga was the following: (1) enhanced oxidation of sulfides in the crust that provided sulfate to the hydrosphere and Pb and Zn to sediments; (2) development of major redox and compositional gradients in the oceans; (3) first formation of significant sulfate-bearing evaporites; (4) formation of red beds and oxidized aquifers, possibly containing easily extractable Pb and Zn; (5) evolution of sulfate-reducing bacteria; and (6) formation of large and long-lived basins on stable cratons.

Although MVT and CD deposits appeared for the first time in Earth history at 2.02 Ga, only CD deposits were important repositories for Pb and Zn in sediments between the Great Oxygenation Event, until after the second oxidation of the atmosphere in the late Neoproterozic. Increased oxygenation of the oceans following the second oxidation event led to an abundance of evaporites, resulting oxidized brines, and a dramatic increase in the volume of coarse-grained and permeable carbonates of the Paleozoic carbonate platforms, which host many of the great MVT deposits. The MVT deposits reached their maximum abundance during the final assembly of Pangea from Devonian into the Carboniferous. This was also a time for important CD mineral deposit formation along passive margins in evaporative belts of Pangea. Following the breakup of Pangea, a new era of MVT ores began with the onset of the assembly of the Neosupercontinent.

A significant limitation on interpreting the secular distribution of the deposits is that there is no way to quantitatively evaluate the removal of deposits from the rock record through tectonic recycling. Considering that most of the sedimentary rock record has been recycled, most sediment-hosted Pb-Zn deposits probably have also been destroyed by subduction and erosion, or modified by metamorphism and tectonism, so that they are no longer recognizable. Thus, the uneven secular distribution of sediment-hosted Pb-Zn deposits reflects the genesis of these deposits, linked to Earth's evolving tectonic and geochemical systems, as well as an unknown amount of recycling of the sedimentary rock record.

Introduction

For more than 30 years, earth scientists have strived to understand the fundamental controls that produced the uneven distribution of many types of ore deposits in Earth history (e.g., Meyer, 1981, 1988; Sawkins; 1984; Veizer et al., 1989; Barley and Groves, 1992; Hutchinson, 1992; Titley, 1993; Goldfarb et al., 2001a, b; Groves et al., 2005a, b; Holland, 2005). Several papers focused on sediment-hosted Pb-Zn deposits in Earth history (Sangster, 1990; Goodfellow et al., 1993; Leach et al., 2001, 2005b; Lydon, 2004; Kesler and Reich, 2006; Lyons et al., 2006; Goodfellow and Lydon, 2007). These authors attributed the deposit distributions to: (1) long-term changes in the tectonic processes of the Earth that are inextricably related to the cooling planet, (2) the change in oxidation state of the atmosphere and hydrosphere, (3) the evolution of life, and (4) the tectonic recycling and /or destruction of ore deposits. Despite advances in our knowledge of the evolution of Earth systems and their controls on ore genesis, there continues to be significant gaps in our understanding of the temporal distribution of ores in the rock record.

The goal of this paper is to provide new insights into the fundamental controls that an evolving Earth had on the genesis

† Corresponding author: e-mail, dleach5100@me.com

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of sediment-hosted Pb-Zn deposits. We examine the distributions of these deposits in time within a context of tectonic and geochemical environments to better understand when and where these deposits formed in the crust. Hopefully, this information will contribute to our understanding of the essential Pb-Zn ore-forming processes in sedimentary rocks and lead to better exploration strategies for undiscovered ores.

The most important sediment-hosted Pb-Zn deposits are those in clastic rock-dominated sedimentary sequences traditionally called sedimentary exhalative (SEDEX) and those in carbonate-dominated sequences that are mainly of the Mississippi Valley-type (MVT). In this paper, we do not discuss sandstone Pb, sandstone-hosted Pb, or Pb-Zn vein districts, such as Freiberg, Germany, and Coeur d'Alene, United States, because these deposits are highly restricted in both space and time and probably represent different ore types. We also exclude fracture-controlled deposits in which fluorite is dominant and barite typically abundant (e.g., Central Kentucky and Hansonburg, New Mexico); strata-bound fluorite-rich, but Pb-Zn–bearing deposits, such as those in southern Illinois, considered a genetic variant of carbonate-hosted Pb-Zn deposits (Leach and Sangster, 1993); and carbonate-hosted skarn and carbonate replacement deposits of probable igneous affinity.

This paper covers four main subjects: (1) description of the two main subtypes of sediment-hosted Pb-Zn ore deposits and their tectonic settings; (2) overview of the geochemical and tectonic controls on ore genesis and the evolution of the Earth's atmosphere and hydrosphere; (3) examination of the secular distribution of sediment-hosted Pb-Zn deposits in clastic rock-dominated sedimentary sequences; and (4) examination of the secular distributions of sediment-hosted Pb-Zn deposits in carbonate-dominated platform sequences.

Description and Classification of Sediment-Hosted Pb-Zn Deposits

Sediment-hosted Pb-Zn deposits are a diverse group of ores hosted by a wide variety of siliciclastic and carbonate rocks that, with few exceptions, have no direct genetic association with igneous activity. They are the products of a range of ore-forming processes in a variety of geologic and tectonic environments. The metals were precipitated through a variety of processes that include synsedimentary precipitation on the sea floor (SEDEX), diagenesis, epigenetic replacement, and low-grade metamorphism. The ores consist mainly of sphalerite, galena, and generally lesser amounts of iron sulfides. Silver is commonly an important commodity, whereas Cu is generally low but is economically important in some deposits. Gold values are reported for a small set of deposits in clastic rock-dominated sequences but absent from ores in host rocks dominated by carbonates. Gangue minerals may include carbonates (dolomite, siderite, ankerite, calcite) and typically minor to major barite. Silicification of the host rocks (or quartz gangue) is generally minor but may be abundant in a few deposits. The deposits have a broad range of relationships with their host rocks that includes stratiform, strata-bound, and discordant ores; in some deposits, vein ore is important. Given that sediment-hosted Pb-Zn deposits originate mainly from sedimentary brines and from similar ore-forming processes, Leach et al. (2005b) concluded that the attributes, ore controls, and nature of the deposits are mainly determined by the tectonic setting where ore deposition occurred.

An indepth review of sediment-hosted Pb-Zn deposits was presented by Leach et al. (2005b); the attributes, genesis, and resource endowments of 248 deposits were described. Classifications of the ores were organized around traditional subgroups: Mississippi Valley-type (MVT), sedimentary exhalative (SEDEX), sandstone-hosted (SSH) and sandstone-lead (Sst-Pb), and further subdivided based on classifications attributed to the deposits in the literature. Leach et al. (2005b) acknowledged a fundamental concern with the genetic model-based classification of SEDEX, which imparts an inherent exhalative genetic component to deposits. Most deposits classified as SEDEX lack unequivocal evidence of an exhalite in the ore or alteration component; consequently, the presence of laminated sulfides parallel to bedding is usually accepted to be permissive evidence for exhalative ore. We regard this as fundamentally unsatisfactory because some deposits traditionally classified as SEDEX did not form from sulfide exhalites. Some SEDEX deposits with ore textures that mimic synsedimentary textures were formed by replacement processes below the sea floor (e.g., Anarraaq and Red Dog deposits: Kelley et al., 2004a, b), whereas some MVT deposits (e.g., Reocin, Metaline) contain extensive (kilometer-scale) laminated and stratiform ores that formed by highly selective carbonate replacement millions of years after deposition of the host rocks. Other deposits containing stratiform and laminated sulfides in a variety of rocks, particularly in metasedimentary rocks, are commonly classified as SEDEX (e.g., Balmat: Whelan et al., 1984; Aguilar: Gemmell et al., 1992) without unequivocal evidence for the ores being syngenetic or even early diagenetic.

In this paper, we minimize process-related, interpretive, and model-driven features to classify the deposits, and instead turn to descriptive terms that reflect the nature of the sedimentary rock sequences determined by the tectonic environment where the ores formed. This approach uses the relationship that ores classified as SEDEX in Leach et al. (2005b) are hosted in clastic rock-dominated sedimentary sequences in mainly passive margins, continental rifts, and sag basins (Fig. 1). We use the term clastic-dominated lead-zinc (CD Pb-Zn) for these deposits and avoid genetic and time (e.g., syngenetic, diagenetic, syndiagenetic) attributes to the deposits. The ores can be hosted in shale, sandstone, siltstone, or mixed clastic rocks, or occur as carbonate replacement ores within a clastic rock-dominated sedimentary sequence. Under the CD type of sediment-hosted Pb-Zn deposits, broad subtypes are used to distinguish specific tectonic or geologic settings of the deposit: passive margin settings, continental rifts, continental sag basins, and back-arc basins.

We retain the traditional term of MVT Pb-Zn for sedimentary rock-hosted Pb-Zn deposits in carbonate-dominated platform sequences because it does not include a genetic component. Although the traditional use of the term MVT does imply a broad time component of simply being epigenetic with respect to its host rocks, we recognize that some MVT ores may have a syngenetic, diagenetic, or burial metamorphic component. The most important characteristics of MVT ores deposits are that they are hosted mainly by dolostone and limestone in platform carbonate sequences and usually located at

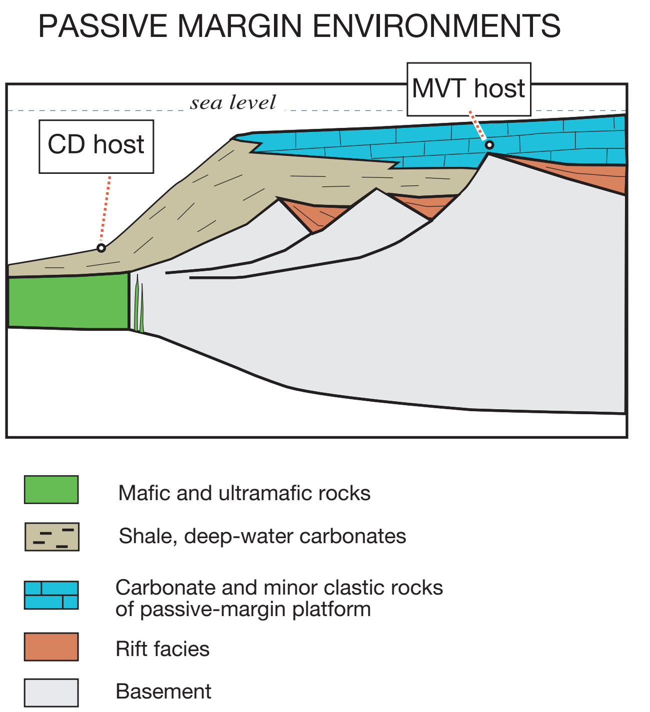


FIG. 1. Tectonic setting of sediment-hosted Pb-Zn deposits in passive margins. Equivalent clastic rock-dominated to platform carbonate sequences are also in continental rift and sag basins. CD sedimentary rock sequences host CD Pb-Zn deposits (traditionally called sedimentary exhalative deposits) that form during sedimentation, or diagenesis to early burial of the sedimentary sequence. The MVT Pb-Zn deposits are located in the carbonate-platform sequences of the passive margin.

flanks of basins, orogenic forelands, or foreland thrust belts inboard of the clastic rock-dominated passive-margin sequences (Fig. 1). They have no spatial or temporal relationship to igneous rocks, which distinguishes them from skarn or other intrusive rock-related Pb-Zn ores.

Many subtypes or alternative classifications have been applied to MVT deposits since their recognition as a distinct ore type by Bastin (1939). These alternative classifications reflect geographic and or specific geologic features that some workers believe set them apart as unique (e.g., Appalachian, Alpine, Reocin, Irish, Viburnum trend types). However, we do not consider these alternative classifications or subtypes to be sufficiently different to warrant using them.

Tectonic Settings of Sediment-Hosted Pb-Zn deposits

The tectonic setting in which the ore deposits form is the defining moment in the formation and eventual destruction of a sediment-hosted Pb-Zn deposit. The tectonic setting determines the host-rock type, ore controls, temperature, and pressure of the depositional processes, as well as the survivability of the deposit during tectonic recycling. Below we define the tectonic settings that form the basis for characterizing and evaluating their distribution in Earth history.

Most sediment-hosted Pb-Zn deposits are in strata that were deposited in rift or passive-margin settings. These tectonic settings are related: passive margins form when continental rifts succeed (Fig. 2B). Certain CD and MVT deposits have been placed by some workers in extensional back-arc settings; we show how these are variants on rifts and passive margins. For each of these tectonic settings, climate and time in Earth history are critical in determining the suite of sedimentary rocks that is deposited.

Continental rifts

"Rifts are fault-bounded elongate troughs, under or near which the entire thickness of the lithosphere has been reduced in extension during their formation" (Sengor and Natalin, 2001, p. 389; Fig. 2A). We use the term "rift" to mean a continental rift, such as the East African rift system. The key characteristics of continental rifts are stretched continental basement, a topographically low axial depression, and elevated flanks or shoulders. Rift shoulders, bounded by normal faults, may rise to several kilometers elevation in response to extensional unloading. The coarse, immature clastic sediments associated with rifts are shed off these highlands and are deposited in alluvial fans along basin-bounding growth faults. Depending on sea level and connections, or lack thereof, to the world oceans, sedimentation along the rift axis may either be marine (e.g., Afar rift, Djibouti), or more commonly, nonmarine (e.g., East African rift, Kenya). Commonly, subsidence is rapid enough for deep-water environments to be produced, and it is here that conditions may favor CD Pb-Zn ore deposition. Some rifts are associated with red beds, evaporites, and mafic or bimodal volcanic rocks, but these rock types are far from universal. Red beds and evaporites form mainly in the arid belts (~15°–35° lat), red beds did not even exist before oxygenation of the atmosphere at ca. 2400 Ma (Holland, 2005), and some rifts are devoid of volcanic rocks.

Passive margins

Continental rifting (Fig. 2A) may or may not proceed all the way to sea-floor spreading. If it does, then the axial valley of a rift evolves into a midoceanic ridge and, over time, the continents on either side drift apart. Passive margins develop on the rifted edges of the two diverging continents (Fig. 2B, C). With plate divergence now being focused at the ridge axis, cooling takes over as the main driver of subsidence on the new continental margins; this is referred to as thermal subsidence. Strata of the passive-margin stage (or postrift or sag) bury the rift-related strata and structures and typically lap onto older continental basement landward of the rift margins. Over time, a seaward-thickening miogeoclinal prism builds upward and outward over the adjacent sea floor, with bathymetric realms referred to as the shelf, slope, and rise.

Water depth, distance from shore, sea level, and climate are the main factors governing the character of sediments deposited across passive margins. Compositionally mature sandstones and siltstones are typical of shelf environments at high latitudes, whereas platform carbonates, the classic assemblage of passive margins, and the eventual host of most MVT deposits, are dominant at low latitudes. Finer grained and shale equivalents are deposited farther offshore on the slope and rise, the prime site for syngenetic or diagenetic CD Pb-Zn deposition.

Collisional demise of passive margins: The vast majority of ancient passive margins ended their tenure by colliding with an arc (Bradley, 2008). In Figure 2C, the passive margin on

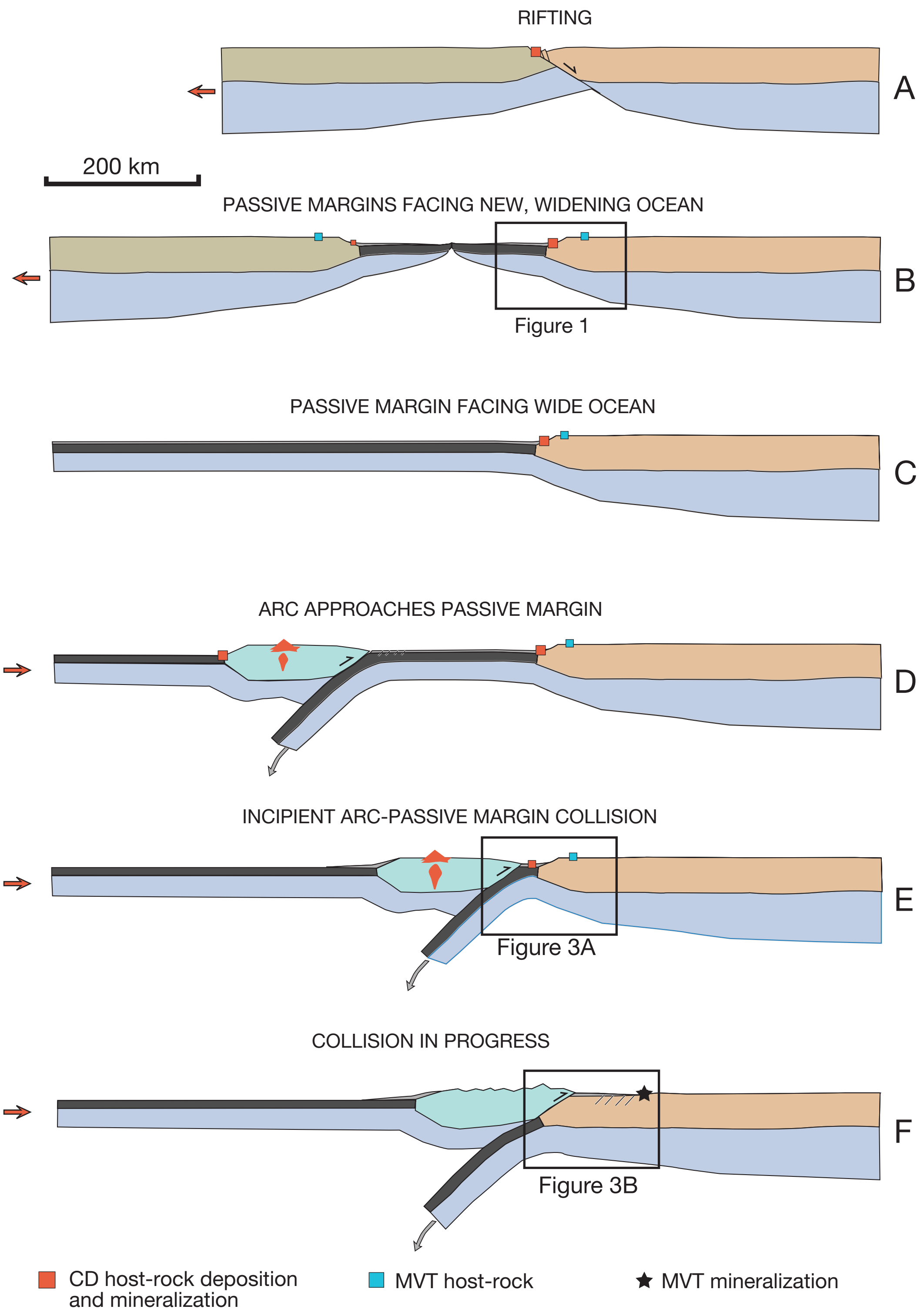


FIG. 2. Schematic, plate-scale cross sections showing settings of host-rock deposition and mineralization that account for the majority of sediment-hosted Pb-Zn deposits, which are shown by colored symbols as indicated. Locations of deposit symbols are highly generalized and should be considered to extend beyond the locations shown. A single continent (A) is extended asymmetrically. Rifting has succeeded (B), and an ocean has begun to open between what is now a pair of continents, each of which is bordered by a young passive margin. The ocean has widened (C) and one continent has been removed. Some time later (D), an arc approaches from the west, consuming the oceanic part of the plate that also includes the continent on the east. Collision is inevitable and begins (E) when the distal passive margin enters the trench. Arc-passive margin collision (F) has nearly run its course.

the left has drifted away to form an ocean basin whereas in Figure 2D, the ocean floor is being subducted and consequently an arc-passive-margin collision is inevitable. Collision begins as the continental rise, or distal passive margin, begins to enter the trench (Fig. 2E). From this time onward, what had been a trench is referred to as a collisional foreland basin, or foredeep (Figs. 2E, 3). As plate convergence continues, the miogeoclinal prism and its underlying stretched continental basement are flexed down into the approaching subduction zone. This is typically a time of minor extension related to flexure (Bradley and Kidd, 1991), synchronous with rapid turbidite sedimentation in a cratonward-advancing foreland basin. Extension at the onset of collision is not to be confused with back-arc extension; the former occurs in the subducting plate and the latter in the overriding plate. A few syngenetic barite deposits (e.g., in Arkansas and Nevada) are known to have formed in extensional foredeep settings (e.g., Maynard and Okita, 1991; Bradley and Leach, 2003). Once plate convergence has ceased (Fig. 2F), the foreland basin stops migrating and fills with sediment, yielding the classic flysch to

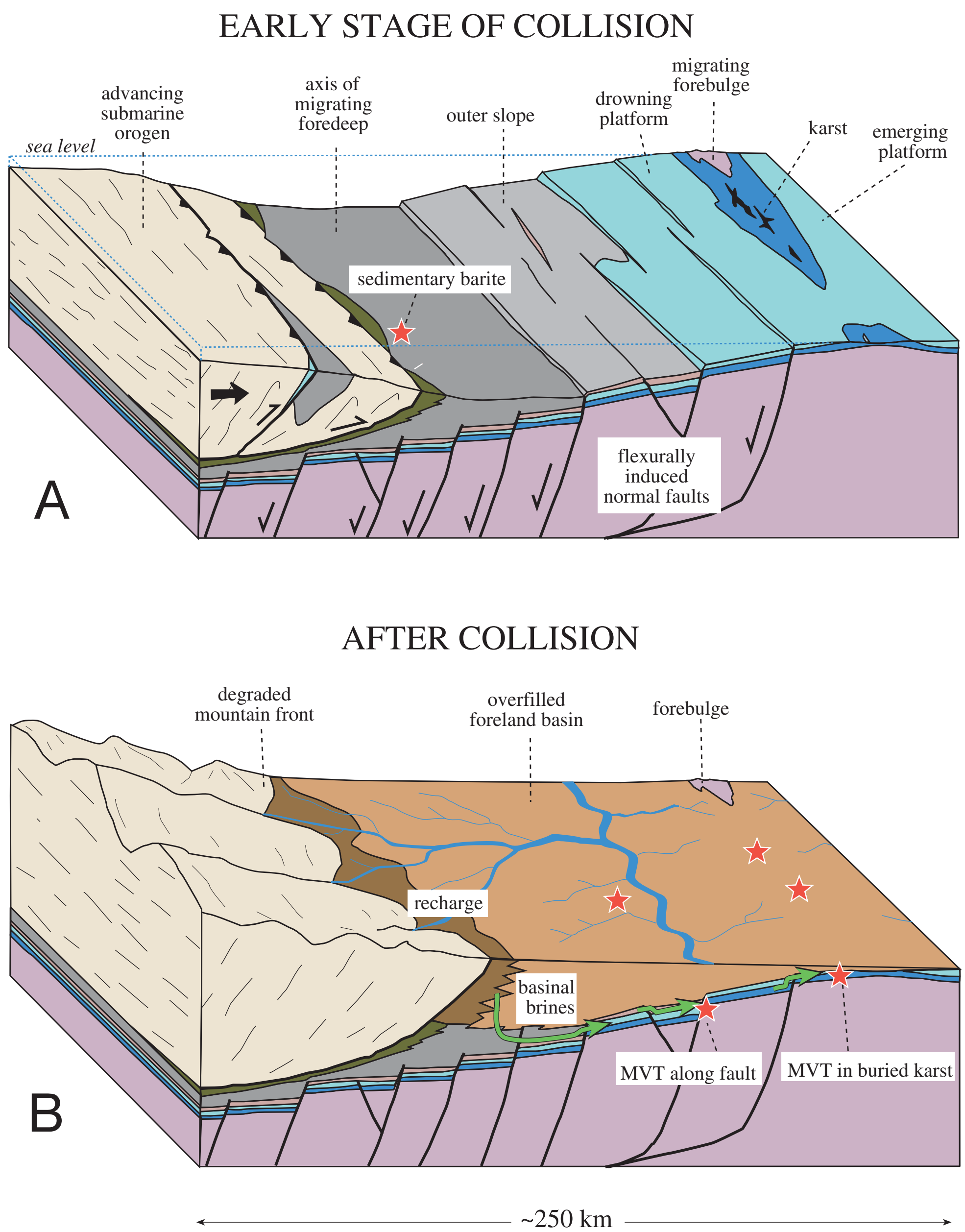


Fig. 3. Block diagrams showing foreland evolution. During plate convergence (A), a submarine thrust belt loads the passive margin, thereby forming the foreland basin, extensional domain, and forebulge. Plate convergence continually causes these features to migrate across the foreland plate. The foreland basin remains underfilled because the depocenter migrates. Barite CD mineralization may occur along the foredeep axis and is based on examples from the Ouachita orogen (Maynard and Okita, 1991). Plate convergence has ceased and the foreland basin has filled with sediment (B), creating hydrologic conditions favorable for MVT mineralization.

molasse transition that was first recognized in the Alps (Sinclair, 1997). The most favorable environment for MVT mineralization (Fig. 3) is in platform carbonates of former passive margins that are eventually located beneath foreland basin deposits in collisional orogenic forelands (Bradley and Leach, 2003).

Extensional arc systems

Upper-plate extension along continental arcs produces variants on the scenario just described. This is relevant because a few CD deposits have been assigned a nonspecific back-arc basin tectonic setting (e.g., Rammelsberg: Mueller, 2008; Selwyn basin: Goodfellow, 2007). Despite being located above convergent plate boundaries (Fig. 4A), continental arcs extend under some circumstances (Dewey, 1980). Where rifting of an arc proceeds all the way to sea-floor spreading, the result is two margins separated by a back-arc basin floored by oceanic crust (Fig. 4B). One of the two margins lies on the backside of the active arc, where any passive-margin–like sedimentation patterns would likely be masked or overwhelmed by arc magmatism. The other margin is like a classic passive margin, despite its somewhat different prior history.

Continental sag basins

If rifting stops short of sea-floor spreading, then ensuing events are somewhat different. Thermally driven subsidence becomes dominant and rift-related strata and structures are blanketed, similar to passive margins. The idealized sag sequence resembles two partial miogeoclines, which mirror each other above the rift axis (Fig. 5).

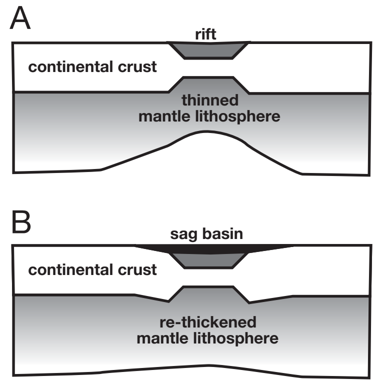


FIG. 5. Rift to sag basin transition illustrating the tectonic setting of some CD deposits (i.e., Sullivan deposit, Canada, in continental rift setting, and Mount Isa, Australia, in sag phase).

Geochemistry of Sediment-Hosted Pb-Zn Ore-Forming Fluids

MVT ore fluids

The homogenization temperatures of ore-stage minerals from MVT deposits range from about 50° to 250°C, with a few as high as 300°C; however, most of the temperatures are between 90° and 150°C (Basuki and Spooner, 2004; Leach et al., 2005b). The salinities of MVT fluids are typically 10 to 30 wt percent NaCl equiv (Basuki and Spooner, 2004; Leach et al., 2005b). Fluid inclusion compositions of ore-stage minerals from MVT districts (Leach et al., 2005b and references therein) are remarkably similar to compositions of present-day basin brines that are formed mainly from evaporated seawater (Carpenter et al., 1974; Kesler et al., 1996; Viets et al., 1996), with lesser amounts of dissolved evaporites.

CD ore fluids

It is generally assumed from mineralogical and geochemical considerations that the CD ore fluids were principally hot metalliferous basinal brines (e.g., Badham, 1981; Lydon, 1983; Cooke et al., 2000) and similar to MVT ore fluids. Definitive fluid inclusion evidence on the temperature and salinity of the CD Pb-Zn ore-forming fluids is limited. The only CD deposits with published fluid inclusion data on ore-stage sphalerite are the Red Dog deposits, United States (Edgerton, 1997; Leach et al., 2004) and the Century deposit, Australia (Polito et al., 2006). Primary fluid inclusions in sphalerite from the Red Dog deposits yielded homogenization temperatures of 100° to 200°C and salinities of 14 to 19 wt percent NaCl equiv (Leach et al., 2004). Prior to fluid mixing at the depositional site, the fluids were about 30 wt percent NaCl equiv. The ore fluids were derived from evaporated seawater and are compositionally similar to MVT fluids (Leach et al., 2004). Fluid inclusion data from the Century deposit in the Burketown mineral field (Polito et al., 2006) show that the ore-stage sphalerite formed between 74° and 125°C from a fluid with salinity of about 22 wt percent NaCl equiv. Late

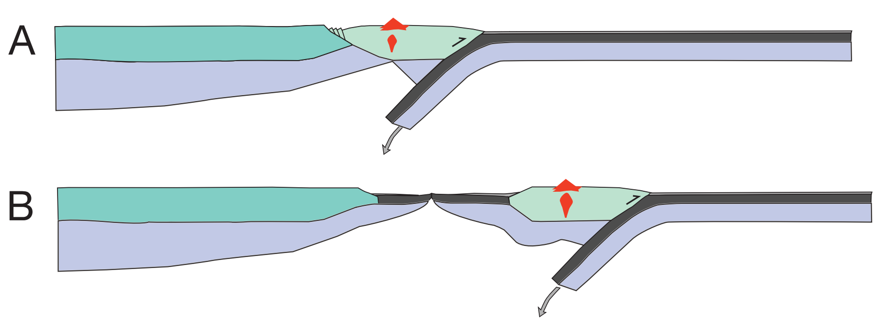


FIG. 4. Tectonic cross sections illustrating the overlapping nature of basin classifications pertinent to sediment-hosted Pb-Zn deposits. Back-arc rifting (A) leading to opening of a back-arc basin floored by oceanic crust (B). The margins of this back-arc basin are passive margins and the one on the left, in particular, differs only subtly from a class Atlantic-type passive margin.

sphalerite lodes in the Burketown mineral field have lower salinities and higher temperatures (~200°C) and fluids with halogen ratios similar to the Red Dog deposits (Leach et al., 2004).

Fluid inclusion data from gangue minerals are available for the Jason (Gardner and Hutcheson, 1985) and Tom (Ansdell et al., 1989) deposits in the Selwyn basin, Canada. Ansdell et al. (1989) reported fluid inclusion data for ankerite in the alteration zone and quartz in veins that cut the main ore zones in the Tom deposit. The salinities range from 2 to ~18 wt percent NaCl equiv and homogenization temperatures range from 234° to 274°C. Both deposits experienced postore deformation and low-grade metamorphism, which casts some doubt on the relevance of the data to ore deposition (Leach et al., 2004). A wide range of salinities (<1 to >45 wt % NaCl equiv) and temperatures (<100°–400°C) are reported for the Sullivan deposit, Canada (Leitch and Lydon, 2000). However, uncertainties as to the geologic context of the veins, and an episodic fluid-flow history, make interpretation of the fluid inclusion data difficult (Lydon, 2004).

Transport and deposition of lead and zinc

The most important factors controlling the solubility of Zn and Pb in the hydrosphere at the surface are temperature, salinity, pH, total sulfur, and redox state of fluids (e.g., Cooke et al., 2000). Therefore, secular changes in Earth processes had profound impacts on these variables that provided fundamental controls on the distribution of sediment-hosted Pb-Zn deposits. The geochemistry of Pb and Zn in crustal fluids is reasonably well understood from thermodynamic modeling, analyses of subsurface fluids, and fluid inclusions (e.g., Anderson, 1973, 1975, 1983; Barnes, 1979; Sverjensky, 1984; Hanor, 1996; Cooke et al., 2000; Giordano, 2002; Yardley, 2005). Whereas temperature and salinity are the most important global controls over a broad range in crustal environments, Yardley (2005) and Hanor (1996) showed that Zn-bearing fluids in sedimentary basins had a chlorinity threshold of about 100 g/l. Above this threshold, the Zn content had an inverse relationship with reduced sulfur content (Carpenter et al., 1974). Furthermore, Hanor (1996) noted no correlation between metal content and temperatures up to 160°C. These observations are consistent with fluid inclusion and metal resource data from global sediment-hosted Pb-Zn deposits, which do not show a consistent relationship between the metal endowment and the salinity and temperature of the fluid inclusions in ore minerals (Leach et al., 2005b).

Discussions on the geochemistry of sediment-hosted Pb-Zn ore fluids generally refer to end-member compositions based on the dominant redox state of sulfur. Oxidized sedimentary brines are those that contain sulfur dominated by sulfate, whereas reduced sedimentary brines contain sulfur dominantly as bisulfide (e.g., Lydon, 1983; Cooke et al., 2000). Modern Zn- and Pb-rich sedimentary brines (Carpenter et al., 1974; Hanor, 1996; Kharaka and Hanor, 2007) are weakly acidic (~4–6 pH) oxidized brines that are believed to be analogs for most sediment-hosted Pb-Zn ore fluids. These observations are consistent with thermodynamic modeling (e.g., Anderson, 1973, 1975, 1983; Plumlee et al., 1994; Cooke et al., 2000; Leach et al., 2006) that shows the dominant control on the content of Pb and Zn in low-temperature (~<250°C) sediment-hosted Pb-Zn ore fluids is the reduced sulfur content. The concentrations of Pb and Zn in modern sedimentary brines vary up to ~300 ppm (Yardley, 2005, and references therein). Calculated concentrations of Pb in sphalerite-hosted fluid inclusions are as high as 3,000 to 5,000 ppm (Stoffell et al., 2008; Wilkinson et al., 2009B). Reduced sedimentary brines with lower pH values (<4) and higher temperatures (>~200°–250°C) can transport Pb and Zn together with reduced sulfur. These reduced brines are stable in higher temperature sedimentary basins with dominantly reduced siliciclastic sediments that are low in carbonate (Cooke et al., 2000).

Secular Distribution of Sediment-Hosted Pb-Zn Metal: Limitations and Constraints

The secular distribution of the total contained Pb + Zn metal in known CD deposits is plotted in 20-m.y. increments (Fig. 6). Most ages reflect the age of the host rocks, but a few represent the measured date of the mineralization. For MVT deposits, Figure 7A shows the distribution of the total contained metal versus the age of their host rocks and Figure 7B presents the distribution of metals in dated MVT deposits and districts. The data used to construct the secular plots are from Taylor et al. (2009). These plots (Figs. 6, 7) provide the basis for the following discussions on the genesis and preservation of sediment-hosted Pb-Zn deposits in Earth history. We examine the uneven secular distribution of MVT and CD metals in Earth history with respect to their contrasting tectonic settings and evolving Earth geochemical systems. However, we first summarize some important limitations on our interpretations

Age of ore deposition

The age of ore formation relative to the host sediments for some CD Pb-Zn deposits are contentiously debated; however, there is reasonable evidence that they formed in syngenetic to early diagenetic environments or during early burial diagenesis. Thus, these ores have depositional ages that are the same or close to the age of the host rocks (Large et al., 2005; Leach et al., 2005b). The CD Pb-Zn ores were precipitated in or with relatively immature sediments, which, at the time of mineral formation, contained abundant primary porosity and well-preserved sedimentary fabrics. Therefore, sulfide textures commonly appear to be syndepositional. Whether the textures are synsedimentary or not, the assumption is that CD ores are close in age to the enclosing sediments. There is good evidence, for example, for syngenetic exhalite (SEDEX) ores at Sullivan (Lydon et al., 2000), subsea-floor diagenetic replacement ores in the Red Dog district (Kelley and Jennings, 2004), and ore formation during burial diagenesis at the Century deposit (Broadbent, 1998). Red Dog is the only CD Zn-Pb deposit that has been dated both by isotopic methods (Morelli et al., 2004) and by paleomagnetic methods (Lewchuk et al., 2004); by either measure, the age of ore formation is indistinguishable from the conodont age of the host rocks (Dumoulin et al., 2004). Although a number of CD Pb-Zn deposits have Pb isotope model ages, only the Australian deposits (discussed below) have been dated using a calibrated local crustal lead isotope evolution model, which provides a more precise age of ore

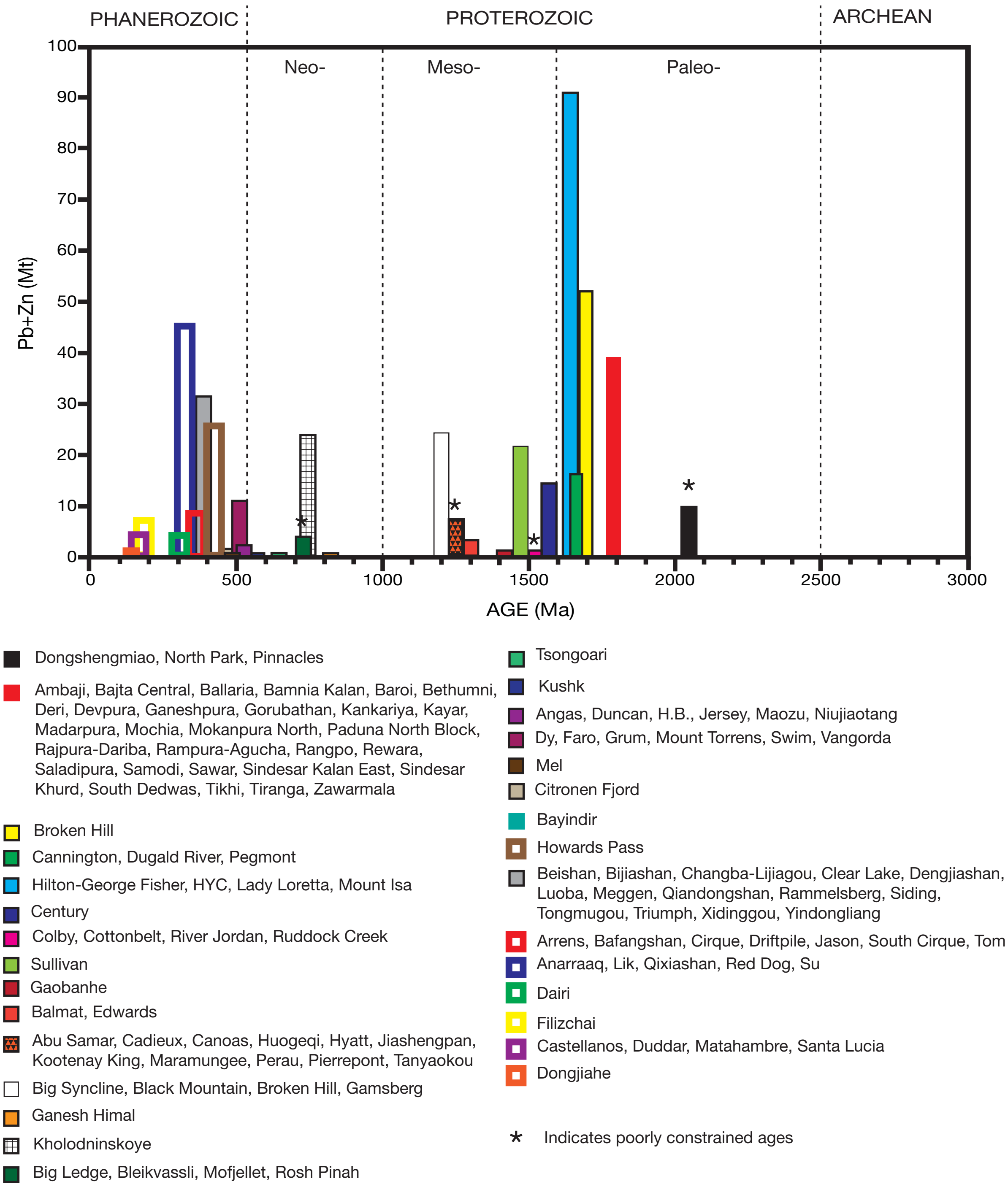


FIG. 6. Distribution of contained Pb + Zn metal in known CD deposits. Age and tonnage data for 121 deposits from Taylor et al. (2009). Deposits are identified and plotted in 20-m.y. age increments for their host rocks, or in a few cases, using the measured date of mineralization. Bins of deposits are listed from oldest to youngest in the legend.

deposition. Some Proterozoic CD Pb-Zn deposits have poor age constraints and are distinguished only as Neoproterozoic, Mesoproterozoic, and Paleoproterozoic.

The MVT deposits are usually low-temperature epigenetic replacement ores and, therefore, the age of ore deposition is inherently difficult to determine. Nearly one-half of the total metal endowments of MVT deposits and districts have been dated by isotopic and paleomagnetic methods (Fig. 7). Ages of mineral deposit formation vary from early diagenesis (e.g., some Irish Midlands deposits, Ireland; Lennard Shelf, Australia) to tens or hundreds of million years younger than the host rocks (Fig. 7A, B).

Classifications

For most deposits, the subtype classifications (CD or MVT) and their tectonic settings are clear (Taylor et al., 2009).

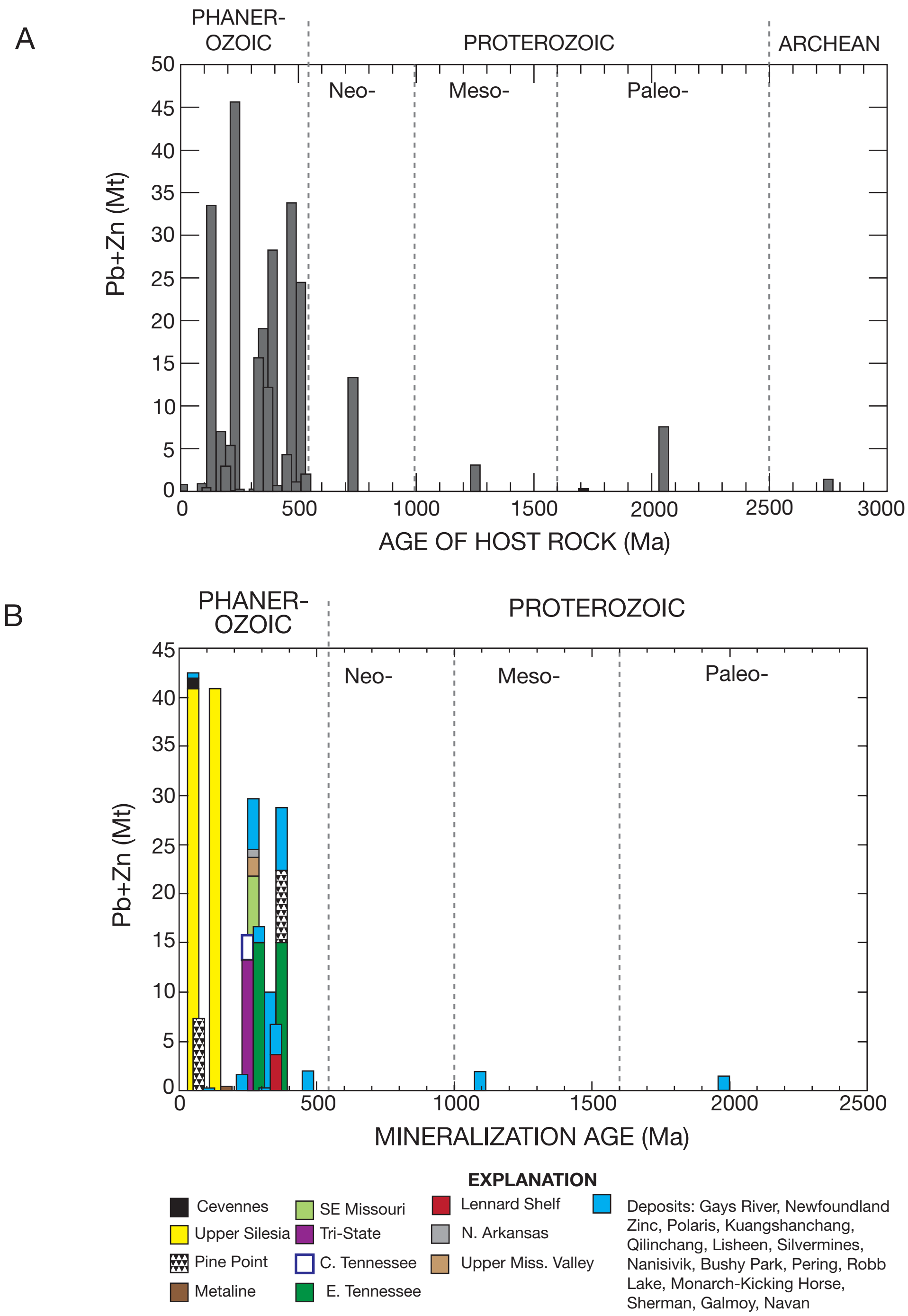


FIG. 7. A. Distribution of total contained Pb + Zn metal in known MVT deposits vs. the age of their host rocks plotted in 20-m.y. age increments. Data from Taylor et al. (2009). B. Distribution of total contained Pb + Zn metal in known MVT deposits vs. the measured age of ore deposition plotted in 20-m.y. age increments. Metal resource data and references for ages are given in Taylor et al. (2009). Note that data for Upper Silesia, East Tennessee, and Pine Point districts are plotted in different time increments (color coded) due to conflicting age determinations.

However, some deposits lack sufficient geologic information to unequivocally classify the ores or to establish the tectonic environment in which they formed. In many cases, the absence of a precise age of ore deposition, together with equivocal ore textures and original deposit morphology, further complicate the problem of classification.

Preservation and destruction of the ores

It is well known that much of the rock record has been eroded, subducted, or metamorphosed and deformed to the extent that the original depositional or tectonic settings are unrecognizable (e.g., Gilluly, 1949; Veizer, 1988; Veizer et al., 1989; Veizer and Mackenzie, 2003). Therefore, the secular distribution of sediment-hosted Pb-Zn ores reflects not only the genesis of the ore deposits but also their preservation or destruction. Veizer et al. (1989) studied the temporal distribution of ore deposits in terms of cycling processes based on estimated destruction rates for groups of metals, but their study was limited in applicability due to the focus on metals, rather than on deposit types. Veizer and Mackenzie (2003) argued that the tectonic regime mainly determines the survival of sedimentary rocks; therefore, the contained ore deposits are transported through time with their host sedimentary rock sequence. For example, the potential for the preservation of CD deposits in passive margins reflects the life span of the ocean basin (Bradley, 2008) and whether the host strata are subducted, metamorphosed, and uplifted in an orogenic belt. Garrels and Mackenzie (1969) suggested that resistance to weathering of various rock types imparts additional variations on survival potential; in certain climate regimes, carbonates will be recycled faster than sandstones due to their lower resistance to chemical weathering (Fig. 8). It is reasonable to assume that a significant, but undefined, number of sediment-hosted Pb-Zn deposits have been removed from the rock record. Consequently, interpretations of the genesis of these ores through time are limited to the deposits that have been preserved.

The Evolution of the Earth's Atmosphere and Hydrosphere

The emergence of CD Pb-Zn deposits between 2.02 Ga, the age of the earliest known deposit of this type, and 1.85 to 1.58 Ga, a major period of CD ore formation in Australia and India, corresponds to a period of major change in the compositions of the atmosphere and hydrosphere. Most workers (e.g., Cloud, 1972; Walker et al., 1983; Rye and Holland, 1998; Huston and Logan, 2004; Farquhar et al., 2010) agree that the atmosphere and, for the most part, the hydrosphere, were reduced prior to about 2.4 Ga. During the time period from about 2.4 and 1.8 Ga, commonly referred to as the Great Oxygenation Event, the atmosphere became progressively oxygenated as the result of the loss of H_2 to space (Tian et al., 2005) and/or the evolution of O_2-producing organisms (Anbar and Knoll, 2002). However, the response of the hydrosphere, including response of basinal brines, was more complex. The main consequence of the oxidation of the atmosphere on the hydrosphere was progressive oxidation caused by input into oceans of riverine sulfate derived by the oxidative weathering of sulfide minerals, equilibration of the upper parts of the oceans with the atmosphere, and significant changes in the ecology of sulfur-utilizing organisms (Farquhar et al., 2010). These processes probably produced major redox and compositional gradients in the oceans.

The change in oceanic composition was most rapid in shallow marginal seas and shelf environments (Fig. 9), which resulted in oxidized, relatively sulfate rich shallow seawater in these basins. As discussed by Lyons et al. (2006), Canfield and Raiswell (1999), and Farquhar et al. (2010), and supported by $\delta^{34}S$ characteristics of pyritic shales, bacteriogenic reduction of sulfate in these deep basins was nearly complete, leading to the persistence of deep, anoxic ocean waters perhaps into the Neoproterozoic. Importantly, the presence of abundant Fe^{2+} in these deep waters would have limited the amount of reduced sulfur, leading, at least prior to ~1.8 Ga (c.f. Huston and Logan, 2004), to reduced and relatively S poor deep seawater. Only after the oceans were scrubbed of Fe^{2+} during extensive deposition of iron formations between 1.95 and 1.85 Ga would S contents of the deep oceans have increased.

The emergence of CD deposits appears to have corresponded to this time period in which shallow, oxygenated, sulfate-rich seawater coexisted with deeper, reduced seawater. Sites and time periods where these contrasting fluid types and their derivative brines and sediments interacted would have been ideal locations or periods for the formation of CD deposits.

Corresponding to the first appearance of significant CD Pb-Zn deposits was the Sudbury impact at 1.85 Ga that Slack and Cannon (2009) suggested affected the SO_4/H_2S ratio of the deep oceans and abruptly altered their redox state to suboxic conditions. Furthermore, they argued that this would explain the end of banded iron formations in the Lake Superior region of North America and may have provided the global redox conditions necessary to effectively produce the first large CD Pb-Zn (SEDEX) ores at ca. 1.85 to 1.80 Ga. We note that the first appearance of CD Pb-Zn deposits at 2.02 Ga, as well as the oldest known MVT deposit at Pering, South Africa (2.1–2.0 Ga), corresponds to the large Vredefort impact at 2.02 Ga.

Subsequent to the Great Oxygenation Event and to about 1.0 Ga was a time described by Hazen et al. (2008) as that of the intermediate ocean in which the hydrosphere and atmosphere were in intermediate oxidation states (Farquhar et al., 2010). This was a time of relative stability in Earth systems, referred to as the Boring Billion by Holland (2009).

Between 0.8 Ga and the end of the Proterozoic at 0.54 Ga was a time of major changes in the redox state of the atmosphere and hydrosphere, referred to as the Second Great

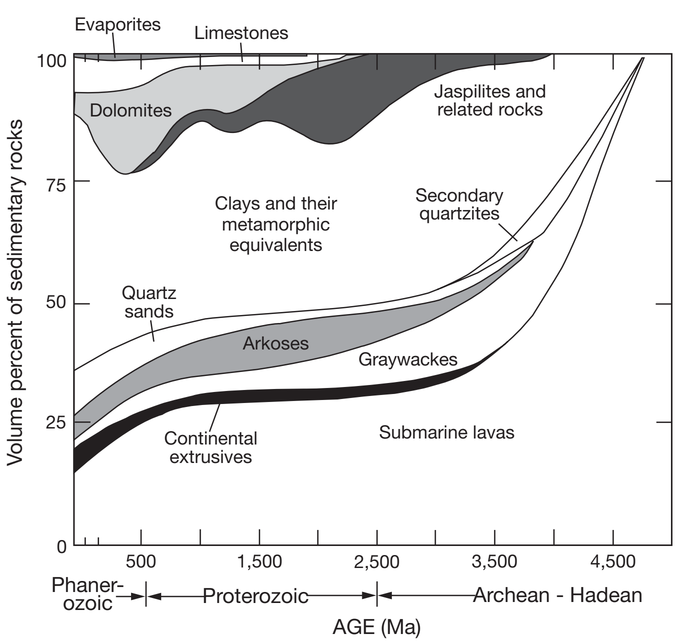


FIG. 8. Volume percent of sedimentary rocks through time. Modified from Ronov (1964) and Veizer and Mackenzie (2003). Note the increase in volume of carbonates in the Neoproterozoic and early Paleozoic discussed in the text.

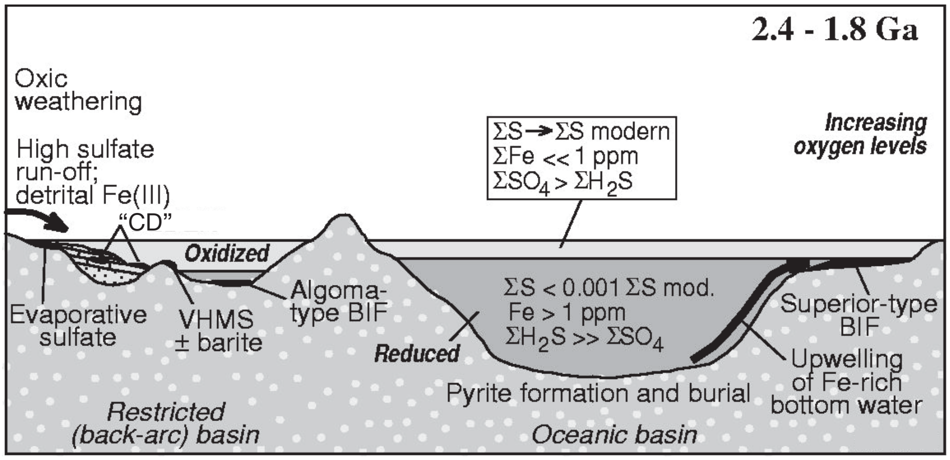


FIG. 9. Progressive oxidation of the hydrosphere between 2.4 and 1.8 Ga as a consequence of the Great Oxygenation Event (after Huston and Logan, 2004). Weathering and oxidation of rock sulfide associated with an oxidizing atmosphere leads to sulfate-bearing runoff. This runoff progressively enriches the upper layer of oceans and shallow basins in sulfate, resulting in an upper oxidized zone. The Sudbury bolide impact at ~1.85 Ga may have caused extensive oceanic mixing to produce a suboxic ocean (Slack and Cannon, 2009).

Oxygenation Event (e.g., Holland, 2005; Hazen et al., 2008). This was a period characterized by the progression to widespread oxygenation of the oceans that was indicated by the rapid reappearance of deep-water iron oxide and sedimentary Mn deposits (e.g., Holland, 2005; Canfield et al., 2007). Perhaps related to these changes in redox states were at least two Snowball Earth events between about 750 to 550 Ma (Hoffman et al., 1998; Kennedy et al., 1998), with a duration of perhaps 10 m.y. each (e.g., Bodiselitsch et al., 2005). Following the glacial cycles were periods of global algae blooms that contributed to an increase in atmospheric oxygen to Phanerozoic levels, increased oxidative weathering that led to increased abundance of seawater sulfate and evaporites (Hazen et al., 2008, and references therein). Canfield and Farquhar (2009) suggested that the increase in sulfate in this period can be attributed to the onset of bioturbation that reduced a significant sink for reduced sulfur in the oceans.

Although not linked to the oxygenation of Earth, a second major change in the composition of the hydrosphere was a decrease in the salinity of seawater through much of the Proterozoic. Fluid inclusion data from the downwelling parts of sea-floor hydrothermal systems indicate a salinity of about 10 wt percent NaCl equiv at 3.24 Ga (Drieberg, 2003), indicating that Archean seawater was as much as three times more saline than modern seawater. Gützmer et al. (2003) estimated a seawater salinity of as much as 5 wt percent NaCl equiv at 2.2 Ga, more than 1.5 times that of modern seawater. These salinity estimates are consistent with the general model for salinity variations of Knauth (2005), who suggested that Proterozoic and Archean seawater was much more saline than modern seawater. He suggested that through the Archean, seawater salinities were high, 1.5 to 2 times modern values, because of the absence of long-lived continents, which prevented the formation of evaporites and basinal brines that sequestered salt. When long-lived cratons developed during the Proterozoic, salinity of the ocean decreased because the development of epicratonic basins allowed sequestration of salt into evaporite deposits and basinal brines. Since the end of the Neoproterozoic, the salinity of the oceans has been relatively constant at modern values (Knauth, 2005).

Secular Tectonics

The secular distribution of total contained Pb and Zn metal in known CD deposits together with their assigned tectonic settings from Taylor et al. (2009) is shown in Figure 10. The secular distribution of the CD metals and the names of the individual deposits that fall within the age bins are presented in Figure 6. It is clear that CD deposits are unevenly distributed in time and in their tectonic settings. Continental rift and sag basin CD deposits are restricted to the Proterozoic, whereas passive margin-hosted deposits are more widely distributed. The abundance of CD ores and the tectonic settings of their host rocks do not strongly correlate (Fig. 10).

Since before the time of the oldest known CD ores in the Paleoproterozoic, Earth's tectonic regime has been dominated by plate tectonics (e.g., Condie, 2005; Brown, 2008). The main global tectonic changes, and those most pertinent to the present topic, have involved the assembly, tenure, and disassembly of a series of supercontinents, which are defined loosely as a large gathering of continents. Each iteration of the supercontinent cycle has taken place against a backdrop of other secular change, for example, in the Earth's heat production, oxidation state of the exosphere, and importance of life as a geologic agent.

One control of the age distribution of sediment-hosted Pb-Zn ores is that the requisite tectonic settings are themselves unevenly distributed through time. Passive margins were relatively abundant at ca. 2640 to 2470, 2000 to 1880, 670 to 560, 540 to 445, and 150 to 0 Ma; they were scarce at ca. 2445 to 2300, 1600 to 1000, and 300 to 275 Ma; and they were absent before ca. 3000 and at 1740 to 1600 Ma (Bradley, 2008). These fluctuations are manifestations of the supercontinent cycle, as discussed further by Bradley (2008). If all other influences were constant, then the secular distribution of ore deposits in passive-margin host rocks would broadly follow this age pattern.

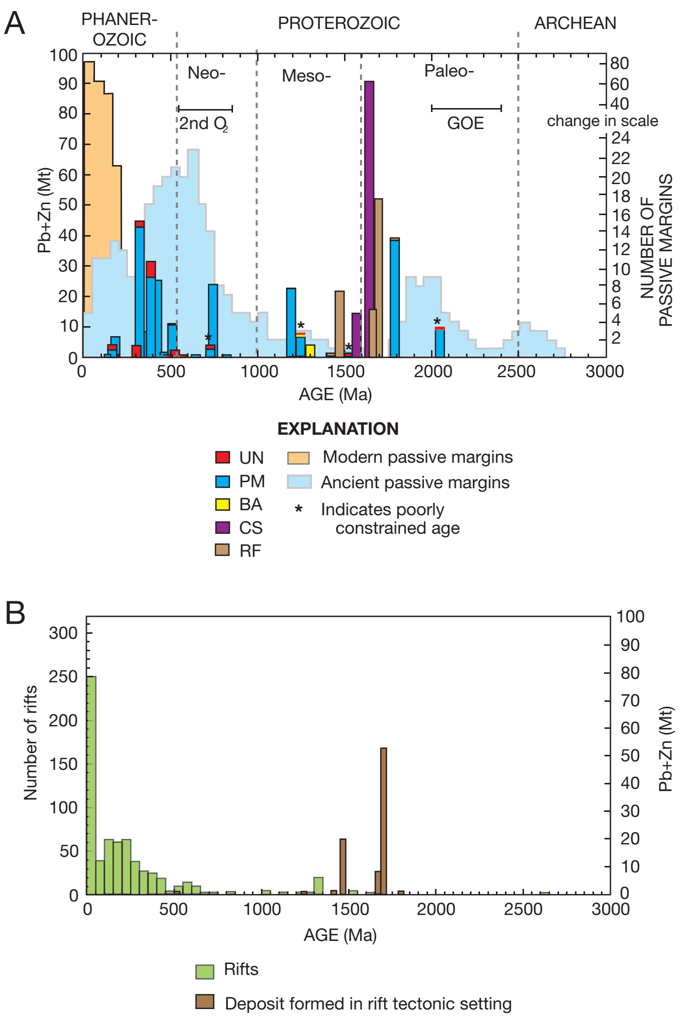


FIG. 10. A. Distribution of total contained Pb + Zn metal in known CD deposits plotted in 20-m.y. age increments of host-rock age and their tectonic setting. Data from Taylor et al. (2009). Abbreviations: BA = back-arc basin, GOE = Great Oxidation Event, CS = continental sag, 2nd O_2= Second Great Oxidation Event, PM = passive margin, RF = continental rift, UN = unclassified tectonic setting. Number of passive margins per age increments shown in blue histogram from Bradley (2008). B. Distribution of rifts from data of Sengor and Natalin (2001) and secular distribution of CD Pb-Zn deposits formed in rift tectonic settings.

The same might be expected to hold for rifts and rift-related CD Pb-Zn deposits, but this is not the case. A census of the world's rifts (Sengor and Natalin, 2001) has been re-plotted as a histogram in Figure 10B. In this inventory, the modern rifts were counted quite accurately because they are obvious. Conversely, three subsets of rifts are underrepresented in the histogram: those in the Precambrian with such poor age control that they could not be accurately plotted, severely deformed rifts that were difficult to recognize for what they originally were, and rifts beneath modern or ancient passive margins, which were deliberately excluded from the inventory of Sengor and Natalin (2001). The resulting age distribution is dominated by Phanerozoic rifts and particularly by the very youngest ones (<50 Ma). There is no indication that Proterozoic CD deposits are abundant because they formed at a time of unusually abundant rifting. Betts et al. (2003) suggested that the far-field, continental back-arc setting of the Australian Proterozoic deposits was particularly favorable for CD mineralization. Why are CD deposits not more abundant in the younger rift and sag basins? One possible factor is basin inversion, the deformation process that can expose the deep, axial portions of rifts that would normally be buried by younger sediments. Thus, the existence of a world-class Proterozoic CD province in Australia is known to exist because the rift system, which formed, fortuitously, in an arid latitude, was inverted. In contrast, classic examples of younger rifts (e.g., East African, Reelfoot, Baikal, and Rhine) are classic because they have not been inverted. Clearly, the tectonic setting is one control on ore formation, but it alone cannot be a deciding factor in whether or not CD deposits will form.

Geology and Geodynamic Settings of Selected CD Pb-Zn Deposits

Phanerozoic and Neoproterozoic CD deposits in passive margins

The Phanerozoic CD deposits are mainly hosted in Atlantic-type passive margins (i.e., Brooks Range, Alaska), a few in a passive margin of a back-arc basin (i.e., Rammelsberg), and some have uncertain tectonic settings. Below we briefly describe selected deposits to illustrate their diversity and the spectrum of tectonic settings.

Red Dog deposits of the Brooks Range, Alaska: The giant Red Dog deposits consist of massive sulfides and barite deposits that are hosted in organic-rich siliceous mudstone and shale, chert, and carbonate rocks of the Carboniferous Kuna Formation in the Brooks Range, Alaska (Moore et al., 1986; Kelley and Jennings, 2004; Kelley et al., 2004b; Young, 2004). It is generally accepted that the rocks of the Brooks Range represent a former passive margin of the Arctic Alaska terrane that separated from the Canadian Arctic during the opening of the Canada Basin (Moore et al., 1986; Lawver and Scotese, 1990; Symons and McCausland, 2006).

The Red Dog deposits contain the world's largest concentration of Zn that formed by subsea-floor replacement of an early sea-floor barite mound (Johnson et al., 2004); possibly some interbedded carbonate turbidites were replaced as well. Based on textural and field evidence (e.g., Kelley and Jennings, 2004; Kelley et al., 2004b), together with isotopic dating (Morelli et al., 2004) and paleomagnetic dating (Lewchuk et al., 2004), sulfide mineralization is interpreted to have been broadly contemporaneous with sedimentation and early diagenesis.

In contrast to the Red Dog deposits where the bulk of the sulfides replaced early barite, massive sulfides and barite are temporally and spatially separate and, in many cases, absent in other nearby Brooks Range deposits. In addition to the Red Dog deposits, other CD deposits of the Brooks Range hosted in rocks of the Carboniferous Kuna Formation include the Anarraaq deposit in which ores replaced a carbonate turbidite deposit in a submarine channel (Kelley et al., 2004a). The sulfide zone is separated by ~100 m from another carbonate turbidite that was replaced by massive barite. The replaced carbonate turbidites at Anarraaq contain more than a billion metric tons of barite (Jennings and King, 2002). In the vicinity of the Red Dog deposits, bimodal igneous material consists of small felsic and mafic diabase sills near the orebody. Igneous rocks are absent at the Anarraaq deposit but volumetrically important at the Drenchwater deposit, another CD deposit about 140 km east of Red Dog.

Leach et al. (2004) proposed a reflux brine model for the genesis of the Red Dog ores in which the brines were produced in time-equivalent coastal marine evaporative environments in supratidal carbonate facies of the Lisburne Group less than 100 km from the Red Dog deposits (Fig. 11). Reconstruction of the paleogeographic position where the Red Dog deposits formed is within Phanerozoic evaporative latitudes (Fig. 12A). It should be noted that the evaporative environment does not contain massive evaporates, but rather, textural evidence shows that gypsum formed in evaporative flats. In this model, seawater evaporative brines infiltrated into the underlying clastic rocks of the Devonian Endicott Group or fractured metasedimentary basement rocks that are believed to be the source of the metals (Ayuso et al., 2004). In the Red Dog area, the metalliferous fluids ascended into the organic-rich rocks of the Kuna Formation and precipitated the ores (Fig. 12B). Some essential requirements for the formation of the Red Dog deposits and possibly other passive-margin CD deposits are (1) a large source of reduced sulfur necessary for the precipitation of Pb and Zn from an oxidized metalliferous fluid, with likely sources of reduced sulfur including sulfate reduction facilitated by organic matter or bacteria in the organic-rich sediments or reduced basin fluids; (2) a proximal brine source in the adjacent coastal carbonate platform; and (3) a permeable and oxidized clastic aquifer or fractured basement underlying the passive-margin sedimentary sequence to provide adequate transport of the oxidized metalliferous brines.

Kholodninskoye CD deposit, Russia: The Kholodninskoye deposit is one of the largest CD deposits in the world, containing 340 Mt ore at 6 percent Zn and 0.9 percent Pb. The deposit is hosted in a metamorphosed and deformed Neoproterozic passive-margin sequence on the southern margin of the Siberian craton (Dobretsov et al., 1987; Dobretsov, 1996; Pisarevsky and Natapov, 2003). The details of the primary ore depositional environment were destroyed by dynamic metamorphism. However, Pb model ages for the ore and host rocks suggest an age of mineralization of 760 to 720 Ma (Dobretsov, 1996), well before terrane collision at ca. 600 Ma.

Deposits of the Selwyn basin, Canada: The Selwyn basin is a long-lived, off-shelf depocenter along the western (present direction) passive margin of Laurentia. This part of the Laurentian margin formed by continental breakup in the late Neoproterozoic (Colpron et al., 2002) and it appears to have undergone later episodes of extension in the Cambrian, Silurian, and Devonian, each synchronous with ore formation. Devonian extension has been variously assigned to settings of an extensional back-arc (e.g., Goodfellow, 2007) or a flexurally extending collisional foreland (Smith et al., 1993). The Selwyn Basin contains four CD districts: MacMillan Pass and

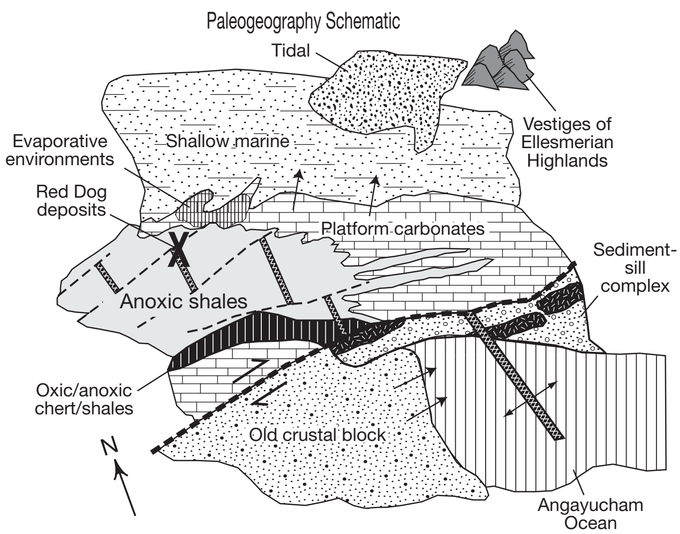


FIG. 11. Restored paleogeography of the Red Dog area in Late Carboniferous (modified from Young, 2004). A possible source for the evaporative concentrated seawater for the ore fluids was a sabkha and/or coastal evaporative environment north of the Red Dog deposits.

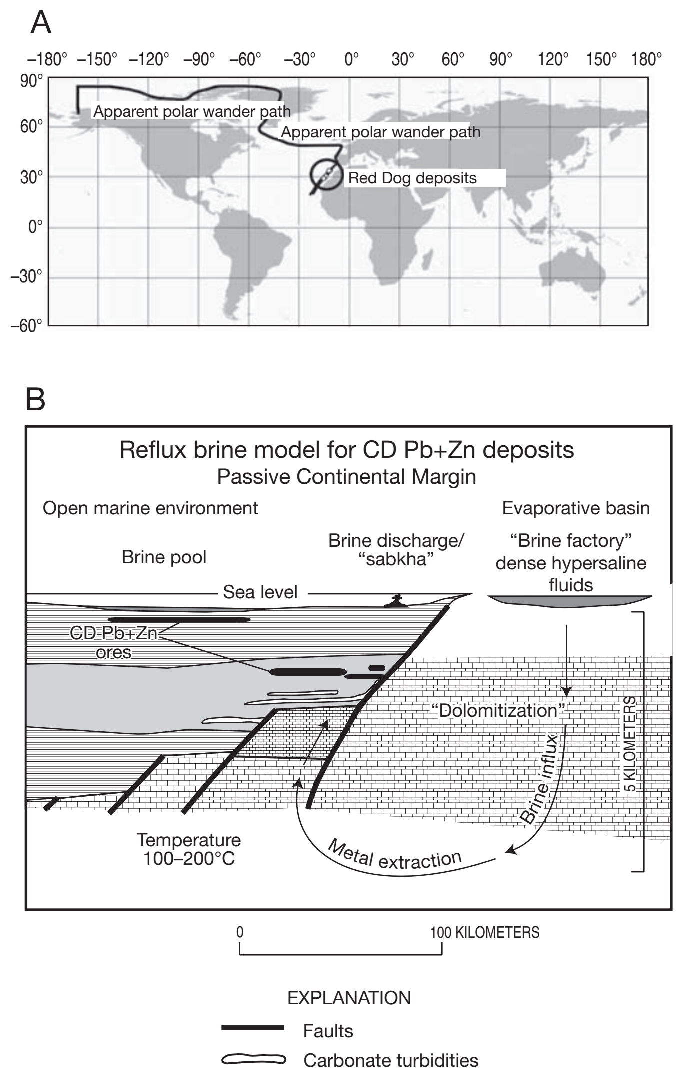


FIG. 12. A. Reconstruction of the paleolatitude where the Red Dog deposits formed at 338 Ma (circle) using a GIS-based plate reconstruction of Scotese (2002). B. Reflux brine model for the giant Red Dog deposits, Alaska, from Leach et al. (2005b).

Gataga (Devonian), Howards Pass (Early Silurian), and Anvil (Late Cambrian). The MacMillan Pass district includes the Tom and Jason, Anvil, Vangorda and Dy deposits. The CD deposits in the Selwyn basin are described in detail by Goodfellow et al. (1993) and Goodfellow (2007). They interpreted the ores as having formed from exhalative processes in anoxic seawater columns in the Selwyn basin. The world-class resource at Howards Pass contains 855 Mt of combined 6.5 percent Zn and Pb (Goodfellow, 2007). Unusual for most CD Pb-Zn ores, anomalous Cu and Au contents are reported for the Devonian Dy and Vangorda deposits at 0.3 percent and 0.8 g/t, respectively (Goodfellow, 2007). Similar to the Red Dog district, base metal-barren stratiform barite deposits are common in the sedimentary sequence in the Selwyn basin. Nevertheless, barite appears to be a significant part of the distal ore assemblage in some deposits (i.e., Jason and Tom) but is notably absent from the giant Howards Pass deposit.

Rammelsberg Zn-Pb-Cu deposit, Germany: The Rammelsberg Zn-Pb-Cu deposit is one of the few Phanerozoic CD deposits with high Cu and Au contents, spatially associated bimodal volcanic rocks, and a high temperature (~300°C) of ore deposition (Large, 2003). The deposit is hosted in organic-rich Middle Devonian siliciclastic rocks of the Rhenohercynian basin on the passive continental margin of the Laurussian continent (Muchez and Stassen, 2006). During the Late Carboniferous Variscan orogeny, the ores were deformed and metamorphosed. Large (2003) and Large and Walcher (1999) described the tectonic setting as the postrift sedimentary sequence of the Laurussian passive margin, whereas Mueller (2008) stated that the tectonic setting was a marine back-arc rift basin. As discussed previously, the difference between the passive-margin and back-arc tectonic classifications with respect to Rammelsberg may reflect more semantics than processes. This 27 Mt ore deposit contains 19 percent Zn + 9 percent Pb, is rich in Cu and Au (1% and 0.5–1.0 g/t, respectively), and is barite bearing. The high temperature of ore deposition and presence of significant Cu, Au, and barite in the deposit is consistent with a reduced fluid model (Cooke et al., 2003; Mueller, 2008). Mueller (2008) described the ore as a vent-proximal deposit that formed from a hot, reducing, and acidic brine pool.

Mesoproterozoic and Paleoproterozoic deposits

The Proterozoic, particularly the latter part of the Paleoproterozoic and the Mesoproterozoic, is the dominant period of Earth's history during which CD deposits formed. Although the earliest known deposits have an age of 2020 Ma, the main period of Proterozoic CD mineralization was between 1850 and 1490 Ma. This period includes formation of major deposits in Sweden, India, Canada, South Africa, United States, and Australia. In Australia, the deposits are located in two subcontinental blocks, the North and South Australian cratons.

CD deposits in the North Australian craton: Although the oldest known Zn-Pb prospect in northern Australia, the Namoona prospect (Ahmad et al., 2006), is hosted by ~2020 Ma rocks (Worden et al., 2008), with a similar lead isotope model age (Sun et al., 1996), the main period of Proterozoic CD ore formation in the North Australian craton was between 1690 and 1575 Ma. Mineralization was episodic and produced the North Australian zinc belt (Fig. 13), which includes deposits of both the sag- and continental rift-hosted classes. This belt contains global (production plus geologic resources) resources of nearly 120 Mt Zn and Pb, which is slightly more than one-half of Australia's global Zn and Pb resources (Huston et al., 2006).

The North Australian zinc belt is comprised of three superbasins overlying the polydeformed basement (Fig. 13). The oldest superbasin, the 1780 to 1740 Ma (Page et al., 2000) Leichhardt superbasin, contains a rift sequence dominated by continental tholeiites, fluvial to lacustrine siliciclastic rocks, and lesser carbonate rocks (Jackson et al., 2000). The second superbasin, the 1740 to 1710 Ma (Page et al., 2000) Calvert superbasin, consists of continental to shallow marine siliciclastic and carbonate rocks, including red beds, which are interlayered with intrusive and extrusive felsic and mafic volcanic rocks that were emplaced in a rift environment (Jackson et al., 2000). Parts of this basin were extensively K-feldspar-hematite altered at ~1640 Ma (Cooke et al., 1998), losing both Zn and Pb, and suggesting that the Calvert superbasin was an important metal source to CD deposits in the overlying Isa superbasin.

The relationship of the eastern part of the Zn belt to the Calvert superbasin is complex. The Soldiers Cap Group is dominated by deep-water turbidites and contains mafic and minor felsic volcanic rocks (Beardsmore et al., 1988). Their ~1676 Ma age (Page and Sun, 1998) postdates deposition of the shallow marine part of the Calvert superbasin but corresponds in time with development of an unconformity and granite emplacement to the west (Neumann et al., 2009). This unconformity, the coeval magmatism, and change in style of sedimentation suggest opening of the rift basin to the east. The oldest CD deposits, the continental rift-hosted Cannington and Pegmont deposits, are hosted by these rocks.

The third superbasin, the 1665 to 1595 Ma Isa superbasin (Page et al., 2000; Neumann et al., 2006), overlies the Calvert superbasin and the Soldiers Cap Group. The older part of the basin comprises fluviatile to shallow-marine sandstone, siltstone, and dolomite, with lesser black shale and minor felsic volcanism, whereas the younger part of the superbasin comprises turbidite, carbonaceous shale, and stromatolitic dolostone deposited in a shallow- to deep-marine environment (Hutton and Sweet, 1982; Southgate et al., 2000; Betts et al., 2006).

Although consensus exists that the Leichhardt and Calvert superbasins and the Soldiers Cap Group filled rifts in an extensional environment (Jackson et al., 2000; Giles et al., 2003; Gibson et al., 2008), opinion regarding the geodynamic setting of the Isa superbasin differs. Historically, deposition of rocks of the Isa superbasin has been considered the consequence of postrift thermal sag (Etheridge and Wall, 1994; Betts and Lister, 2001; Betts et al., 2003, 2006). Alternatively, Southgate et al. (2000) suggested a model whereby deposition of the Isa superbasin rocks was controlled by the development of pull-apart basins associated with dilational jogs related to north- to northeast-trending sinistral faults. In yet another alternative, Gibson et al. (2008) indicated that the Isa superbasin comprises two parts, an extensional older (1670–1640 Ma) sequence and a postextensional younger (1640–1595 Ma) sequence. In this model, the early phase of

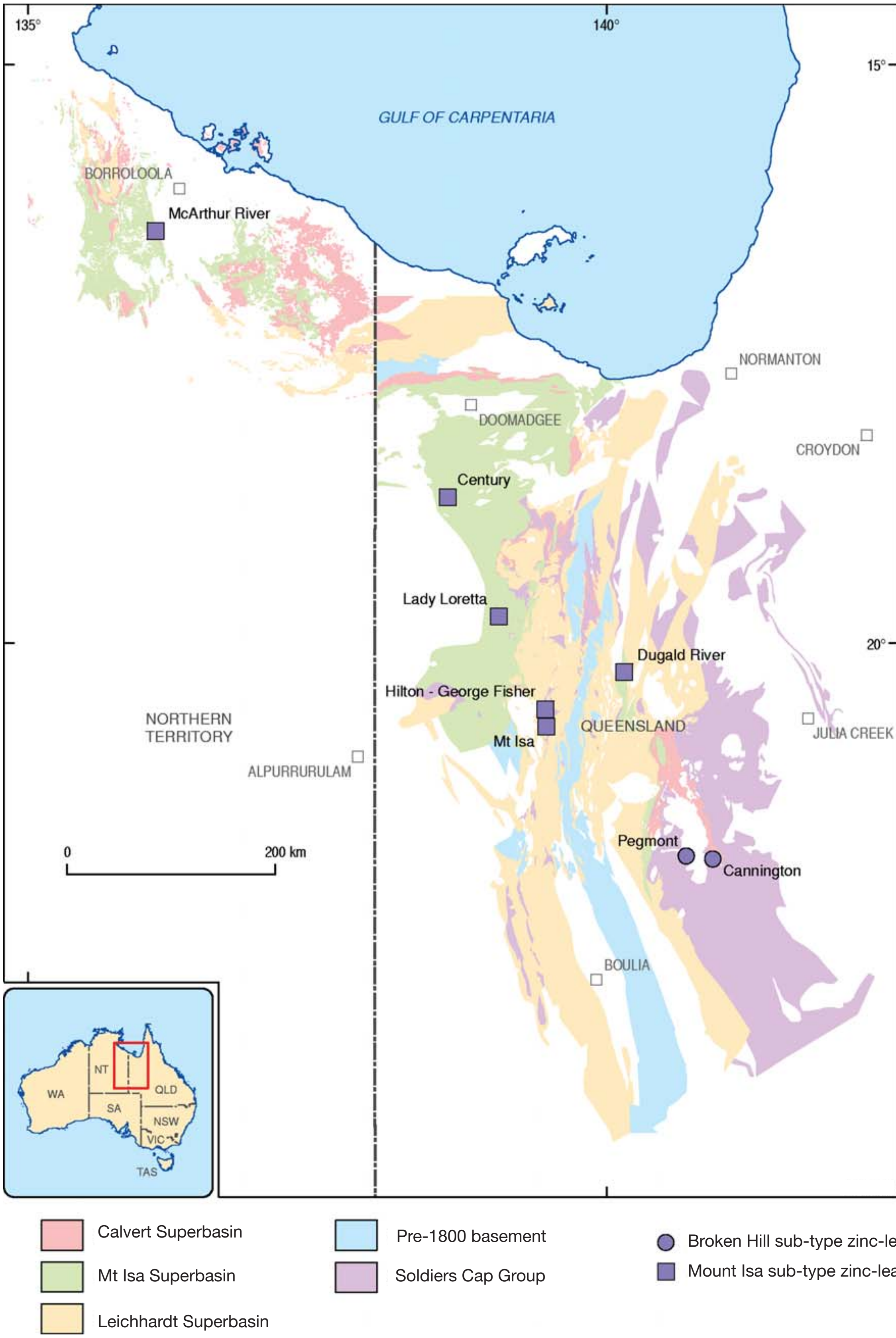


FIG. 13. Map of North Australian zinc belt showing the mapped distributions of basement, the Soldiers Cap Group, the Leichhardt, Calvert, and Mount Isa superbasins, and major Zn-Pb-Ag deposits.

the basin was formed through continuation of rifting initiated during Calvert time. However, the later phase is interpreted as postrift (Gibson et al., 2008).

Additional constraints on the geodynamic evolution of the North Australian zinc belt are provided by the Paleoproterozoic to Mesoproterozoic apparent polar wander path for the North Australia craton (Idnurm, 2000), which defines a series of bends that reflect plate reorganization. Major flexures at ~1650 Ma (B3) and ~1590 Ma (B5) and a U-turn at ~1640 Ma (B4) overlap the evolution of the Mount Isa basin. The ~1650 Ma bend and the ~1640 Ma U-turn correspond to major periods of continental sag-hosted Zn-Pb mineralization, and a sharp bend at ~1680 Ma (B2) corresponds to continental rift-hosted mineralization in rocks of the Soldiers Cap Group. Although the bend at ~1650 Ma cannot be correlated with known geodynamic events, the bend at ~1590 Ma corresponds with cessation of deposition in the Isa superbasin and initiation of the first phase of the Isan orogeny (Betts et al., 2006). The U-turn corresponds to the 1640 to 1635 Ma Liebig orogeny, the result of accretion of the Warumpi province along the southern margin of the North Australian craton (Scrimgeour et al., 2005). Paleomagnetic and geochronological data constrain formation of a syncline at the HYC deposit, 900 km to the north of the craton margin, to ~1639 to 1636 Ma (Symons, 2007). Hence, CD deposits in the North Australian zinc belt appear to correspond to significant tectonic changes that were well removed from mineralization.

Continental rift-hosted deposits at Cannington and Pegmont, which are hosted by rocks of the ~1676 Ma Soldiers Cap Group (Page and Sun, 1998; Walters and Bailey, 1998), are the oldest deposits in the North Australian zinc belt. The Pb isotope model age of ~1665 Ma for the Cannington deposit is similar to the age of the host unit. In addition to turbiditic rocks, the Soldiers Cap Group contains significant tholeiitic amphibolite and metabasalt, along with minor felsic volcaniclastic rocks (Beardsmore et al., 1988). The Ag-rich Cannington deposit, which is hosted by amphibolite facies migmatitic quartzofeldspathic gneiss, is comprised of four separate, apparently stratiform lenses associated with skarn-like alteration assemblages, including pyroxene, garnet, olivine, fluorite, apatite, and quartz (Bodon, 1998; Chapman and Williams, 1998; Walters and Bailey, 1998).

Most Zn-Pb-Ag ores in the North Australian zinc belt are hosted by rocks of the Isa superbasin, were deposited between ~1655 and 1635 Ma, and are interpreted as continental sag-hosted deposits. The oldest group of these deposits includes the Mount Isa and Hilton-George Fisher deposits. These deposits are hosted by ~1655 Ma (Page et al., 2000) dolomitic and variably carbonaceous, pyrite-rich siltstone (Forrestal, 1990; Chapman, 2004). The deposits consist of a series of discrete, stacked lenses that are as thick as 80 m (Forrestal, 1990). Although the Hilton and George Fisher deposits have been considered to be separate deposits, the two deposits appear to be part of one ore system that was subsequently offset by later faulting (c.f. Chapman, 2004). The Dugald River deposit, which has a Pb isotope model age of ~1662 Ma (Carr et al., 2001), is hosted by metamorphosed dolomitic and carbonaceous siltstone, now schist, and interpreted as a continental sag deposit broadly coeval with the Mount Isa and Hilton-George Fisher deposits.

Other continental sag-hosted deposits in the North Australian zinc belt are hosted by similar units, although at higher stratigraphic positions: HYC is hosted by ~1639 Ma rocks; Lady Loretta is hosted by ~1647 Ma rocks; and Century is hosted by ~1595 Ma rocks (Page et al., 2000). Similar to the older deposits, these deposits are comprised of multiple stacked, stratiform lenses in pyritic, dolomitic, and carbonaceous siltstone (Hancock and Purvis, 1990; Broadbent et al., 1998; Large et al., 2005).

Geodynamic setting of CD deposits in the North Australian craton: In the Mount Isa province, continental rift-hosted deposits (Cannington and Pegmont) are hosted by a deep-water turbiditic basin in the east that developed during incision and granite emplacement to the west (Neumann et al., 2009). This basin formed in a rift setting and it contains significant intrusive tholeiites, which reflect the extension and a relatively high heat flow (Beardsmore et al., 1988; Huston et al., 2006). In contrast, the continental sag-hosted deposits formed in the overlying Isa superbasin, which, with the exception of minor tuffs and peperites, is amagmatic and is interpreted as a thermal sag or foreland basin (Southgate et al., 2000; Gibson et al., 2008). This superbasin unconformably overlies the Calvert basin in the west but may be partly conformable with the Soldiers Cap Group to the east (Gibson et al., 2008; Neumann et al., 2009). As already noted, these changes and the timing of mineralization correspond with major changes in the North Australian apparent polar wander path (Idnurm, 2000), suggesting a close relationship to external tectonic events.

The deposits also display a systematic change in Pb isotope systematics (Fig. 14), both in time and in space. As also discussed in Carr et al. (2001), Large et al. (2005), and Kositcin et al. (2009), the older continental rift-hosted deposits hosted by rocks of the Soldiers Cap Group in the east are characterized by relatively juvenile Pb (μ = 12.74–12.76). In contrast, the younger continental sag-hosted deposits to the west in the Isa superbasin are characterized by more evolved Pb (μ = 12–87–12.90), with the Dugald River deposit having intermediate Pb (μ = 12.80). Although juvenile relative to overall Pb from the North Australian craton (D. Huston, unpub. data), Pb from the continental rift-hosted deposits is more evolved in comparison with similar-aged deposits hosted in back-arc settings, such as the United Verde deposit in Arizona (Fig. 14). These data are compatible with models whereby the continental rift-hosted deposits sourced Pb from rifted continental crust, whereas the continental sag-hosted deposits sourced Pb mostly from the underlying basins and continental crust.

Proterozoic CD deposits in the South Australian craton: Although the known Zn and Pb content of the South Australian craton is less than one-half that of the North Australian craton, this craton contains the Broken Hill deposit which is the world's largest single accumulation of Zn and Pb; before mining began in the late 1880s, Broken Hill contained >50 Mt Zn and Pb. The South Australian craton comprises two provinces, the Curnamona province, which contains the Broken Hill deposit, and the larger Gawler province to the west. Only the Curnamona province is discussed below.

The exposed part of the Curnamona province comprises medium- to high-grade siliciclastic metasedimentary rocks

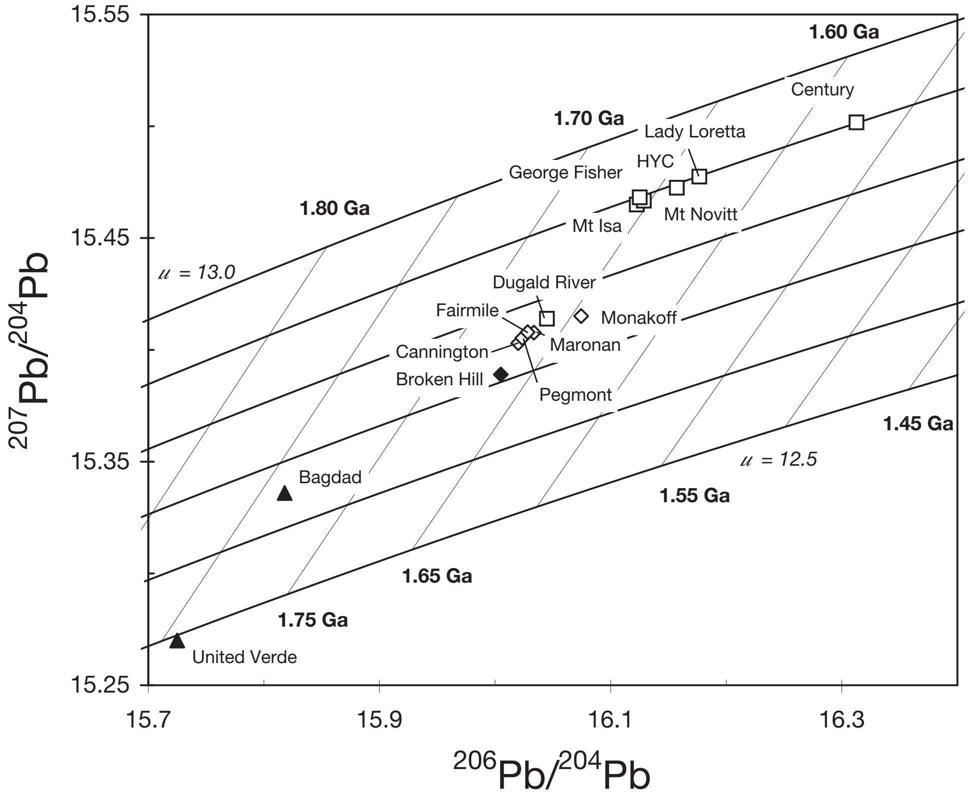


FIG. 14. $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ diagram showing the least radiogenic isotopic composition of galena from CD Zn-Pb deposits in the North Australian zinc belt (open symbols) and the Broken Hill domain (solid symbol) in comparison to the isotopic composition of galena from volcanic rock-hosted massive sulfide deposits in southwestern Laurentia (gray symbols). Squares denote continental sag-hosted deposits, diamonds denote continental rift-hosted deposits, and triangles denote volcanic-hosted massive sulfide deposits. Data are from Carr et al. (2001) and Wooden and DeWitt (1991).

that are dated at 1720 to 1640 Ma (Conor and Preiss, 2008). The lower part (1720–1670 Ma) of this sequence is characterized by bimodal volcanic and intrusive rocks and is interpreted to have formed in a rift environment, whereas the upper part lacks these rocks and is interpreted to have formed in a sag environment (Willis et al., 1983; James et al., 1987; Barovich and Hand, 2008; Conor and Preiss, 2008). The Broken Hill deposit is located near the top of the lower part of the stratigraphy, at a similar position to ~1685 Ma volcaniclastic rocks. These rocks are coeval with extensive intrusion of tholeiitic amphibolites and mafic granulites, and emplacement of felsic sills (Donaghy et al., 1998; Nutman and Ehlers, 1998; Page et al., 2005). These felsic and mafic igneous rocks are not known to extend above the Broken Hill position into the upper part of the Curnmona stratigraphy.

The lower part of the stratigraphy is also characterized by extensive albitites, particularly 500 to 2,000 m stratigraphically below the Broken Hill ore horizon. These rocks are depleted in Pb and Zn, suggesting that they are possible sources for metals in the deposit (Huston et al., 1998). Alternatively, Crawford and Maas (2009) suggested a magmatic-hydrothermal source of metals that was ultimately derived from the mantle.

The Curnamona province contains a large number of Zn-Pb mineral occurrences, the vast majority within the Broken Hill domain. However, only the Broken Hill deposit contains significant amounts of metal; the next largest deposit, the Pinnacles deposit, contains less than one percent the amount of metal contained in the Broken Hill deposit. The Broken Hill deposit is comprised of six separate lenses hosted by metamorphosed psammite of the Broken Hill Group (Haydon and McConachy, 1987). Adjacent to the ore lenses, the host rocks include quartz-garnet and quartz-gahnite-pyrrhotite rocks that are interpreted as metamorphosed alteration assemblages (Groves et al., 2008).

Following the pioneering concepts of King and Thomson (1953), the Broken Hill deposit has been considered by most workers to be a syngenetic deposit (e.g., Stanton, 1976). However, there are widely contrasting interpretations of the genesis of the deposit. Haydon and McConachy (1987) suggested an epigenetic origin similar to sandstone-hosted Pb deposits, and Gibson and Nutman (2004) suggested an epigenetic origin associated with an extensional detachment associated with basin development.

Geodynamic relationship between the South and North Australian cratons: During the past two decades, lithologic and geochronologic similarities between the Curnamona province and, particularly the eastern part of the Mount Isa inlier, have led many authors (e.g., Laing, 1996; Betts et al., 2002; Giles et al., 2002; Gibson et al., 2008) to propose that the North and South Australian cratons were contiguous at least between 1700 and 1670 Ma. If this proposal is correct, continental rift-hosted deposits hosted in the Curnamona province and by rocks of the Soldiers Cap Group would have formed in the same rift, a hypothetical Soldiers Cap-Broken Hill rift. Unlike the Isa superbasin, the Paragon Group and equivalents in the Curnamona province do not have known continental sag-hosted deposits despite being of similar age. However, the lithologic make-up of these two units is quite different; the Paragon-Strathearn Groups are composed entirely of metamorphosed psammo-pelitic units (Conor and Priess, 2008) and lack the dolomitic rocks that are abundant in the Isa superbasin (Southgate et al., 2000). This may suggest that linkage of depositional systems between the South and North Australian cratons had been broken following the development of the hypothesized Soldiers Cap-Broken Hill rift.

Sullivan CD deposit: The Sullivan deposit and the geology of the Belt-Purcell basin are described in detail by Lydon et al. (2000) and Lydon (2007). Other than the Australian deposits, the Sullivan deposit is the most economically significant continental rift-hosted CD deposit in the world. This world-class deposit is hosted in the Mesoprotozoic Aldridge Formation of the Belt-Purcell basin in northwestern United States and adjacent Canada. The deposit consists of a well-defined vent complex containing pyrrhotite, galena, and sphalerite and an upper zone of bedded ores and distal thinly banded sulfides. Lydon et al. (2000) presented evidence that the bedded ores formed as an exhalite. Intense alteration zones consist of tourmaline, chlorite, albite, and sericite.

The Belt-Purcell basin is generally described as a continental rift-sag basin (e.g., Chandler, 2000; Goodfellow, 2000; Lydon et al., 2000; Lydon, 2007, and references therein) that contains >10 to 12 km of reduced marine sediments, turbidites, and interlayered mafic sills, and >4 km of sag facies of fine clastics, and carbonates that show abundant evidence for evaporative conditions, such as gypsum casts. In the vicinity of the Sullivan deposit, mafic sills constitute as much as 40 percent of the Aldridge Formation. Isotopic dating of the sills in and surrounding the Sullivan deposit yields ages between 1.47 and 1.40 Ga (Anderson and Parrish, 2000; Schandl and Davis, 2000). Although the Belt-Purcell basin has traditionally been classified as a continental rift-sag basin, Ross and Villeneuve (2003) interpreted the basin to be an extensional basin that formed in a continental back-arc. Both interpretations can be viewed as minor variants. Some continental reconstructions place the basin near the margin of Laurentia and positioned near the Northern Australian CD deposits (Lydon et al., 2000, and references therein). However, our reconstruction (Fig. 15) places the Belt-Purcell basin distal from the ~200-m.y. older deposits in the North Australian mineral belts. There is abundant evidence for evaporative conditions, including sabkha and/or playa environments during sedimentation of the Belt-Purcell Supergroup (Chandler, 2000), which likely played a role in the genesis of the Sullivan ores.

CD Pb-Zn Deposits in the Rock Record

Some important questions arising from the secular distribution of the total contained Pb and Zn metal in known CD Pb-Zn deposits and their tectonic setting (Fig. 10) distribution are (1) why do CD deposits first appear in the Paleoproterozoic? (2) why are passive-margin environments important hosts for CD ores? (3) why are CD deposits between ~1.7 and 1.4 Ga so richly endowed with Pb-Zn? (4) why are CD deposits in continental rift sag basins apparently restricted to the late Paleoproterozoic to middle Mesoproterozoic? (5) why are CD deposits less common in the period ~1.40 to 0.76 Ga? and (6) why are some passive-margin and rift-sag basins fertile and others not?

FIG. 15. Paleogeographic reconstruction at 1650 Ma based on the Global Paleomagnetic Database (Pisarevsky, 2005). Euler rotation parameters: Laurentia to absolute framework: 13.1°N, 39.1°W, -83.5°; Baltica to Laurentia: 45.0°N, 7.5°E, +44.9°; Australia to Laurentia: 35.5°N, 80.5°E, +99.7°; Siberia to Laurentia: 66.6°N, 139.3°E, +134.8°; Kalahari to Laurentia: 18.2°N, 69.7°W, +160.7°.

Emergence of CD Pb-Zn deposits

The oldest well-established occurrence (~2.02 Ga) of CD mineralization is a Zn-Pb prospect in northern Australia as discussed above. The Paleoproterozoic Dongshengmiao, North Park, and Pinnacles deposits have poorly constrained ages; therefore, they are plotted as mid-Paleoproterozoic. The better age-constrained passive-margin deposits in India are about 1.85 to 1.80 Ga (Deb and Thorpe, 2004), which marks the first significant appearance of CD deposits in the Paleoproterozoic. The apparent absence of ores in rocks older than about ~2.02 to 1.85 Ga could simply be due to the tectonic recycling and destruction of the deposits. However, given the strong redox control on formation of these ores, the absence of these ores in older rocks probably reflects the reducing character of the atmosphere and hydrosphere that limited the mobility of Pb and Zn in surface and near-surface environments. Prior to the Great Oxygenation Event, the dominant repositories of Zn were volcanic rock-hosted massive sulfide deposits in Archean and Proterozoic greenstone belts (Huston et al., 2010). In contrast, the major repositories of Zn between 1.85 and 1.45 Ga were CD deposits. Before 1.85 Ga, the only saline crustal fluid available was reduced seawater, and the transport and deposition of Zn, Pb, and Ag required heating of this seawater to temperatures in excess of 250°C to form significant CD Pb-Zn deposits. After 1.85 Ga, the availability of highly saline, oxidized brines allowed transport of significant amounts of Zn, Pb, and Ag at lower temperatures to efficiently form CD deposits.

The oldest significant CD deposits may be associated with the hypothetical Mesoproterozoic supercontinent variously termed Nuna, Columbia, or Hudsonland (e.g., Condie, 2000, Meert, 2002; Rogers and Santosh, 2002, Pesonen et al., 2003; Zhao et al., 2004). The exact configuration of this supercontinent is debated, but limited reliable paleomagnetic data suggest medium to low (<45°) paleolatitudes for some of its building blocks (e.g., Australia and Kalahari; Fig. 15), which is consistent with evaporative processes that generated brines that are the ore fluids for CD deposits. Abundant evidence, including pseudomorphs of gypsum and halite (Walker et al., 1983; Page et al., 2000), barite occurrences, and colloform chert nodules that are indicative of silicified barite (Warren, 2006, and references therein), suggests that oxidized brines were being produced at the time of formation of continental sag-hosted deposits of the North Australian zinc belt (Huston and Logan, 2004; P. Southgate and J. Jackson, oral commun., 2010). Because these brines were developed after the oxidation of the hydrosphere, they would for the first time have been highly oxidized. The combination of evaporative and oxidized conditions would produce low-temperature (<200°C) brines capable of transporting sufficient Zn and Pb to form continental sag-hosted deposits (Cooke et al., 2000). Another aspect that may have been important was the flowering of sulfate-reducing bacteria by this period (Huston and Logan, 2004; Farquhar et al., 2010). These bacteria, essential in producing the sulfidic deep oceans of Canfield and Raiswell (1999), would also have been critical in the production of H_2S at the site of ore deposition for sag-hosted deposits (Huston et al., 2006).

Continental rift-hosted deposits differ from sag-hosted deposits in that they form from moderate-temperature, reduced brines. As with the sag-hosted deposits, initial brine formation may be tied to evaporative conditions associated with Nuna during the late Paleoproterozoic. However, the fluids characteristic of rift-hosted deposits require both a heat source and a reductant. As discussed by Huston et al. (2006), a rift environment could provide Fe-rich, tholeiitic basalt to serve as both a heat source and a reductant. Hence, initiation of rifting, combined with the presence of highly saline brines, may have been the trigger for formation of major continental rift-hosted deposits. Prior to this time, Zn-Pb (Cu) deposits formed from moderate- to high-temperature reduced fluids that were dominated by volcanic rock-hosted massive sulfide deposits. These deposits, although forming mostly in back-arc and arc settings (Huston et al., 2010), have a number of similarities with rift-hosted deposits, with one subclass of Barrie and Hannington (1999), the siliciclastic-mafic subclass characterized by a siliciclastic sequence with significant intercalated basalt.

Passive-margins CD Pb-Zn deposits

The most common tectonic setting for CD Pb-Zn deposits is a passive continental margin. Some CD deposits formed in the early rift phase (e.g., Rammelsberg), most formed in the drift phases (e.g., Red Dog), and they are rare in the closure phase of a passive margin (e.g., Arkansas barite, Fig. 3). The distribution of passive-margin environments in Earth history (from Bradley, 2008) and the metal endowment of CD deposits are shown in Figure 10. The age distribution is based on a global survey of 85 ancient passive margins and shows the number of different passive margins that existed during each 50-m.y.-wide bin. The age distribution shows close parallels to other geologic time series, including the Condie (2005) census of juvenile continental crust and the Shields (2007) plot of the continental component of seawater strontium. Bradley (2008) argued that these independent associations confirm that the passive-margin age distribution is broadly correct and not merely an artifact of a flawed census. The distribution of CD ores in passive margins (Fig. 10) broadly correlates with the distribution of passive margins in Earth history; that is, both are abundant in the Phanerozoic and Neoproterozoic, uncommon in the Mesoproterozoic, and important in the late Paleoproterozoic. Therefore, a first-order control on the distribution of CD deposits is simply the abundance of passive margins. The second major factor contributing to the observed passive margins and contained CD Pb-Zn deposits must be the tectonic recycling and destruction of these environments (Veizer et al., 1989). The fate of most passive margins is to be involved with an ocean closure (Bradley, 2008). Ocean closure will involve subduction of passive-margin successions, or their deformation, metamorphism, and subsequent erosion during uplift of the collisional orogenic belts. Clearly, many CD deposits in passive margins have probably been destroyed or are no longer recognizable for what they once were. Thus, the distribution of CD deposits in passive-margin environments reflects favorable factors for the formation of CD deposits, as well as their destruction.

Excluding the Paleoproterozoic deposits plotted as middle Paleoproterozoic due to poor age constraints, the most significant Paleoproterozoic passive-margin CD deposits are those in India (e.g., Rampura-Rajasthan) that formed about 1.85 to 1.80 Ga (Deb and Thorpe, 2004). Passive margins as old as Archean are recognized (Bradley, 2008); however, CD Pb-Zn mineralization was obviously limited by the reducing atmosphere and hydrosphere. There are only a few known CD deposits between 1800 and 800 Ma that are clearly related to bona fide passive margins. As argued above, the dearth of passive margins during this interval appears to be real and not an artifact. The same argument would thus apply to the ore deposits themselves.

The abundant passive margins between ~1 Ga and the present host the giant Phanerozoic CD deposits of the Brooks Range, United States, and Selwyn basin, Canada, and the Neoprotrozoic Kholodninskoye deposit in Russia. The abundance of passive-margin deposits between ~550 to 300 Ma corresponds to the formation of Gondwana and Pangea, which apparently provided many fertile environments for the genesis of CD deposits.

Why are some passive margins fertile and others not? Considering the vast distribution of passive-margin sequences in time and space, a natural question is why are so few CD deposits known? Studies from the world's largest passive-margin CD deposits, the Red Dog deposits (Kelley and Jennings, 2004; Leach et al., 2004), suggest a critical element in ore formation was the reflux of seawater brines, generated from a passive continental margin evaporative "factory" into organic-rich clastic rock sequences. To test if the brine reflux model can be applied to other passive-margin deposits, Leach et al. (2005a) determined the distribution of the paleolatitudes of the deposits at the time of mineralization. This was accomplished by an analysis of the distribution of the ore deposits in a Geographical Information System (GIS) plate-tectonics database. The approach used GIS to query results from plate-tectonic reconstructions (Scotese, 2005) and quantify both spatial and temporal patterns. The percentage of metal content of all Phanerozoic deposits vs. paleolatitudes at the time of ore deposition is summarized in Figure 16. The analysis was limited to the Phanerozoic because of the higher confidence in the plate reconstructions relative to reconstructions for the Proterozoic. The results remarkably mimic the favorable latitudes of evaporative belts in Earth history (Evans, 2006; Warren, 2006). This suggests that the presence of a brine factory on a passive margin may be a key factor in determining which passive margins host CD Pb-Zn deposits.

Except for the giant Kholodninskoye deposit, passive margin-hosted CD deposits are scarce in the Neoproterozoic (Fig. 10), despite the abundance of passive margins associated with continental rifting of Rodinia at low latitudes (Kirschvink, 1992; Hoffman et al., 1998). This was also a time of major changes in the redox state of the atmosphere and hydrosphere, the Second Great Oxygenation Event, and increased abundance of seawater sulfate and evaporites. Two or more Snowball Earth events occurred during this time. It is puzzling that so few CD Pb-Zn deposits are known given the increased potential for formation of oxidized brines in evaporative environments along the abundant Neoproterozoic passive margins.

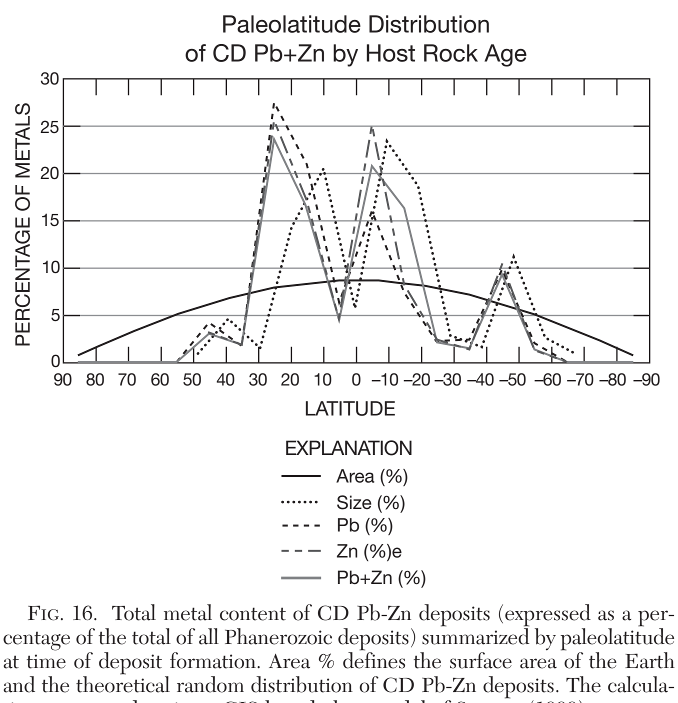


FIG. 16. Total metal content of CD Pb-Zn deposits (expressed as a percentage of the total of all Phanerozoic deposits) summarized by paleolatitude at time of deposit formation. Area % defines the surface area of the Earth and the theoretical random distribution of CD Pb-Zn deposits. The calculations were made using a GIS-based plate model of Scotese (1999).

In view of the above observations, in order for the reflux evaporative brines to become potential ore fluids in passive-margin environments, other factors must enter into the process. These may include the presence of oxidized and permeable aquifers or fractured basement rocks with permissive redox buffering to allow the extraction and transport of metals to sites of deposition. Sites that are rich in reduced sulfur, or those capable of efficiently reducing sulfate in the ore fluid, such as those that are anoxic, have highly reduced water columns or pore fluids, or contain organic-rich sediments, are essential for most CD ore deposition. The association between CD deposits and highly reduced host rocks is well established (e.g., Goodfellow and Jonasson, 1987; Goodfellow et al., 1993; Dumoulin et al., 2004; Young, 2004). An additional factor that may determine when or if a passive-margin CD deposit forms is a tectonic trigger discussed below.

Continental rift and sag basin environments

Perhaps the most intriguing aspect of the distribution of CD deposits is the unusual abundance of giant CD Pb-Zn deposits in continental rift or sag basins between ~1690 and 1300 Ma. Contributing to the dominance of continental rift and sag basin environments as hosts for CD ores is the paucity of passive-margin environments (Fig. 10). Significant CD deposits are not recognized as such in continental rift or sag basins in younger rocks, whereas passive-margin environments are the main repositories of CD ores. Does the restricted distribution at ~1690 to 1300 Ma reflect a period in Earth history when CD deposits flourished only in continental rift and sag basins, or is it a result of selective preservation or destruction of the deposits?

Most of the continental rift and sag basin ores are located within the Proterozoic Australian craton and this raises the question as to what was special about these rift and sag basins? Part of the answer is that the Australian craton was at the right place and time in Earth history to form giant CD deposits. These deposits appear after the Great Oxygenation Event, when oxygenated shallow ocean water coexisted with deeper reduced seawater. Farquhar et al. (2010) describe the striking contrast between sulfidic, nonsulfidic, and anoxic pools in the oceans at this time. These contrasts in redox character of the hydrosphere, and presumably in the basin sediments, would have led to extremely efficient redox-controlled precipitation of CD ores either in the water column or in deep-basin sediments. Furthermore, the Australian craton was located at favorable latitudes (Fig. 15) for the formation of oxidized brines capable of transporting Pb and Zn. Abundant evidence exists for evaporative environments in the Australian basins that host the giant CD deposits (Large et al., 2002, 2005) attesting to potential brine factories at the time of ore formation.

Large et al. (2002, 2005) argued that the fertility of CD deposits in the Australian Proterozoic craton was due to the long life of these intracratonic marine basins with sediment fill that included extensive oxidized clastic aquifers and extensive aquitards. This explanation could also be applied to the Sullivan deposit in the Belt-Purcell basin. The Belt-Purcell basin was a long-lived continental rift basin that was located in evaporative latitudes during the formation of the Sullivan deposit. The Belt-Purcell basin can be viewed as a marine embayment on continental crust that eventually opened to an ocean basin. Perhaps these long-lived continental rift basins with marine sedimentary sequences share the same essential ore-forming attributes as passive margins. Thus, there may not be fundamental differences between the CD ore-forming potential of passive margins and long-lived continental rift basins. Regardless of the basin classification, the critical parts of the ore-forming puzzle may be the infiltration of sedimentary brines into reduced marine sequences from underlying continental sedimentary sequences, together with a large-scale tectonic trigger for the ascent of the brines.

The answer to why the Australian and Sullivan deposits are preserved could be related to limited inversion and erosion of the deep-water axis of the basins. The distribution of rift basins suggests that Proterozoic rift basins are significantly less abundant than Phanerozoic basins (Fig. 10). Although Proterozoic rift basins were slightly undercounted in Figure 10, they are clearly less abundant relative to Phanerozoic basins. Therefore, the apparent reduction of the number of preserved continental rift environments in older rocks is consistent with their destruction through tectonic recycling, which may include uplift and/or erosion and metamorphism and/or deformation. Consequently, the frequency of preserved continental rift CD deposits would be less.

Could there be a factor of enhanced preservation of these Paleoproterozoic and Mesoproterozoic rift or sag basins? Groves et al. (2005a, b) proposed that changes in a thick and buoyant Precambrian subcontinental mantle to thinner and less buoyant Phanerozoic subcontinental mantle led to a decrease in preservation potential for the younger orogenic gold deposits. Following this logic, continental rifts and sag basin environments on old Archean and Paleoproterozoic lithosphere, such as that containing the Australian and Sullivan CD deposits, may more likely be preserved than those on younger lithosphere. However, no more than 5 to 10 percent of the cataloged rifts (Sengor and Natalin, 2001) appear to be older than Paleozoic. Thus, there is no unequivocal evidence that Archean and/or Paleoproterozoic rooted rift basins have been selectively preserved. Perhaps these are just rare examples where such basins escaped serious deformation but yet experienced sufficient inversion to bring the deposit to the surface and not be eroded. If preservation is the reason why the Proterozoic CD continental rift deposits are present in the rock record, then there could be a number of undiscovered CD Pb-Zn deposits in younger rifts that have not undergone significant inversion. This remains an enigma.

The low abundance of ores in rocks between ~1350 and 760 Ma

Another curious aspect of the distribution of CD deposits is the absence of CD ores in the interval ~1350 to 760 Ma. The absence of CD ores could be related to the relatively low sulfate concentrations in the Proterozoic oceans. Low sulfate contents in the Proterozoic oceans would limit the potential for precipitation of sulfate-bearing evaporites to locally restricted basins as suggested for the Australian CD deposits. This period in Earth history is one of the most complex and perplexing in terms of the chemistry of the oceans and marine sediments (Farqurhar et al., 2010). Farqurhar et al. (2010) suggested this was a time of extreme variation in the ocean chemistry, when the ocean contained "pools" of sulfidic to nonsulfidic and oxic to anoxic water. Canfield (2004) suggested that this was a time of sulfur limitations on a global scale. Considering the evidence for restricted sulfur in the oceans, the potential for formation of CD deposits would likely be lower.

The paucity of CD ores between ca. 1350 and 760 Ma coincides with the assembly of Rodinia and the first half of a protracted breakup. One factor may be that, unlike the assembly of all other supercontinents, the assembly of Rodinia did not result in the deformation and uplift of many passive margins and any contained ores. Instead, the main Rodinia-forming event, the Grenville orogeny, involved collisions between a series of arcs and a long-lived convergent margin on the southeast side of Nuna (Karlstrom et al., 2001).

Global anoxia events and CD deposits

It has been suggested that the CD ores in the Selwyn basin are related to the development of euxinic deep waters that were part of global anoxia events when the world's oceans were strongly redox stratified (e.g., Goodfellow, 1987, 2000; Goodfellow and Jonasson, 1987). Suggestions that the secular distribution of most CD ores reflect global events are difficult to evaluate, particularly in light of the intense debate on secular distribution of the redox state of the Earth's oceans (Farquhar et al., 2010). Nevertheless, there is general agreement that the precipitation of CD ores from oxidized brines within the basin sediments requires reducing conditions, particularly in the form of organic matter. If the ores precipitated in a seawater column, then reduced and sulfidic conditions were necessary for precipitation of the ores. The reduced environments in the sediment fill or water column required for CD ore genesis does not have to be part of global events but rather can be local or regional scale.

Tectonic triggers of CD ore-forming systems

The 338 Ma age of deposits in the Red Dog district corresponds to an ~130° change in the plate motion of North America (Van der Voo, 1993). Such a dramatic change in drift of North America could be responsible for the development of the transtensional subbasin that hosts the Red Dog deposits and provided a mechanism for the ascent of hydrothermal fluids. Idnurm (2000) demonstrated that the ages of continental sag-hosted CD deposits in the North Australian superbasin correspond closely with the ages of major bends in the Paleoproterozoic to Mesoproterozoic Australian apparent polar wander path. This relationship was interpreted to indicate that fluid flow and CD mineralization were triggered by major tectonic events, including collisions and rifting, that changed the relative motion of the North Australian craton. These events are not expressed locally as deformation events, confirming a relationship with distant tectonic events. Furthermore, the ca. 1470 Ma Sullivan deposit (Jiang et al., 2000) is within error of a major bend on the Mesoproterozoic Laurentian apparent polar wander path (Elston et al., 2002).

In the North Australian craton, mineralization in at least the HYC and Century deposits cannot be correlated with local deformation events, although distant tectonic events could have been responsible. For the HYC deposit and some U deposits, the age of mineralization corresponds to the

~1640 to 1635 Ma Leibig Event, at which time the Warumpi province accreted onto the North Australian craton. Similarly, formation of the Century deposit corresponds in time with the ~1575 Ma Chewings Event, which also affected the southern margin of the North Australian craton. Although the ~1655 Ma age of mineralization at Mount Isa and Hilton does not correspond to tectonic events in the North Australian craton, this age corresponds to the Mazatzal orogeny in western North America (Bauer and Williams, 1994; Shaw and Karlstrom, 1999), which, according to some paleogeographic constructions (Burrett and Berry, 2000; Karlstrom et al., 2001), was adjacent to the North Australian craton at this time. These relationships suggest that for many CD deposits, mineralization was triggered by tectonic events well removed from the region of hydrothermal activity.

Mississippi Valley-Type Pb-Zn Deposits in the Rock Record

It has long been recognized that MVT ores are mainly hosted in Phanerozoic carbonates and are significantly less abundant in Archean and Proterozoic rocks (Fig. 7A; Sangster, 1983, 1986; Leach et al., 2001, 2005a; Kesler and Reich, 2006). This contrast in abundance is more pronounced when the ages of ore formation are plotted against tons of contained metal (Fig. 7B). The MVT ores hosted in Phanerozoic rocks account for 88.9 percent Zn and 76.8 percent Pb of the known global endowment. If we exclude the large equivocal Gorevskoye deposit in Siberia as a Proterozoic MVT (discussed below), then the percent increases to 91 percent Zn and 96.6 percent Pb. The top ten deposits in terms of contained metal are hosted in Phanerozoic rocks, whereas for the remaining smaller deposits, there is no apparent difference in size and grade (Fig. 17) between Proterozoic rock- and Phanerozoic rock-hosted deposits. The major difference is that the Phanerozoic, despite being significantly shorter than the Proterozoic, contains significantly more MVT Pb and Zn relative to the Proterozoic.

Insight into why so few deposits are hosted in Archean and Proterozoic rocks is limited by the small population of deposits and particularly by the few deposits with dates (Fig. 7B). Table 1 lists the host-rock age, size, and metal content of Precambrian MVT deposits. Only the deposits of the Archean Transvaal Supergroup and the Mesoproterozoic rock-hosted Nanisivik are dated. The Proterozoic rock-hosted ores have similar fluid inclusion homogenization temperatures and salinities compared to their Phanerozoic counterparts (Leach et al., 2005b; Kesler and Reich, 2006), and they also formed mainly from sedimentary brines derived from evaporated seawater. Although Proterozoic ores have many similarities with their Phanerozoic counterparts, the reasons for the contrasting abundances remain unclear.

Does the contrast in abundance reflect a poor preservation of MVT ores or did secular changes in Earth systems limit ore-forming processes? Based on studies by Ronov (1964) and Veiser and Mackenzie (2003), relative to CD deposits, platform carbonate-hosted MVT ores would more likely be recycled during the eventual closure of the facing ocean basin. Whether this is actually the case or not depends on the

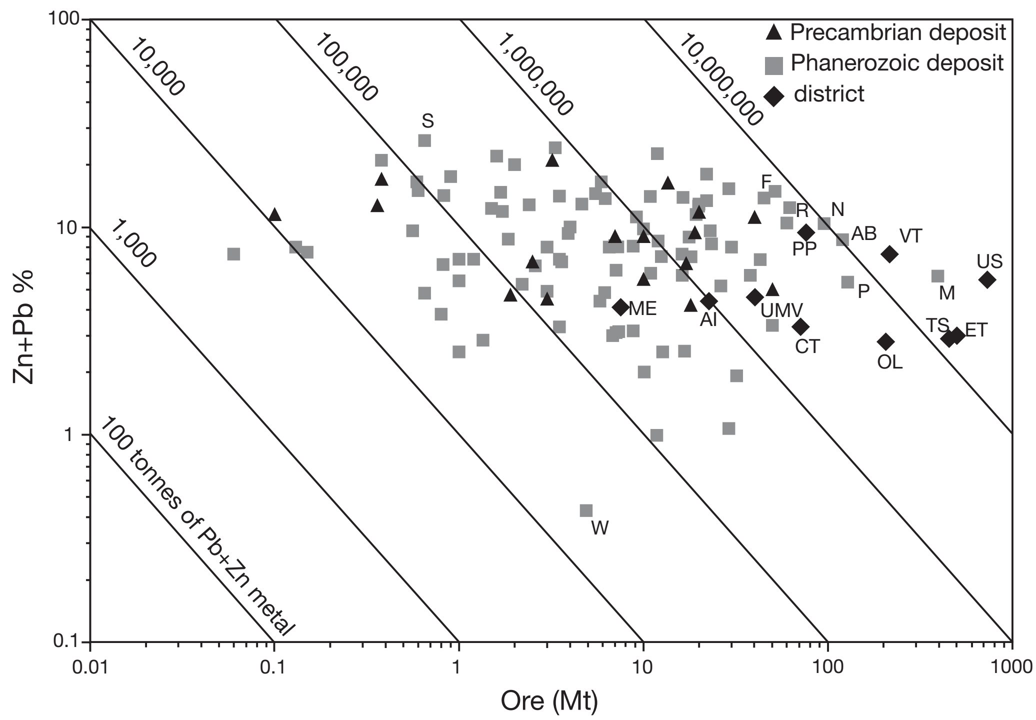


Fig. 17. Grade-tonnage for 113 MVT deposits and 10 districts. Diagonal lines represent tonnage of Pb and Zn metal. Select districts and deposits are labeled as: AB = Admiral Bay, AI = Austinville-Ivanhoe, CT = Central Tennessee, ET = East Tennessee, F = Fankou, M = Mehdiabad, ME = Metaline, N = Navan, OLB = Old Lead Belt, P = Pavlovskoye, PP = Pine Point, R = Reocin, S = Schmalgraf, TS = Tri-State, UMV = Upper Mississippi Valley, US = Upper Silesia, VT = Viburnum Trend, W = Walton. Data from Taylor et al. (2009). Note that all of the districts are Phanerozoic.

TABLE 1. Precambrian MVT Deposits and Host-Rock Ages

Deposit	Location	Formation/Supergroup	Host-rock age (Ga)	Size (Mt)	Pb (%)	Zn (%)	Reference
Late Archean carbonate-hosted Pb-Zn mineralization							
Bushy Park	South Africa	Campbellrand /Transvaal SG	2.52–2.65[1]	10	0.6	5.0	Wheatley et al. (1986); Greyling (2000)
Pering	South Africa	Campbellrand /Transvaal SG	2.52–2.65	18	0.6	3.6	Wheatley et al. (1986); Greyling (2000)
Paleoproterozoic dolostone-hosted Pb-Zn mineralization							
Esker	Canada	Rocknest Fm/Coronation SG	1.89	1.9	1.2	3.5	Gummer et al. (1996)
Kamarga	Australia	Lawn Hill Platform/Mt Isa inlier	1.6–1.8	50	?	?	Jones et al. (1999)
Bulman	Australia	Dolomite, limestone,chert	??	0.4	2.0	15.0	Plumb et al. (1998)
Mesoproterozoic dolostone-hosted Pb-Zn mineralization							
Nanisivik	Canada	Society Cliffs Fm, Bylot SG	1.2	19	0.7	8.7	Sutherland and Dumka (1995); Sherlock et al. (2004)
Neoproterozoic dolostone-hosted Pb-Zn mineralization							
Morro Agudo	Brazil	Bambui SG	0.75	17	1.5	5.1	Hitzman et al. (1995)
Tianbaoshan	China	Dengying Fm	??	20	1.4	10.4	Wang et al. (2000)
Gayna River	Canada	Little Dal Group	??	50	0.3	4.7	Hewton (1982); Gibbins (1983)
Goz Creek	Canada	Backbone Ranges Fm	??	2.5	?	?	Gibbins (1983); Cordilleran Engineering Limited (1974)
Daliangzi	China	Algal dolomite	??	40	0.8	10.4	Cromie et al. (1996); Zheng and Wang (1991)
Fagundes	Brazil	Dolarenite, dolomite breccia	??	3	?	4.5	Touahri (1991)
Januaria	Brazil	Dolomitic limestone	??	0.1	7.5	4.0	Robertson (1963)
Nova Redencao	Brazil	Silicified dolarenite	??	2.5	6.3	0.5	Misi et al. (1999)
Sardana	Russia	Limestone, dolomite	??	10	3.0	6.0	Zapolnov (1997)
Tres Irmas	Brazil	Limestone, dolomite	??	7	1.4	7.6	Kyle and Misi (1997)

Notes: Fm = Formation; SG = Supergroup; ?? = host-rock age unknown; ? = Pb% or Zn% unknown
[1] Mineralization age for the Archean deposits of the Transvaal Supergroup have been established as 2.0 to 2.1Ga (Schaefer, 2002; Duane et al., 2004)

nature and extent of the orogenic event and the width and thickness of the carbonate platform. Nevertheless, whereas the destruction of a significant number of MVT deposits is probable, there is presently no way to quantitatively assess the attrition of platform carbonate sequences spanning the Archean to present. Consequently, we focus on evaluation of the evolution of Earth systems to gain insight into the secular controls on ore genesis. Clues to the problem are possible from the observations discussed above regarding the distribution of CD Pb-Zn ores in Earth history and from new studies on the deposits of the Neoarchean platform carbonates of the Transvaal Supergroup (Gutzmer, 2005; Huizenga et al., 2006).

MVT deposits in Archean rocks

The oldest known MVT deposits are Pering and the related Bushy Park, which are the only carbonate-hosted deposits in Archean rocks. Paleoproterozoic mineralization ages of 2.1 to 2.0 Ga have been reported (Duane et al., 2004; Schaefer et al., 2004). It is noteworthy that these ores have broadly the same age as the oldest CD deposit, the Namoona prospect hosted by ~2020 Ma rocks (Worden et al., 2008). Thus it appears that the emergence of CD deposits and the oldest known MVT ores correspond to a time after the Great Oxygenation Event when shallow, oxygenated, sulfate-rich seawater coexisted with deeper, reduced seawater. Furthermore, as pointed out previously, these ores formed about the time of the large Vredefort impact in South Africa at 2.02 Ga (Kamo et al., 1996). Following the arguments of Slack and Cannon (2009), it is conceivable that the huge Vredefort impact may have triggered the migration of brines in the subsurface in the South African craton.

The ores are hosted in the stromatolitic dolostone of the Campbellrand Subgroup (2.52–2.65 Ga), Transvaal Supergroup in South Africa. Gutzmer (2005) attributed the Pering mineralization to the ascent and formation of an intense hydrothermal dissolution collapse breccia that created vertical permeability for the ore fluids in the impervious carbonate platform (Gutzmer, 2005). Huizenga et al. (2006) showed the ore deposition involved the mixing of an evaporated seawater brine with meteoric and carbonic fluids at temperatures of 200° to 210°C and at depths of 4 to 5 km.

Proterozoic MVT deposits

Paleoproterozoic rock-hosted MVT deposits: The most significant Paleoproterozoic rock-hosted MVT deposits are the Esker and related deposits in the Rocknest Formation. Esker is a large low-grade deposit in the 1.8 Ga Rocknest Formation in the northwestern Canadian Arctic (Gummer et al., 1997). The ore occurs as sulfide matrix breccias that may be related to evaporite facies in the Rocknest Formation (Kesler and Reich, 2006).

The Kamarga deposit is hosted in rocks of the McNamara Group in North Australia and is located in the important North Proterozoic CD-rich basins (Plumb et al., 1990). Kamarga ores occur in breccias and as massive replacement bodies that are believed to have been former evaporites in the Gunpowder Creek Formation (Plumb et al., 1990).

Mesoproterozoic rock-hosted MVT deposits: The only known significant MVT ore deposit hosted in Mesoproterozoic rocks is the Nanisivik deposit in the Society Cliffs Formation, Nunavut Territory, Canada, which is an evaporite-rich stromatolitic carbonate unit with abundant collapse breccias (Olson, 1984; Ghazban et al., 1990). Considering evidence for in situ sulfate reduction in the deposition of the ores (Ghazban et al., 1990) and the unusual vertical keel-like deposit morphology (Olson, 1984), the sulfides may have replaced an evaporite mass in the Society Cliffs Formation. Although hosted in Mesoproterozoic carbonates, two different ages have been determined for the deposit. These include a paleomagnetic date of 1.09 Ga (Symons et al., 2000) and an Ordovician age from an Ar-Ar measurement on altered orthoclase in a crosscutting dike (Sherlock et al., 2004).

Neoproterozoic rock-hosted MVT deposits: The Neoproterozoic rocks are better endowed with MVT ores than other Proterozoic sequences. The Gorevskoye deposit in the Riphean fold belt of the Siberian craton (Khiltova and Pleskach, 1997) may be the largest MVT of this age. The deposit was classified as a CD Pb Zn deposit in Leach et al. (2005b). We consider it a probable MVT deposit based on descriptions of the hosting Tunguisk Group as a sedimentary rock sequence dominated by shallow-water carbonates. However, in the absence of more specific information, the MVT classification is equivocal.

The Gayna River deposit in the Mackenzie Mountains in northwestern Canada is hosted by stromatolitic carbonates of the Little Dal Group (Hardy, 1979). The ore occurs in dissolution collapse breccias that may have been derived from the dissolution of evaporites in the sequence. The age of ore deposition is probably much younger than Neoproterozoic based on Pb isotope studies that suggest derivation of the metals from Phanerozoic rocks (Gleeson and Sharp, 2009).

Other Neoproterozoic deposits classified as MVTs include the fracture-controlled ore of Morro Agudo, Brazil, and the strata-bound, dominantly vein ores of Tianbaoshan and Daliangzi, China. There are insufficient data and descriptions in the literature on the Chinese deposits to confidently classify them as MVT deposits.

Nature and extent of carbonate platforms

The permeability of carbonate rocks has a fundamental control on the transmissivity of MVT ore-forming fluids and the sites where MVT deposits form (e.g., Leach and Sangster, 1993; Leach et al., 2005b). Therefore, secular changes in the nature and extent of the carbonate platform sequences must have influenced the distribution of MVT deposits in the rock record. The first massive carbonate sequences, consisting primarily of stromatolites and sea-floor precipitates, appear about 3.2 to 2.4 Ga (e.g., Sumner, 1997; Ericksson et al., 2001). These ancient carbonate platforms were vast and as compositionally diverse as their Phanerozoic counterparts (Grotzinger and James, 2000). These early platform carbonate successions were nearly impermeable due to early lithification, diagenetic dolomitization and silicification, and lack of bioturbation (Grotzinger, 1989).

Neoproterozoic platform carbonate successions mark a shift from in situ precipitation of carbonate to the incorporation of carbonate sediments in Neoproterozoic stromatolites with increased complexity and porosity for the first time in Earth history (Grotzinger and James, 2000). A dramatic change in the relative abundance of carbonates and an increase in coarse skeletal carbonate minerals occurred in the Cambrian (Hazen et al., 2008, and references therein). Considering the increase in permeability from fine-grained carbonate mudstone to carbonate grainstone (Lucia, 2007), Phanerozoic carbonate platforms should have a greater potential relative to Proterozoic platforms for the migration of sedimentary brines and the formation of MVT ores. Consistent with this suggestion is the fact that the world's great petroleum reservoirs are in Phanerozoic carbonates, whereas hydrocarbon resources are rarely hosted in older carbonates. Furthermore, the interconnected karst networks that reflect extensive preore permeability of many MVT districts in Phanerozoic carbonate platforms (i.e., East Tennessee) are absent in the Proterozoic deposits. Proterozoic rock-hosted deposits are localized in vertical pipelike hydrothermal dissolution breccias (e.g., Pering and Nanisivik) or as fracture-controlled ores (e.g., Morro Agudo) that do not depend on primary permeability controls. Most Proterozoic rock-hosted MVT deposits appear to be restricted to evaporite dissolution breccias or associated with evaporite-rich areas of normally impermeable stromatolitic sequences (Table 1). Furthermore, Proterozoic platform carbonates lack the extensive reef facies transitions of fine-grained carbonate and/or shale (back reef) to coarse-grained carbonate (fore reef; i.e., Viburnum Trend, United States), characteristic of many younger deposits.

In addition to the secular variation in the nature of carbonate platforms, there appears to be a decline in the amount of carbonate in the sedimentary rock volume older than the Neoproterozoic-Phanerozoic maximum (Fig. 8), which Veizer and Mackenzie (2003) attributed to the rapid tectonic recycling of carbonates relative to other sedimentary rocks. The decline in the volume of carbonates is also consistent with the secular distribution of passive-margin environments (Bradley, 2008), with a decrease in abundance from the Neoproterozoic back to the Paleoproterozoic. Furthermore, the large volume of carbonate sediments during the Neoproterozoic-Phanerozoic maximum (Fig. 8) also reflects the explosion and diversification of carbonate-secreting life following the second Great Oxygenation Event. Thus, the few MVT ores in the Archean-Proterozoic reflect, in part, the secular changes that occurred in the character and extent of the carbonate sediments, as well as their tectonic recycling in Earth history.

Oxygenation of the hydrosphere, evaporates, and MVT deposits

Both CD and MVT deposits appear in the rock record at about 2.02 to 2.00 Ga, just after the Great Oxygenation Event. However, whereas CD deposits flourished during the Paleoproterozoic to Middle Mesoproterozoic, MVT deposits remained scarce. Kesler and Reich (2006) argued that the few MVT deposits in Proterozoic rocks are the consequence of the low sulfate in Proterozoic seawater that produced fewer evaporites. Kesler and Reich (2006) also suggested that Proterozoic MVT deposits were localized by reduced sulfur traps produced by the reduction of sulfate evaporites. If the low-sulfate content of the Proterozoic oceans was the only factor controlling the presence of MVT deposits, then it raises the question as to why CD ores reached their maximum mass during the Proterozoic? Perhaps the contrast is due to more efficient tectonic recycling of MVT deposits in carbonate platforms relative to the Proterozoic CD deposits, which at the time formed mainly in continental rift and sag basins.

The MVT ores were most abundant in the Phanerozoic (Fig. 18), following the last of the Neoproterozoic glaciations and after the rise of oxygen in the atmosphere to modern levels (the second Great Oxygenation Event; Holland, 2005; Hazen et al., 2008, and references therein). A consequence of the rise of oxygen in the atmosphere was an increased flux of sulfate from oxidative weathering into the ocean and the formation of abundant evaporites (Fig. 18B). It has also been suggested that the increase in sulfate in the Neoproterozoic can be attributed to the onset of bioturbation that removed a significant sink for reduced sulfur in the oceans (Canfield and Farquhar, 2009; Farquhar et al., 2010). Considering that MVT ore-forming fluids consist mainly of evaporated seawater, the late Neoproterozoic and Phanerozoic must have been favorable for the formation of such fluids. However, there is a poor correspondence between the ages of evaporites and MVT deposits (Fig. 18B). A possible explanation for this poor correspondence is that MVT deposits formed from evaporated seawater produced in earlier evaporative events. The seawater was trapped in the platform sedimentary sequences or crystalline basement until a tectonic trigger set the fluids in motion.

Another consequence of the second Great Oxygenation Event was that the oceans became fully oxygenated, which produced an extraordinary diversification of life and a huge increase in the volume of coarse-grained skeletal carbonates at the start of the Cambrian (Fig. 8). As discussed above, the increased abundance of coarse-grained and permeable carbonate platform sequences in the Phanerozoic is probably a major control on the abundance of MVT ores in the rock record.

Tectonic triggers

For many years, MVT deposits were thought to be unrelated to tectonic events. As a consequence of remarkable dating efforts on most major MVT deposits and districts in the past 20 years, it is now generally accepted that most Phanerozoic ores formed during major contractional events (Fig. 19; Leach et al., 2001, 2005, and references therein).

Within these overall contractional settings, the single most important tectonic controls at the deposit or district scale are extensional faults (normal, transtensional, and wrench faults) and associated fractures and dilatancy zones. This relationship applies to most MVT districts, including the Ozark MVT province (e.g., Clendenin and Duane, 1990). Bradley and Leach (2003) discussed MVT deposits that formed within extensional domains that developed due to lithospheric flexure (Fig. 3) or in large dilational zones within bounding strike-slip faults during large-scale contractional events. Nevertheless, some workers argue that the ores formed during purely extensional events (e.g., Heijlen et al., 2003). As Leach et al. (2001) and Bradley and Leach (2003) pointed out, MVT districts are typically controlled by district-scale extensional faults which are inextricably linked to contractional events in a nearby orogeny and related to closure of a facing ocean basin. The only uncontested example of a MVT district that does not fit this characteristic tectonic setting is the Canning basin district of Australia, where there appears to be no associated closure of an ocean basin.

Perhaps the most controversial and significant problem relating MVT ore genesis to supercontinent cycles is centered on the conflicting ages for the giant Upper Silesia district, Poland. An Rb/Sr date on insoluble residues extracted from sulfides is interpreted to date mineralization during Jurassic platform extension (Heijlen et al., 2003) that was associated with the breakup of Pangea. In contrast, Symons et al. (1995) reported a Tertiary paleomagnetic age that corresponds to extensional faulting during closure of the Tethyan ocean basin during the Carpathian orogeny.

Phanerozoic supercontinents and MVT ore genesis

During the assembly of Pangea, the fundamental requirements to form MVT deposits converged, which resulted in the most prolific time for MVT mineralization in Earth history (Leach et al., 2001). The exceptional endowment of Pangea, and particularly North America, with MVT Pb-Zn deposits may be explained by a number of facts. First, Laurentia, which formed a prominent part of Pangea and the core of North America, remained at low latitudes during the Paleozoic, allowing the development of vast carbonate platforms. Second, after the second Great Oxygenation Event, Pangea was positioned at the best latitudes for the formation of oxidized brines that are the ore-forming fluids for MVT deposits. The increased oxygenation of the atmosphere after the second Great Oxygenation Event, to concentrations exceeding today's levels, produced the highest content of sulfate in seawater in Earth history. This led to the abundance of sulfate-rich evaporites, development of oxidized brines, and the explosion of diverse carbonate skeletal organisms and coarse-grained carbonate sediments. Third, extensive Pangean paleoclimates with high evaporation rates led to the evaporation of seawater in continental margin basins and infiltration of sedimentary brines into basement rocks and deep basin aquifers (Rowan and Marsily, 2001). Fourth, intense orogenic activity during the assembly of Pangea created ground preparation for many MVT districts through farfield deformation of the craton. Important crustal extension zones formed, such as forebulges and associated karst networks (Bradley and Leach, 2003), that produced drains for sedimentary brines. Finally, uplifted orogenic belts along Pangea suture zones established areas of large-scale migration of basin fluids inboard of the orogenic belts and regions of density-driven upwelling of sedimentary brines into depositional sites.

The second most important period for MVT deposit genesis was Cretaceous to Tertiary, when the assembly of the projected Neosupercontinent (Condie, 2000; Groves et al., 2005) began. Microplate collisions along the western margin of North America and Africa-Eurasia produced the giant deposits of Upper Silesia, Poland, and Reocin, Spain. Based on the deposits that have been dated, it appears that few MVT deposits were formed during periods of major plate dispersion represented by the Neoproterozoic to early Paleozoic or during the rapid breakup of Pangea in Triassic through Jurassic.

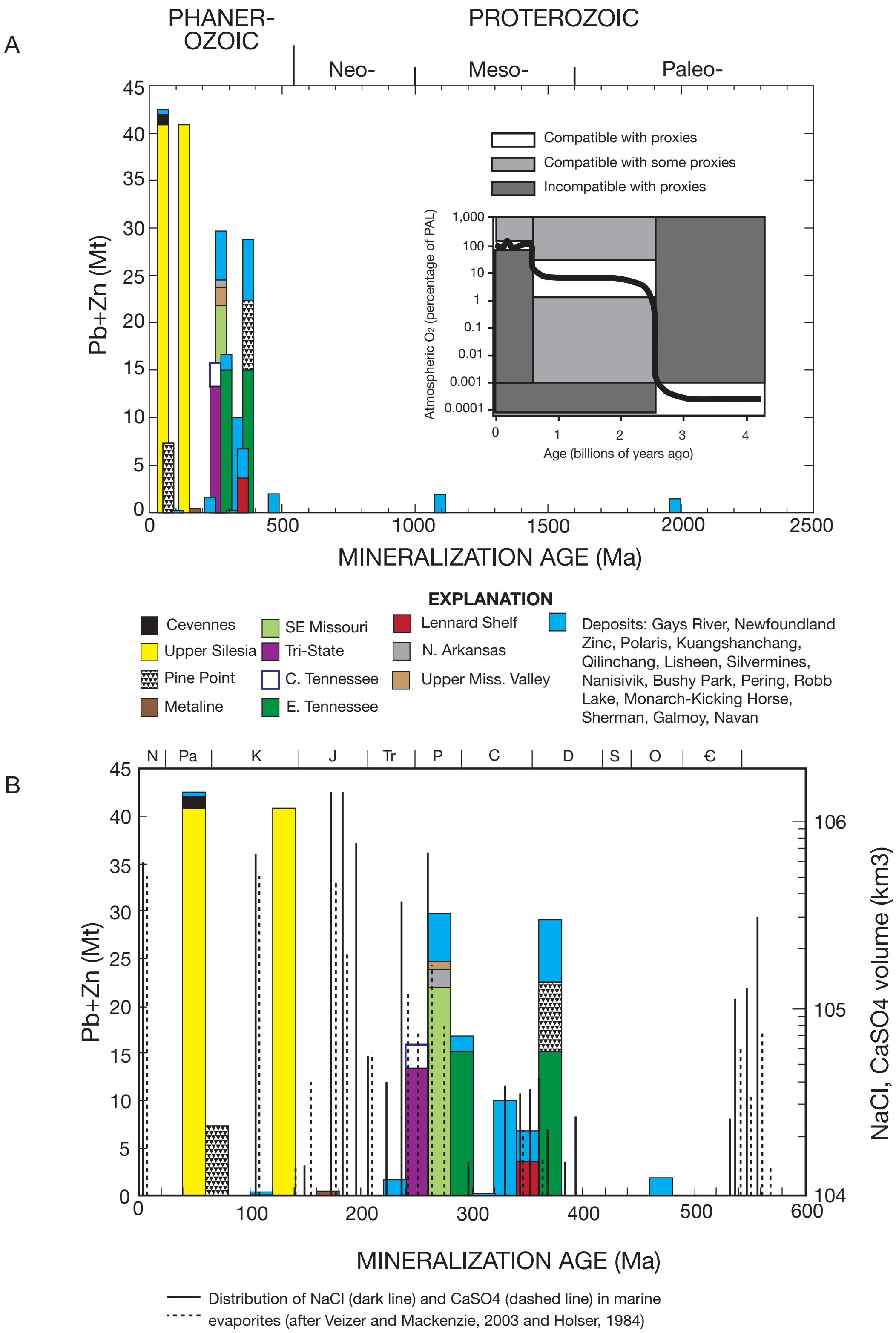
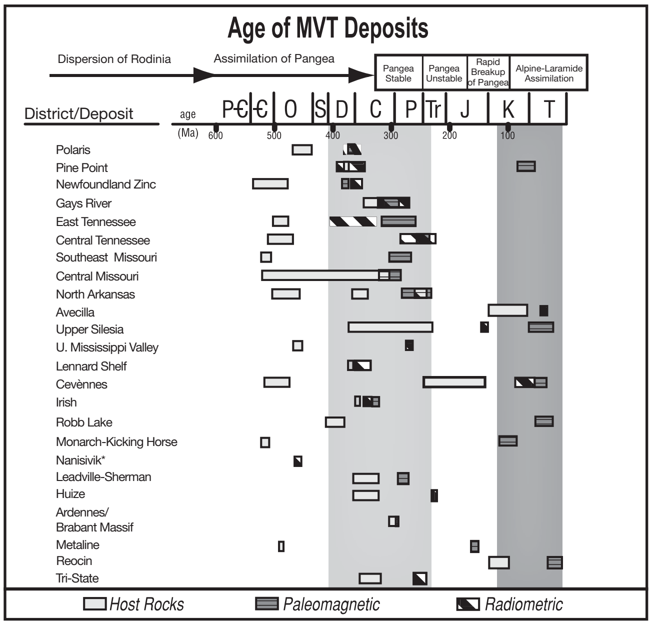


FIG. 18. A. Distribution of total contained Pb + Zn metal in known MVT deposits vs. the measured age of ore deposition plotted in 20-m.y. age increments. Prevailing view of the atmospheric oxygen over time (modified from Kump, 2008). Data from Taylor et al. (2009). Inset of (A) adapted by permission from Macmillan Publishers Ltd. (Nature), copyright 2008 and Lee Kump. B. Secular distributions of MVT deposits (dated) and volume of halite and gypsum evaporites. Note that data for Upper Silesia, East Tennessee, and Pine Point districts are plotted in different time bins (color coded) due to conflicting age determinations. Deposit resource data from Taylor et al. (2009). Permission to adapt the distribution of evaporites in Veiser and Mackenzie (2003) from Springer-Verlag.



* Paleomagnetic age for Nanisivik 1100 Ma

FIG. 19. Distribution of isotopic and paleomagnetic ages of MVT deposits and their host rocks in the Phanerozoic (modified from Leach et al., 2001, 2005). Ages from Leach et al. (2001, 2005, and reference therein); Symons et al. (2000, 2005, 2009); Zegers et al. (2003); Li et al. (2006); Pannalal et al. (2004, 2007); and Mudan et al. (2009).

Summary and Concluding Remarks

The MVT and CD Pb-Zn deposits formed mainly from oxidized sedimentary brines derived from evaporated seawater. With few exceptions (i.e., Broken Hill subtype), these sedimentary rock-hosted ores formed within a few kilometers of the surface by similar depositional processes (e.g., fluid mixing, changes in redox state, fluid-rock reactions). Considering that sulfur redox reactions are one of the major controls on the extraction, transport, and deposition at shallow crustal sites, these ores can be considered as sensitive indicators that have recorded the oxygenation of Earth's hydrosphere. A consequence of the Great Oxygenation Event was the increased input of sulfate into the oceans derived by the oxidative weathering of sulfide minerals together with changes in the rate of sulfate removal from the oceans (Farquhar et al., 2010). Banded iron formations disappeared as a common rock type after the first major oxygenation of the oceans, whereas sediment-hosted Pb-Zn deposits bloomed in clastic rock-dominated sedimentary sequences in certain basins from ca. 1.85 to 1.4 Ga. Contributing to the abundance of CD deposits during this time was (1) increased oxidation of sulfides at the surface that provided sulfate to the hydrosphere and Pb and Zn to the sediments; (2) major redox and compositional gradients in the oceans; (3) first formation of significant sulfate-bearing evaporites; (4) formation of red beds and oxidized aquifers: (5) evolution of sulfate-reducing bacteria; and (6) formation of large and long-lived basins on stable cratons.

Although MVT and CD deposits appeared for the first time in Earth history at 2.02 to 2.00 Ga, only CD deposits were important repositories for Pb and Zn between the onset of the Great Oxygenation Event and the second oxidation of the atmosphere that followed the Neoproterozoic glaciations. Increased oxygenation of the oceans following the second Great Oxygenation Event led to an abundance of evaporites and an explosion of marine organisms with coarse skeletal carbonates. These coarse-grained carbonates comprise the vast Paleozoic carbonate platforms that host many of the giant MVT deposits. The MVT deposits reached their maximum abundance during the assembly of Pangea from Devonian to Carboniferous. By this time, vast and permeable carbonate platforms and abundant evaporites had formed. The intense orogenic activity during the assembly of Pangea in relatively low latitudes created abundant opportunities for the migration of sedimentary brines into the interior carbonate platforms and within extensional domains landward of the orogenic belts to form MVT deposits. This was also a time for important CD mineral deposit formation along passive margins in evaporative belts of Pangea. Following the breakup of Pangea, a new era of MVT ore deposition began with the onset of the assembly of the Neosupercontinent.

The genesis of sediment-hosted Pb-Zn deposits in Earth history resulted from the convergence of a number of important ore-forming elements. The essential element was the presence of sufficient oxygen in the atmosphere that enabled the mobility of Pb and Zn in the hydrosphere. In addition, there seem to be other critical factors that must exist to form large deposits or a metallogenic province. These include the presence of oxidizing sedimentary brines; a tectonic trigger that may be regional or continental in scale; the presence of a site where sulfur can be efficiently reduced or trapped, such as organic-rich or sulfate evaporites; oxidized aquifers in the basin or flow path of the metal-bearing fluids; and, for MVT deposits, geologic features that allow the mixing of large volumes of metal-bearing and reduced-sulfur fluids and the presence of large volumes of permeable carbonate platform. Another critical factor for the formation of large ore deposits may be the involvement of special source rocks enriched in extractable metals. There are few studies that provide direct evidence for special source rocks for the ore metals. Goldhaber et al. (1995) provided Pb isotope evidence that oxidized basal sandstone and the underlying basement regolith were the main sources of metals for the Viburnum Trend district. Wilkinson (2009a, b) provided a case study tracing metal transport in the Irish Midlands ore field that suggests the efficient extraction of metals from the source rocks is critical for the formation of economic deposits.

The most important feature that shaped the rather uneven secular distribution of sediment-hosted Pb-Zn deposits after the Great Oxygenation Event is the destruction and tectonic recycling of the deposits. Veizer and Mackenzie (2003) concluded that the sedimentary cycle is about 90 percent cannibalistic and that most older sedimentary rocks have been recycled. If this is correct, then most sediment-hosted Pb-Zn deposits that formed in Earth history have been destroyed or deformed and metamorphosed beyond recognition. Thus, the inability to quantify the destruction of the deposits imposes a significant limitation on interpreting their secular distribution. Perhaps the best constraints on the survival potential for sediment-hosted Pb-Zn deposits are for those hosted in clastic rock sedimentary sequences in passive margins. Here, the potential for the preservation of CD deposits in passive margins can be examined within a context of the life span of ocean basins (Bradley, 2008) and it can be determined whether the host strata were subducted, metamorphosed, and/or uplifted and eroded in an orogenic belt. Life spans vary from tens of millions to several hundreds of millions years. Relative to MVT deposits in platform carbonate sequences, CD deposits in passive margins appear to be more prone to destruction. This point is based on the observation that few MVT deposits in the Phanerozoic have been metamorphosed, whereas many CD deposits have been deformed and metamorphosed. Although significant passive-margin CD deposits are present in the rock record as far back as 1.85 Ga, a large proportion of passive-margin CD deposits have been removed from the rock record.

The potential for destruction of CD deposits in rift and sag basins is another critical issue. The most significant CD Pb-Zn deposits are those hosted in Proterozoic continental rift and sag basins between about 1.65 and 1.4 Ga, but yet no large CD deposits are known in similar younger basins. This observation remains to be explained in a convincing way.

Some important questions for future research that address the issues of preservation and survivability of the ore and their tectonic environments include the following: (1) why are there so few sediment-hosted Pb-Zn deposits from about 1.4 to 0.7 Ga, within the Boring Billion of Holland (2005)? Is it a lack of ore genesis or destruction of deposits?; (2) why are there no CD Pb-Zn deposits in rift basins younger than 1.4 Ga? Is it a lack of formation or have the basins not been sufficiently inverted to expose the deposits?; (3) why are there so few sediment-hosted Pb-Zn deposits in the late Neoproterozoic, after the rise of oxygen in the atmosphere and the formation of the important Neoproterozoic evaporites?; (4) Can we quantify the destruction of sediment-hosted Pb-Zn deposits in the tectonic environments that host the deposits?; and (5) do metal-rich source rocks that may have been deposited after the Great Oxygenation Event provide the link to the genesis of the giant CD Pb-Zn in the Paleoproterozoic? Certainly, more work is needed to identify the sources of ore metals for sediment-hosted Pb-Zn deposits.

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REFERENCES

Ahmad, M., Lally, J.H., and McCready, A.J., 2006, Geology and mineral deposits of the Rum Jungle mineral field, Northern Territory: Northern Territory Geological Survey Report 19, 81 p.

Anbar, A.D., and Knoll, A.H., 2002, Proterozoic ocean chemistry and evolution: A bioinorganic bridge?: Science, v. 297, p. 1137–1142.

Anderson, G.M., 1973, The hydrothermal transport and deposition of galena and sphalerite near 100°C: ECONOMIC GEOLOGY, v. 68, p. 480–492.

——1975, Precipitation of Mississippi Valley-type ores: ECONOMIC GEOLOGY, v. 70, p. 937–942.

——1983, Some geochemical aspects of sulfide precipitation in carbonate rocks, *in* Kisvarsanyi, E., et al., eds., Proceedings of International conference on Mississippi Valley-type lead-zinc deposits: Rolla, Missouri, University of Missouri-Rolla Press, p. 61–76.

Anderson, H.E., and Parrish, R.R., 2000, U-Pb geochronological evidence for the geological history of the Belt-Purcell Supergroup, southeastern British Columbia, *in* Lydon, J.W., Hoy, T., Slack, J.F., and Knapp, M.E., eds., The geological environment of the Sullivan deposit, British Columbia: Geological Association of Canada, Mineral Deposits Division, p. 113–126.

Ansdell, K.M., Nesbitt, B.E., and Longstaffe, F.J., 1989, A fluid inclusion and stable isotope study of the Tom Ba-Pb-Zn deposit, Yukon Territory, Canada: ECONOMIC GEOLOGY, v. 84, p. 841–856.

Ayuso, R.A., Kelley, K.D., Leach, D.L., Young, L.E., Slack, J.F., Wandless, J.F., Lyon, A.M., and Dillingham, J.L., 2004, Origin of the Red Dog Zn-Pb-Ag deposits, Brooks Range, Alaska: Evidence from regional Pb and Sr isotope sources: ECONOMIC GEOLOGY, v. 99, p. 1533–1553.

Badham, J.P.N., 1981, Shale-hosted Pb-Zn deposits: Products of exhalation of formation waters: Institution of Mining and Metallurgy Transactions, v. 90, sec. B, p. B70–B76.

Barley, M.E., and Groves, D.I., 1992, Supercontinent cycles and the distribution of metal deposits through time: Geology, v. 20, p. 291–294.

Barnes, H.L., 1979, Solubilities of ore minerals, *in* Barnes, H.L., ed., Geochemistry of hydrothermal ore deposits, 2nd ed.: New York, Wiley, p. 404–459.

Barovich, K.M., and Hand, M., 2008, Tectonic setting and provenance of the Paleoproterozoic Willyama Supergroup, Curnamona province, Australian geochemical and Nd isotopic constraints on contrasting source terrain components: Precambrian Research, v. 166, p. 318–337.

Barrie, C.T., and Hannington, M.D., 1999, Classification of volcanic-associated massive sulfide deposits based on host-rock composition: Reviews in Economic Geology, v. 8, p. 2–11.

Bastin, E.S., 1939, Theories of formation of ore deposits: Scientific American, v. 49, no. 6, p. 538–547.

Basuki, N.I., and Spooner, E.T.C., 2004, A review of fluid inclusion temperatures and salinities in Mississippi Valley-type Zn-Pb deposits: Identifying thresholds for metal transport: Exploration and Mining Geology, v. 11, nos. 1–4, p. 1–17.

Bauer, P.W., and Williams, M.L., 1994, The age of Proterozoic orogenesis in New Mexico, U.S.A.: Precambrian Research, v. 67, p. 349–356.

Beardsmore, T.J., Newberry, S.P., and Laing, W.P., 1988, The Maronan Supergroup: An inferred early volcanosedimentary rift sequence in the Mount Isa inlier, and its implications for ensialic rifting in the Middle Proterozoic of northwest Queensland: Precambrian Research, v. 40/41, p. 487–507.

Betts, P.G., and Lister, G.S., 2001, Comparison of the "strike-slip" versus the "episodic rift-sag" models for the origin of the Isa superbasin: Australian Journal of Earth Sciences, v. 48, p. 265–280.

Betts, P.G., Giles, D., Lister, G.S., and Frik, L.R., 2002, Evolution of the Australian lithosphere: Australian Journal of Earth Sciences, v. 49, p. 661–698.

Betts, P.G., Giles, D., and Lister, G.S., 2003, Tectonic environment of shale-hosted massive sulfide Pb-Zn-Ag deposits of Proterozoic northeastern Australia: ECONOMIC GEOLOGY, v. 98, p. 557–576.

Betts, P.G., Giles, D., Lister, G.S., Goleby, B.R., and Ailleres, L., 2006, Synthesis of the Proterozoic evolution of the Mt. Isa inlier: Australian Journal of Earth Sciences, v. 53, p. 187–211.

Bodiselitsch, B., Koeberl, C., Master, S., and Reimold, W.U., 2005, Estimating duration and intensity of Neoproterozoic snowball glaciations from Ir anomalies: Science, v. 308, p. 230–242.

Bodon, S.B., 1998, Paragenetic relationships and their implications for ore genesis at the Cannington Ag-Pb-Zn deposit, Mount Isa inlier, Queensland, Australia: ECONOMIC GEOLOGY, v. 93, p. 1463–1488.

Bradley, D.C., 2008, Passive margins through Earth history: Earth-Science Reviews, v. 91, p. 1–36.

Bradley, D.C., and Kidd, W.S.F., 1991, Flexural extension of the upper continental crust in collisional foredeeps: Geological Society of America Bulletin, v.103, p. 1416–1438.

Bradley, D.C., and Leach, D.L., 2003, Tectonic controls of Mississippi Valley-type lead-zinc mineralization in orogenic forelands: Mineralium Deposita, v. 38, p. 652–667.

Broadbent, G.C., Myers, R.E., and Wright, J.V., 1998, Geology and origin of shale-hosted Zn-Pb-Ag mineralization at the Century deposit, northwest Queensland, Australia: ECONOMIC GEOLOGY, v. 93, p. 1264–1294.

Brown, M., 2008, Characteristic thermal regimes of plate tectonics and their metamorphic imprint throughout Earth history: When did Earth first adopt a plate tectonics mode of behavior?: Geological Society of America Special Paper 440, p. 97–128.

Burrett, C., and Berry, R., 2000, Proterozoic Australia-Western United States (AUSWUS) fit between Laurentia and Australia: Geology, v. 28, p. 103–106.

Canfield, D.E., 2004, The evolution of the Earth surface sulfur reservoir: American Journal of Science, v. 304, p. 839–861.

Canfield, D.E., and Farquhar, J., 2009, Animal evolution, bioturbation, and the sulfate concentration of the oceans: Proceedings of the National Academy Science, v. 106, p. 8123–8127.

Canfield, D.E., and Raiswell, R., 1999, The evolution of the sulfur cycle: American Journal of Science, v. 299, p. 697–723.

Canfield, D.E., Poulton, S.W., and Narbonee, G.M., 2007, Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life: Science, v. 315, p. 92–95.

Carpenter, A.B., Trout, M.L., and Pickett, E.E., 1974, Preliminary report on the origin and chemical evolution of lead- and zinc-rich oil field brines in Central Mississippi: ECONOMIC GEOLOGY, v. 69, p. 1191–1206.

Carr, G.R., Denton, G.J., Korsch, M.J., Gardner, B.L., Parr, Andrew, A.S., Whitford, D.J., Wyborn, L.A.I., and Sun, S-S., 2001, User friendly isotope technologies in mineral exploration: Pb isotope applications, Northern Australian Proterozoic basins: CSIRO Report 713C, 127 p.

Chandler, F.W., 2000, The Belt-Purcell basin as a low-latitude passive rift: Implications for the geological environment of Sullivan-type deposits, *in* Lydon, J.W., Hoy, T., Slack, J.F., and Knapp, M.E., eds., The geological environment of the Sullivan deposit, British Columbia: Geological Association of Canada, Mineral Deposits Division, p. 82–112.

Chapman, L.H., 2004, Geology and mineralization styles of the George Fisher Zn-Pb-Ag deposit, Mt. Isa: ECONOMIC GEOLOGY, v. 99, p. 233–255.

Chapman, L.H., and Williams, P.J., 1998, Evolution of pyroxene-pyroxenoid-garnet alteration at the Cannington Ag-Pb-Zn deposit, Cloncurry district, Queensland Australia: ECONOMIC GEOLOGY, v. 93, p. 1390–1405.

Clendenin, C.W. and Duane, M.J., 1990, Focused fluid flow and Ozark Mississippi Valley-type deposits: Geology, v. 18, p. 116–119.

Cloud, P.E., Jr., 1972, A working model of the primitive Earth: American Journal of Science, v. 272, p. 537–548.

Colpron, M., Logan, J.M., and Mortensen, J.K., 2002, U-Pb zircon age constraint for late Neoproterozoic rifting and initiation of the lower Paleozoic passive margin of western Laurentia: Canadian Journal of Earth Sciences, v. 39, p. 133–143.

Condie, K.C., 2000, Episodic continental growth models: Afterthoughts and extensions: Tectonophysics, v. 322, p. 207–215.

——2005, Earth as an evolving planetary system: Amsterdam, Elsevier Academic Press, 447 p.

Conor, C.H.H., and Preiss, W.V., 2008, Understanding the 1720–1640 Ma Palaeoproterozoic Willyama Supergroup, Curnamona province, southeastern Australia: Implications for tectonics, basin evolution and ore genesis: Precambrian Research, v. 166, p. 297–317.

Cooke, D.R., Bull, S.W., Donovan, S., and Rogers, J.R., 1998, K metasomatism and base metal depletion in volcanic rocks from the McArthur basin, Northern Territory—implications for base metal mineralization: ECONOMIC GEOLOGY, v. 93, p. 1237–1263.

Cooke, D.R., Bull, S.W., Large, R.R., and McGoldrick, P.J., 2000, The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (Sedex) deposits: ECONOMIC GEOLOGY, v. 95, p. 1–18.

Cordilleran Engineering Limited, 1974, Summary report on the Goz Creek property: Cordilleran Engineering Limited, 1418–355 Burrard St., Vancouver, B.C., Property Report, 54 p.

Crawford, J.C., and Maas, R., 2009, A magmatic-hydrothermal origin for the giant Broken Hill Pb-Zn deposit: Biennial SGA Meeting, 10th, Townsville, 2009, Proceedings, p. 421–423.

Cromie, P.W., Gosse, R.R., Zhang, P., and Zhu, X., 1996, Exploration for carbonate-hosted Pb-Zn deposits, Sichua, P.R.C. [abs.]: International Geological Congress, 30th, Beijing, China, Abstracts, p. 412.

Deb, M., and Thorpe, R.I., 2004, Geochronological constraints in the Precambrian geology of Rajasthan and their metallogenic implications, *in* Deb, M., and Goodfellow, W.D., eds., Sediment-hosted lead-zinc sulphide deposits: New Delhi, India, Narosa Publishing House, p. 246–263.

Dewey, J.F., 1980, Episodicity, sequence, and style at convergent plate boundaries: Geological Association of Canada Special Paper 20, p. 553–573.

Dobretsov, N.L., 1996, Ore formation and global geological processes: Evolution and problems of periodicity, *in* Smirnovskii Sbornik, ed., General problems of ore formation and metallogeny: Moscow, Akademik Smirnov Fund, p. 38–60 (in Russian).

Dobretsov, N.L., Melyakhovetskiy, A.A., Ashchepkov, I.V., Kartavchenko, V.G., Gabov, N.F., Mogilev, V.A., Shadayev, M.A., Rip, G.S., and Sklyarov, Y. V., 1987, Structural-mineralogical criteria for metamorphogenetic ore mineralization: An example of pyrite deposits: Novosibirsk, USSR, Izd. Nauka, P. 168 p.

Donaghy, T., Hall, M., and Gibson, G., 1998, The Palaeoproterozoic Thackeringa Group: Deposition, deformation, and stratigraphy [abs.]: ASGO Record 1998/25, p. 17–20.

Drieberg, S.L., 2003, The magmatic-hydrothermal architecture of the Archean volcanic massive sulfide (VMS) system at Panorama, Pilbara, Western Australia: Unpublished Ph.D. thesis, Perth, WA, University of Western Australia, 370 p.

Duane, M.J., Kruger, F.J., Turner, A.M., Whitelaw, H.T., Coetzee, H., and Verhagen, B., 2004, The timing and isotopic character of regional hydrothermal alteration and associated epigenetic mineralization in the western sector of the Kaapvaal craton (South Africa): Journal of African Earth Science, v. 38, p. 461–476.

Dumoulin, J.A., Harris, A.G., Blome, C.D., and Young, L.E., 2004, Depositional settings, correlation, and age of Carboniferous rocks in the western Brooks Range, Alaska: ECONOMIC GEOLOGY, v. 99, p. 1355–1384.

Edgerton, D., 1997, Reconstruction of the Red Dog Zn-Pb-Ba orebody, Alaska: Implications for the vent environment during the mineralizing event: Canadian Journal of Earth Science, v. 34, p. 1581–1602.

Elston, D.P., Enkin, R.J., Baker, J., and Kisilivsky, D.K., 2002, Tightening the belt: Paleomagnetic-stratigraphic constraints on deposition, correlation, and deformation of the Middle Proterozoic (ca. 1.4 Ga) Belt-Purcell Supergroup, United States and Canada: Geological Society of America Bulletin, v. 114, p. 619–638.

Eriksson, P.B., Martins-Neto, M.A., Nelson, D.R., Aspler, L.B., Chiarenzelli, J.R., Catuneau, O., Sarker, S., Altermann, W., and Rautenbach, C.J. de W., 2001, An introduction to Precambrian basins: Their characteristics and genesis: Sedimentary Geology, v. 141–142, p. 1–35.

Etheridge, M., and Wall, V.J., 1994, Tectonic and structural evolution of the Australian Proterozoic [abs.]: Geological Society of Australia Abstracts, v. 37, p. 927–934.

Evans, D.A.D, 2006, Proterozoic low orbital obliquity and axial-dipolar geomagnetic field from evaporite palaeolatitudes: Nature, v. 444, p. 51–55.

Farquhar, J., Namping, W., Canfield, D.E, and Oduro, H., 2010, Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits: ECONOMIC GEOLOGY, v. 105, p. 509–533.

Forrestal, P.J., 1990, Mount Isa and Hilton silver-lead-zinc deposits: Australasian Institute of Mining and Metallurgy Monograph 14, p. 927–934.

Gardner, H.D., and Hutcheson, I., 1985, Geochemistry, mineralogy, and geology of the Jason Pb-Zn deposits, Macmillan Pass, Yukon, Canada: ECONOMIC GEOLOGY, v. 80, p. 1257–1276.

Garrels, R.M., and Mackenzie, F.T., 1969, Sedimentary rock types: Relative proportions as a function of geological time: Science, v. 163(3867), p. 570–571.

Gemmel, J.B., Zantop, H., and Meinert, L.D., 1992, Genesis of the Aguilar zinc-lead-silver deposit, Argentina; contact metasomatic vs. sedimentary exhalative: ECONOMIC GEOLOGY, v. 87, p. 2085–2112.

Ghazban, F., Schjwarcz, H.P., and Ford, D.C., 1990, Carbon and sulfur isotope evidence for in situ reduction of sulfate, Nanisivik lead-zinc deposits, Northwest Territories, Baffin Island, Canada: ECONOMIC GEOLOGY, v. 85, p. 360–375.

Gibbins, W.A., 1983, Mississippi Valley-type lead-zinc districts of northern Canada, *in*, Kisvarsanyi, G., Grant, S.K., Pratt, W.P., and Koenig, J.W., eds.,

International conference on Mississippi Valley-type lead-zinc deposits. Proceedings volume: Rolla, Missouri, University of Missouri, Rolla, p. 403–414.
Gibson, G.M., and Nutman, A.P., 2004, Detachment faulting and bimodal magmatism in the Palaeoproterozoic Willyama Supergroup, south-central Australia: Keys to recognition of a multiply deformed Precambrian metamorphic core complex: Journal of the Geological Society of London, v. 161, p. 55–66.
Gibson, G.M., Rubenach, M.J., Neumann, N.L., Southgate, P.N., and Hutton, L.J., 2008, Syn-and post-extensional tectonic activity in the Palaeoproterozoic sequences of Broken Hill and Mount Isa and its bearing on reconstructions of Rodinia: Precambrian Research v. 166, p. 350–369.
Giles, D., Betts, P.G., and Lister, G.S., 2002, Far-field continental backarc setting for 1.80–1.67 Ga basins of northern Australia: Geology, v. 30, p. 823–826.
Giles, D., Betts, P., and Aillieres, L., 2003, Insights into the early Isan orogeny from the Snake Creek anticline: A regional scale recumbent fold at the eastern margin of the Mount Isa inlier [abs.]: Geological Society of Australia Abstracts 72, p. 65.
Gilluly, A.K., 1949, Distribution of mountain building in geologic time: Geological Society of America Bulletin, v. 60, p. 561–590, v. 120, p. 135–139.
Giordano, T.H., 2002, Transport of Pb and Zn by carboxylate complexes in basinal ore fluids and related petroleum-field brines at 100°C: the influence of pH and oxygen fugacity: Geochemical Transactions, v. 38. p. 56–72.
Glesson, S.A., and Sharp, R.J., 2009, A regional mineralizing event in the Mackenzie Mountains, Northwest Territories, Canada: Science for Exploration and Mining, SGA Biennial Meeting, 9th, Townsville, Australia, Proceedings, p. 442–443.
Goldhaber, M.B., Church, S.E., Doe, B.R., Aleinikoff, J.N., Brannon, J.C., Podosek, F.A., Mosier, E.L., Taylor, C.D., and Gent, C.A., 1995, Lead and sulfur isotope investigation of Paleozoic sedimentary rocks from the southern midcontinent of the United States: Implications for paleohydrology and ore genesis of the southeast Missouri lead belts: Economic Geology, v. 90, p. 1875–1910.
Goldfarb, R.J., Groves, D.I., and Gardoll, S., 2001a, Orogenic gold and geologic time: A global synthesis: Ore Geology Reviews, v. 18, p. 1–75.
——2001b, Rotund versus skinny orogens: Well-nourished or malnourished gold?: Geology, v. 29, p. 539–542.
Goodfellow, W.D., 1987, Anoxic stratified oceans a source of sulphur in sediment-hosted stratiform Zn-Pb deposits (Selwyn basin, Yukon, Canada): Chemical Geology, v. 65, p. 359–382.
——2000, Anoxic conditions in the Aldridge basin during formation of the Sullivan Zn-Pb deposit: Implications for the genesis of massive sulphides and distal hydrothermal sediments: Geological Association of Canada, Mineral Deposits Division, Special Publication 1, p. 218–250.
——2007, Base metal metallogeny of the Selwyn basin, Canada, *in* Goodfellow, W.E., ed., Mineral deposits of Canada: A synthesis of major deposit-types, district metallogeny, the evolution of geological provinces, and exploration methods: Geological Association of Canada, Mineral Deposits Division, p. 553–579.
Goodfellow, W.D., and Jonasson, I.R., 1987, Environment of formation of the Howards Pass (XY) Zn-Pb deposit, Selwyn basin, Yukon: Canadian Institute of Mining and Metallurgy Special Volume 37, p. 19–50.
Goodfellow, W.D., and Lydon, J.W., 2007, Sedimentary-exhalative (SEDEX) deposits: Geological Association of Canada, Mineral Deposits Division, Special Publication 5, p. 163–183.
Goodfellow, W.D., Jonasson, I.R., and Morganti, J.M., 1983, Zonation of chalcophile elements about the Howard's Pass (XY) Zn-Pb deposit, Selwyn basin, Yukon, *in* Parslow, G.R., ed., Geochemical Exploration Journal of Geochemical Exploration 1982: Elsevier, Amsterdam-New York, p. 503–542.
Goodfellow, W.D., Lydon, J.W., and Turner, R.J.W., 1993, Geology and genesis of stratiform sediment-hosted (SEDEX) zinc-lead-silver sulphide deposits: Geological Association of Canada Special Paper 40, p. 201–251.
Greyling, L.N., 2000, The Paleoproterozoic carbonate-hosted Pering lead-zinc deposit, South Africa: Unpublished M.Sc. thesis, Johannesburg, Rand Afrikaans University, 129 p.
Grotzinger, J.P., 1989, Facies and evolution of Precambrian depositional systems: Emergence of the modern platform archetype: Society for Sedimentary Geology Special Publication 44, p. 79–106.
Grotzinger, J.P., and James, N.P., 2000, Precambrian carbonates: Evolution of understanding: Society for Sedimentary Geology Special Publication 67, p. 3–20.
Groves, D.I., Condie, K.C., Goldfarb, R.J., Hronsky, J.M.A., and Vielreicher, R.M., 2005a, Secular changes in global tectonic processes and their influence on the temporal distribution of gold-bearing mineral deposits: Economic Geology, v. 100, p. 203–224.
Groves, D.I., Vielreicher, R.M., Goldfarb. R.J., and Condie, K.C., 2005b, Controls on the heterogeneous distribution of mineral deposits through time: Geological Society of London Special Publication 248, p. 71–101.
Groves, I.M., Groves, D.I., Bierlein, F.P., Broome, J., and Penhall, J., 2008, Recognition of the hydrothermal feeder to the structurally inverted, giant Broken Hill deposit, New South Wales, Australia: Economic Geology, v. 103, p. 1389–1394.
Gummer, P.K., Plint, H.E., and Rainbird, R.H., 1996, The Esker Lake prospect: Stratabound Pb-Zn-Cu-Ag in emergent inner shelf carbonates, Rocknest Formation, Coronation Supergroup, NWT, 1996 exploration overview: Canada Department of Indian Affairs and Northern Development, p. 18–19.
——1997, The Esker Lake prospect: Stratabound Pb-Zn-Cu-Ag in emergent inner shelf carbonates, Rocknest Formation, Coronation Supergroup, NWT: Canada Department of Indian and Northern Affairs, p. 18–19.
Gützmer, J., 2005, Paleoproterozoic carbonate-hosted Pering Zn-Pb deposit, South Africa: I. Styles of brecciation and mineralization: Mineralium Deposita, v. 40, p. 664–685.
Gützmer, J., Banks, D.A., Luders, V., Hoefs, J., Beukes, N.J., and von Bexing, K.L., 2003, Ancient subsea-floor alteration of basaltic andesites of the Ongeluk Formation, South Africa: Implications for the chemistry of Paleoproterozoic seawater: Chemical Geology, v. 201, p. 37–53.
Hancock, M.C., and Purvis, A.H., 1990, Lady Loretta silver-lead-zinc deposit: Australasian Institute of Mining and Metallurgy Monograph 14, v. 943–948.
Hanor, J.S., 1996, Controls on the solubilization of lead and zinc in basin brines: Society of Economic Geologists Special Publication 4, p. 483–500.
Hardy, J.L., 1979, Stratigraphy, brecciation and mineralization, Gayna River, N.W.T.: Unpublished M.Sc. thesis, Toronto, University of Toronto, 64 p.
Haydon, R.C., and McConachy, G.W., 1987, The stratigraphic setting of Pb-Zn-Ag mineralization at Broken Hill: Economic Geology, v. 82, p. 826–856.
Hazen, R.M., Papineau, D., Bleeker, W., Downs, R.T., Ferry, J.M., McCoy, T.J., Sverjensky, D.A., and Yang, H., 2008, Mineral evolution: American Minerologist, v. 93, p. 1693–1720.
Heijlen, W., Muchez, P., Banks, D.A., Schneider, J., Kucha, H., and Keppens, E., 2003, Carbonate-hosted Zn-Pb deposits in Upper Silesia, Poland: Origin and evolution of mineralizing fluids and constraints on genetic models: Economic Geology, v. 98, p. 911–932.
Hewton, R.S., 1982, Gayna River: A Proterozoic Mississippi Valley-type zinc-lead deposit: Geological Association of Canada Special Paper 25, p. 667–700.
Hitzman, M.W., Thorman, C.H., Romagna, G., Oliviera, R.F., Dardenne, M.A., and Drew, L.J., 1995, The Morro Agudo Zn-Pb deposits, Minas Gerais, Brazil: A Proterozoic Irish-type carbonate-hosted sedex-replacement deposit [abs.]: Geological Society of America Abstracts with Programs, v. 27, p. 408.
Hoffman, P.F., Kaufman, A.J., Halverson, G.P., and Schrag, D.P., 1998, A Neoproterozoic snowball Earth: Science, v. 281, p. 1342–1346.
Holland, H.D., 2005, Sedimentary mineral deposits and the evolution of Earth's near-surface environments: Economic Geology, v. 100, p. 1489–1509.
——2009, Why the atmosphere became oxygenated: A proposal: Geochimica et Cosmochimica Acta, v. 73, p. 5241–5255.
Huizenga, J-M., Gutzmer, J., Banks, D., and Greyling, L., 2006, The Paleoproterozoic carbonate-hosted Pering Zn-Pb deposit, South Africa. II: Fluid inclusion, fluid chemistry and stable isotope constraints: Mineralium Deposita, v. 40, p. 686–706.
Huston, D.L., and Logan, G.A., 2004, Barite, BIFs and bugs: Evidence for the evolution of the Earth's early hydrosphere: Earth and Planetary Science Letters, v. 220, p. 41–55.
Huston, D.L., Wyborn, L., and Stevens, B., 1998, Pb-Zn-Ag mineral systems: An example from Broken Hill: Australian Geological Survey Organisation Report1998/25, p. 59–63.
Huston, D.L., Stevens, B., Southgate, P.N., Muhling, P., and Wyborn, L., 2006, Australian Zn-Pb-Ag ore-forming systems: A review and analysis: Economic Geology, v. 101, p. 1117–1157.
Huston, D.L., Pehrsson, S., Eglington, B.M., and Zaw, K., 2010, The geology and metallogeny of volcanic-hosted massive sulfide deposits: Variations through geologic time and with tectonic setting: Economic Geology, v. 105, p. 571–591.
Hutchinson, R.W., 1992, Mineral deposits and metallogeny: Indicators of Earth's evolution, *in* Schidlowski, M., ed., Early organic evolution: Implications for mineral and energy resources: Berlin Heidenberg, Springer-Verlag, p. 521–544.

Hutton, L.J., and Sweet, I.P., 1982, Geological evolution, tectonic style and economic potential of the Lawn Hill Platform cover, northwest Queensland: BMR Journal of Australian Geology and Geophysics, v. 7, p. 125–134.

Idnurm, M., 2000, Toward a high resolution Late Palaeoproterozoic-earliest Mesoproterozoic apparent polar wander path for northern Australia: Australian Journal of Earth Sciences, v. 47, p. 405–430.

Jackson, M.J., Scott, D.L., and Rawlings, D.J., 2000, Stratigraphic framework for the Leichardt and Calvert superbasins: Review and correlations of the pre-1700 Ma successions between Mt. Isa and McArthur River: Australian Journal of Earth Sciences, v. 47, p. 381–408.

James, S.D., Pearce, J.A., and Oliver, R.A., 1987, The geochemistry of the lower Proterozoic Willyama Complex volcanics, Broken Hill block, New South Wales: Geological Society Special Publication 1, p. 395–408.

Jennings, S., and King, A.R., 2002, Geology, exploration history and future discoveries in the Red Dog district, western Brooks Range, Alaska: Centre for Ore Deposit Research Special Publication 4, p. 151–158.

Jiang, S.Y., Slack, J.F., and Palmer, M.R., 2000, Sm-Nd dating of the giant Sullivan Pb-Zn-Ag deposit, British Columbia: Geology, v.28, p. 751–754.

Johnson, C.A., Kelley, K.D., and Leach, D.L., 2004, Sulfur and oxygen isotopes in barite deposits of the western Brooks Range, Alaska, and implications for the origin of the Red Dog massive sulfide deposits: ECONOMIC GEOLOGY, v. 99, p. 1435–1448.

Jones, D.J., Bull, S., and McGoldrick, P., 1999, The Kamarga deposit: A large, low grade, stratabound zinc resource in the Proterozoic “Carpentaria zinc belt” of northern Australia, *in* Stanley, C.J., ed., Mineral deposits: Processes to processing: Rotterdam, A.A. Balkema, p. 873–876.

Kamo, S.L., Reimoldb, W.U., Krogha, T.E., and Collistonc, W.P., 1996, A 2.023 Ga age for the Vredefort impact event and a first report of shock metamorphosed zircons in pseudotachylitic breccias and Granophyre: Earth and Planetary Science Letters v. 144, p. 369–387.

Karlstrom, K.E., Ahall, K.I., Harlan, S.S., Williams, M.L., McLelland, J., and Geissman, J.W., 2001, Long-lived (1,8–1.0 Ga) convergent orogen in southern Laurentia, its extensions to Australia and Baltica, and implications for refining Rodinia: Precambrian Research, v. 111, p. 5–30.

Kelley, K.D., and Jennings, S., 2004, A special issue devoted to barite and Zn-Pb-Ag deposits in the Red Dog district, Western Brooks Range, northern Alaska: ECONOMIC GEOLOGY, v. 99, p. 1–14.

Kelley, K.D., Dumoulin, J.A., and Jennings, S., 2004a, The Anarraaq Zn-Pb-Ag and barite deposit, northern Alaska: Evidence for replacement of carbonate by barite and sulfides: ECONOMIC GEOLOGY, v. 99, p. 1577–1591.

Kelley, K.D., Leach, D.L., Johnson, C.A., Clark, J.L., Fayek, M., Slack, J.F., Anderson, V.M., Ayuso, R.A., and Ridley, W.I., 2004b, Textural, compositional, and sulfur isotope variations of sulfide minerals in the Red Dog Zn-Pb-Ag deposits, Brooks Range, Alaska: Implications for ore formation: ECONOMIC GEOLOGY, v. 99, p. 1509–1533.

Kennedy, M.J., Runnegar, B., Prave, A.R., Hoffman, K.H., and Arthur, M.A., 1998, Two or four Neoproterozoic glaciations?: Geology, v. 26, p. 1059–1063.

Kesler, S.E., and Reich, M.H., 2006, Precambrian Mississippi Valley-type deposits: Relation to changes in composition of the hydrosphere and atmosphere: Geological Society of America Memoir 198, p. 185–204.

Kesler, S.E., Martini, A.M., Appold, M.S., Walter, L.M., Huston, T.J., and Furman, F.C., 1996, Na-Cl-Br systematic of fluid inclusions from Mississippi Valley-type deposits, Appalachian Basin: Constraints on solute origin and migration paths: Geochimica et Cosmochimica Acta, v. 60, p. 225–233.

Kharaka, Y.K., and Hanor, J.S., 2007, Deep fluids in the continents: I. Sedimentary basins: Treatise on Geochemistry Volume 5, p. 1–48,

King, H.F., and Thomson, B.P., 1953, The geology of the Broken Hill district: Australasian Institute of Mining and Metallurgy Publication 1, p. 533–577.

Khiltova, V.Y., and Pleskach, G.P., 1997, Yenisey fold belt: Developments in Economic Geology, v. 30, p. 289–316.

Kirschvink, J.L., 1992, Late Proterozoic low-latitude global glaciatioin: The snowball Earth, *in* Schopf, J.W., and Klein, C., eds., The Proterozoic biosphere: A multidisciplinary study: Cambridge, UK, Cambridge University Press, p. 51–52.

Knauth, L.P., 2005, Temperature and salinity history of the Precambrian ocean: Implications for the course of microbial evolution: Paleaeogeography, Palaeoclimatology, Palaeoecology, v. 219, p. 53–69.

Kositcin, N., Champion, D.C., and Huston, D.L., 2009, Geodynamic synthesis of the North Queensland region and implications for metallogeny: Geoscience Australia Record 2009/30, 196 p.

Kump, L.R., 2008, The rise of atmospheric oxygen: Nature, v. 451, p. 277–278.

Kyle, J.R., and Misi, A., 1997, Origin of Zn-Pb-Ag sulfide mineralization within upper Proterozoic phosphate-rich carbonate strata, Irece basin, Bahia, Brazil: International Geology Review, v. 39, p. 383–399.

Laing, W.P., 1996, The Diamantina orogen linking the Willyama and Cloncurry terranes, eastern Australia: University of Tasmania, Centre for Ore Deposit and Exploration Studies Special Publication 1, p. 67–70.

Large, D.E., 2003, The tectonic setting of base-metal mineralization in the Rhenohercynian terranes of central Europe, *in* Kelly, J.G., Andrew, C.J., Ashton, J.H, Boland, M.B., Earls, G., Fusciardi. L., and Stanley, G. eds., Europe’s major base metal deposits: Dublin, Irish Association for Economic Geology, p. 155–168.

Large, D.E., and Walcher, E., 1999, The Rammelsberg massive sulphide Cu-Zn-Pb-Ba deposit, Germany: An example of sediment hosted, massive sulphide mineralization: Mineralium Deposita, v. 34, p. 522–538.

Large, R.R., Bull, S.W., Yang, J., Cooke, D.R., Garven, G., McGoldrick, P.J., and Selley, D., 2002, Controls on the formation of giant stratiform sediment-hosted Zn-Pb-Ag deposits with particular reference to the north Australian Proterozoic: University of Tasmania, Centre for Special Ore Deposit and Exploration (CODES) Studies Publication 4, p. 107–149.

Large, R.R., Bull, S.W., McGoldrick, P.J., Derrick, G., Carr, G., and Walters, S., 2005, Stratiform and strata-bound Zn-Pb-Ag deposits of the Proterozoic sedimentary basins of northern Australia: ECONOMIC GEOLOGY 100TH ANNIVERSARY VOLUME, p. 931–963.

Lawver, L.A., and Scotese, C.R., 1990, A review of tectonic models for the evolution of the Canada basin: Geological Society of America, Geology of North America, v. L, p. 593–618.

Leach, D.L., and Sangster, D.F., 1993, Mississippi Valley-type lead-zinc deposits: Geological Association of Canada Special Paper 40, p 289–314.

Leach, D.L., Bradley, D., Lewchuk, M.T., Symons, D.T.A., de Marsily, G., and Brannon, J., 2001, Mississippi Valley-type lead-zinc deposits through geological time: Implications from recent age-dating research: Mineralium Deposita, v. 36, p. 711–740.

Leach, D.L., Marsh, E., Emsbo, P., Rombach, C.S., Kelley, K.D., Reynolds, J., and Anthony, M., 2004, Nature of hydrothermal fluids at the shale-hosted Red Dog Zn-Pb-Ag deposits, Brooks Range, Alaska: ECONOMIC GEOLOGY, v. 99, p. 1449–1480.

Leach, D. L., Bradley, D., Gardoll, S., Huston, D., and Marsh, E., 2005a, The distribution of SEDEX Pb-Zn deposits through Earth history: Mineral Deposit Research: Meeting the Global Challenge, Biennial SGA Meeting, 8th, Beijing, China, August 2005, Proceedings, p. 145–149.

Leach, D.L., Sangster, D.F. Kelley, K. D., Large, R. R., Garven, G., Allen, C. R., Gutzmer,J., and Walters, S., 2005b, Sediment-hosted lead-zinc deposits: A global perspective: ECONOMIC GEOLOGY 100TH ANNIVERSARY VOLUME, p. 561–608,

Leach, D., Macquar J.-C., Lagneau, V., Leventhal, J., Emsbo, P., and Premo, W., 2006 Precipitation of lead-zinc ores in the Mississippi Valley-type deposit at Trèves, Cévennes region of Southern, France: Geofluids, v. 6, p. 24–44.

Leitch, C.H.B., and Lydon, J.W., 2000, Fluid inclusion petrography and microthermometry of the Sullivan deposit and surrounding area: Geological Association of Canada, Mineral Deposits Division Special Volume 1, p. 617–632.

Lewchuk, M.T., Leach, D.L., Kelley, K.D., and Symons, D.T.A., 2004, Paleomagnetism of the Red Dog Zn-Pb massive sulfide deposit in northern Alaska: ECONOMIC GEOLOGY, v. 99, p. 1555–1567.

Li, W., Huang, Z., and Yin, M., 2006, Dating of the giant Huize Zn-Pb orefield of Yunnan province, southwest China: Constraints from the Sm-Nd system in hydrothermal calcite: Resource Geology, v. 57, p. 90–97.

Lucia, F.J., 2007, Carbonate reservoir characterization—an integrated approach, 2nd ed.: Berlin, New York, Springer, 336 p.

Lydon, J.W., 1983, Chemical parameters controlling the origin and deposition of sediment-hosted stratiform lead-zinc deposits: Mineralogical Association of Canada Short Course Handbook 9, p. 175–250.

——2004, Geology of the Belt-Purcell basin and the Sullivan deposit, *in* Deb, M., and Goodfellow, W.D., eds., Sediment-hosted lead-zinc sulfide deposits: Attributes and models of some major deposits in India, Australia, and Canada: New Delhi, India, Narosa Publishing House, p. 100–148.

——2007, Geology and metallogeny of the Belt-Purcell basin: Geological Association of Canada, Mineral Deposits Division Special Publication 5, p. 581–607.

Lydon, J.W., Hoy, T., Slack, J.F., and Knapp, M.E., eds., 2000, The geological environment of the Sullivan deposit, B.C.: Geological Association of Canada, Mineral Deposits Division Special Publication 1, 834 p.

Lyons, T.W., Gellatly, S.W. McGoldrick, P.J., and Kah, L.C., 2006, Proterozoic sedimentary exhalative (SEDEX) deposits and links to evolving global ocean chemistry: Geological Society of America Memoir 198, p. 169–184.

Maynard, J.B., and Okita, P.M., 1991, Bedded barite deposits in the United States, Canada, Germany, and China: Two major types based on tectonic setting: ECONOMIC GEOLOGY, v. 86, p. 364–376.

Meert, J.G., 2002, Paleomagnetic evidence for a Paleo-Mesoproterozoic Supercontinent Columbia: Gondwana Research, v. 5, p. 207–215.

Meyer, C., 1981, Ore-forming processes in geologic history: ECONOMIC GEOLOGY 75TH ANNIVERSARY VOLUME, p. 6–41.

——1988, Ore deposits as guides to geologic history of the earth: Annual Review of Earth and Planetary Science, v. 16, p. 147–171.

Misi, A., Iyer, S.S., Tassinari, C.C.G., Kyle, J.R., Coelho, C.E.S., Franca-Rocha, W.J.S., Gomes, A.S.R., and Cunha, I.A., 1999, Geological and isotopic constraints on the metallogenic evolution of the Proterozoic sediment-hosted Pb-Zn (Ag) deposits of Brazil: Gondwana Research, v. 2, p. 47–68.

Moore, D.E., Young, L.E., Modene, J.S., and Plahuta, J.T., 1986, Geologic setting and genesis of the Red Dog zinc-lead-silver deposit, Western Brooks Range, Alaska: ECONOMIC GEOLOGY, v. 81, p. 1696–1727.

Morelli, R.M., Creaser, R.A., Selby, D., Kelley, K.D., Leach, D.L., and King, A.R., 2004, Re-Os Sulfide Geochronology of the Red Dog Sediment-Hosted Zn-Pb-Ag Deposit, Brooks Range, Alaska: ECONOMIC GEOLOGY, v. 99, p. 1569–1576.

Muchez, P., and Stassen, P., 2006, Multiple origins of the “Kniest feeder zone” of the stratiform Zn-Pb-Cu ore deposit of Rammelsberg, Germany: Mineralium Deposita, v. 41, p. 46–51.

Mudan, Y., Wenbo, L., and Xiwen, S., 2009, Rb-Sr isotopic dating of sphalerite from the giant Huize Zn-Pb ore field, Yunnan province, southwestern China: Chinese Journal of Geochemistry, v. 28, p. 70–75.

Mueller, A.G., 2008, Rammelsberg Cu-Zn-Pb SEDEX deposit, Germany: SGA Web Mineral Deposit Archive (www.e-sga.org, 34 p.)

Neumann, N.L., Southgate, P.N., Gibson, G.M., and McIntyre, A., 2006, New SHRIMP geochronology for the Western fold belt of the Mount Isa inlier: Developing a 1800–1650 Ma event framework: Australian Journal of Earth Sciences, v. 53, p. 1023–1039.

Neumann, N.L., Southgate, P.N., and Gibson, G.M., 2009, Defining unconformities in Proterozoic sedimentary basins using detrital geochronology and basin analysis—an example from the Mount Isa inlier, Australia: Precambrian Research, v. 168, p. 149–166.

Nutman, A.P., and Ehlers, P.D., 1998, Evidence for multiple Palaeoproterozoic thermal events and magmatism adjacent to the Broken Hill Pb-Zn-Ag orebody, Australia: Precambrian Research, v. 90, p. 203–238.

Olson, R.A., 1984, Genesis of paleokarst and strata-bound zinc-lead sulfide deposits in a Proterozoic dolostone, northern Baffin Island, Canada: ECONOMIC GEOLOGY, v. 79, p. 1056–1103.

Page, R.W., and Sun, S.-S., 1998, Aspects of geochronology and crustal evolution in the Eastern fold belt, Mt. Isa inlier: Australian Journal of Earth Sciences, v. 45, p. 343–362.

Page, R.W., Jackson, M.J., and Krassay, A.A., 2000, Constraining sequence stratigraphy in north Australia basins: SHRIMP U-Pb zircon geochronology between Mt. Isa and McArthur River: Australian Journal of Earth Sciences, v. 47, p. 431–460.

Page, R.W., Conor, C.H.H., Stevens, B.P.J., Gibson, G.M., Preiss, W.V., and Southgate, P.N., 2005, Correlation of Olary and Broken Hill domains, Curnamona province: Possible relationship to Mount Isa and other North Australian Pb-Zn-Ag–bearing successions: ECONOMIC GEOLOGY, v. 100, p. 663–676.

Pannalal, S.J., Symons, D.T.A., and Sangster, D.F., 2004, Paleomagnetic dating of Upper Mississippi Valley zinc-lead mineralisation, WI, USA: Journal of Applied Geophysics, v. 56, p. 135–153.

Pannalal, S.J., Symons, D.T.A., and Leach, D.L., 2007, Paleomagnetic and mineral magnetic constraints on Zn-Pb ore genesis in the Pend Oreille mine, Metaline district, Washington, USA: Canadian Journal of Earth Science, v. 44, p. 1661–1673.

Pesonen, L.J., Elming, S.A., Mertanen, S., Pisarevsky, S.A., D’Agrella-Filho, M.S., Meert, J., Schmidt, P.W., Abrahamsen, N., and Bylund, G., 2003, Palaeomagnetic configuration of continents during the Proterozoic: Tectonophysics v. 375, p. 289–324.

Pisarevsky, S.A., 2005, New edition of the Global Paleomagnetic Database: EOS Transactions, v. 86, no. 17, p. 170.

Pisarevsky, S.A., and Natapov, L.M., 2003, Siberia and Rodinia: Tectonophysics v. 375, p. 221–245.

Plumb, K.A., Ahmad, M., and Wygralak, A.S., 1990, Mid-Proterozoic basins of north Australian craton—regional geology and mineralization, *in* Hughes, F.E., ed., Geology of the mineral deposits of Australia and Papua New Guinea: Melbourne, Australasian Institute of Mining and Metallurgy, p. 881–902.

——1998, Mid-Proterozoic basins of the North Australian craton: Australasian Institute of Mining and Metallurgy Monograph 22, p. 881–902.

Plumlee, G., Leach, D.L., Hofstra, A.H., Landis, G.P., Rowan, E.L., and Viets, J.G., 1994, Chemical reaction path modeling of ore deposition in Mississippi Valley-type deposits of the Ozark region, U.S. mid-continent: ECONOMIC GEOLOGY, v. 89, p.1361–1383.

Polito, P.A., Kyser, K.T., Golding, S.D., and Southgate, P.N., 2006, Zinc deposits and related mineralization of the Burketown mineral field, including the world-class Century deposit, Northern Australia: Fluid inclusion and stable isotope evidence for basin fluid sources: ECONOMIC GEOLOGY, v. 101, p. 1251–1273.

Robertson, J.F., 1963, Geology of the lead-zinc deposits in the Municipio de Januaria State of Minais Gerais Brazil: U.S. Geological Survey Bulletin 1110-B, 109 p.

Rogers, J.J.W., and Santosh, M., 2002, Configuration of Columbia, a Mesoproterozoic Supercontinent: Gondwana Research, v. 5, p. 5–22.

Ronov, A.B., 1964, Common tendencies in the chemical evolution of the Earth’s crust, ocean and atmosphere: Geochemistry International, v. 1, p. 713–737.

Ross, G.M., and Villeneuve, M., 2003, Provenance of the Mesoproterozoic (1.45 Ga) Belt basin (western North America): Another piece in the pre-Rodinia paleogeographic puzzle: Geological Society of America Bulletin, v. 115, p. 1191–1217.

Rowan, E.L., and Marsily, G., 2001, Infiltration of Late Paleozoic evaporative brines in the Reelfoot rift: A possible source for Illinois basin formation waters and MVT mineralizing fluids: Petroleum Geoscience, v. 7, p. 269–279.

Rye, R., and Holland, H.D., 1998, Paleosols and the evolution of atmospheric oxygen: A critical review: American Journal of Science, v. 298, p. 621–672.

Sangster, D.F., 1983, Mississippi Valley-type deposits: A geological mélange, *in* Kisvarsanyi, G., Grant, S.K., Pratt, W.P. and Koenig, J.W., eds., Proceedings of International Conference on Mississippi Valley-type lead-zinc deposits: Rolla, MO, University of Missouri-Rolla Press, p. 7–19.

——1986, Age of mineralization in Mississippi Valley-type (MVT) deposits: A critical requirement for genetic modeling, *in* Andrew, C.J., Crowe, R.W.A., Finlay, S., Pennell, W.M. and Pyne, J.F., eds., Geology and genesis of mineral deposits in Ireland: Dublin, Ireland, Irish Association for Economic Geology, p. 625–634.

——1990, Mississippi Valley-type and sedex lead-zinc deposits: A comparative examination: Institution of Mining and Metallurgy Transactions, v. 99, sec. B, p. B21–B42.

Sawkins, F.J., 1984, Metal deposits in relation to plate tectonics: Minerals and Rocks, v. 17, Berlin, Springer Verlag, 325 p.

Schaefer, M.O., 2002, Paleoproterozoic Mississippi Valley-type Pb-Zn deposits of the Ghaap Group, Transvaal Supergroup in Griqualand West, South Africa: Unpublished Ph.D. thesis, Johannesburg, South Africa, Rand Afrikaans University, 367 p.

Schaefer, M.O., Gutzmer, J., Beukes, N.J., and Greyling, N.L., 2004, Mineral chemistry of sphalerite and galena from Pb-Zn mineralization hosted by the Transvaal Supergroup, in Griqualand West, South Africa: South African Journal of Geology, v. 107, p. 341–354.

Schandl, E.S., and Davis, D.W., 2000, Geochronology of the Sullivan deposit: U-Pb and Pb-Pb ages of zircons and titanites, *in* Lydon, J.W., Hoy, T., Slack, J.F., and Knapp, M.E., The geological environment of the Sullivan deposit, British Columbia: Geological Association of Canada, Mineral Deposits Division, p. 127–135.

Scrimgeour, I.R., Kinny, P.D., Close, D.F., and Edgoose, C.J., 2005, High-T granulites and polymetamorphism in the southern Arunta region, central Australia: Evidence for a 1.64 Ga accretional event: Precambrian Research, v. 142, p. 1–27.

Scotese, C.R, 2002, PALEOMAP Project (http://www. scotese.com/earth.htm).

——2005, Plate tectonic and paleographic maps and animations: PALEOMAP Project (www. scotese. com), 2005.

Sengor, A.M.C., and Natal’in, B.A., 2001, Back-arc basins: Rifts of the world: Geological Society of America Special Paper 352, p. 389–482.

Shaw, C.A., and Karlstrom, K.E., 1999, The Yavapai-Mazatzal crustal boundary in the southern Rocky Mountains: Rocky Mountain Geology, v. 34, p. 37–52.

Sherlock, R.L., Lee, J.K.W., and Cousens, B.L., 2004, Geologic and geochronologic constraints on the timing of mineralization at the Nanisivik zinc-lead Mississippi Valley-type deposit, northern Baffin Island, Nanavut, Canada: ECONOMIC GEOLOGY, v. 99, p. 279–293.

Shields, G.A., 2007, A normalised seawater strontium isotope curve: Possible implications for Neoproterozoic-Cambrian weathering rates and the further oxygenation of the Earth: eEarth, v. 2, p. 35–42.

Sinclair, H.D., 1997, Flysch to molasse transition in peripheral foreland basins: The role of the passive margin versus slab breakoff: Geology, v. 25, p. 1123–1126.

Slack, J.F., and Cannon, W.F., 2009, Extraterrestrial demise of banded iron formation ca 1.86: Geology, v. 37, p. 1011–1014.

Smith, M.T., Dickinson, W.R., and Gehrels, G.E., 1993, Contractional nature of Devonian-Mississippian tectonism along the North American margin: Geology, v. 21, p. 21–24.

Southgate, P.N., Bradshaw, B.E., Domalga, J., Jackson, M.J., Idnurm, M., Krassay, A.A., Page, R.W., Sami, T.T., Scott, D.L., Lindsay, J.F., McConachie, B.A., and Tarlowski, C., 2000, Chronostratigraphic basin framework for Palaeoproterozoic rocks (1730–1575 Ma) in northern Australian and implications for base-metal mineralisation: Australian Journal of Earth Sciences, v. 47, p. 461–484.

Stanton, R.L., 1976, Petrochemical studies of the ore environment at Broken Hill, New South Wales: 1. Constituents of "banded iron formations:" Institution of Mining and Metallurgy Transactions, v. 85, sec. B, p. B33–B46.

Stoffell, B., Appold, M.S., Wilkinson, J.J., McClean, N.A., and Jeffries, T.E., 2008, Geochemistry and evolution of Mississippi Valley-type mineralizing brines from the Tri-State and northern Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions: ECONOMIC GEOLOGY, v. 103, p. 1411–1435.

Sumner, D.W., 1997, Carbonate precipitation and oxygen stratification in late Archean seawater as deduced from facies and stratigraphy of the Gamohaan and Frisco Formations, Transvaal Supergroup, South Africa: American Journal of Science, v. 297, p. 455–487.

Sun, S.-S., Carr, G.R., and Page, R.W., 1996, A continued effort to improve lead-isotope model ages: AGSO Research Newsletter 24, p. 19–20.

Sutherland, R.A., and Dumka, D., 1995, Geology of the Nanisivik mine, N.W.T., Canada: Society of Economic Geologists Guidebook Series, v. 22, p. 4–18.

Sverjensky, D.A., 1984, Oil field brines as ore-forming solutions: ECONOMIC GEOLOGY, v. 79, p. 23–37.

Symons, D.T.A., 2007, Paleomagnetism of the HYC Zn-Pb SEDEX deposit, Australia: Evidence of an epigenetic origin: ECONOMIC GEOLOGY, v. 102, p. 1295–1310.

Symons, D.T.A. and McCausland, P.J.A., 2006, Paleomagnetism of the Fort Knox Stock, Alaska, and rotation of the Yukon–Tanana terrane after 92.5 Ma: Tectonophysics, v. 419, p. 13–26.

Symons, D.T.A., Sangster, D.F., and Leach. D.L., 1995, A Tertiary age from paleomagnetism for the Mississippi Valley-type zinc-lead mineralization in Upper Silesia, Poland: ECONOMIC GEOLOGY, v. 90, p. 782–794.

Symons, D.T.A., Symons, T.B., and Sangster, D.F., 2000, Paleomagnetism of the Society Cliffs dolostone and the age of the Nanisivik zinc deposits, Baffin Island, Canada: Mineralium Deposita, v. 35, p. 672–682.

Symons, D.T.A., Pannalal, S.J., Coveney, R.M., Jr., and Sangster, D.F., 2005, Paleomagnetism of late Paleozoic strata and mineralization in the Tri-State lead-zinc ore district: ECONOMIC GEOLOGY, v. 100, p. 295–309.

Symons, D.T.A., Lewchuck, M.T., Kawasaki, K., Velasco, F., Leach, D.L., 2009, The Reocin zinc-lead deposit, Spain: Paleomagnetic dating of a late Tertiary ore body: Mineralium Deposita, v. 44, p. 867–880.

Taylor, R.D., Leach, D.L., Bradley, D.C., and Pisarevsky, S.A., 2009, Compilation of mineral resource data for Mississippi Valley-type and CD sediment-hosted lead-zinc deposits: U.S. Geological Survey Open-File Report 2009-1297, 42 p.

Tian, F., Toon, O.B., Pavlov, A.A., and De Sterck, H., 2005, A hydrogen rich early Earth atmosphere: Science, v. 308, p. 1014–1017.

Titley, S.R., 1993, Relationship of stratabound ores with tectonic cycles of the Phanerozoic and Proterozoic: Precambrian Research, v. 61, p. 295–322.

Touahri, B, 1991, Geochimie et Metallogenie des Mineralisations a Plomb et Zinc du Nord de l'AlgerieOffice National de la Geologie, 18A Avenue Mustapha el Ouali, Alger: Memoires 4, 260 p.

Van der Voo, R., 1993, Paleomagnetism of the Atlantic, Tethys and Iapetus Oceans: Cambridge, Cambridge University Press, 411 p.

Veizer, J., 1988, Solid Earth as a recycling system: Temporal dimensions of global tectonics, *in* Lerman, A., and Meyback, M. eds., Physical and chemical weathering in geochemical cycle: Dordrecht, Reidel, p. 357–372.

Veizer, J., and Mackenzie, F.T., 2003, Evolution of sedimentary rocks: Treatise on Geochemistry, v. 7, p. 369–407.

Veizer, J., Laznicka, P., and Jansen, S.L., 1989, Mineralization through geologic time: Recycling perspective: American Journal of Science, v. 289, p. 484–524.

Viets, J.G., Hofstra, A.H., and Emsbo, P., 1996, Solute composition of fluid inclusions in sphalerite from North American and European Mississippi Valley-type ore deposits: Ore fluids derived from evaporated seawater: Society of Economic Geologists Special Publication 4, p. 465–482.

Walker, J.C.G., Klein, C., Sachidlowski, M., Schopf, J.W., Stevenson, D.J., and Walter, M.R., 1983, Environmental evolution of the Archean-Early Proterozoic Earth, *in* Schopf, J.W., ed., Earth's earliest biosphere-its origin and evolution: Princeton, NJ, Princeton University Press, p. 260–290.

Walker, R.N., Gulson, B., and Smith, J., 1983, The Coxco deposit—a Proterozoic Mississippi Valley-type deposit in the McArthur River district, Northern Territory, Australia: ECONOMIC GEOLOGY, v. 78, p. 214–249.

Walters, S., and Bailey, A., 1998, Geology and mineralization of the Cannington Ag-Pb-Zn deposit: An example of Broken Hill-Type mineralization in the Eastern Succession, Mount Isa inlier, Australia: ECONOMIC GEOLOGY, v. 93, p. 1307–1329.

Wang, X., Zhang, Z., Zheng, M., and Xu, X., 2000, Metallogenic mechanism of the Tianbaoshan Pb-Zn deposit, Sichuan: Chinese Journal of Geochemistry, v. 19, p. 121–133.

Warren, J.K., 2006, Evaporites, sediments, resources, and hydrocarbons: Heidelberg, Germany, Springer-Verlag, 1035 p.

Wheatley, C.J.V., Whitfield, G.G., Kenny, K.J., and Birch, A., 1986, The Pering carbonate-hosted zinc-lead deposit, Griqualand West, *in* Anhaeusser, C.R., and Maske, S., eds., Mineral deposits of southern Africa: Johannesburg, Geological Society of South Africa, p. 867–874.

Whelan, J.F., Rye, R.O., and De Lorraine, W.F., 1984, The Balmat-Edwards zinc-lead deposits—synsedimentary ore from Mississippi Valley-type fluids: ECONOMIC GEOLOGY, v. 79, p. 239–265. p. 2085–2112.

Wilkinson, J.J., Cooke, D.R., Weiss, D.J., Crowther, H.L., Coles, B.J. Jeffries, T.E., Ryan, C.G., and Laird, J., 2009a, Making metal super-charged ore fluids: the key to hydrothermal base-metal ore formation?: Science for Exploration and Mining, Biennial SGA Meeting of the Society for Geology Applied to Mineral Deposits, 10th, Townsville, Australia, August, 2009, Proceedings, v. 1, p. 40–42.

Wilkinson, J.J., Stoffell, B., Wilkinson, C.C., Jeffries, T.E., and Appold, M.S., 2009b, Anomalously metal-rich fluids form hydrothermal ore deposits: Science, v. 323, p. 764–767.

Willis, I.L., Brown, R.E., Stroud, W.J., and Stevens, B.J.P., 1983, The early Proterozoic Willyama Supergroup: Stratigraphic subdivision and interpretation of high- to low-grade metamorphic rocks in the Broken Hill block, New South Wales: Journal of the Geological Society of Australia, v. 30, p. 195–224.

Wooden, J.L., and DeWitt, E., 1991, Pb isotope evidence for the boundary between the Early Proterozoic Mojave and Central Arizona crustal provinces in western Arizona: Arizona Geological Society Digest, v. 19, p. 27–50.

Worden, K., Carson, C., Scrimgeour, I., Lally, J., and Doyle, N., 2008, A revised Palaeoproterozoic chronostratigraphy for the Pine Creek orogen, northern Australia: Evidence from SHRIMP U-Pb zircon geochronology: Precambrian Research, v. 166, p. 122–144.

Yardley, B.W.D., 2005, Metal concentrations in crustal fluids and their relationship to ore formation: ECONOMIC GEOLOGY, v. 100, p. 613–632.

Young, L.E., 2004, A geologic framework for mineralization in the western Brooks Range, Alaska: ECONOMIC GEOLOGY, v. 99, p. 1281–1306.

Zapolnov, A.K., 1997, Tectonic evolution and metallogeny, *in* Rundqvist, D.V., and Gillen, C., eds., Precambrian ore deposits of the East European and Siberian cratons: Amsterdam, New York, Elsevier Science, p. 365–379.

Zegers, T.E., Dekkers, M.J., and Bailly, S., 2003, Late Carboniferous to Permian remagnetization of Devonian limestones in the Ardennes: Role of temperature, fluids, and deformation: Journal of Geophysical Research, v. 108, no. B7, p. 5.1–5.19.

Zhao, G., Sun, M., Wilde, S.A., and Li, S., 2004. A Paleo-Mesoproterozoic supercontinent: Assembly, growth and breakup: Earth-Science Reviews, v. 67, p. 91–123.

Zheng, M., and Wang, X., 1991, Ore genesis of the Daliangzi Pb-Zn deposit in Sichuan, China: ECONOMIC GEOLOGY, v. 86, p. 831–846.