Current Perspectives on Zinc Deposits

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The front cover shows a jumbo drill rig collaring a new drift in the Navan Mine operated by Boliden Tara Mines Limited, Co. Meath, Ireland. The mine was discovered in 1970, and started production in 1977. It is Europe's largest zinc mine with annual production averaging 2.5 Mt grading 7.2% Zn, 1.4% Pb over the last 5 years. (Picture provided by Boliden Tara Mines Limited).

The metallogeny of zinc through time: links to secular changes in the atmosphere, hydrosphere, and the supercontinent cycle

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Abstract

The distribution of zinc deposits through time is episodic, involving relatively short time periods of high zinc productivity and long periods of low productivity. This distribution is principally related to the geodynamic evolution of the Earth. Many deposits are associated with the assembly and break-up of supercontinents: preserved stratiform deposits hosted by volcanic-dominated successions (volcanic-hosted massive sulfide deposits) and deposits hosted by carbonate-dominant succession (Mississippi Valley-type and Irish-type deposits) mainly formed during supercontinent assembly, whereas stratiform deposits hosted by clastic-dominated successions (shale-hosted massive sulfide or "SEDEX" deposits) are associated with the assembly, stability and break-up of supercontinents.

The secular distributions of zinc deposits also reflect the preservation potential of their tectonic environment of formation. Volcanic-dominated deposits formed at mid-oceanic ridges and deposits formed on advancing accretionary orogens are unlikely to be preserved. Skarn and related deposits are generally a young feature; this distribution is likely a consequence of their poor long-term potential for preservation.

The lack of zinc deposits, with the exception of carbonate-hosted deposits linked to orogenesis, during the assembly of Rodinia points to the possibility that this assembly was dominated by advancing accretionary orogenesis. This tectonic style not suitable for the formation and preservation of a range of mineral deposits, including most zinc deposits.

Although changes in the composition of the atmosphere and hydrosphere are an important control on some characteristics of zinc ores, they are second-order controls on the secular distribution of zinc concentrations. The main change of importance is the oxidation of the atmosphere and portions of the hydrosphere that occurred in the Paleoproterozoic, during the Great Oxidation Event at ca. 2400 Ma. After this event, oxidized fluids evolved in basins, which allowed the formation of deposits hosted by carbonate-dominant successions and some deposits hosted by clastic-dominated successions. Other effects of changes in the hydrosphere relate mainly to gangue mineralogy and sulphur isotopes. After the Great Oxidation Event, sulphates became important gangue minerals in many zinc deposits, and sulphur isotope characteristics became more variable, reflecting the isotopic signatures of coeval seawater sulphate.

Introduction

Although it has been recognized for decades that many types of ore deposits have a non-uniform distribution in time (Lambert and Groves, 1981; Meyer, 1988; Goldfarb et al., 2010), advances in the understanding of secular changes in geodynamic processes and in the evolution of the coupled atmosphere-hydrosphere system have allowed a better linkage of metallogenesis to the evolution of the Earth. In this contribution, which builds upon early analyses by Lambert and Groves (1981), Meyer (1988) and Groves et al. (2005), and more recent ones by Huston et al. (2010) and Leach et al. (2010), we describe the secular distributions of major classes of zinc deposits and summarize major secular changes in Earth processes, in order to establish the drivers of changes in zinc metallogeny through time.

The metallogeny of zinc deposits through time

Unlike many other elements of economic interest (i.e., gold and lead), the distribution of zinc is relatively even among major geochemical reservoirs of the solid Earth, excepting the core (Table 1). The crust and mantle have similar bulk zinc concentrations; different reservoirs within the crust have remarkably uniform zinc levels. This generalization extends to most rock types. With the exception of clean carbonate, quartzose sandstone, and black shale, common igneous and sedimentary rock types typically have zinc concentrations of between 30 and 130 ppm (Table 1). This uniformity suggests that the major drivers of zinc metallogeny are not sources, but instead are processes that extract and concentrate zinc

This contrasts with lead, which is commonly a major component of zinc-bearing ores. Lead is characterized by much greater variations in concentrations between major reservoirs. Relative to zinc, which has variability of less than an order of magnitude, the concentration of lead ranges from 0.15 ppm to 8 ppm from the mantle to bulk crust. Moreover, the concentration of lead varies considerably within the crust (Table 1). As a consequence, the concentration of lead in zinc-bearing deposits is highly variable, with a major control being the metal source.

Figure 1 is based on an updated database, which was built on previous data sets (e.g., Franklin et al., 2005; Meinert et al.,

Table 1. Average zinc concentrations in geochemical reservoirs and rocks

	Zn (ppm)	Pb (ppm)	Reference
Reservoir			
Solid Earth	40	0.23	McDonough (2003)
Core	8.6	0.40	McDonough (2003)[1]
Silicate Earth	55	0.185	McDonough (2003)
Mantle	53.5	0.15	Palme and O'Neill (2007)
Bulk crust[2]	80	8	Palme and O'Neill (2007)
Oceanic crust	78		Wedepohl and Hartmann (1994)
Total continental crust	72	11	Rudnick and Gao (2003)
Lower continental crust	78	4	Rudnick and Gao (2003)
Middle continental crust	69.5	15.2	Rudnick and Gao (2003)
Upper continental crust	67	17	Rudnick and Gao (2003)
Rock			
Basalt			
Mid-oceanic basalt	67	0.38	Kelemen et al. (2007)
Island-arc basalt	72	8.5	Kelemen et al. (2007)
Continental-arc basalt	81	6.0	Kelemen et al. (2007)
Rhyolite-granite[3]	30-70[4]	6-60[4]	Wedepohl (1972a), Wedepohl (1974a)
Graywacke	70-120[4]	4-50[4]	Wedepohl (1972b), Wedepohl (1974b)
Quartzose and arkosic sandstone	25-50[4]	5-25[4]	Wedepohl (1972b), Wedepohl (1974b)
Shale	50-130[4]	18-28[4]	Wedepohl (1972b), Wedepohl (1974b)
Black shale	200[4]	20[4]	Wedepohl (1972b), Wedepohl (1974b)
Limestone	20[4]	0.4-10[4]	Wedepohl (1972b), Wedepohl (1974b)

[1]Calculated from data in McDonough (2004) using mass balance constraints
[2]Bulk crust is higher that crustal components because of different studies used
[3]A-type granites have higher Zn content of 120 pm (Whalen et al., 1987)
[4]Cited range is the range of average values of studies cited by Wedepohl (1972a,b, 1974a,b)

2005; Taylor et al., 2009; Mosier et al., 2009a,b; Huston et al., 2010) and includes information on the name and location of deposits, production and resource data, and age data. This database is available upon request from the authors and most of the information is also available online from the StratDB database (Eglington et al., 2009) at http://sil.usask.ca/databases.htm. The deposits are divided into four groups based on characteristics of the host succession and alteration assemblages: volcanic-dominated, clastic-dominated, carbonate-dominated, and skarn.

The volcanic-dominated (equivalent to volcanogenic or volcanic-hosted massive sulfide) group has five subgroups based on characteristics of the underlying lithological succession. This classification follows that of Barrie and Hannington (1999), as modified by Franklin et al. (2005), and includes bimodal-mafic, mafic, pelitic-mafic, bimodal-felsic and siliciclastic-felsic groups.

The clastic-dominated group was divided into two subgroups, siliciclastic-mafic and siliciclastic-carbonate. Like the classification of Barrie and Hannington (1999) for the volcanic-dominated group, this classification is based on characteristics of the underlying succession. It has some similarities with classifications of Morganti (1981), Cooke et al. (2000), Huston et al. (2006) and Leach et al. (2010), but is more empirical. Deposits of the siliciclastic-mafic group are underlain and hosted by successions that are dominated by fine-grained siliciclastic rocks, are associated with *coeval* mafic magmatism, and lack significant carbonate rocks. Siliciclastic-carbonate group deposits are underlain and hosted by siliciclastic-dominated successions that have a significant carbonate content and lack significant *coeval* mafic volcanic or sub-volcanic rocks. The host units to siliciclastic-carbonate group deposits are commonly carbonate-bearing.

The carbonate-hosted group includes low-temperature (<200°C) deposits hosted largely by platform carbonate successions that are not associated with coeval magmatism. This group includes a subgroup that is thought to significantly post-date sedimentation, Mississippi Valley-type deposits, and a second group that is thought to be syngenetic or early diagenetic, Irish-type deposits (see discussion in Leach et al., 2005).

Skarn (including manto and chimney) deposits are epigenetic, carbonate-replacement deposits that are characterized by calc-silicate (or skarn) mineral assemblages. These deposits are generally interpreted to be genetically related to magmatic activity (Meinert et al., 2005).

We do not discuss non-sulphide zinc deposits separately because these are generally either metamorphosed or weathered examples of our four groups. A few, including the Vazante willemite deposit in Brazil, formed by hypogene processes (Hitzman et al., 2003). A small number of zinc sulfide deposits do not fit into our classification (e.g., Coeur d'Alene vein deposits in Idaho and Endeavor, New South Wales), but their collective production and resources contribute less than one percent to global zinc resources and they are not considered further.

We have chosen to use a descriptive rather than a genetic classification as some processes used in genetic classifications are not universally accepted (e.g. SEDEX – SEDimentary EXhaltive – implies a syngenetic process of deposition that may not apply to some deposits in this group). We have retained the terms Mississippi Valley-type and Irish-type for subgroups of carbonate-hosted deposits as they are non-genetic and well-established in the literature.

Aside from grade and tonnage data, the most critical data in this analysis is the age of ore formation. With advances in geochronological techniques over the last several decades, constraints on the age of mineralization have improved signifi-
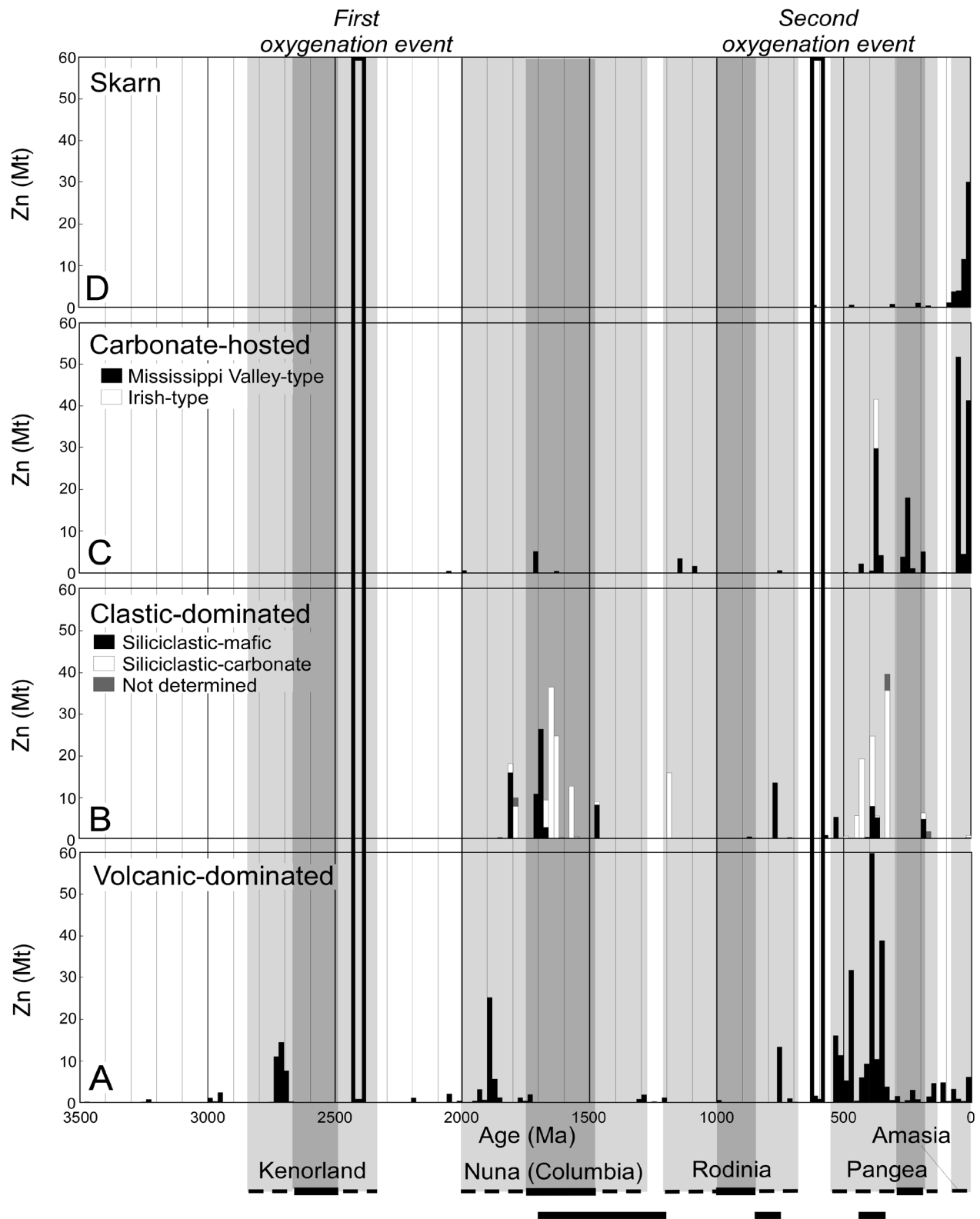
Figure 1. Secular variations in amounts of total contained zinc of (A) volcanic-dominated, (B) clastic-dominated, (C) carbonate-dominated, and (D) skarn deposits. Data are updated from Franklin et al. (2005), Leach et al. (2005), Meinert et al. (2005), Mosier et al. (2009a,b) and Taylor et al. (2009). Horizontal black lines at bottom indicate periods of supercontinent assembly (dashed; also dark shading), stability (heavy solid) and breakup (dashed; also light shading). Periods of juvenile crust formation (Roberts, 2012) are shown as horizontal lines at the bottom of the diagram. Heavy boxes indicate global oxygenation events.

cantly, although some deposits remain poorly constrained. Age constraints fall into two broad groups: ages that directly date ore deposition (direct ages), and ages that date rocks or events inferred to be related to mineralization or bracket the timing of ore deposition (inferred ages). Examples of a direct age might be Re-Os ages of molybdenite or lead model ages of galena. Examples of inferred ages include the age of the host succession for a syngenetic or early diagenetic deposit, the age of a mineral interpreted to be an alteration product related to ore formation, or the age of a magmatic rock inferred to be genetically related to ore deposition. Inferred ages require some assumption about the relationship between ore formation and the dated mineral, and have a lower degree of certainty than direct ages.

In addition to the uncertainties associated with inferred ages, uncertainty also must be applied to the method of age determination. For example, a lead isotope model age, even using a well-constrained local model, has much less certainty than a molybdenite Re-Os age, even though both are "direct" age determinations. For inferred ages, a U-Pb zircon age determined from a magmatic rock genetically associated with ore should have higher certainty than a [40]Ar-[39]Ar age on an alteration min-

eral. To allow the reader to assess the ages, we have included metadata on the type of age in the database. We have also included conflicting ages. Although we indicate our preferred ages in these situations, the data user can use metadata to evaluate alternative ages.

Volcanic-dominated deposits

Figure 1A shows the secular distribution of contained zinc within volcanic-dominated deposits. As also discussed by Huston et al. (2010), the distribution of zinc in these deposits is episodic, with major peaks occurring at 2740-2680 Ma, 1900-1760 Ma, and 520-300 Ma. Outside of these periods, the formation and/or preservation of volcanic-dominated deposits was poor. These peaks correspond to the assembly of the Kenorland, Nuna and Gondwana-Euramerica-Pangea supercontinents/supercratons.

Clastic-dominated deposits

Figures 1B shows the secular distribution of zinc contained by deposits within clastic-dominated successions (see also Leach et al. 2010), including both the siliciclastic-mafic and siliciclastic-carbonate subgroups. Well-dated, major deposits of both
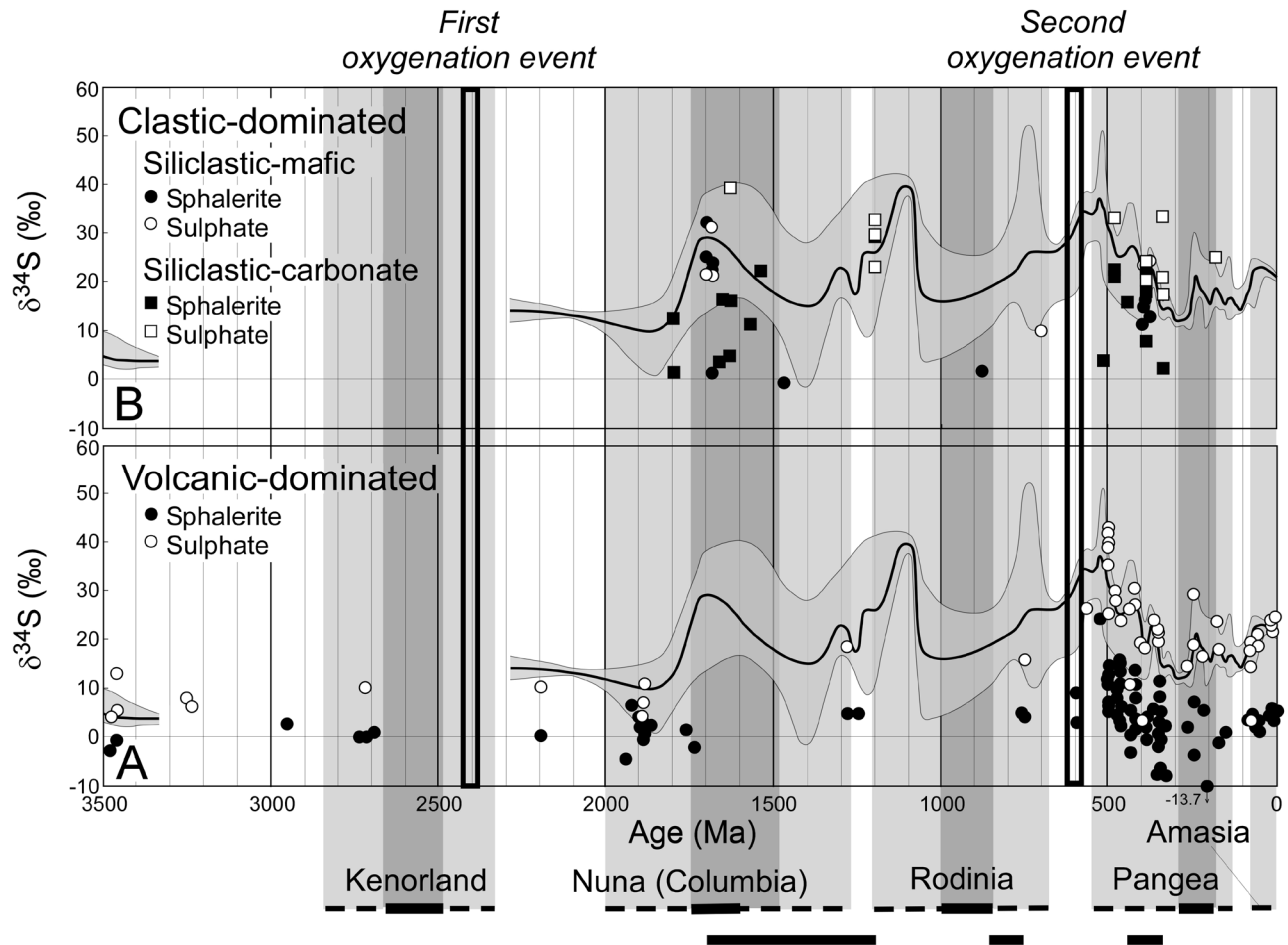

Figure 2. Secular variations in δ^{34}S from (A) volcanic-dominated, and (B) clastic-dominated deposits superimposed on variations in δ^{34}S of seawater sulphate. The light grey field indicates the evolution of seawater sulphate δ^{34}S based on Claypool et al. (1980) and Strauss (2004). The heavy line in the center indicates the mean evolution path. Data for the deposits are from a compilation available from the authors. In part (A), closed and open circles indicate median δ^{34}S values of spalerite and sulphate minerals, respectively, from volcanic-dominated deposits. In part (B) closed and open symbols indicate median δ^{34}S values of spalerite and sulphate minerals, respectively, from clastic-dominated deposits. Circles and squares indicate siliciclastic-mafic and siliciclatic-carbonate subgroups, respectively. Periods of juvenile crust formation (Roberts, 2012) are shown as horizontal lines at the bottom of the diagram. Heavy boxes indicate global oxygenation events.

subgroups are concentrated in two periods, the latest Palaeo- to Mesoproterozoic (1690-1470 Ma), which corresponds to the period of stability and earliest break-up of the Earth's first supercontinent, Nuna, and the first half of the Palaeozoic (550-250 Ma), which corresponds to the assembly of the latest supercontinent, Gondwana-Euramerica-Pangea.

Outside of these two major periods, there are three other significant peaks. The first, at ~1800 Ma, corresponds to deposits in the Aravalli-Delhi Province of India. The ages of these deposits, however, are poorly constrained by lead isotope model ages (Deb and Thorpe, 2004). The second peak, at 1200-1150 Ma, corresponds to temporally well-constrained siliciclastic-carbonate deposits in the Aggeneys district of South Africa (McClung, 2006; Cornell et al., 2009), which may have formed during the beginnings of Rodinia assembly. The Aggeneys and Gamsberg deposits exhibit high model source $^{238}U/^{204}Pb$ compositions (Reid et al., 1997), indicating significant involvement of lead from substantially older crustal sources. The third peak, at ~750 Ma, corresponds to the siliciclastic-carbonate Kholodninskoye deposit in the Siberian Craton of Russia. Although this age is a lead isotope model age (Larin et al., 1997), it corresponds with the break-up of Rodinia.

The oldest known clastic-dominated deposit is the Namoona prospect in the North Australian Craton (not shown on Figure 1B due to its small size). This deposit, which is of the siliciclastic-carbonate subgroup, has an age of ~2020 Ma based on the age of the host succession (Worden et al., 2008) and on a locally constrained lead isotope model age (Jaireth, 2011). The oldest siliciclastic-mafic deposits are ~1800 Ma deposits in the Aravalli-Delhi Craton in India, based on a locally constrained lead isotope model age (Deb and Thorpe, 2004).

Carbonate-hosted deposits

Figure 1C shows the secular distribution of zinc contained within carbonate-hosted deposits, including both the Mississippi Valley-type and Irish-type subgroups. With a few important exceptions, all carbonate-hosted deposits formed during the Palaeozoic, in two periods that correspond to the assembly of Gondwana-Euramerica-Pangea and to the very early (i.e., the closing of the Tethys Sea) assembly of Amasia, a supercontinent that is predicted to amalgamate 250 m.y. into the future (Santosh et al., 2009). Like clastic-dominated deposits, the oldest Mississippi Valley-type deposits (Pering, Bushy Park and others in South Africa: (Wheatley et al., 1986a,b; Duane et al., 1991a,b) have a middle Palaeoproterozoic (~2100 Ma) age. These deposits, along with additional deposits from the Zawar district in India (Sarkar and Banerjee, 2004; Deb and Thorpe, 2004) define a small peak at 2100-1700 Ma that roughly corresponds to Nuna assembly. In addition, a peak at 1100-1000 Ma, which includes deposits at Nanisivik, Canada (Symons et al., 2000; Hnatyshin et al., 2011) and in the Balmat-Edwards district, New York (Fletcher and Farquhar, 1982; Steers, 2003), corresponds to Rodinia assembly, the only significant zinc mineralization associated with Rodinia.

Skarn, manto and chimney deposits

Figure 1D shows the secular distribution of zinc contained within skarn, manto and chimney deposits. We have grouped these three deposit types together as the ores form mostly by replacement of carbonate-bearing rocks. In most cases there is a spatial and/or temporal association to granitic, *sensu lato*, intrusions; many manto and chimney deposits have calc-silicate alteration assemblages (as in skarns); and the ores are thought to have formed at moderate to high temperatures (>250°C), contrasting with the low temperatures (<200°C) that characterize carbonate-hosted Mississippi Valley-type and Irish-type deposits. Although skarn and related deposits are in general Cenozoic in age, a few examples of older deposits exist. The oldest deposit known to the authors is the Evelyn prospect in the North Australian Craton, which has an age of ~1818 Ma, based upon

the age of the spatially associated intrusion (Jaireth, 2011). The oldest significant deposit is O'Callaghans (0.39 Mt Zn) in the Paterson Province in Australia, which has an age of ~607 Ma based on titanite U-Pb TIMS and zircon U-Pb SIMS ages of the associated intrusion suite (Maidment et al., 2010).

Secular changes in earth processes and conditions

It has become increasingly clear over the last several decades that for many Earth processes, the present is not necessarily the key to the deep past. Not only climate, but the composition of the atmosphere and hydrosphere, and the size, shape and distribution of continents have also changed over geological time. It is likely that the nature and style of tectonic processes have varied through Earth history. These changes are likely to have driven secular variations in the distribution of zinc deposits. In the following pages, we summarize these changes and then discuss how each has affected zinc metallogeny.

Secular changes in the compositions of the atmosphere and hydrosphere

The compositions of both the atmosphere and the hydrosphere have changed substantially over geologic time. As a consequence, ore fluids that formed zinc deposits have also varied with time, producing not only secular changes in the abundance of deposits, but also in their characteristics. Two processes that have most affected the compositions of the atmosphere and hydrosphere are the oxidation of the atmosphere and the sequestration of salt from oceanic water into the rock record by evaporative processes.

Oxidation of the atmosphere and the hydrosphere: There is general consensus that prior to about 2450 Ma, the atmosphere was reduced and lacked significant free oxygen (Cloud, 1973; Rye and Holland, 1998; Farquhar et al., 2000). In addition to nitrogen, the main gases in the Hadean and Archean atmosphere were likely CO_2 and methane, accompanied by minor SO_2 and, possibly, hydrogen and higher-order hydrocarbons (Kasting, 1993; Catling et al., 2001). Co-existing oceans and meteoric waters also had different compositions relative to the present. With the possible exception of a thin, more oxidized surface layer (see below), oceanic waters were reduced and lacked dissolved oxidized species such as sulphate, but had significant dissolved Fe^{2+}, derived either from anoxic weathering of landmasses or from submarine-hydrothermal contributions (Cloud, 1973; Isley, 1995). Moreover, because of the high concentrations of Fe^{2+} in Archean seawater, the concentration of sulphur species (mainly H_2S) was likely low (Huston and Logan, 2004).

Beginning in the very earliest Palaeoproterozoic at ~2400 Ma, the atmosphere began to oxidize by a process that continued for several hundred m.y. and is known as the Great Oxidation Event (Farquhar et al., 2000). This process of oxidation was driven by the evolution of photosynthesis (Kopp et al., 2005), gradual changes in the composition or pressure of volcanic gases (Holland, 2002; Gaillard et al., 2011) and/or the loss of hydrogen to space (Catling et al., 2001; Tian et al., 2005).

The oceans responded to the Great Oxidation Event in a complicated manner. Run-off from oxidative weathering produced a progressively thicker oxidized surface layer on the ocean (Huston and Logan, 2004; Farquhar et al., 2010). The presence of sulphate in this surface layer allowed the deposition of sulphate minerals in evaporative and hydrothermal environments, and, consequently, the production of oxidized basinal brines.

Deep oceanic waters also changed. According to Canfield (2004) and Farquhar et al. (2010), these became sulfidic beginning at ~1800 Ma, whereas, in contrast, Holland (1984) and Huston and Logan (2004) suggested that deep seawater progressively became oxidized. Either change caused iron to become insoluble (Huston and Logan, 2004), hence the end of this period of
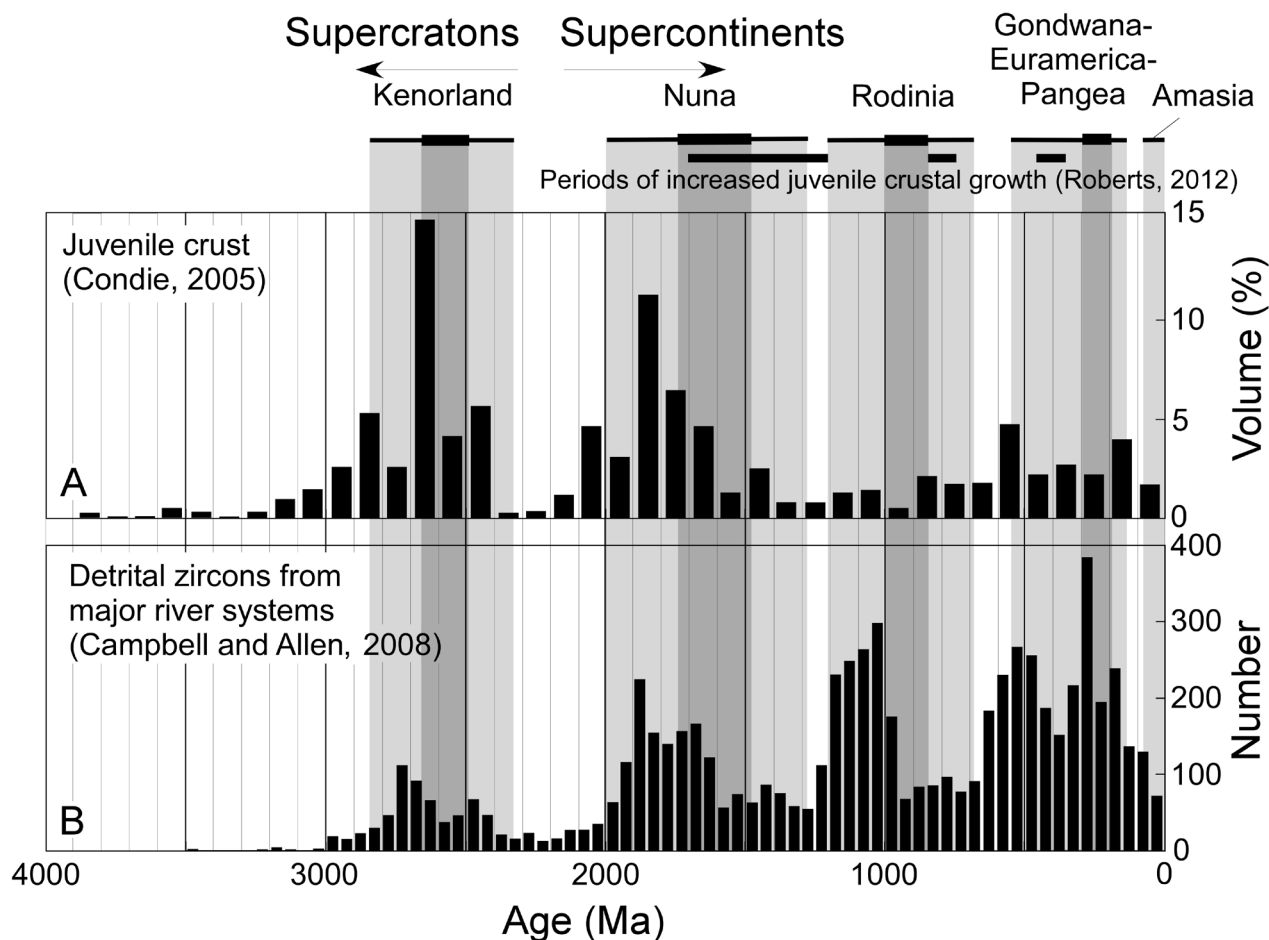
Figure 3. Secular variations in the abundance of (A) juvenile crust (after Condie, 2005), and (B) detrital zircons from major river systems (after Campbell and Allen, 2008). This diagram is modified slightly from that of Hawkesworth et al. (2009). The juvenile crust diagram of Condie (2005) is based upon the distribution of zircon U-Pb age data of igneous rocks supplemented by Sm-Nd data. Periods of juvenile crust formation (Roberts, 2012) are shown as horizontal lines at the top of the diagram.

change saw termination of major banded iron formation deposition between 1900 and 1850 Ma (Bekker et al., 2010). Alternatively, other workers (e.g., Poulton et al., 2010; Planevsky et al., 2011; Poulton and Canfield, 2011) have suggested that deep ocean waters were anoxic, Fe^{2+}-rich and H_2S-poor from ~1900 Ma to ~580 Ma, at which time the oceans finally became fully oxidized. A critical aspect of all of these models is the presence of an oxidized (and presumably sulphate-bearing) surface layer beginning in the Palaeoproterozoic.

Changes in sulphur isotope characteristics of seawater: One of the more important isotopic discoveries of the last two decades is the recognition of mass-independent ^{33}S fractionation in syngenetic or diagenetic sulfide and sulphate minerals of Archean to earliest Proterozoic age (Farquhar et al., 2000). This distinctive isotopic fractionation has been interpreted to be the consequence of photolytic decomposition of atmospheric SO_2 to produce sulphate (Farquhar et al., 2000; Farquhar and Wing, 2003), which rained-out to form a thin, sulphate-rich layer near the surface of otherwise reduced oceans (Huston and Logan, 2004; Poulton and Canfield, 2011). Between 2450 and 2090 Ma, mass independent fractionation of ^{33}S decreased, a trend interpreted to indicate gradual oxidation of the atmosphere and loss of SO_2 (Farquhar et al., 2000).

Although recognition of mass independent ^{33}S fractionation is recent, it has long been established that $\delta^{34}S$ of seawater sulphate has varied through geologic time (e.g., Claypool et al.,

1980; Strauss, 2004). Figure 2 shows this variation based on compilations by Strauss (2004) and Huston and Logan (2004) of $\delta^{34}S$ values for anhydrite/gypsum, stratiform (non-VHMS-related) barite and structurally-substituted sulphate in carbonate. In the Paleoarchean (3550-3230 Ma) $\delta^{34}S_{sulphate}$ was relatively uniform, showing a total range of -2 to 15‰, with most data between 3 and 8‰. This sulphate is generally interpreted as having formed as rainout from photolytic decomposition of atmospheric SO_2 prior to the Great Oxidation Event (Huston and Logan, 2004).

Between the end of the Paleoarchean at 3200 Ma and the beginning of the Great Oxidation Event at 2400 Ma, there are no data for non-hydrothermal sulphate deposits, probably because of low sulphate concentrations in coeval seawater. However, beginning at ~2300 Ma, stratiform and diagenetic sulphate deposits progressively increased in the geologic record. As the atmosphere oxidized, seawater $\delta^{34}S_{sulphate}$ initially was relatively uniform, with most values ~10‰, but after ~1800 Ma, it became much more variable, showing a total range of 0 to 50‰, and significant secular changes in values (Fig. 2). Strauss (2004) interpreted seawater $\delta^{34}S_{sulphate}$ variations in the Palaeozoic as reflecting tectonic controls upon the relative influx of riverine (i.e. weathering) versus hydrothermal inputs of sulphur into the ocean. Another possible control on $\delta^{34}S_{sulphate}$ variations could be the relative size of reduced and oxidized oceanic water reservoirs in stratified oceans, sulphate-sulphide fractionation factors and the rate of removal of reduced sulphur from the ocean by Fe

sulphide precipitation (Holser, 1977, Goodfellow and Jonasson, 1984; Goodfellow, 1987). It is interesting to note that in a broad sense, the large variations in $\delta^{34}S_{sulphate}$ began as Nuna stabilized, perhaps supporting the concept of a tectonic link to variations in oceanic $\delta^{34}S_{sulphate}$.

Changes in seawater salinity and temperature: Another important change in seawater composition that has significant implications for zinc metallogenesis is an apparent decrease in salinity with time, particularly in the Neoproterozoic to Mesozoic. Based on the secular distribution and abundance of halite deposits, Knauth (2005) suggested that seawater salinity decreased by a factor of 1.5-2 between the Neoproterozoic and Jurassic. Limited studies that have inferred Proterozoic to Archean seawater compositions from fluid inclusion data support this interpretation, thus possibly indicating an even larger decrease in salinity with time (Huston et al., 2010). This inferred change has several potential implications for zinc metallogenesis and metallogenic studies in general. Older seawater-derived fluids, including some basinal brines, would have been more saline than at present, making them capable of transporting higher concentrations of zinc as chloride complexes. Moreover, the presence of denser, high salinity ambient seawater has implications for the behaviour of hydrothermal fluids after venting on the seafloor (c.f., Sato, 1972). The discharge of highly saline brines into epicratonic basins could have produced highly stratified basinal water columns, with anoxic bottom waters critical to the preservation of seafloor sulfide deposits (W Goodfellow, pers. comm., 2013). Importantly, secular changes in seawater salinities should be considered when using halogen ratios of fluid inclusions in the evaluation of potential hydrothermal fluid sources.

Another possible change to the hydrosphere is variations in temperature. Based on systematic secular changes in $\delta^{18}O$ values of chert, some workers have suggested that during much of the Archean the Earth's oceans were substantially warmer than now, with estimated temperatures of up to 55°C (Knauth and Lowe, 2003: van den Boorn et al., 2010). In addition, there were periods of time, such as during "snowball" periods of the late Neoproterozoic (Hoffman et al., 1998), when the Earth was substantially colder than at present.

Secular changes in tectonics and the supercontinent cycle

Since the paradigm shift to plate tectonics theory in the 1960s and 1970s, it has become clear that tectonic processes may have changed through geologic time, both irreversibly and episodically. The most important driver of irreversible changes to tectonic processes has been cooling of the Earth: upper mantle temperatures have decreased between 100°C and 200°C since the Archean (van Hunen et al. 2008). As mantle cooling drives tectonic activity, hotter mantle temperatures early in Earth's history are generally interpreted to have generated faster plate motion (Phillips and Bunge, 2005), more plates (Bleeker, 2003), and thicker crust and sub-continental lithospheric mantle (Davies, 1992; Poudjom-Djomani et al., 2001) relative to present. However, modeling of mantle dynamics by Korenaga (2006) suggested that the Archean was characterized by slower plate motion, in contrast to the more widely accepted interpretation.

In addition, processes other than modern-style subduction may have been responsible for the formation of some early cratons. Smithies et al. (2005a), for example, proposed that the Palaeo- to Mesoarchean North Pilbara Terrane in Western Australia formed as an oceanic plateau early in its history, with subduction processes only becoming important after ~3120 Ma (Smithies et al., 2005b), an interpretation supported by the first appearance of eclogitic diamonds after ca. 3200 Ga (Shirey and Richardson, 2011). Other workers have suggested that subduction-like processes were active through virtually all recorded geological his-

tory, with the earliest putative evidence of subduction recorded at ~3800 Ma in west Greenland (Polat et al, 2002). It is possible, even probable, that during its early history, both plate-tectonic and non-plate-tectonic processes formed crust on Earth.

The supercontinent cycle

The tectonic evolution of Earth has been marked by repeated assembly and breakup of supercontinents. At least three major supercontinents assembled during Earth's history: *Nuna* (Evans and Mitchell, 2011; aka *Columbia*, Zhao et al., 2004), which formed in the late Palaeoproterozoic; *Rodinia* (Li et al., 2008), which amalgamated in the Neoproterozoic, and *Pangea* (including Euramerica and Gondwana: Kearey et al., 2009), which formed in the Palaeozoic (Fig. 1). An additional latest Archean-early Palaeoproterozoic supercontinent, termed *Kenorland*, also may have existed (Reddy and Evans, 2009).

The assembly and breakup of these landmasses define the super-continent cycle, which typically lasts ~700 m.y. Supercontinents were only stable for at most 150 m.y., and generally much shorter periods. The Archean is regarded as being characterized by the assembly of smaller blocks, or supercratons, such as Superia and Vaalbara (Bleeker, 2003). At present the Earth may be in the earliest stage of assembly of the next super-continent, Amasia (Santosh et al., 2009). Figure 1 illustrates periods of assembly, stability and breakup of these supercontinents.

It has been established that a temporal correlation exists between the assembly and break-up of supercontinents/supercratons and the apparent distribution of juvenile continental crust (Taylor and McLennan, 1995; Condie, 2005; Campbell and Allen, 2008; Hawkesworth et al., 2009, 2010). The most prominent peaks in the age distribution of preserved juvenile continental crust (Condie, 2005: Fig. 3A) correspond to the periods of assembly and break-up of the Kenorland and Vaalbara supercratons and the Nuna supercontinent, with a third, diffuse peak that corresponds to the assembly and break-up of Pangea-Gondwana. Notably, there is not a peak associated with the assembly and break-up of Rodinia.

Peaks in the distribution of detrital zircons from modern rivers and dunes also correspond to periods of assembly and break-up of supercontinents/supercratons (Campbell and Allen, 2008), but have a different pattern (Fig. 3B). The largest peaks are associated with the assembly of Pangea-Gondwana and Rodinia, with smaller peaks related to Nuna and Kenorland/Vaalbara.

In detail, the largest peaks are coeval with supercontinent assembly, followed by a trough during supercontinent stability and a smaller peak associated with the initiation of supercontinent break-up. Multiple peaks and troughs present during Pangea assembly probably relate to the initial formation of the smaller landmasses of Gondwana and Euramerica beginning at 550 Ma and 440 Ma, respectively, and the closure of the Iapetus and Rheic oceans prior to the final amalgamation of Pangea at 370-280 Ma. It is important to bear in mind that the datasets presented in Figure 3 are largely based on zircon geochronology, a mineral that generally does not crystallize in mafic magmatic rocks. Hence, the production of mafic crust, which dominates extensional environments (i.e., during supercontinent break-up), is under-represented in these data.

Preservation of newly-formed crust

Although the distributions of both datasets shown in Figure 3 show correlations with the supercontinent cycle, in detail there are important differences. The most striking is the contrast between an apparent increase in the volume of juvenile crust formation through time as shown by the Condie (2005) dataset and an apparent decrease in the intensity of peaks in older detrital zircons from active river systems as shown by Campbell and Allen (2008). Although this difference may be partly accounted for by winnowing out of older, U-rich zircons from the dataset by metamictization and isotopic disturbance (J. Claoue-Long,
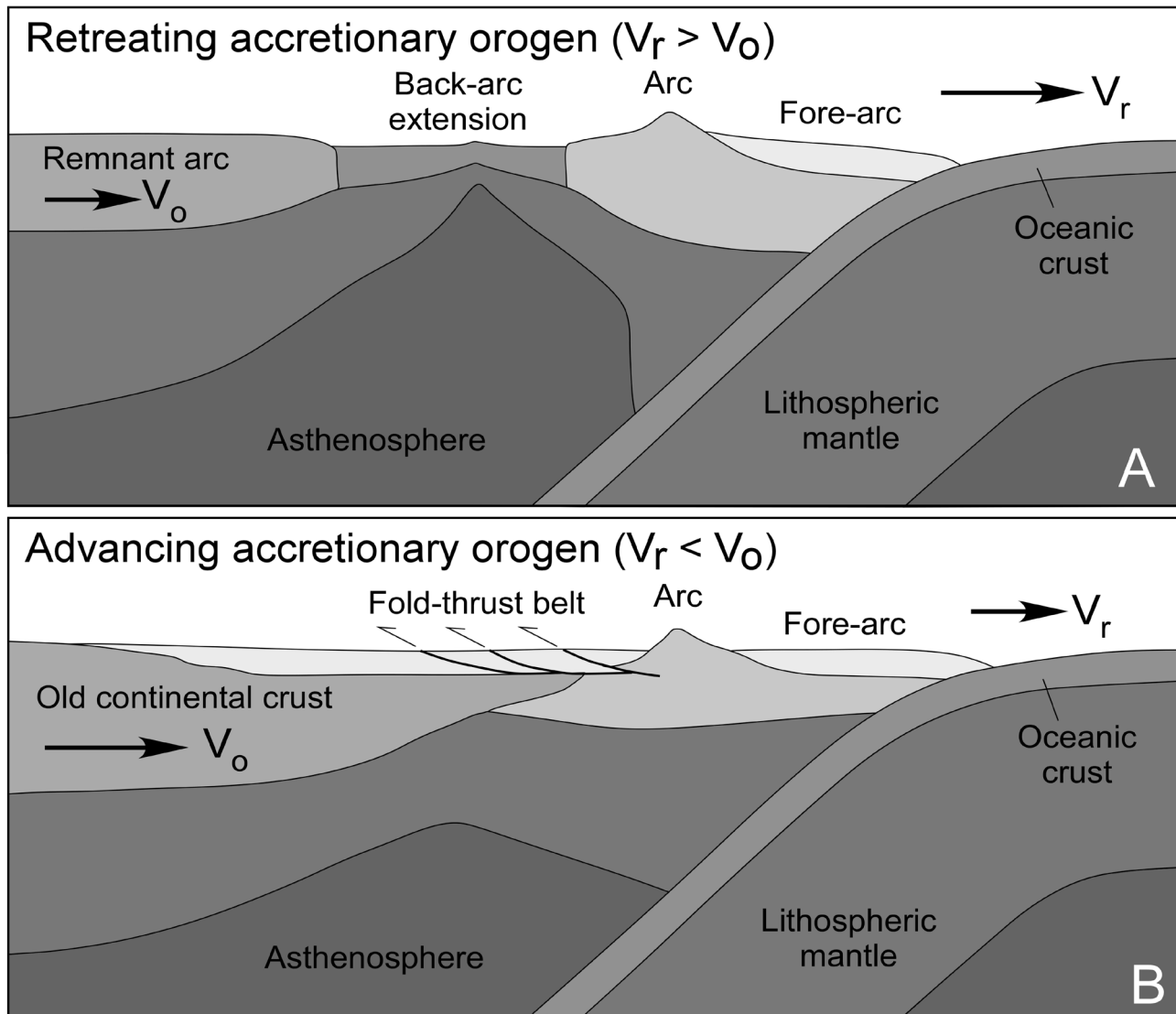
Figure 4. Styles of accretion along convergent margins: (A) retreating accretionary orogenesis, and (B) advancing accretionary orogenesis (modified after Cawood and Buchan, 2007). Vr is the velocity at which the subducting plate is retreating. Vo is the velocity at which the overriding plate is advancing.

pers. comm., 2011), it may also relate to the preservation of newly-formed crust (Hawkesworth et al., 2009, 2010) and re-cycling of older crust via erosion and subduction of sediments with long term residence and mixing in the mantle. For instance, Hawkesworth et al. (2010) argued that the large peak in juvenile crustal ages that corresponds to the assembly of supercratons actually reflects the preferential preservation of these rocks in the geological record.

Another factor that influences the preservation of new crust, at least in recent geological times, is that in many modern magmatic arcs, particularly continental ones, the rate of crust loss through subduction is equal to or greater than the rate of crust generated through magmatism (Clift and Vannuchi, 2004). A decrease in the relative rate of crust generation to crust loss along convergent margins with geological time could be partly responsible for the observed secular differences between apparent abundance of juvenile crust production and detrital zircon populations.

A third factor that could influence the preservation of new crust is the style of subduction along convergent margins. Cawood and Buchan (2007) identified two styles of orogenesis along accretionary convergent margins: retreating accretionary orogen-

esis and advancing accretionary orogenesis. During the former, the velocity of slab rollback exceeds that of the over-riding plate, putting the over-riding plate in extension and forming back-arc basins (Fig. 4A): this style of convergence is characteristic of modern tectonics in the modern western Pacific Ocean. In contrast, during advancing orogenesis, the velocity of slab roll-back is less than that of the over-riding plate, putting this plate in contraction (Fig. 4B): this style of convergence is characteristic of the eastern Pacific Ocean, in particular the Andean margin.

Hawkesworth et al. (2009, 2010) suggested that the amount of juvenile crust preserved along convergent margins is the product of the volume of magmatic rocks produced along the margin and their preservation potential (Fig. 5). Production of magmatic rocks is interpreted to be highest during subduction, lowest during collision, and intermediate during break-up. In contrast, preservation potential is low during subduction and break-up, but high during collision. More importantly, the preservation potential is higher for retreating subduction (i.e. retreating accretionary orogenesis) relative to advancing subduction.

These differences mean that the preservation of juvenile crust, and the mineral deposits hosted by such crust, is higher along retreating subduction margins relative to advancing subduction

margins. The differences between the patterns shown in Figure 3 probably relate, at least in part, to preservation of juvenile crust. Despite the caveats discussed above, the secular distribution of detrital zircon ages in modern sediments is the best approximation of the production of felsic magma, whereas the distribution of observed juvenile crustal ages best approximates the preservation of such crust. The greatest discrepancy in these two distributions relates to the assembly of Rodinia, which is marked by a large spike in detrital zircon ages, but apparently without coeval production of juvenile crust (Fig. 3). This contrasts suggests very low preservation of juvenile crust that formed along Rodinian margins, consistent with a model in which these margins were dominated by advancing accretionary orogenesis.

Roberts (2012) combined the riverine detitral zircon data of Campbell and Allen (2008) with a global compilation of zircon ε_{Hf} data (Belousova et al., 2010; Lancaster et al., 2011) to show that zircons formed between periods of supercontinent assembly (i.e., 1700-1200 Ma, 850-750 Ma and 450-350 Ma) have a more juvenile character, indicating a greater rate of juvenile crust formation during these times.

Implications for zinc metallogeny

The above discussion indicates that the Earth has experienced major episodic and irreversible changes over its long history, and that the changes are complicated by important differences in the make-up and likely preservation of juvenile crust depending on tectonic setting and the style of convergence. Periodic and irreversible changes also characterize the secular distribution of zinc deposits, suggesting that this distribution relates directly to secular changes in Earth processes. Moreover, the characteristics of some classes of zinc deposits also change with time, again providing a link to changes in Earth processes.

Changes in zinc metallogeny due to changes in tectonics and the supercontinent cycle

As discussed above, the observed secular abundance of juvenile felsic crust is a function of the rate at which this crust was produced, and the extent of preservation over geologic time. The same logic applies to mineral deposits. The secular distribution of porphyry copper, epithermal gold-silver and zinc skarn deposits, most of which have young ages (Seedorf et al., 2005; Simmons et al., 2005; Meinert et al., 2005; Lydon; 2007; Fig. 1D), is most likely the consequence of a poor likelihood of preservation of the uppermost parts of magmatic arcs rather than a lack of formation through geologic time: porphyry copper and epithermal deposits are some of the oldest mineral deposits known on Earth (Huston et al., 2007).

The episodic distribution of zinc deposits in volcanic-dominated successions probably reflects a combination of formational and preservational factors. Submarine black smoker deposits, the modern analogues of volcanic-dominated deposits, form in a number of tectonic environments, both in divergent settings such as mid-oceanic ridges, and in convergent settings such as back-arc basins and rifted arcs (Hannington et al., 2005). However, the likelihood of preservation of these settings differs significantly. The oldest preserved seafloor crust has an age of only 180 Ma (Müller et al., 2008), and ophiolites are uncommon prior to Rodinia-time and unknown prior to 1900 Ma (Dann, 1991; Moores, 2002; Peltonen et al., 2003). Moreover, sulfide deposits exposed to oxic water columns are less likely to survive, especially during the Phanerozoic. Hence oceanic crust that formed along divergent mid-oceanic ridges, and its contained mineral deposits, are unlikely to survive into the ancient rock record, whereas deposits that formed in back-arc basins and rifted arcs should predominate. These latter two tectonic settings, though present to some extent throughout the Wilson cycle, are most abundant during supercontinent assembly, thus accounting for the strong temporal link between zinc deposits hosted by volcanic-dominated successions and the assembly of supercontinents (Fig. 1A).

In detail, there appear to be systematic patterns in both the type and possibly the tectonic setting of volcanic-dominated deposits through time. Deposits hosted by mafic-dominated successions are dominant in Archean to Proterozoic rocks, whereas deposits hosted by felsic-dominated successions are most common in Phanerozoic rocks (Huston et al., 2010). Moreover, the geochemical characteristics of felsic rocks within the host successions have also changed with time. Although mostly in mafic-dominated successions, in detail Archean deposits are mostly associated with tholeiitic rhyodacite to high silica rhyolite that display relatively flat rare earth element (REE) patterns ($[La/Yb]_{CN}$ ~ 1-5), negative Eu/Eu*, low Zr/Y (1.7-6.2) and moderately to highly enriched high field strength elements (FIIIa and FIIIb types of Lesher et al., 1986), whereas younger deposits have a progressively closer association with calc-alkaline dacites to rhyolites that have moderately sloping REE patterns ($[La/Yb]_{CN}$ ~ 2-9), negative Eu/Eu*, moderate Zr/Y (3-12) and moderately enriched high field strength elements (FII type: Lentz, 1998; Piercey et al., 2001; Hart et al., 2004). Both the changes in the lithological make-up of the host succession and the geochemistry of the associated felsic volcanic rocks suggest a change in tectonic environment and crustal substrate with time. Hart et al. (2004) attributed changes in felsic igneous geochemistry to a change in the depth of melting, with FIIIa and FIIIb rocks having formed from magmas that originated at shallow depth and higher temperature, and FII rocks having crystallized from melts generated at moderate depth and temperature. These changes could relate either to a general cooling of the upper mantle, longer stability of arc systems, the increasing importance of evolved continental crust as a substrate to the arc systems, and/or to an increasing importance of (peri-)continental rifted arc and back-arc (as opposed to oceanic back-arc) environments as preferential loci for the formation of volcanic-dominated deposits (e.g., Lentz, 1998; Piercey et al., 2001; Piercey, 2011).

The first appearance of clastic-dominated and carbonate-hosted zinc deposits after 2100-2000 Ma may be controlled by the confluence of two important events in Earth's evolution, a higher rate of juvenile crustal growth at 1700-1200 Ma (Roberts, 2012), and the Great Oxidation Event. High heat flow associated with juvenile crust growth produced higher temperature (>200°C) ore fluids that transported zinc under reduced conditions and formed siliciclastic-mafic deposits (e.g., Cooke et al., 2000). As passive margins formed during as Nuna stabilized, heat flow in the evolving basins decreased, resulting in a decreasing temperature of basinal fluids. This period of increased crustal growth occurred after the Great Oxidation Event, which, for the first time, allowed large quantities of oxidized fluids – meteoric water, seawater and derived brines – to migrate at or near the Earth's surface. Oxidized, H_2S-poor fluids are highly-potent ore fluids that allow transport of zinc at the low temperatures (<200°C) characteristic of siliciclastic-carbonate deposits (Cooke et al., 2000; Huston et al., 2006). The presence of these oxidized, low-temperature fluids also allowed the development of early, economically significant carbonate-hosted (Mississippi Valley-type) deposits, such as those in southern Africa (Fig. 1C).

Unlike volcanic-dominated deposits, clastic-dominated deposits formed and were preserved during periods of supercontinent assembly, stability and break-up (Figs, 1B and 2). In most cases, however, the deposits formed in extensional settings – ensialic rifts, rifted passive margins or back-arc basins, suggesting that local extensional environments, and not the type of margin, controlled the formation and preservation of these deposits. It may be that timing in basin evolution may influence the type of deposit. In the Mount Isa Province of Queensland, siliciclastic-mafic deposits (Cannington and Pegmont) formed a few tens of millions of years earlier than siliciclastic-carbonate deposits (Dugald River, Mount Isa, Hilton-George Fisher). This age pattern probably relates to the evolution of a rift or back-arc basin

Table 2. Temporal changes in the abundance of sulphate (excluding supergene) gangue for deposits hosted by volcanic - and clastic-dominated successions.

Age range (Ma)	Volcanic-dominated		Clastic-dominated	
	Deposits containing sulphate gangue minerals (%)	Total deposits	Deposits containing sulphate gangue minerals (%)	Total deposits
600-0	43	532	64	50
1000-600	46	26	33	3
1700-1000	21	14	47	30
2000-1700	8	133	0	22
2500-2000	50	6	—	—
2800-2500	2	116	—	—
3200-2800	0	27	—	—
3500-3200	70	10	—	—

to a passive margin and to changes in the temperature and redox state of the ore fluids, as discussed above.

Carbonate-hosted deposits are most strongly associated with the assembly of Gondwana-Euramerica-Pangea (Fig. 1C), with some very young deposits (<50 Ma) possibly linked to the early stages of Amasia assembly. It has been shown in many mineral districts that the timing of mineralization is closely tied to orogenesis in the hinterland and, in some cases, to basin inversion, which likely drove fluid flow on a regional scale (Leach et al., 2005, 2010, and references therein). Hence, the temporal association of carbonate-hosted deposits with supercontinent assembly is most likely the consequence of increased orogenesis during assembly as ocean basins close and crustal blocks amalgamate. However, recent dating of alteration minerals associated with the Kaapvaal deposits suggests that they may be due to fluid flow induced by intrusion of the massive Bushveld Complex and associated deformation (Gleason et al., 2011)

One of the more enigmatic features of the secular distribution of zinc deposits is the virtual lack of deposits associated with Rodinia assembly (Fig. 1). As discussed above, differences between observed abundances of detrital zircon ages and the inferred abundance of preserved juvenile crust ages may indicate that advancing accretionary orogenesis predominated during Rodinia assembly. As a consequence, back-arc basins, which form mainly during retreating accretionary orogenesis (e.g., Cawood

and Buchan, 2007), were not abundant. Hence, zinc deposits, which commonly form in back-arc basins during supercontinent assembly, formed infrequently during Rodinia assembly. An important exception are carbonate-hosted deposits, which form in response to orogenesis. A small but important peak of these deposits is associated with Rodinia assembly (Fig. 1C).

Changes in zinc metallogeny due to the evolution of the atmosphere and hydrosphere

Although the main controls of the secular distribution of zinc deposits as a whole are secular changes in tectonic processes, changes in the composition of the atmosphere and, particularly, the hydrosphere also appear to be important for the distribution of clastic-dominated and carbonate-hosted deposits. Moreover, changes in the composition of the hydrosphere have been important controls on the composition and isotopic characteristics of zinc deposits of all types and ages, and may influence the composition and possibly preservation potential of volcanic-dominated deposits.

The first examples of both siliciclastic-carbonate clastic-dominated deposits and carbonate-hosted deposits formed after the Great Oxidation Event (~2400 Ma), between 2100 and 2000 Ma. These types of deposits are thought to form from oxidized, H_2S-poor basinal brines (Sangster, 1990; Cooke et al., 2000; Leach et al., 2005), which would have only become available in large quantities after the upper layer of the ocean became oxidized and was trapped as basinal brines in marginal and intracratonic basins. The delay of ~300 m.y. between the Great Oxidation Event and the initiation of these deposits points possibly to tectonic settings as providing additional controls on their formation. For carbonate-hosted deposits, orogenesis accompanying Nuna assembly was probably an important driver. For siliciclastic-dominated deposits, the development of rift-sag basins may have been important.

Although sulphate minerals, such as barite, gypsum and anhydrite, are gangue minerals in many zinc deposits, their distribution is restricted in time (Table 2). Although common in Paleoarchean volcanic-dominated deposits, sulphate minerals are virtually absent between 3200 Ma and 1700 Ma, becoming increasingly common after the Paleoproterozoic assembly of Nuna and generally very abundant during the Phanerozoic (Table 2; Huston and Logan, 2004). The only exception to this generalization is between 2500 Ma and 2000 Ma, just after the Great Oxidation Event, where 50% of the deposits contain sulphate gangue minerals, although based on a small number of deposits.

The overall distribution probably relates to the oxidation of the hydrosphere: sulphate became increasingly common in the hydrosphere only after the Great Oxidation Event. The presence of sulphate gangue minerals in Palaeoarchean zinc deposits is probably related to photolytic disproportionation of SO_2 in a reduced atmosphere, an interpretation supported by $\Delta^{33}S$ values of the sulphate minerals (Farquhar and Wing, 2003).
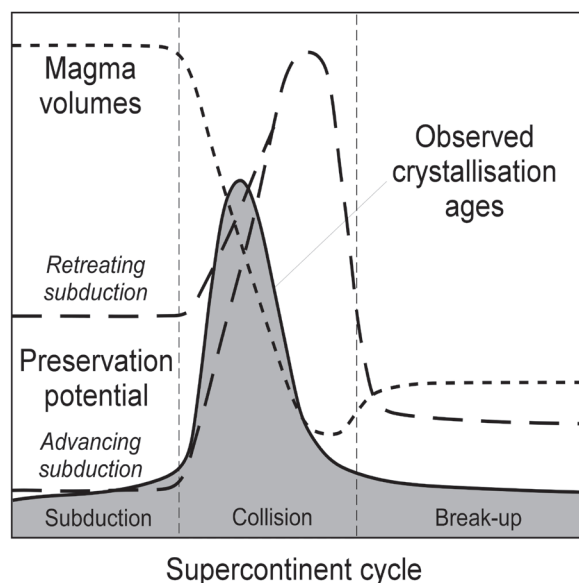

Figure 5. Preservation potential of magmatic rocks during the supercontinent cycle (after Hawkesworth et al., 2009).
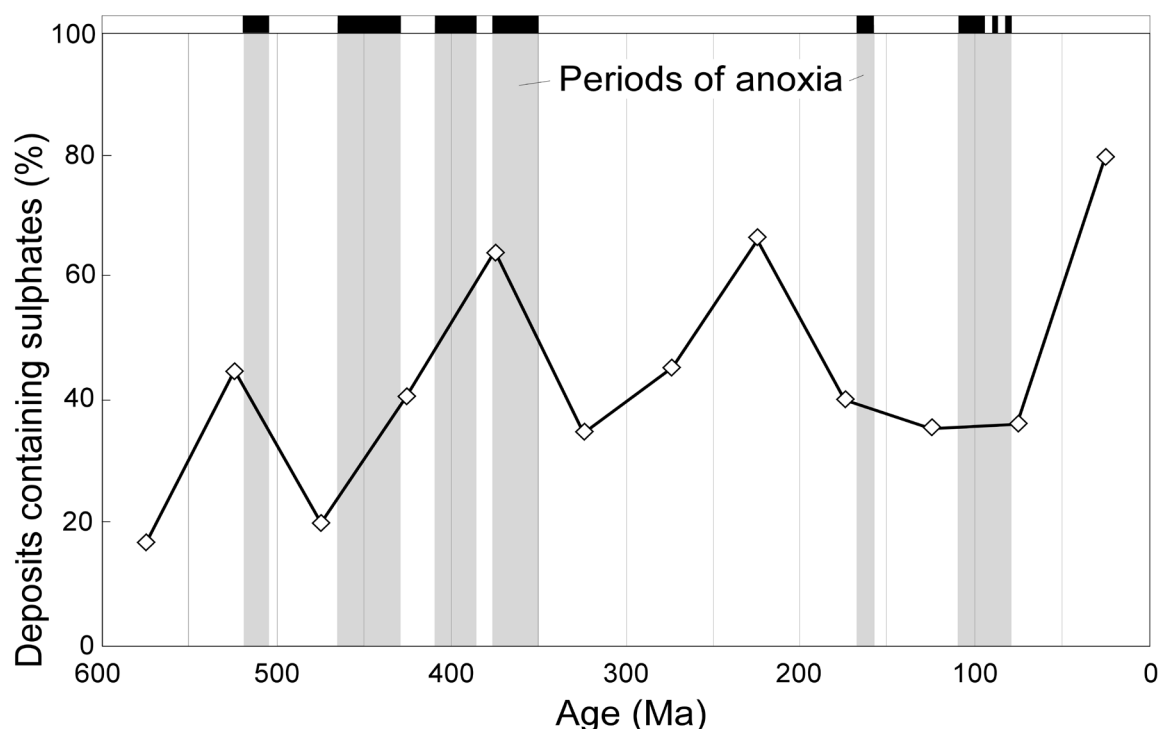
Figure 6. Temporal variations in the abundance of sulphate gangue minerals (excluding those of supergene origin) in stratiform zinc deposits hosted by volcanic-dominated successions from 600 Ma to 90 Ma. Periods of anoxia are indicated by solid bars and grey areas.

Although the sulphate abundance of deposits from both the volcanic-dominated and clastic-dominated groups is in general high in the Phanerozoic, there are significant differences in abundances, even during this time period. Figure 6 illustrates variations in sulphate abundances in volcanic-dominated deposits using a bin of 50 m.y. to determine distributions; the large number of deposits of this type during this period makes these abundances fairly robust. In general, about 40% of volcanic-dominated deposits contain sulphate gangue from 600 Ma to 0 Ma, with the periods of 600-550 Ma and 500-450 Ma having a low abundance (<20%) of sulphate-bearing deposits and the periods 400-350 Ma, 250-200 Ma and 50-0 Ma characterized by higher abundances (>60%) of sulphate-bearing deposits. Periods of anoxia, as compiled by Eastoe and Gustin (1996), are superimposed on this distribution. Although the correlation is not that strong, the well-defined low in sulphate abundances at 500-450 Ma does correlate to the beginning of a proposed major period of anoxia at around 450 Ma, and a less intense period of low sulphate abundance between 200 Ma and 50 Ma corresponds to proposed anoxic periods between 160 Ma and 80 Ma (c.f., Eastoe and Gustin, 1996). These data are consistent with a period of anoxia during the formation of the Bathurst district in New Brunswick, which Goodfellow et al. (2003) argued was critical for the preservation of this giant district.

Sulphur isotope data indicate differences in the source of sulphur in zinc deposits and changes in that source with time. For Precambrian volcanic-hosted deposits, the range in $\delta^{34}S_{sulphide}$ is restricted, mostly between 0‰ and 5‰ (Huston, 1999 and references therein; Fig. 2A), but during the Phanerozoic it is highly variable and generally ~15‰ lower than coeval seawater, a relationship first recognized by Sangster (1968). Proterozoic siliciclastic-mafic clastic-dominated deposits also have a relatively restricted range in $\delta^{34}S_{sulphide}$, again between 0‰ and 5‰ (Fig 2B), whereas siliciclastic-carbonate and Phanerozoic

siliciclastic-mafic clastic-dominated deposits have highly variable $\delta^{34}S_{sulphide}$ (Fig. 2B). In these two latter groups of deposits, the variability is both between and within deposits. Reasons for these differences relate to both the source and redox state of sulphur in the ore-forming fluids and potentially the $\delta^{34}S$ composition of H_2S in ambient euxinic water columns (e.g., Goodfellow and Jonasson, 1984; Goodfellow, 1987; Shanks et al., 1987).

As discussed above, it is likely that during the early history (Archean to early Mesoproterozoic) of the Earth the oceans were sulphur-poor (Huston and Logan, 2004), with total sulphur contents below one part per million. As a consequence, seawater during this time would not have been a sulphur source, rather the rocks through which the ore fluids passed would be the sulphur source. If that source was dominated by volcanic or high level magmatic rocks, the leached sulphur would have $\delta^{34}S_{sulphide}$ values similar to those of igneous rocks, which mainly range from 0‰ to 5‰ (Ohmoto and Rye, 1979). Hence, the reason for the uniform, near-magmatic $\delta^{34}S_{sulphide}$ for Precambrian volcanic-dominated deposits is the lack of sulphur in coeval seawater and its leaching from surrounding country rocks.

Ore fluids that formed siliciclastic-carbonate clastic-dominated and carbonate-hosted deposits are generally interpreted as oxidized, with sulphur in the fluid travelling as sulphate (Sangster, 1990; Cooke et al., 2000; Leach et al., 2005). To deposit metals, this sulphate must be reduced, either inorganically or biogenically, or reduced sulphur has to be present at the site of ore deposition. Reduction of sulphate to sulphide typically involves large and variable sulphur isotope fractionation (Ohmoto and Rye, 1979), possibly accounting for the highly variable $\delta^{34}S_{sulphide}$ of these deposit types. If reduced sulphur was present at the site of deposition, it is likely to have been sourced from sedimentary or diagenetic sulfide minerals, which, again, are characterized by large variations in $\delta^{34}S$ (Canfield, 2004).

Conclusions

Zinc deposits of different types all show systematic secular trends in the abundance of contained zinc. These trends relate mostly to changes in global geodynamic evolution, and also to changes in the compositions of the atmosphere and hydrosphere with time. The vast majority of stratiform deposits hosted by volcanic-dominated successions are linked to the amalgamation of supercontinents through geological time. These deposits form and are most effectively preserved in convergent margins, largely in back-arc basins or in rifted arcs, which were more abundant during supercontinent amalgamation. Such deposits also form in oceanic spreading centers, but deposits formed in this environment were not likely to be preserved in Precambrian terranes.

Carbonate-hosted deposits also are most abundant during supercontinent amalgamation as orogenesis associated with amalgamation is a driver of regional fluid flow. They are also restricted in time to after the Great Oxidation Event as this fostered production of oxidized basinal brines that were critical to formation of these deposits.

Stratiform deposits hosted by clastic-dominated successions are also temporally restricted to after the Great Oxidation Event, similarly because many of these deposits require oxidized basinal brines as ore fluids. In contrast to the previous two deposit types, these deposits formed during supercontinent amalgamation, stability and break-up.

Skarn and related deposits, for the most part, are geologically young, probably because environments in which they commonly formed, the high level parts of arcs, are less likely to be preserved in older rocks.

Changes in the composition of seawater also influence characteristics such as the presence of sulphate gangue minerals and the sulphur isotopic composition of the ores. These changes reflect processes and environments such as the Great Oxidation Event and anoxic conditions later in Earth's geological history, both of which exerted significant control on the characteristics and preservation of deposits hosted by both volcanic-dominated and clastic-dominated deposits.

With the exception of carbonate-hosted Mississippi Valley-type deposits, zinc deposits are absent during the amalgamation of Rodinia, unlike other supercontinents. This distribution is interpreted as the consequence of the dominance of advancing accretionary orogenesis, which does not produce back-arc basins that are critical for the formation of zinc deposits hosted by volcanic-dominated and clastic-dominated successions. In contrast, orogenesis – the driver of Mississippi Valley-type metallogenesis – occurred during Rodinia assembly as well as the assembly of other supercontinents.

Acknowledgements

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