

# Earth's evolution and mineral resources, with particular emphasis on volcanic-hosted massive sulphide deposits and banded iron formations

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Oh, never let us never, never doubt  
What nobody is sure about  
*The Microbe (Hilaire Belloc)*

From 3.5 Ga the overall uniformity of the composition and character of sedimentary and mantle- and crustal-derived igneous rocks, and the persistence of ore types related to convergent continental margins (e.g. volcanic-hosted massive sulphide, porphyry Cu-Mo, Sn-W and lode Au), indicates continuity of tectonic processes broadly similar to the present. Secular variations in abundance of these ores reflect tectonic cycles having periods of perhaps several hundred million years, but other ores reflect long-term changes in tectonic style and the composition of the ocean and atmosphere. Thus the development of extensive continental margins and depositional basins from about 3.0 Ga heralded development of giant Au-U conglomerate and banded iron formation deposits, with at least the former suppressed in the Palaeoproterozoic as a result of increased atmospheric PO<sub>2</sub>. Aggregation of large continents and the development of extensive basins allowed formation of giant Cu-Co, Pb-Zn and U-platinum group elements-Au ores from about 2.0 Ga. There is no firm evidence that mantle

heterogeneity has contributed to ore distribution, nor that Archaean crust or mantle was anomalously enriched in Au or platinum group elements.

Mineralogical and isotopic data from volcanic-hosted massive sulphide deposits support the hypothesis that there was abundant sulphate in deep oceans from 3.5 Ga, and the lack of Pb and barite in Late Archaean ores may be related to the mafic-rich composition of the local shallow crust, steep thermal gradients, anoxic, sulphate basin waters or the compositions of particular magma types. Both the ocean margin (Holland 1973) and the hydrothermal plume/gravity current models for the origin of banded iron formations are broadly compatible with their composition, secular distribution and timing with respect to glaciation, ocean anoxia and tectonic activity. In the gravity current model the possible impact of the hydrothermal activity on climate warrants further investigation.

## Introduction

The origins of many of Earth's mineral resources are closely linked to the physical and chemical evolution of the planet and the life it supports, and particularly its atmosphere and hydrosphere. Many mineral deposits are sensitive signatures of particular tectonic and magmatic environments so that there are periods in Earth's history that favour specific ore types. In this paper we focus on those deposits that by their distribution patterns and composition contribute to the debate on the evolution of the Earth, and particularly volcanic-hosted massive sulphide deposits and Fe and Mn ores related to banded iron formations. Recent reviews of mineral deposit distribution include Meyer (1985, 1988), Hutchinson (1992), Barley & Groves (1992), Lambert et al. (1992) and Kirkham & Roscoe (1993).

Our time scale to the beginning of the Proterozoic is as follows: Hadean: 4.5 to 3.9 billion years (Ga); Early Archaean: 3.9 to 3.5 Ga; Middle Archaean: 3.5 to 3.0 Ga; Late Archaean: 3.0 to 2.5 Ga.

## The evolving Earth

### The Hadean

The possibility that there are 'enriched' mantle sources favourable for some styles of mineralisation raises questions on secular and spatial variations in abundance of the ore-forming elements in the mantle and crust, and particularly the possibility of mantle heterogeneity generated during Earth's accretionary stage (see discussion by Taylor, and Taylor & McLennan in this issue on the accretional history of Earth and evolution and composition of the continental crust). Core formation was probably contemporaneous with the accretion of planetesimals at ~4.5 Ga as a result of temperature increase and melting caused by accretional energy and heat generated by short-lived nuclides (Stevenson 1983). During core formation highly siderophile elements, such as platinum group elements and Au, were effectively concentrated into the core. After the

completion of core formation, addition of a small amount (<1 mass %) of oxidised accretional 'veener' introduced the currently observed highly siderophile elements into Earth's mantle (Kimura et al. 1974, McDonough & Sun 1995, Taylor this issue), and it is possible that this process led to heterogeneous distributions of platinum group elements and Au in the mantle. In addition, core-mantle interaction and rising of their boundary layer may have introduced some platinum group elements and Au, a process especially important in Hadean time (McDonough, Harvard University, pers. comm. 1994), and Tredoux et al. (1989) and McDonald et al. (1995) speculated that such enrichment may have occurred in the Archaean through underplating of mantle plume-derived and subducted lithosphere.

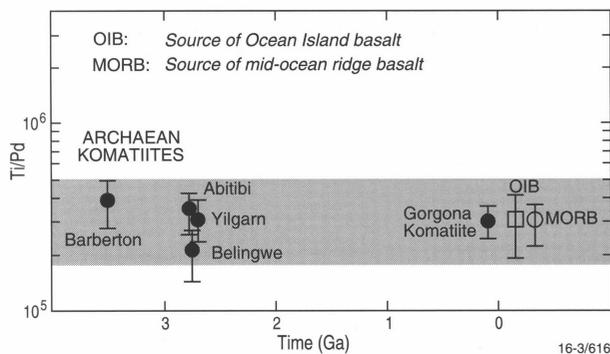
During Hadean time a circum-global magma ocean may have existed in the upper mantle and its evolution and final solidification could have resulted in mineralogical and chemical layering of the mantle, i.e. large scale mantle heterogeneity. However, this would probably have been counterbalanced by vigorous mantle convection. Although debate continues, available geophysical and geochemical observations favour a 'pyrolite' type mantle without major differences in composition between upper and lower mantle (McDonough & Sun 1995).

### The Archaean

Judging from dates close to 4 Ga on gneisses in Canada, China and the USA, and of detrital zircons aged 4.1–4.2 Ga from Western Australia, the crust, atmosphere and hydrosphere may be several hundred million years older than the 3.87 Ga rocks of the Isua Supercrustal Belt. The overall uniformity of both chemical composition and range of types of sedimentary and igneous rocks from 3.87 Ga points strongly to the continuity of tectonic processes broadly similar to those of Recent Earth (Lowe 1992a, Lowe & Ernst 1992, Windley 1992, 1993). A survey of the abundance ratios between Ti (a lithophile element) and Pd (a chalcophile element) in S-undersaturated, high temperature, mantle-derived melts, including komatiites and picrites ranging in age from 3.4 Ga to ~90 million years (Ma) and fertile mantle peridotites, shows near constant values of 2–3.10<sup>5</sup> (Sun et al. 1991, McDonough & Sun 1995; Fig. 1).

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**Figure 1.** Ti/Pd values in the convecting mantle over time, based on study of komatiites from 3.45 to 0.06 Ga and ultramafic mantle xenoliths, ophiolites and alpine peridotites (Sun et al. 1991, McDonough & Sun 1995, McDonough pers. comm. 1995).

This indicates a lack of obvious secular variation in the abundance of Pd (and other platinum group elements) in the convecting mantle, and the same can be inferred for gold. Similarly, Jochum et al. (1993) found that Sn/Sm appears to be constant in mantle-derived rocks for the last 3.4 Ga at a value  $\sim 0.32$ . Nevertheless, secondary enrichment of Pd, Pt and Au can occur in komatiites, boninites and some shoshonites and plume-related picrites and tholeiites due to S-undersaturation and second-stage melting (Sun et al. 1991).

Continuity of crustal processes is also indicated by the similarity and persistence of certain ore types from the Early Archaean to the present, particularly volcanic-hosted massive sulphide (from 3.5 Ga), porphyry copper (from 3.3 Ga), and Sn-W and syndeformational lode gold deposits (from about 2.7 Ga), all typical of Phanerozoic convergent continental margins before, during and after orogenesis (Hutchinson 1981, Sawkins 1990a, Barley & Groves 1992; Fig. 2). Archaean mesothermal lode Au provinces are no richer in that metal than Phanerozoic examples (see below).

Earth's surface rind in the earliest Archaean probably consisted of thin platelets of simatic and lesser sialic material undergoing movement and subduction under the influence of shallow convection, involving relatively rapid flow due to the hotter mantle (Lowe & Ernst 1992). Deep penetration of the mantle by subducted material may have been inhibited by shallow melting in earlier Archaean times and the few crustal blocks probably grew by rapid accretion, with little interference from neighbours, to reach diameters  $>1000$  km (Lowe & Ernst 1992, McCulloch 1993). Periodically, large volumes of crust, both ultramafic-mafic and felsic, could have formed, been recycled back into the mantle and reprocessed in the crustal environment through lithosphere subduction, meteorite impact to about 3.7 Ga (Maher & Stevenson 1988), and crustal remelting. Stein & Hofmann (1995) proposed periods of rapid crustal growth as a result of mantle overturn and major orogenesis when two-layer mantle convection gave way to single-cell, whole-mantle convection, during which magmas generated by buoyant plumes underplated crust or formed oceanic plateaus, and subduction slabs penetrated deep into the mantle. The chemical composition of the continental crust cannot be maintained by long-term depletion of the isolated upper mantle, requiring episodic or continuous replenishment from the lower mantle. Recent numerical modelling by Davies (1995) indicates that for a two-layered convecting mantle the 'cold finger' effect of lithosphere subduction would effectively buffer the temperature in the Archaean upper mantle to only  $\sim 100^\circ\text{C}$  hotter than the present day upper mantle (with a potential temperature of  $\sim 1300^\circ\text{C}$  and an adiabatic gradient of  $\sim 0.3^\circ\text{C}/\text{km}$ ) while the potential temperature of the lower mantle could have been about three hundred degrees hotter.

Mantle plumes originating at the thermal boundary layers,

the core/lower mantle and/or the upper/lower mantle, could have played a major role in generation of the voluminous Archaean continental flood basalts and oceanic plateaux from the plume heads (Campbell & Griffiths 1990), as well as introducing large layered mafic-ultramafic intrusions and kimberlites from the deep mantle and causing magma underplating, crustal melting, and growth of refractory, and thus lighter, lithospheric mantle and continental lithosphere. Survival of diamonds formed in the Archaean would be favoured in this way, eventually being brought to the surface by kimberlites generated by later melting of the mantle plume at great depths.

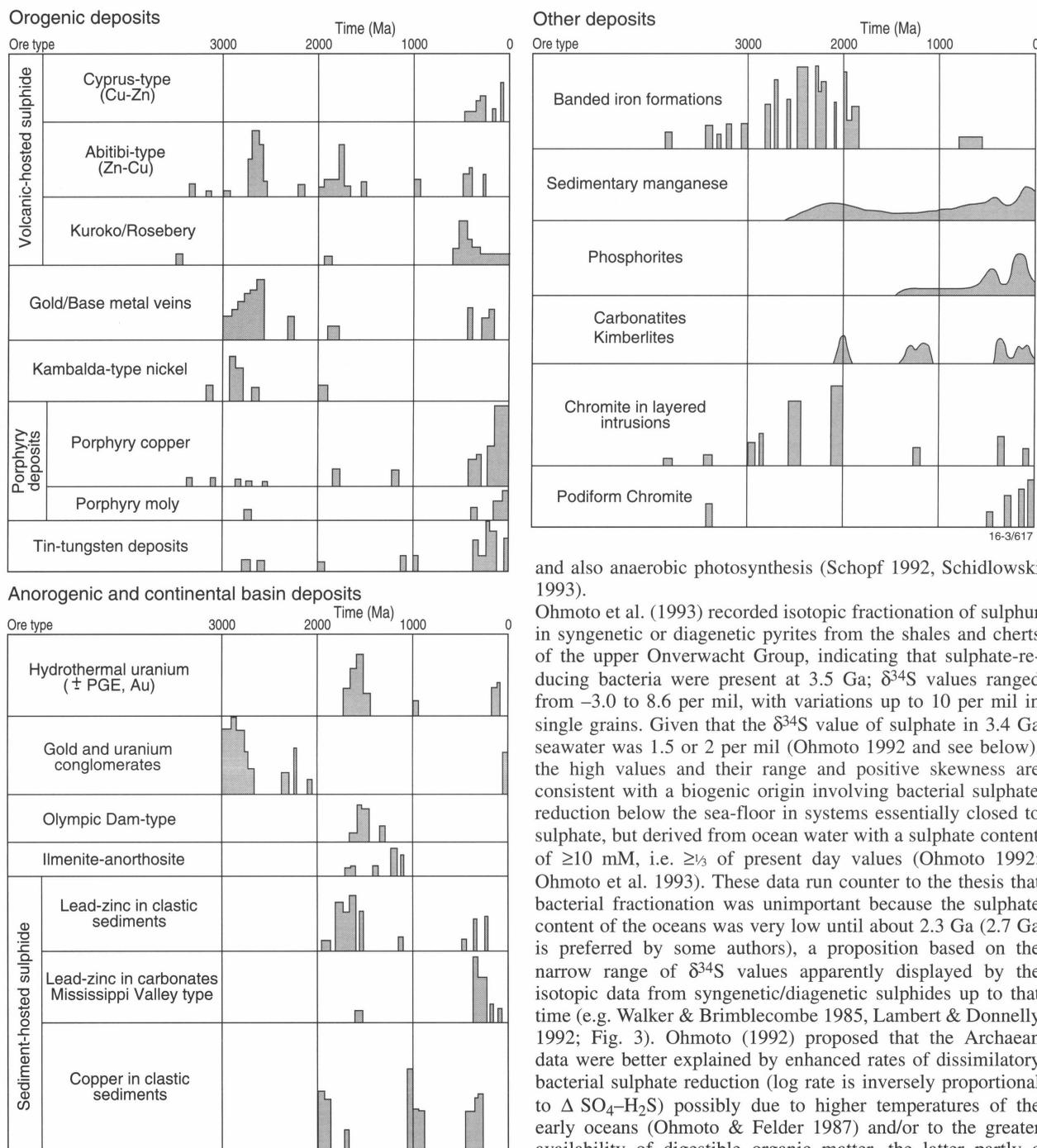
Des Marais (1994a) proposed that much of the earlier Archaean crustal material was probably submerged, restricting the influence of weathering on the compositions of the oceans and atmosphere. However, the report of an unconformity at 3.5–3.46 Ga in the Pilbara Block, with a possible related palaeosol, indicates that orogenesis, exposure and weathering were occurring at that time (Buick et al. 1995). Domal intrusion of intermediate to silicic plutons from about 3.4 Ga (e.g. the Pilbara Block, Bickle et al. 1993) or earlier, and regional metamorphism and anatexis (the high grade gneiss terrains), caused stabilisation and thickening of crustal platelets with increasing recycling in the crustal environment as evidenced by the growing Eu anomaly (Taylor & McLennan 1995).

The Late Archaean saw the merging of terrains along convergent margins, accretion of volcanic arcs in greenstone belts and the development of cratonic and craton margin sequences. Extensive platforms were established with major rifts and passive margins generated in extensional settings, and foreland basins in convergent settings (Lowe & Ernst 1992, Grotzinger & Ingersoll 1992). For example, Witt (1995) identified Late Archaean tholeiitic and high-Mg sills in the Kalgoorlie Terrane in Western Australia that are consistent with formation in the marine continental margin basins proposed by Barley et al. (1989) for this terrane. The identification of a 2.7 Ga suture extending into the upper mantle to a depth of 65 km in the Abitibi Belt implies collisional events and deep subduction similar to that of recent times (Calvert et al. 1995). Major Ni-Cu, Au and base metal mineralisation in the Yilgarn and Superior provinces was associated with orogenesis between 2.8 and 2.6 Ga (Barley et al. 1995). One of the earliest large basins (covering some 26 000 km<sup>2</sup>), the foreland-type Witwatersrand Basin dated at between 3.1 and 2.7 Ga, contained sediments with detrital uraninite and gold, probably derived from hydrothermally altered  $\leq 3.05$  Ga U- and Au-rich granites (Robb & Meyer 1990), though the amount of Au therein must have been exceptionally high (Kirkham & Roscoe 1993).

The Late Archaean was a period of rapid growth of continental crust, particularly near 2.7 Ga, and by the end of the Archaean more than half of the Earth's continental crust may have been formed (e.g. Taylor & McLennan, this issue). Gradual changes occurred in the overall composition of the upper crust, owing to a reduction of melting of the subducted oceanic crust when the mantle cooled, an increase in melting and reprocessing of the pre-existing crust, and cordilleran as well as island arc-type, calcalkaline magmatism becoming more common. Thus average Palaeoproterozoic upper continental crust was enriched in large ion lithophile elements (e.g. K, Rb, Pb, U) compared to average upper Archaean crust (Taylor & McLennan this issue).

#### *The evolution of life and the early oceans*

The earliest organic compounds on Earth may have formed by photochemical reactions in the atmosphere and on the surface, or as a result of the introduction of material by extraterrestrial bodies during impact (see Kasting 1993). Another possibility of increasing interest is an origin using the chemical energy developed as a result of mixing hot



**Figure 2.** The distribution in time of some important types of mineral deposit, from Meyer (1985, 1988), Lambert et al. (1992), Klein & Beukes (1992) and Barley & Groves (1992). The vertical bars for each ore type represent the approximate proportions of the total tonnage from 3.8 Ga.

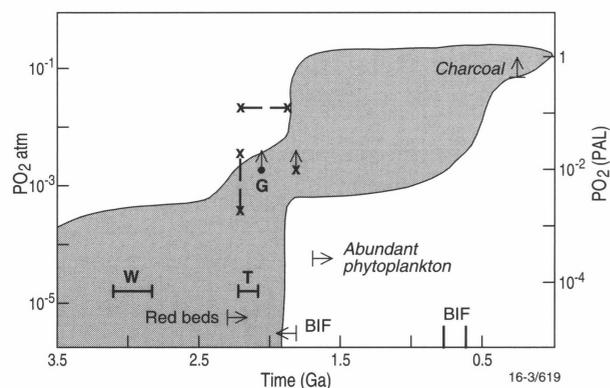
seafloor vent waters with cold ocean waters (Russell et al. 1993, Shock et al. 1995). The oldest fossils known appear to be the prokaryotic stromatolites and cellularly preserved filamentous and colonial microfossils in the carbonaceous cherts of the Warrawoona Group in Western Australia, probably  $\leq 3.47$  Ga (Schopf & Packer 1987, Thorpe et al. 1992, M.E. Barley pers. comm. 1995), and in cherts of the Onverwacht and Fig Tree groups of the Barberton Greenstone Belt, dated at about 3.45 Ga and 3.45–3.23 Ga, respectively (Byerly et al. 1986, de Ronde & de Wit 1994). The microfossils indicate the presence of autotrophic and heterotrophic organisms, which probably included cyanobacteria capable of oxygen-producing

and also anaerobic photosynthesis (Schopf 1992, Schidlowski 1993).

Ohmoto et al. (1993) recorded isotopic fractionation of sulphur in syngenetic or diagenetic pyrites from the shales and cherts of the upper Onverwacht Group, indicating that sulphate-reducing bacteria were present at 3.5 Ga;  $\delta^{34}\text{S}$  values ranged from  $-3.0$  to  $8.6$  per mil, with variations up to 10 per mil in single grains. Given that the  $\delta^{34}\text{S}$  value of sulphate in 3.4 Ga seawater was 1.5 or 2 per mil (Ohmoto 1992 and see below), the high values and their range and positive skewness are consistent with a biogenic origin involving bacterial sulphate reduction below the sea-floor in systems essentially closed to sulphate, but derived from ocean water with a sulphate content of  $\geq 10$  mM, i.e.  $\geq 1/3$  of present day values (Ohmoto 1992; Ohmoto et al. 1993). These data run counter to the thesis that bacterial fractionation was unimportant because the sulphate content of the oceans was very low until about 2.3 Ga (2.7 Ga is preferred by some authors), a proposition based on the narrow range of  $\delta^{34}\text{S}$  values apparently displayed by the isotopic data from syngenetic/diagenetic sulphides up to that time (e.g. Walker & Brimblecombe 1985, Lambert & Donnelly 1992; Fig. 3). Ohmoto (1992) proposed that the Archaean data were better explained by enhanced rates of dissimilatory bacterial sulphate reduction (log rate is inversely proportional to  $\Delta \text{SO}_4\text{-H}_2\text{S}$ ) possibly due to higher temperatures of the early oceans (Ohmoto & Felder 1987) and/or to the greater availability of digestible organic matter, the latter partly a function of higher atmospheric  $\text{P}_{\text{CO}_2}$ . Trudinger (1992) suggested that if the phylogeny of archaeobacteria is correctly understood then bacterial sulphate reduction probably predated 3.45 Ga, and he raised the possibility of the existence of other bacterial sulphate reducers in the past than the groups presently known, groups having different fractionation characteristics that may have evolved to sulphate reduction via sulphur and then sulphite reduction.

Abundant sulphate in the Early/Middle Archaean oceans is also indicated by the barite lenses at North Pole in the Warrawoona Group in Western Australia and in the Fig Tree Group in Africa. These barites are believed to be replacements of evaporative gypsum (Perry et al. 1971, Lambert et al. 1978, Buick & Dunlop 1990, Ohmoto 1992), and the associated sedimentary rocks in Western Australia indicate extensive areas of shallow, nearshore probably (but not proven) marine environments (Buick & Dunlop 1990). Other barites of broadly similar age in the Onverwacht Group in South Africa and in





**Figure 4.** The variation in atmospheric  $\text{PO}_2$  with time according to Kasting (1993). Crosses indicate tentative estimates and ranges of  $\text{PO}_2$  from palaeosol studies (Holland et al. 1989, Holland & Beukes 1990, Holland 1992a). G: the requirements for *Grypania spiralis* from the Michicopoten Iron Formation (Han & Runnegar 1992, Runnegar 1993). W: the approximate possible age range of the uraninite-pyrite-bearing Witwatersrand Basin (Robb & Meyer 1990). T: the age of the hematite-magnetite-bearing Tarkwaian conglomerates (Krupp et al. 1994). The time of redbed formation is from Lowe (1992b). The cessation of significant banded iron formation coincides approximately with the sharp rise in  $\text{PO}_2$  from about 2.0 to 1.8 Ga, but banded iron formations reappear in the period 0.8–0.6 Ga. The very low  $\text{PO}_2$  values for the Archaean atmosphere seem unlikely in view of the evidence of substantial sulphate in Archaean oceans.

of more  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  than at present. High Mg/Ca ratios (a corollary of extensive carbonate precipitation) and high Fe contents of the oceans is indicated by the abundance of sedimentary ferroan (and manganiferous) dolomite and ankerite in Early and Middle Archaean sequences, and of ferroan dolomite and siderite in regional alteration assemblages (Veizer et al. 1989a, b). The Mg-rich chlorite commonly present in the altered footwalls of Archaean volcanic-hosted massive sulphide deposits (Franklin et al. 1981, Meyer 1988) may be due to relatively high  $\text{Mg}^{2+}$  contents in seawater-derived ore solutions compared to those of the Phanerozoic. Increase in oceanic pH may have been a factor (additional to increased  $\text{PO}_2$ ) in shutting off giant-sized banded iron formation from about 1.8 Ga.

Despite intensive research, particularly in Australia, it seems that biological activity has been essential to metal fixation in only a few types of ore deposit, for example, pyritic shales (e.g. Brukungu in South Australia, Seccombe et al. 1985), sediment-hosted Pb-Zn deposits in Ireland (e.g. Anderson et al. 1989) and possibly some Cu-Co ores (e.g. the Kupferschiefer; Fig. 3). Proposals that the stratiform Pb-Zn deposits of the Phanerozoic Selwyn Basin in Canada contain largely biogenic sulphide have been seriously undermined by Ohmoto et al. (1990). Sulphide microbialites have been reported from the Silvermines Pb-Zn deposit in Ireland (Russell 1996). A complex biota was probably associated with other seafloor ore-forming systems (e.g. volcanic-hosted massive sulphide deposits and Au-U conglomerates), but does not appear to have been crucial to ore formation, though hydrothermal processes may have been vital to the development of the earliest organisms (Russell 1996).

### The Proterozoic-Phanerozoic

Collisional and obducted material and sediments of the craton margin are more common in Palaeoproterozoic than Archaean sequences, and long-lived platforms (passive margins?) of Palaeoproterozoic age provided the environment for a surge in BIF and Mn sedimentation (Fig. 2), perhaps during periods of continental fragmentation and dispersal (see *Banded iron formations and manganese deposits*, below). During the late

Palaeoproterozoic large continental masses supported extensive basins in which the earliest sedex Pb-Zn-Ag deposits were formed, e.g. in northern Australia from about 1.7 Ga (e.g. Mount Isa), and in Korea and north China, possibly from ~1.9 Ga (e.g. Jiande). Hairpin bends of the palaeomagnetic apparent polar wandering path of north Australia for the mid-Proterozoic, probably related to major changes in relative plate motion, coincided with basin mineralisation (Idnurm et al. 1994, Loutit et al. 1994). Other giant basin deposits include the Cu-Co ores of Udokan at about 2.0 Ga and the Zambia/Zaire deposits at about 1.0 Ga, and the earliest important hydrothermal U-Au-platinum group element assemblages were formed in extensive, fractured cratonic basins in Australia and Canada from about 1.7 Ga (e.g. Jabiluka, Rabbit Lake). The period from about 2.0 Ga through the Mesoproterozoic saw abundant felsic magmatism in and on the continents, and some oxidised, alkaline, S-poor granitic magmas yielded large tonnages of hydrothermal Fe (e.g. Kiruna at 1.9 Ga, Olympic Dam at 1.6 Ga). The scarcity of greenstones (Condie 1994) and lack of volcanic-hosted massive sulphide and porphyry-related ores between about 1.7 and 1.4 Ga may be related to development of a supercontinent during this period (Hoffman 1989). According to Veizer et al. (1989c) and Lowe (1992a), there was steady-state equilibrium between addition and consumption of crustal material from about 1.8–1.5 Ga, with less new crust added and craton rifting and associated sedimentation prominent.

There is no longer any support for the model proposed by Etheridge et al. (1987) that envisaged Palaeoproterozoic orogeny and crustal growth (e.g. in the Pine Creek Inlier) as a result of mantle upwelling and underplating beneath large sialic masses rather than plate tectonic processes (Windley 1992, 1993, Myers 1993, Solomon & Groves 1994). Nevertheless the origin of the extensive felsic magmatic activity that characterised northern Australia and other continents in the late Palaeoproterozoic has been much debated (Hoffman 1989).

The lack of significant redbeds before about 2.2 Ga, the presence of large deposits of detrital uraninite and pyrite and the removal of Fe and other components from palaeosols before that time suggest there may have been low atmospheric  $\text{PO}_2/\text{PCO}_2$  during the Archaean and into the earliest Proterozoic (Lowe 1992b, Holland 1992a, Kirkham & Roscoe 1993, Krupp et al. 1994; Fig. 4). A significant rise or rises between about 2.0 and 2.3 Ga (Kirkham & Roscoe 1993 suggest between 2.3 and 2.4 Ga) is indicated by the appearance of redbeds and iron oxide-bearing conglomerates, and also by retention of  $\text{Fe}^{\text{III}}$  in palaeosols. Holland (1992a) tentatively suggested a value of  $\text{PO}_2$  of about  $4 \times 10^{-3}$ – $3 \times 10^{-4}$  atm ( $2 \times 10^{-2}$ – $1.5 \times 10^{-3}$  PAL) for the pre-(?) 2.2 Ga Heckpoort palaeosol, while Mossman & Farrow (1992) obtained values of  $2 \times 10^{-2}$  and  $< 10^{-2}$  PAL for the pre-2.2 Ga pre-Huronian Supergroup profiles of the Elliot Lake palaeosol (Kirkham & Roscoe 1993). Holland & Beukes (1990) thought that the Kuruman banded iron formation profile, with weathering between 2.2 and 1.9 Ga, probably formed at  $\text{PO}_2$  levels of  $1.5 \times 10^{-1}$  PAL. The presence of *Grypania spiralis* in 2.1 Ga iron formations from Michigan indicates a  $\text{PO}_2$  level of  $\geq 10^{-2}$  PAL (Han & Runnegar 1992), probably in both ocean and atmosphere (Runnegar 1993), and formation of the 2.0 Ga Udokan Cu-Co ores involved reduction of Cu-bearing oxidised solutions. Highly oxidised shallow groundwaters (of meteoric origin?) were probably vital to the generation of the 1.6 Ga hematite-Cu-U-REE ores at Olympic Dam and the 1.5–1.7 Ga Pine Creek U-platinum group element-Au deposits (Solomon & Groves 1994, Haynes et al. 1995).  $\text{PO}_2$  must have reached at least 6–10% of the present value by the close of the Proterozoic to have supported the newly diversifying biota (Holland 1992b).

The causes of the Palaeoproterozoic increase in atmospheric  $\text{PO}_2$  may have been biological, e.g. increased photosynthesis

(Holland 1992b), or increased burial rate caused by evolutionary changes to the biota (Logan et al. 1995), or the result of increased and faster burial of reduced organic C from about 2.9 Ga, mostly during periods of continental breakup and development of extensive sedimentary basins on new continental margins (Des Marais et al. 1992, Des Marais 1994b). The latter authors based their opinions on the  $\delta^{13}\text{C}$  values of organic C and survival of C-bearing sediments, both at a maximum in the periods 2.3–2.0 Ga and 1.1–0.7 Ga. As reviewed by Kirkham & Roscoe (1993) these are also periods of glaciation (related to lowering of  $\text{P}_{\text{CO}_2}$ ) and development of large provinces of banded iron formations. With respect to the latter, it is noted that Fe is an essential component of the modern photosynthetic production of organic compounds, and that addition of Fe to ocean surface water dramatically stimulates the phytoplankton growth rate, lowers ocean  $\text{P}_{\text{CO}_2}$  and increases the concentration of dimethyl sulphide, a potential precursor of atmospheric sulphate particles, raising the possibility of lowering ocean and atmospheric temperature (see the Ironex experiments, Martin et al. 1994, Kumar et al. 1995, Frost 1996 and related papers). Is it possible that the substantial and protracted Palaeoproterozoic and Neoproterozoic oceanic inputs of Fe envisaged for banded iron formations (see *Banded iron formations and manganese deposits*) had significant impacts on the fauna and climate, possibly lowering temperature to the extent that glaciation occurred?

Cyclic changes in atmospheric  $\text{P}_{\text{O}_2}$ , such as modelled for the late Palaeozoic by Graham et al. (1995), were probably superimposed on the overall increase through the Palaeoproterozoic. The cause and effect relationship between atmospheric  $\text{P}_{\text{O}_2}/\text{P}_{\text{CO}_2}$  and biological activity is complex (e.g. Kasting 1993, Graham et al. 1995), and other factors such as a decline in release of reduced gases (possibly related to mantle oxidation) may also be important (Kasting et al. 1993).

Similar evidence of relatively sulphate-rich oceans in the Early and Middle Archaean (see above) is also seen in Late Archaean and Palaeoproterozoic rocks. For example, the sulphur of apparently stratiform barite lenses from the area of the 2.7 Ga Hemlo deposit in Canada ( $\delta^{34}\text{S}$  of about 2–12 per mil; Cameron & Hattori 1985) may be a product of mixing seawater sulphate partially reduced during seawater cycling with ambient seawater sulphate, indicating abundant ocean sulphate and a Late Archaean isotopic composition close to Early Archaean values (Ohmoto 1996). Anhydrite is present in the Archaean Geco and the Palaeoproterozoic Anderson Lake deposits, both of volcanic-hosted massive sulphide type (i.e. involving seawater cycling) though highly metamorphosed (Franklin et al. 1981). Stratiform barite ( $\delta^{34}\text{S} = 17.1\text{--}21.2$  per mil) and sulphides (6.2–8.5 per mil) from the 1.9 Ga Aravalli Supergroup in India (Deb et al. 1991), and the 1.8 Ga Åsen barite ( $\delta^{34}\text{S} = 1.5\text{--}15.0$  per mil) in the Skellefte district of Sweden (from Strauss 1993), may be of similar origin.

Vein barite at the Eastern Creek deposit (18.4–24.7 per mil) in the 1.6–1.7 Ga McArthur Basin in Australia was probably deposited from basin water ultimately of marine origin (Muir et al. 1985), as were barite grains disseminated in McArthur Basin sediments (19.9–31.5 per mil, Walker et al. 1983). There is abundant evidence of precursor gypsum in the McArthur Basin (Jackson et al. 1987), and bedded anhydrites are common from about 1.4 Ga (Strauss 1993). These late Palaeoproterozoic results indicate oceanic sulphate  $\delta^{34}\text{S}$  values substantially higher than those of the Archaean by about 1.9 Ga. In part at least, the lack of evaporitic sulphates in the Palaeoproterozoic might reflect the increasing likelihood of dissolution of anhydrite and gypsum with increasing age (but see earlier discussion of changes in ocean composition).

Superimposed on the overall crustal evolution from at least 2.9 Ga are second-order cycles of several hundred million years, involving continental assembly, culmination and breakup.

Greenhouse conditions and oceanic anoxia are associated with new ocean basins and enhanced ocean ridge exhalative activity following breakup, and glaciation is attendant on continental aggregation (e.g. Veevers 1990, Barley et al. 1995), so there is a strong link between the tectonic cycles and climatic changes. The distribution of ore deposit types in time reflects the various stages. For example, major phosphate and manganese ores (e.g. the Cambrian Georgina phosphates and the Cretaceous Groote Eylandt Mn ores in Australia) follow sea level changes resulting from continental breakup, and peaks in abundance of volcanic-hosted massive sulphide ores worldwide in the Ordovician–Silurian and Mesozoic–Tertiary reflect volcanism related to enhanced oceanic growth and subduction following continental fragmentation (Rona 1988, Barley & Groves 1992). These post-breakup periods were also characterised by development of extensive shale basins, some of which were anoxic (see below), deposition of turbidites, and by low  $\delta^{13}\text{C}$  in carbonates and high  $\delta^{34}\text{S}$  in evaporites (Holser et al. 1988, Tittley 1991).

Palaeoproterozoic phosphorites are known from the Baltic Platform, but phosphate deposits are most abundant worldwide in the Neoproterozoic–Cambrian period (Fig. 2), probably reflecting the surge in diversification of eukaryotes at that time and the appearance of shelly faunas (Cook et al. 1990). Another surge in biological diversification occurred in the Ordovician, tying in with formation of anoxic basins, and enhanced volcanic arc and mid-ocean ridge activity.

## A review of mineralisation through time

Most major mineral deposit types have characteristic first-order age/frequency distributions (Fig. 2), reflecting evolutionary trends in the compositions of the mantle, crust and hydrosphere, changes in tectonic style and the increasing significance of recycling with time (Veizer et al. 1989c, Lambert et al. 1992). The influence of second-order variations, of the order of 100 my, has been noted above. Here we discuss a few of the important ore types.

### *Magmatic platinum group element, nickel, copper and chromite deposits derived from mafic and ultramafic magmas*

Deposits of this group occur in orogenic belts and in large cratonic intrusions from about 3.0 Ga. Layered mafic/ultramafic complexes with important platinum group element deposits, such as Stillwater (2.7 Ga) and the Bushveld Complex (2.0 Ga), are probably related to mantle plumes, and the Ni-Cu-platinum group element deposits of the Norilsk region in Siberia are hosted by 0.25 Ga flood basalts of mantle plume origin (Naldrett et al. 1995). Mixing of S-undersaturated magma and sulphide-bearing magma or crustal S was commonly critical to Ni-Cu and platinum group element ore formation; for example, under certain conditions ground erosion and assimilation of sulphide-bearing sediments by Ni-rich, S-undersaturated komatiitic lavas produced massive Ni-Cu lenses at the base of the flows (Groves et al. 1986), particularly in the Late Archaean of the Yilgarn Block and the Superior Province.

### *Magmatic porphyry copper-gold and copper-molybdenum deposits, and tin-tungsten and tungsten-molybdenum deposits*

Porphyry-related Cu-Au ores generally formed in subduction-related island arcs with little or no continental crust, and Cu-Mo ores typically in convergent continental margins with thick crust (Tittley & Beane 1981). Because of their shallow level of emplacement and terrestrial setting their frequencies decline rapidly, particularly for the island arc types, of which the oldest are probably the Late Ordovician Goonumbla and Copper Hill in New South Wales. The Cu-Mo types, however,

extend into the Middle Archaean (e.g. 3.32 Ga at Gobbos in the Pilbara Block, ME Barley, University of WA, pers. comm. 1995). Their presence supports the uniformity of related tectonic processes throughout the greater part of Earth's history. Most of the surviving examples relate to the formation of subduction-related magmatic arcs following the breakup of Pangaea.

Orogenic Sn-W and W-Mo deposits are also essentially of magmatic origin. They are related to mostly post-orogenic emplacement of highly fractionated felsic melts (tin granites) on the craton side of magmatic arcs in continental convergent margins during subduction (Sawkins 1990a). Emplacement levels range from subvolcanic to pegmatitic, the former surviving erosion like the Cu-Mo ores, but the latter, and also intermediate-depth vein and greisen types, being relatively common in Late Archaean rocks (e.g. Blockley 1980). Anorogenic Sn-W deposits, like those of northern Nigeria (0.6–0.7 Ga), Rondonia (2.0 Ga) and in the Bushveld complex (e.g. Zaiplaats, 2.05 Ga), are found in stable cratons and have a better survival record. Sawkins (1976, 1990a) tied these magmatic events to melting attendant on mantle hotspot activity (mantle plumes?) related to continental fragmentation.

The Sm/Nd signatures in two Australian tin granites of orogenic type suggest that melting in the sialic crust was related to emplacement of mantle-derived melts (Mackenzie et al. 1988, Sun & Higgins 1996). Orogenic Sn-W provinces lie within (mostly) extensive linear granitic magmatic belts, but are commonly circular or oval in outline with sharp boundaries — perhaps the provinces also reflect the size and position of large mantle-derived melts emplaced in the deep sialic crust.

### ***Mesothermal lode gold deposits***

Gold-bearing quartz veins approximately contemporaneous with collision-induced deformation are found in greenstone belts and turbidite-rich greywacke-sandstone-mudstone sequences of the continental margin from about 2.7 Ga to 0.1 Ga, with major peaks at about 2.6–2.7, 0.38 and <0.2 Ga. The low salinity, CO<sub>2</sub>-bearing fluids were probably derived from metamorphic dewatering at temperatures of more than 350°C and travelled via deep fractures and terrane boundaries. While post-Archaean examples originated mostly near the brittle-ductile transition, Archaean examples formed over a greater range of pressure and temperature. Syn- and post-ore intrusion of granitoids is characteristic (e.g. the Victorian and Pine Creek goldfields in Australia). The Late Archaean deposits of the Yilgarn Block and the Abitibi belt are of similar age and style, mostly forming in the period 2.6–2.7 Ga as part of a chain of events that culminated in the formation of one or more large continents (Myers 1995). The overall Au production/km<sup>2</sup> of such famous fields as the Yilgarn (~2.7 Ga) and Victoria (~0.38 Ga) in Australia is similar, suggesting that secular changes in the Au content of upper crustal rocks are not significant to ore formation. Titley (1991) noted that lode Au deposits were particularly common in early Palaeozoic and late Mesozoic turbidites and suggested that the Au was sourced in the host sediments during oceanic anoxia that followed continental fragmentation. However, it seems more likely that the physical make-up of the sandstone-shale sequences (favouring formation of, for instance, saddle reefs) and the reducing nature of the shales may be the more significant factors in gold deposition (Solomon & Groves 1994).

### ***Sediment-hosted stratiform copper-cobalt and lead-zinc deposits***

In contrast to the three groups outlined above, the commonly giant-sized sediment-hosted Cu ± Ag ± Co and Pb-Zn-Ag deposits make their first appearances at about 2.0 Ga (Gustafson & Williams 1981, Kirkham 1989). These deposits formed in large, cratonic or epicratonic, mostly mudstone-carbonate-sand-

stone sedimentary basins from probable high salinity basinal fluids during basin formation. Essential requirements to ore formation probably included the development of thick continental crust over regions large enough to support extensive shallow platforms at least locally undergoing evaporation to provide fluid salinity (e.g. northern Australia at 1.7–1.6 Ga, the Zechstein Sea at 0.28 Ga) and, in the case of most Pb-Zn ores, abundant biota to allow fluid reduction by organic matter. Broken Hill-type Pb-Zn deposits are associated with felsic volcanic rocks and may have a different genesis (Beeson 1990). Many Pb-Zn deposits other than the Broken Hill type appear to have formed in reduced marine environments (e.g. in mid-Proterozoic northern Australia) and from reduced, deep basinal fluids, but the Cu-Co ores were probably derived by reduction of shallow-circulating, oxidised, Cu-rich fluids (Gustafson & Williams 1981). High heat producing granites have been suggested as heat sources for circulating Pb-Zn fluids in northern Australia (Solomon & Heinrich 1992). The argument that these giant Pb-Zn ore deposits did not form until the crust had been enriched in Pb and Zn by late Palaeoproterozoic felsic magmatism (Sawkins 1989, Barley & Groves 1992, Lambert et al. 1992) is not supported by analytical data for earlier Palaeoproterozoic and Archaean sedimentary and igneous rocks (e.g. Bickle et al. 1993, Solomon & Groves 1994), but it is true that Palaeoproterozoic upper crust is richer in K, Rb, U and Pb than Archaean upper crust.

Sawkins (1990a) suggested these deposits formed during advanced rifting of basins, and drew attention to the concentration of sediment-hosted Cu ores in the early Neoproterozoic, a probable time of continental breakup. Hinman et al. (1994) demonstrated complex transpressional faulting during formation of the 1.64 Ga (R.W. Page unpublished data) HYC Pb-Zn-Ag deposit in northern Australia, also a time of rapid changes of plate motion, interplate tectonism and basin-wide hydrothermal activity (Idnurm et al. 1994).

### **Volcanic-hosted massive sulphide deposits and ocean compositions**

Volcanic-hosted massive sulphide deposits, present intermittently from 3.5 Ga to today, may be classified as Cu-Zn ophiolite-related, Zn-Cu ± Pb and Zn-Pb-Cu (e.g. Franklin 1986). They form today mostly in back-arc basins of various types and at mid-ocean ridges, testifying to the persistence and consistency of plate tectonic and associated hydrothermal processes from 3.5 Ga. The 3.46 and 3.26 Ga Zn-Pb-Cu deposits from the eastern Pilbara Craton (Barley 1992, 1993; Vearncombe et al. 1995), probably the oldest base metal ores on Earth, contain barite, confirming abundant sulphate in at least some of the Early and Middle Archaean oceans, as suggested independently by Ohmoto (1992). They are broadly similar in form, textures and mineral and metal content to the Tertiary Kuroko deposits in Japan and/or some modern seafloor deposits of back-arc basins. This implies that they formed under conditions that inhibited boiling of the ore solutions (water depth was ≥1.8 km for the Japanese deposits; Pisutha-Arnond & Ohmoto 1983). Barite in the Big Stubby deposit has δ<sup>34</sup>S values of 11–13 per mil (Lambert et al. 1978), which may be interpreted, following Ohmoto et al. (1983), as mixtures of hydrothermal sulphate (partially reduced oceanic sulphate, possibly via anhydrite) and ambient oceanic sulphate having a value of about 1.5 per mil (Ohmoto 1992). The sulphide-sulphur (about -4.3 to -0.9 per mil) probably represents mixtures of reduced sulphur derived from oceanic sulphate, and of sulphide-sulphur of direct magmatic origin or dissolved from mostly volcanic rocks having δ<sup>34</sup>S values near zero per mil.

Zn-Cu volcanic-hosted massive sulphide deposits without Pb and mostly without sulphate are common in the 3.1–2.7 Ga greenstone belts of the Superior province of Canada, and occur in other cratons. Local host rocks are almost invariably felsic

volcanics. In the Yilgarn Block deposits of similar age and also without sulphate have minor Pb, for example, Zn/Pb ratios of 13.4 and 14.6 at Teutonic Bore and Scuddles, respectively (Barley 1992), compared to 3.0 for Kuroko deposits (Tanimura et al. 1983) and 3.0–4.1 for 3.5 Ga deposits in the Pilbara Block (Barley 1992). Sawkins (1990b) and Barley (1992) argued that volcanic-hosted massive sulphide ores are of magmatic origin, the metal content of ore solutions being related to the composition of the coeval magma, and Barley (1992) suggested that lack of barite is related to ore formation in anoxic, sulphate-free, ocean water. Similar sulphate-free basin water has been proposed for the source of the solutions responsible for the Early Proterozoic volcanic-hosted massive sulphide deposits of Arizona (Eastoe et al. 1990), and also the Late Palaeozoic, pyrrhotite-bearing, barite-free Zn-Cu ± Pb deposits of the West Shasta district, California (Eastoe & Gustin 1996). One of the difficulties of this model is that if, as proposed, the ores are deposited from solutions that are buoyant in seawater, they will not form the sulphate chimneys that appear to be vital to the process of trapping sulphides and building the mounds (e.g. Goldfarb et al. 1983).

There are other possible explanations for both lack of Pb and absence of barite. Ohmoto (1996) suggested these features resulted from a greater degree of reworking of the massive sulphide ore (= leaching of barite and galena) at the high temperature stage due to the higher mass flux caused by an elevated temperature gradient in the Archaean compared to that in subsequent periods (see Ohmoto et al. 1983). Coeval and older Pb-bearing deposits in the Pilbara suggest steep temperature gradients were confined to certain terranes. An alternative explanation, discussed by Franklin et al. (1981), is that most of the metallic components of the Cu-Zn ores, whether Archaean or younger, were derived by dissolution in underlying terrains dominated by mafic rocks which, containing more reductants, such as Fe<sup>II</sup>, and low Pb contents, cause total reduction of oceanic sulphate during hydrothermal circulation and low Pb contents in the ore solutions. Modern mid-ocean ridge fluids sourced in basalts have these characteristics (Von Damm et al. 1985), and Franklin et al. (1981) noted that Canadian Archaean greenstone belts, which contain mostly Cu-Zn, low Pb deposits, have >90% of mafic rocks by volume.

Eastoe & Gustin (1996) postulated that few volcanic-hosted massive sulphide deposits on the sea-floor would survive in oxidised seawater and that preservation ideally requires anoxic conditions. They pointed out that Ordovician rocks contain more deposits than any other period, an anomaly enhanced when the preservation potential is taken into account, and this was a period of widespread oceanic anoxia and enhanced volcanic arc activity following continental breakup (Veevers 1990). However, there are other factors to consider, as noted by Eastoe & Gustin (1996), including rapid burial and the observation that some volcanic-hosted massive sulphide deposits differ from those discussed so far in being mostly much larger in area and tonnage, rather sheet-like and rich in Zn and mostly rich in Pb. They appear to have formed from reduced, saline solutions that reversed buoyancy on exhalation and precipitated much of the total metal content of the solutions in basins, the resulting deposits being shielded from oxic seawater by the spent ore fluids. High salinities postulated for this group (Solomon 1981, Green et al. 1981) have recently been found in fluid inclusions at Hellyer, Tasmania (Khin Zaw et al. 1996, Solomon & Khin Zaw in press), and a partial or wholly magmatic origin for the Hellyer fluids is likely, this being the only reasonable source of chloride.

## Banded iron formations and manganese deposits

Banded iron formations are potentially important as indicators

of ancient atmospheric and oceanic conditions (e.g. Towe 1991, Holland 1992b, Kasting 1993, Morris 1993). They are chemical sediments found in rocks from 3.8 Ga (Isua) to about 0.6 Ga (Rapitan and others) but there is a marked peak in occurrence between about 2.75 and 1.9 Ga, and there are none between about 1.8 and 0.8 Ga and post-0.6 Ga (Klein & Beukes 1992; Fig. 2). Until about 2.6 Ga banded iron formation occurrences tend to be smaller (<50 m thick and strike lengths <10 km; Guilbert & Park 1986) than those of Palaeoproterozoic age, although several Late Archaean banded iron formations extend along strike for more than 30 km, for example at Koolyanobbing in Western Australia (BHP Staff 1975) and in the Chitradurga Schist Belt in India (Rao & Naqvi 1995). About 90% of known iron formations are Palaeoproterozoic in age, and occur in five provinces (from a review by Kirkham & Roscoe 1993); they reach maximum size in the ~2.5 Ga Hamersley Basin, which originally probably covered some 150 000 km<sup>2</sup> and contained some 3×10<sup>17</sup> kg Fe (Trendall 1975, Morris & Trendall 1988). The Archaean banded iron formations are commonly associated with mafic volcanic rocks, but evidence of volcanic activity is generally more limited or absent in Proterozoic types, except in the Hamersley province, where Barley et al. (1997) have shown that some 30 000 km<sup>3</sup> of bimodal igneous rocks were more or less coeval at 2470 ± 4 to 24491 ± 3 Ma with the development of the Hamersley iron formations.

The Dales Gorge member of the Hamersley banded iron formations, perhaps the most intensively studied banded iron formation unit (Trendall & Blockley 1970, and review in Morris 1993), consists of 17 banded iron formation macrobands (chert-iron oxide, 2–15 m thick) that alternate with 16 thinner ferruginous shale macrobands (chert-carbonate-silicate with shale bands). Many of the macrobands can be traced over the whole basin (Trendall 1975), and Ewers & Morris (1981) found some had near-constant composition over distances of more than 100 km. Mesobands of chert (5–15 mm thick) and Fe-rich material occur in macrobands, and the chert mesobands commonly display microlaminae (0.2–1.5 mm thick, Morris 1993). The probable primary minerals in the Hamersley banded iron formation were microcrystalline chert and hydrated iron oxide, carbonate (mostly siderite) and greenalite/stilpnomelane or some silicate precursor (Ayres 1972, Morris 1993); haematite was probably generated during early diagenesis. The similar (and probably contemporaneous) banded iron formations of the Kuruman Iron Formation of the western Transvaal Basin are thought to have formed in water 100–700 m deep, below wave base and the photic zone, during marine transgression over a shallow-water carbonate platform or shelf that may have been part of a back-arc basin (Klein & Beukes 1989, Beukes et al. 1990).

### *The genesis of banded iron formations*

Most recent workers, following Gross (1983 and earlier papers) and Morris & Horwitz (1983), have favoured a hydrothermal source for a large part of the Fe and silica of banded iron formations, for example, Towe (1991), Klein & Beukes (1992) and Morris (1993), with deposition in continental margin basins or on platforms. The Fe-Si-rich waters may have arrived by (a) upwelling related to winds or currents of reduced ocean water, Fe<sup>III</sup> depositing as a result of mixing with shallow, oxidised waters (Holland 1973, 1984; Beukes et al. 1990; Fig. 5A), or (b) convective upwelling initiated by ocean ridge activity (Morris 1993), or (c) buoyancy forces generated at ocean ridge vents, with Fe and silica being deposited from gravity currents driven towards the coastal sites (Solomon & Groves 1994, Isley 1995; Fig. 5B).

In the *upwelling models* the waters contain ≥1 ppm Fe and up to 120 ppm SiO<sub>2</sub> (Holland 1984, Dove & Rimstidt 1992) and come from a markedly stratified ocean with large, deep, fluid reservoirs carrying the reduced Fe and connected to open

oceans. With each upwelling pulse or phase the Fe or Fe-rich water must be resupplied to the reduced ocean, ultimately by ridge vent activity. The REE compositions and the marked positive Eu anomaly in many banded iron formations (normalised to North American Shale), particularly the high-Fe Dales Gorge material of Morris (1993), cannot be explained by continental weathering and indicate significant input from reduced ocean-floor vent fluids that have reacted with basalt at high temperatures (e.g. Klein & Beukes 1989, Danielson et al. 1992). Alibert & McCulloch (1993) estimated  $50 \pm 10\%$  of Nd was supplied to the Dales Gorge-Joffre banded iron formation units from hydrothermal sources.

To supply the  $3 \times 10^{17}$  kg Fe of the Hamersley Basin, and allowing say 50% Fe from terrestrial input and 1 ppm Fe in the fluid, requires  $1.5 \times 10^{23}$  kg of reduced, possibly slightly acid, Fe-bearing ocean water. At Hollands (1984) annual rate of upwelling of  $3 \times 10^{16}$  kg water, the Hamersley banded iron formation deposits could be laid down in about  $5 \times 10^6$  years, well within the  $20 \times 10^6$  years allowed by the dates of Barley

et al. (1997). Modern annual upwelling rates are substantially higher along several passive continental margins (e.g. Smith 1992), and the Fe supply could also have been faster, owing to a more acid, reduced and warmer ocean (see earlier discussion). The *convection* model of Morris (1993) differs only slightly from the above and has the problem that vigorous convection would return fluids to the deep ocean rather than direct them to the continental margin, and would tend to mix the oxygenated and anoxic waters. In the modern oceans, mid-ocean ridge plume dispersal is affected by ocean circulation, not the reverse (Edmond et al. 1982).

Morris (1993) has discussed in some detail the precipitation of Fe and  $\text{SiO}_2$  following mixing of oxidised and reduced waters, highlighting the difficulties in accounting for more or less coeval but physically distinguished chert and Fe deposition. His models for the varve-like bands involve photochemical oxidation of  $\text{Fe}^{2+}$  in the surface zone, storm mixing of reduced and oxidised waters to resupply the shallow water, and evaporation to deposit carbonate and silica, implying seasonal

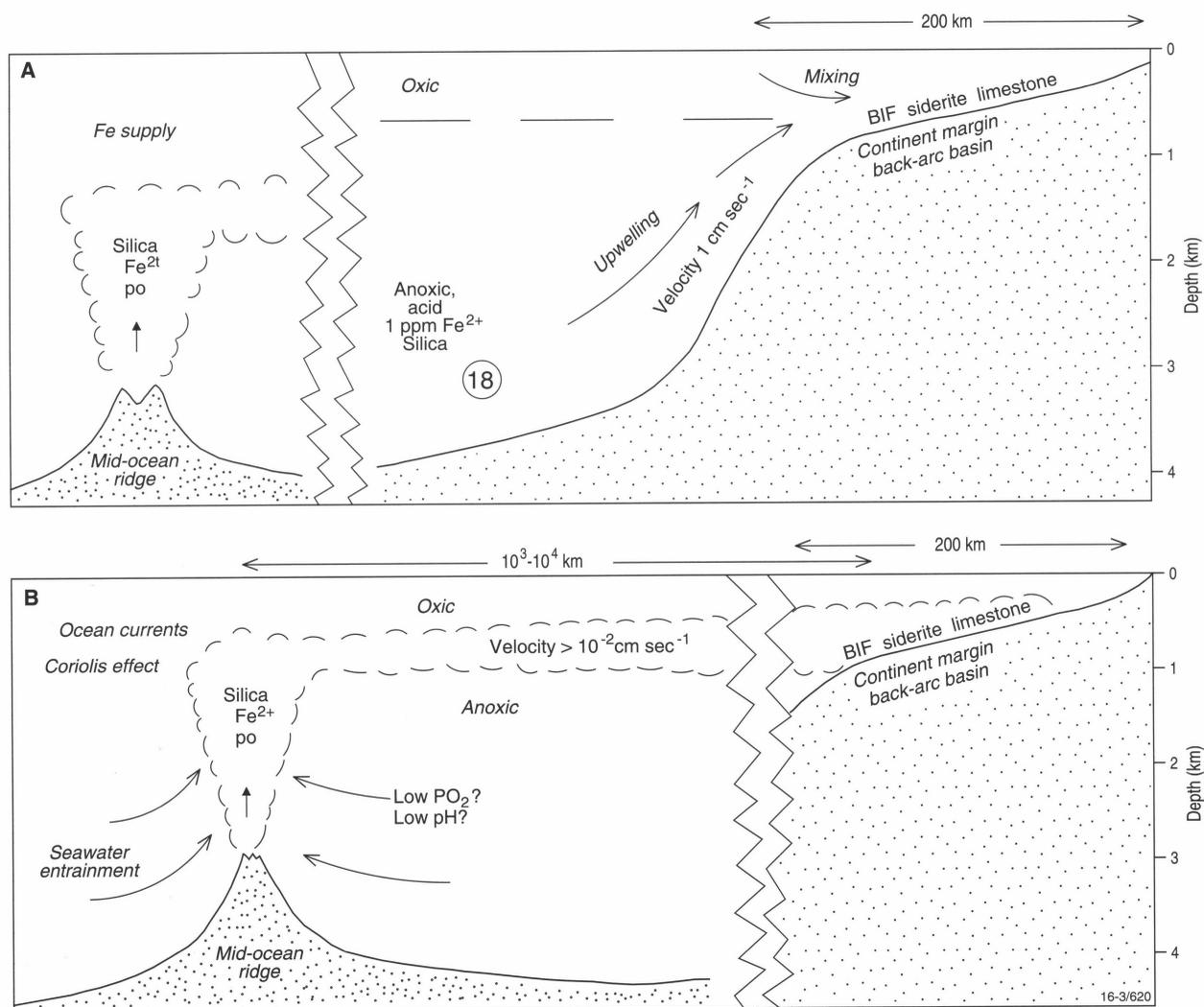


Figure 5. Sketches to illustrate the major competing models for supplying Fe to giant BIF basins in the Palaeoproterozoic.

A. The upwelling model of Holland (1973, 1984), with alongshore currents creating upwelling of deep, reduced, slightly acid(?) ocean waters into shallow, oxidised ocean water where oxidation of  $\text{Fe}^{2+}$  leads to precipitation of Fe hydroxide gels. Fe is re-supplied by exhalative ocean ridge activity greater than the present. The banded iron formation-siderite-limestone transition is from Beukes et al. (1990). Possible mechanisms of silica and Fe(hydroxide?) deposition are discussed by Morris (1993).

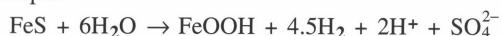
B. The hydrothermal plume/gravity current model of Solomon & Groves (1994) and Isley (1995), with pyrrhotite (and possibly  $\text{Fe}^{2+}$ ) transported vertically and then laterally to basins on the continental margin, with the mass flux and fluid temperature at the sea-floor considerably greater than the present. If oxidation of sulphide and reduced Fe is effected it is likely to occur in the plume (cf. Isley 1995). The oxidised products are carried to the continental margin in the gravity current in which mixing with ocean water is minimal and the velocity is more or less maintained. Stratification of the ocean with respect to  $\text{PO}_2$  is not an essential ingredient of this model (see text for discussion).

controls. Mn is at low levels in most, but not all, Palaeoproterozoic banded iron formations and probably remains in solution as reduced species (Holland 1984, Nelsen et al. 1987). For those banded iron formations with significant Mn, a higher  $P_{O_2}$  is indicated or perhaps a longer transport time, Mn oxidation being notably sluggish (Roy 1992).

For the *hydrothermal plume model* to supply the Fe of the Hamersley Basin requires ridge activity much more vigorous than that observed today, involving relatively high geothermal gradients, and/or higher magmatic temperatures, and/or larger magma bodies. These factors could create larger and hotter sub-seafloor convection systems and thereby higher vent temperatures, higher buoyancy flux, including higher mass flux (see Cathles 1981, 1983) and, most critically, higher Fe contents in the fluids. The recognition of a major basalt-rhyolite province coeval with Hamersley banded iron formations supports the idea of an increased Fe input to the oceans at that time (Barley et al. 1997).

The present-day global flux of  $Fe^{2+}$  at mid-ocean ridges is about  $2 \times 10^9$  kg a year and the fluids at 350°C carry about 100 ppm Fe (composition from Von Damm et al. 1985; fluid flux from Wolery & Sleep 1988). Fluids 50–75°C hotter might carry 1000 ppm Fe and 1000 ppm  $SiO_2$  (Seyfried et al. 1991). Doubling the modern mass flux and focusing the *global* Fe output to the Hamersley Basin yields  $4 \times 10^{10}$  kg Fe a year, requiring nearly  $5 \times 10^6$  years to deposit the Hamersley banded iron formations, assuming 50% from terrestrial sources, just matching the upwelling model. The hydrothermal Fe supply could have been further augmented if  $Fe > H_2S$  in early Precambrian vent fluids (Walker & Brimblecombe 1985, Wolery & Sleep 1988, Holland & Kasting 1992), limiting the proportion of  $Fe^{2+}$  trapped as sulphides in the chimneys and mounds (see below), a condition that might arise partly because of the high temperature, partly because of a lower oceanic sulphate content (and hence lower contribution to the vent fluids via sulphate reduction), and also possibly because the source mafic rocks were sulphide-undersaturated. Total oxidation of modern hydrothermal reductants is possible at a  $P_{O_2}$  of  $10^{-3}$  PAL (Holland 1992b) so even the enhanced outputs envisaged here would only require an oxygen pressure near  $10^{-2}$  PAL, even with abundant Mn deposition. Increased terrestrial input of Fe to offshore basins compared to the present is also likely, because during glaciations (see *Proterozoic-Phanerozoic*) there may be an increased supply of aeolian dust, as recorded in Antarctic ice formed during the last maximum glaciation (Kumar et al. 1995).

In modern mid-ocean ridge vents the escaping  $Fe^{2+}$  (i.e. the fraction not trapped in basal mounds) is precipitated as sulphide (mostly pyrrhotite) almost immediately on mixing with ambient seawater (Fe and  $H_2S$  are approximately balanced, Edmond et al. 1982). It is then carried upwards by the plume, only a few per cent being lost through fallout from the plume flanks (Converse et al. 1984). Rising a few hundred metres in the plume the sulphide oxidises to various hydroxides, for example:



probably forming submicron size particles like those found by Nelsen et al. (1987) over the Mid-Atlantic Ridge. Excess  $Fe^{2+}$  in plumes could form Fe hydroxides directly, for example:



If the vent fluids entered anoxic, sulphate-free water, thus inhibiting chimney and hence mound formation (Goldfarb et al. 1983), then almost the entire Fe content of the fluid might be vented. Silica would also have precipitated on cooling, perhaps as silica gel, albeit more slowly, due to kinetic effects (Rimstidt & Barnes 1980). The reduced Fe must eventually be oxidised, requiring at least an oxygenated ocean layer, but a stratified ocean is not required as in the upwelling model. Isley (1995) calculated a supply of  $2.5 \times 10^{10}$  kg  $Fe^{2+}$  a year

to the depositional site by first removing  $H_2S$  and various oxidants from the plume fluids, and allowing oxidation in the gravity current near the continental margin. However, pyrrhotite deposition would be immediate upon quenching even in anoxic conditions, and particulate sulphides would be transported (with any excess  $Fe^{2+}$ ) until oxidation occurred on entering oxygenated water. Spreading laterally at depth on becoming neutrally buoyant on a pycnocline, or at the surface, the horizontal velocity of the gravity current would be maintained almost indefinitely in a calm ocean (provided the mass flux was maintained at source) because mixing with ambient water is minimal, but in modern oceans the plumes are bent by currents and Coriolis forces, thereby focusing the lateral spread of the current (e.g. Edmond et al. 1982). The particulate-rich fluids may have spread over distances of the order of  $10^3$ – $10^4$  km from the source, like modern vent fluids (as evidenced by their  $^3He$  and Mn contents, Lupton et al. 1980, Klinkhammer & Hudson 1986). Deposition presumably occurred when current velocities fell below particle settling velocities, but there is no obvious explanation in this model for the finer scale banding of the Transvaal and Hamersley banded iron formations.

The lack or scarcity of silica in Phanerozoic ironstones can be explained in both plume and upwelling models by the emergence of silica-secreting organisms at the beginning of the Phanerozoic, assuming there was sufficient time during Fe transport in the gravity current model for the biota to consume most of the silica. The sustained surge in Fe and other nutrients into the ocean waters entrained in the plume probably accelerated both consumption and overall biomass (e.g. Frost 1996 and related papers).

### Tectonics

During the Late Archaean/Palaeoproterozoic period, continental masses developed of sufficient size to support long-lived and extensive basins. Wide continental margins originated during continental breakup, providing for the first time the extensive, stable, clastic-starved basins in which banded iron formations accumulated (Gross 1983, Schissel & Aro 1992, Alibert & McCulloch 1993). The combination of large marginal basins with abundant ocean ridge activity and appropriate chemical conditions in the oceans could have set up ideal conditions for formation of the giant Proterozoic Fe deposits. The marine transgressions recognised by Klein & Beukes (1989) in the Transvaal Supergroup would be more likely products of increased ocean spreading. Buhn et al. (1992) proposed that the Neoproterozoic banded iron formation and Mn deposits at Otjosondu in Namibia are related to opening of the Khomas Sea.

On the southern margin of the Pilbara Block the Fortescue Group basalt lavas and dykes (which include some komatiites), aged 2.77–2.69 Ga (Blake & Barley 1992), may be expressions of mantle plume activity, the protracted thermal decay and volcanism continuing during subsidence of the Hamersley Basin (Barley et al. 1997), and a similar story may apply to the Ventersdorp lavas of southern Africa and the Transvaal Basin.

Isley (1995) suggested that mid-ocean ridge crests were probably at shallower depths than today, but unless the water was  $\geq 3$  km deep, fluids such as those discussed above would have boiled below the rock surface, a process likely to have deposited Fe and Cu sulphides, significantly lowering the Fe content of the fluids (see Drummond & Ohmoto 1985).

### Sedimentary manganese deposits

Manganese deposits are as old as 3.0 Ga, but are most common in the Mesozoic and Cainozoic (Roy 1992; Fig. 2). Large deposits in sedimentary rocks may have been deposited from upwelling oxygenated water at the margins of more reduced basins in which Mn remained in solution, in many cases following marine transgression accompanied by development

of anoxic basins (Roy 1992). The manganese of those deposits accompanying banded iron formations, which include the largest (the 2.2 Ga Kalahari deposit), and even non-banded iron formation-related occurrences, may be ultimately sourced in ocean ridge vents (Fe/Mn  $\sim$ 3 at 21°N, Edmond et al. 1982).

### Review of banded iron formation

The upwelling-stratified ocean model accounts fairly well for the distribution of banded iron formations in time, with increased atmospheric  $\text{PO}_2$  (for which there is independent evidence) inhibiting the development of large anoxic ocean basins from about 1.8 Ga, perhaps combined with increased oceanic pH (Figs 2, 4, 5). However, the fundamental controls over basin formation and size were probably tectonic, with extensive platforms and sufficiently large anoxic basins not developing until the earliest Proterozoic. The Neoproterozoic banded iron formations can also be related to an important period of continental rifting and oceanic basin development. Oscillations in oceanic  $\text{PO}_2$  related to tectonic cycles of a few hundred million years were probably of minor significance. Attendant surges in biological activity and burial of organic residues might have triggered changes in atmospheric  $\text{PO}_2$  that led to the Proterozoic glaciations, of which the major were more or less coeval with banded iron formations.

The plume/gravity current model is quite clearly related to tectonic processes, but perhaps more directly than previously realised if the dramatic increase in Fe and nutrient content due to ocean ridge and other volcanic vent activity can drive increased biological activity and export production to anoxic basins to a level sufficient to cause glaciation. The giant banded iron formation provinces are not synchronous worldwide and do not involve entire oceans so there is doubt as to the significance of the hydrothermal and related processes to climate.

### Summary

Several features relating to both ore formation and Earth's evolution have emerged in this review.

- The secular stability of the chemical composition of igneous and sedimentary rocks points to the operation of similar tectonic processes to those of the present, and this is supported by the occurrence from 3.5 Ga of mineral deposits having essentially present-day appearance and composition (e.g. volcanic-hosted massive sulphide, porphyry Cu, Sn-W, mesothermal lode Au, etc).
- Secular changes in other ore types (other than due to preservation) follow the long-term thermal and chemical evolution of the Earth, for example:
  - (i) the restriction of komatiite-related Ni-Cu ores to the early Precambrian, perhaps because of the cooling mantle, and
  - (ii) the lack of deposits such as the stratiform, sediment-hosted Cu-Co, Zn-Pb and U-PGE types before the increase of atmospheric  $\text{PO}_2$  during the Palaeoproterozoic.
- Mantle heterogeneity does not appear to be important in controlling ore distribution in time or place, nor is there evidence in Au and platinum group element occurrences that these elements were enriched in the Archaean crust or mantle.
- Mantle plumes released from the core/mantle boundary at various stages through Earth's history were probably the direct or indirect (e.g. secondary melting) cause of formation of several ore types (e.g. large platinum group elements, Cr), and large bodies of mantle-derived melts emplaced in the continental crust may be responsible for the development of orogenic as well as anorogenic Sn-W provinces.

- Long-term changes in tectonic style have profoundly affected variation in mineralisation. For example, extensive passive margins and large intracratonic basins developed during the Late Archaean and Palaeoproterozoic as sialic crustal masses enlarged and began to interfere with their neighbours, changes that allowed formation of the giant Palaeoproterozoic banded iron formations and Late Archaean U-Au conglomerates, and, from 2.0 Ga, sediment-hosted Pb-Zn and Cu-Co ores and hydrothermal U deposits.
- Tectonic cycles of a few hundred million years, involving compilation, fracturing and breakup of continental masses, account for much of the second-order (a few hundred m.y.) variation in secular occurrence of, for example, volcanic-hosted massive sulphide, syndeformational lode Au, porphyry Cu and Sn-W ores, and also sedimentary Mn and phosphate deposits.
- There was probably substantial sulphate in at least some deep and shallow oceans from at least 3.5 Ga, a finding based on the occurrences of evaporitic sulphate, the sulphur isotope studies of Ohmoto (1992) and Ohmoto et al. (1993), and the presence of volcanic-hosted massive sulphide deposits in the eastern Pilbara Block; sulphates then appear intermittently in mineral deposits until about 1.4 Ga, from which time bedded evaporitic sulphates are common.
- The  $\delta^{34}\text{S}$  value of oceanic sulphate was about 1.0–1.5 per mil from 3.5 Ga into the Palaeoproterozoic, after which it rose rapidly (and the sulphate content probably also increased), reaching Phanerozoic values by about 1.7 Ga.
- Atmospheric  $\text{PO}_2$  probably increased over the period 2.3–2.0 Ga, based on palaeosol and palaeontological evidence, together with the appearance of redbeds and disappearance of significant detrital uraninite and pyrite. Both the upwelling current and hydrothermal plume models for the origin of banded iron formation are viable, but we raise the possibility that surges in banded iron formation related to intense hydrothermal vent activity might possibly have contributed to atmospheric composition rather than being controlled by it.

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