Miner Deposita (2015) 50:5–23
DOI 10.1007/s00126-014-0574-8

INVITED PAPER

First whiffs of atmospheric oxygen triggered onset of crustal gold cycle

Hartwig E. Frimmel · Quinton Hennigh

Received: 4 December 2014 / Accepted: 23 December 2014 / Published online: 15 January 2015

Abstract Lack of a suitable gold source has long been regarded as a major argument against a palaeoplacer model for the exceptionally well-endowed Witwatersrand gold province. By comparing worldwide Witwatersrand-type deposits/occurrences, ranging in age from 3.1 to 1.8 Ga, we propose that the primary concentration of gold in the continental crust resulted from atmospheric and biological evolution in the Mesoarchaean. A high Au flux off the Archaean land surface (orders of magnitude greater than today's) was a consequence of the chemistry of the Mesoarchaean atmosphere and hydrosphere. When early life gradually changed from anaerobic anoxygenic to oxygenic photosynthesizers at around 3.0 Ga, the first 'whiffs' of free oxygen produced by photosynthesis under an overall reducing atmosphere provided the ideal trap for Au dissolved in the huge reservoir in meteoric and shallow sea water. Oxidative precipitation of gold on the surface of the O_2-producing microbes, probably cyanobacteria, could fix huge amounts of gold over large areas. Some of this microbially mediated gold is still preserved in thin kerogen layers ("carbon seams") that typically developed on erosional unconformities, scour surfaces and bedding planes in nearshore environments at around 2.9 Ga. This gold provided the principal source for the very rich placer deposits that formed by the subsequent sedimentary reworking of the delicate microbial mats on aeolian deflation surfaces, into fluvial channels and delta deposits, represented by Meso- to Neoarchaean auriferous conglomerates. Tectonic reworking of these first gold-rich sediments by orogenic processes explains the temporal peak of orogenic-type gold formation at around 2.7 to 2.4 Ga. With time, the strongly gold-enriched Archaean sediments became progressively eroded, covered or tectonically reworked, and their role as potential source of younger placer deposits diminished. This explains why Witwatersrand-type deposits younger than 2.4 Ga are rare and far less well-endowed and effectively missing in the rock record after 1.8 Ga.

Keywords Gold · Oxygenic photosynthesis · Palaeoplacer · Mesoarchaean · Witwatersrand

Editorial handling: B. Lehmann

Electronic supplementary material The online version of this article (doi:10.1007/s00126-014-0574-8) contains supplementary material, which is available to authorized users.

H. E. Frimmel
Bavarian Georesources Centre, Institute of Geography and Geology, University of Würzburg, Am Hubland, 97074 Würzburg, Germany

H. E. Frimmel (✉)
Department of Geological Sciences, University of Cape Town, Rondebosch, Cape Town 7701, South Africa
e-mail: hartwig.frimmel@uni-wuerzburg.de

Q. Hennigh
Novo Resources Corporation, 500 Coffman Street, Unit 106, Longmont, CO 80504, USA

Introduction

Gold has been concentrated in a huge variety of deposit types through a diverse range of magmatic, hydrothermal and physical processes. By far, the two most important gold deposit types are conglomerate-hosted (Witwatersrand-type) and orogenic-type deposits. In spite of the fact that gold production from the Witwatersrand Basin has steadily decreased over the past quarter century, historic production (>52,000 t gold mined; 32 % of all gold ever mined) combined with enormous remaining reserves and resources (>44,000 t reported in 2012, revised to 16,400 t Au in 2014) make the Witwatersrand Basin, and hence Witwatersrand-type deposits, the world's foremost depository of gold (Frimmel 2014). In terms of

overall gold endowment (past production + reserves + resources), Witwatersrand-type deposits rank first (31 % of total) followed closely by orogenic-type deposits (30 % of total). Porphyry deposits (16 % of total), epithermal deposits (12 % of total), Carlin-type deposits (4 % of total) and all other deposit types (7 % of total) are of much less significance (Frimmel 2008; see also Lipson 2014). Temporal distribution of orogenic gold deposits is closely linked with periods of enhanced crustal growth between 2.7 and 1.9 Ga as well as lesser peaks at around 2.9, 0.6, 0.28 and 0.12 Ga (Goldfarb et al. 2001; Groves et al. 2005a, b). Mode of deposition and timing of Witwatersrand gold mineralization has been a source of extreme controversy with disparate depositional models, syngenetic (palaeoplacer) and epigenetic, having been proposed (e.g. Robb and Meyer 1991; Minter et al. 1993; Barnicoat et al. 1997; Phillips and Law 2000). Data gathered over the past two decades clearly indicates that a purely epigenetic model is untenable, however, and that the principle stage of mineralization was indeed synsedimentary. Limited local remobilization of gold and other ore constituents by post-depositional fluids has occurred (modified palaeoplacer model of Robb and Meyer 1991); for a review and arguments for/against the various models, see Frimmel et al. (2005a).

It has been estimated that more than 80 % of all known gold was deposited in continental crust of Mesoarchaean age, and this gold was likely mantle derived (Frimmel 2008). Melts and hydrothermal fluids in the course of tectonic recycling of Archaean crust undoubtedly remobilized much of this early gold. Critical evidence for the repeated recycling of gold comes from Os concentrations and isotope ratios obtained from gold from various deposit types (Kirk et al. 2001, 2002; Frimmel et al. 2005a; Saunders et al. 2011). Witwatersrand gold can be regarded as 'primitive', not only because it is older than gold from most other deposits but more importantly because it contains orders of magnitude more Os than any other gold analyzed so far (Fig. 1). The wide range in Os concentrations obtained for Witwatersrand gold is controversial, however, and is presumably an artefact of sampling. Bulk analyses of gold from different reefs yielded the highest Os concentrations of as much as 4 ppm (Kirk et al. 2001), and these extraordinary concentrations are most likely due to osmiridium inclusions within the gold. Detrital osmiridium grains are rare but a conspicuous feature of the Witwatersrand ore mineralogy (Malitch and Merkle 2004). To overcome this potential contamination problem, carefully selected individual gold particles, rounded or toroidal, detrital and dendritic, secondary ones, as described in detail by Minter et al. (1993), were subsequently analyzed (Frimmel et al. 2005a, b). They yielded significantly lower Os concentrations on the order of 10 ppb—a level that is here taken as most representative of the true composition of Witwatersrand gold. Importantly, this level is still remarkable, considering that generally Os contents in gold are extremely low (Saunders et al.

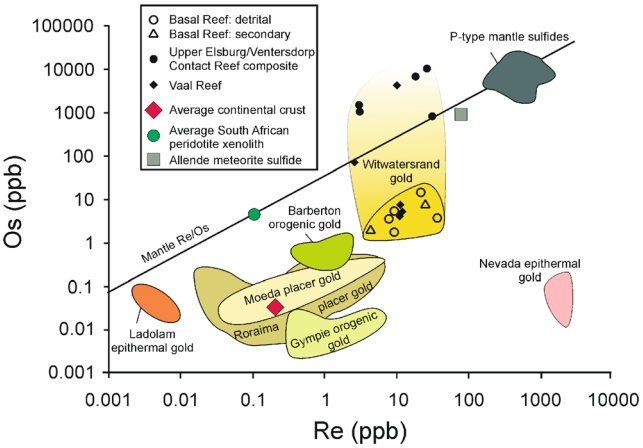


Fig. 1 Re versus Os concentrations for gold of different age and origin, compared with average continental crust, average South African peridotite xenolith and Allende meteorite and P-type mantle sulfide (modified after Frimmel et al. 2005a); note that the Mesoarchaean Witwatersrand gold has orders of magnitude higher Os contents than any younger gold (i.e. Neoarchaean Moeda palaeoplacer, Palaeoproterozoic Roraima palaeoplacer, Permo-Triassic Gympie orogenic-type gold, Tertiary Nevada epithermal gold and Holocene epithermal gold from Ladolam); the higher Os concentrations in the Witwatersrand samples are most likely an artefact of contamination with osmiridium inclusions, whereas the lower end of the range represents the true Witwatersrand gold composition

2011). Thus, the fact remains that Witwatersrand gold is considerably richer in Os than gold from any other deposit. Considering the low solubility of Os in aqueous fluids (Xiong and Wood 2000), the exceptionally high Os contents in the Witwatersrand gold effectively rule out a hydrothermal provenance, such as orogenic lode gold, volcanic-hosted massive sulfide (VMS) or epithermal deposits in eroded equivalents of surrounding greenstone belts, such as the 3.09–2.97 Ga Murchison Greenstone Belt (Jaguin et al. 2012), 3.08 to 3.04 Ga orogenic gold mineralization in the Barberton Greenstone Belt (Dziggel et al. 2010), syndepositional exhalative gold sources along the former basin margin (Hutchinson and Viljoen 1987) or gold from hydrothermally altered granites in the hinterland (Hallbauer and Barton 1987; Robb and Meyer 1990). Gold from some of Earth's oldest orogenic gold deposits, those of the Barberton greenstone belt, contains at least an order of magnitude less Os (Fig. 1) than Witwatersrand gold but still more than all younger gold, be it Palaeoproterozoic or Phanerozoic in age, and regardless of depositional origin (epithermal, orogenic or placer gold derived from orogenic-type deposits). Recycling of primitive Mesoarchaean gold by crustal fluid- and/or melt-rock interaction in the course of tectonic overprinting of Archaean crust perhaps resulted in progressively decreasing Os concentrations in gold (Frimmel 2008). Given the strong evidence for recycling of gold, it is conceivable that Witwatersrand-type gold deposits may have been widespread during the Mesoarchaean, but were consumed and their gold recycled by tectonic reworking of old crust. Only in a few

places that remained protected from tectonic reworking, such as the middle of the buoyant Kaapvaal Craton, were these original concentrations of gold preserved.

A syngenetic model for Witwatersrand deposits requires a mega-gold depositional event during the Mesoarchaean. Although the ultimate source of gold is likely the mantle, the question of how this gold was concentrated into Witwatersrand-type deposits is entirely unresolved. This enigma constitutes the focus of this paper in which it will be demonstrated that the evolution of life, coupled to that of the atmosphere, most likely played the critical role in the concentration of gold in early continental crust.

The Witwatersrand deposits in comparison to other conglomerate-hosted gold deposits

Conglomerate-hosted gold mineralization is by no means restricted to the Mesoarchaean Witwatersrand Basin but is a style of mineralization observed on almost all cratons and is common to many siliciclastic successions that developed on Archaean to Palaeoproterozoic basement. In a recent comparative compilation of worldwide Witwatersrand-type deposits (Frimmel 2014), a number of similarities, all of which confirm a syngenetic origin, but also some systematic differences came to the fore. They provide revealing clues as to the principal gold sources for these various deposits (Table 1).

The overall ore mineralogy of the Witwatersrand-type deposits/occurrences is strikingly similar, with differences being related primarily to age. Deposits that are older than the Great Oxidation Event (GOE) at c. 2.4 Ga are rich in both detrital and synsedimentary pyrite as well as detrital uraninite, whereas those younger than the GOE contain detrital Fe-oxides (haematite, magnetite). Moreover, many of the older Archaean examples, especially those that are particularly well-endowed in gold, contain more or less abundant stratiform kerogen layers (carbon seams) that represent former microbial mats (Hallbauer 1975; Minter 1991; Mossman et al. 2008; Horscroft et al. 2011; Frimmel 2014). Such carbon seams are conspicuously missing in all the younger, Palaeoproterozoic examples.

A further significant difference lies in the shape and size of gold particles in the various deposits. The presence of detrital gold particles has been ascertained in almost all examples, but much of that gold had been remobilized into texturally late positions in those deposits that had experienced low- to medium-grade metamorphic overprint. This is well documented for the Witwatersrand deposits (Frimmel et al. 1993; Gartz and Frimmel 1999; Hayward et al. 2005), those in the Huronian Supergroup (Long et al. 2011), the Jacobina (Milesi et al. 2002) and Moeda (Koglin et al. 2012) palaeoplacers (for location maps and stratigraphic columns, see Figs. A1–A5 in online supplementary material). This notwithstanding, many of these deposits, except for those in the Witwatersrand Basin, contain well-preserved gold nuggets that display variable degrees of mechanical abrasion and deformation, thus reflecting a range of transport distances from their respective sources in a former hinterland. Good examples are gold particles released by digestion in HF from the Moeda Formation and from the Roraima Supergroup (Fig. 2a, b, c and g) as well as gold nuggets of up to >1 mm diameter recovered from the deposits in the Hardey Formation in the Fortescue Group (Fig. 2j). Observations of primary gold inclusions within detrital quartz clasts (Fig. 2d) or within greenstone clasts (Fig. 2i) clearly attest to a greenstone-hosted orogenic-type gold-quartz vein system as source. Systematic differences in degree of rounding from proximal to distal depositional environments, together with sedimentological analyses, such as palaeocurrent directions, help in deciphering specific point sources—eroded former gold deposits in the hinterland. Such specific sources in the form of older, eroded gold deposits, be it greenstone-hosted gold-quartz veins or older conglomerate-hosted placer deposits, are indicated for many of the Witwatersrand-type deposits that are younger than 2.8 Ga, such as those in the Fortescue, Caraça, Jacobina and Tarkwa groups, the Roraima Supergroup, as well as in the younger deposits in the Kaapvaal Craton, specifically the Elsberg Reefs, Ventersdorp Contact Reef and the Black Reef. In contrast, no specific sources are known for the older examples in the Witwatersrand Supergroup, which has posed a major problem for the (modified) palaeoplacer model and has been used as critical argument by those favouring an epigenetic gold mineralization (e.g. Phillips and Law 2000).

Although the greenstone belts surrounding the Witwatersrand Basin host several orogenic-type gold deposits, some of which in the Barberton greenstone belt even have the same age (3.08 and 3.04 Ga, Dziggel et al. 2010) as indicated for the detrital heavy minerals (including some gold) in the Witwatersrand reefs, several lines of evidence speak against a derivation of the Witwatersrand gold from such greenstone-hosted gold-quartz veins. Apart from significant differences in the chemical composition between Barberton greenstone-hosted gold and Witwatersrand gold (Hallbauer and Barton 1987; Frimmel et al. 2005a), there is an insurmountable mass-balance problem. Total gold production from the greenstone belts in the Kaapvaal Craton (mainly from the Barberton goldfield) is approximately 385 t. Bearing in mind that the total area of exposed Archaean greenstone terrains in the craton is not significantly smaller than that of Central Rand Group subcrop, the main depository of Witwatersrand gold, the amount of gold mined from greenstone-hosted orogenic gold deposits is miniscule in comparison to the >52,000 t of gold recovered from the Witwatersrand goldfields so far. This comparison clearly highlights that the hypothetical amount of orogenic-type gold in the Palaeo- to Mesoarchaean hinterland is by far not sufficient to explain the huge amount of gold in the Witwatersrand Basin.

Table 1 Comparison of main features of known conglomerate-hosted gold deposits/occurrences

Supergroup/ group	Formation/reef	Age (Ma)	Metam. (low grade) overprint	Detrital gold	Gold nuggets >150 μ	Detrital Fe-phase	Detrital uraninite	Kerogen seams	Bitumen globules	Gold source	Gold endowment (t)[a]
Kaapvaal Craton											
Dominion	Dominion	3074	●	○	x	Pyrite	●	?	○	No evidence of specific gold deposits as point source(s)	<1
Witwatersrand/ West Rand	Bonanza	c. 2940	●	○	x	Pyrite	●	○	?		c. 3000
	Coronation/Rivas/ Government	c. 2935	●	○	x	Pyrite	●	○	?		
	Buffelsdoorn	c. 2930	●	○	x	Pyrite	●	○	?		
	Veldskoen	c. 2920	●	○	x	Pyrite	●	○	?		
Witwatersrand/ Central Rand	Ada May, Beisa, North, Main, South, Carbon Leader, Commonage	2900	●	●	x	Pyrite	●	●	●		c. 54000
	Middelvlei	c. 2890	●	●	x	Pyrite	●	○	○		
	Livingstone	c. 2870	●	●	x	Pyrite	●	○	○		c. 25000
	Basal, Steyn, Vaal, Saaiplaas, Leader, Monarch, Bird	2870	●	●	x	Pyrite	●	●	●		
	Crystalkop, Kalkoenkrans, A, B, Kimberley	c. 2850	●	○	x	Pyrite	●	○	○		c. 7000
	Denny's, Beatrix, Composite, Elsburg, EA, Bastard	c. 2850	●	○	x	Pyrite	●	○	○	Older Witwatersrand ore	
Ventersdorp	Ventersdorp Contact	2714	●	○	x	Pyrite	○	○	●	Witwatersrand ore	c. 7000
Transvaal	Black Reef	2664	x	●	○	Pyrite	●	x	●	Witwatersrand ore	c. 80
Pietersburg	Uitkyk	c. 2880–2670	●	○	?	Pyrite	?	x	○	VMS in Pietersburg Greenstone Belt	?
Pilbara Craton											
Fortescue	Hardey	c. 2760	x	●	●	Pyrite	●	x	○	Archaean basement	>55
Dharwar Craton											
Bababudan	Karthikere (basal congl.)	<2910>2720	●	?	?	Pyrite	●	?	?	Archaean basement	?
Chitradurga	Basal conglomerate	>c. 2500	●	○	?	Pyrite	○	?	?	Bababudan ore/ Archaean basement?	?
Singhbhum Craton											
Iron Ore	Basal conglomerate	>3000	●	○	?	Pyrite	●	?	?	?	?
Dhanjori	Basal conglomerate	<2900, ?	●	○	?	?	●	?	?	?	?
Sáo Francisco Craton											
Minas/Caraça	Moeda	2650	●	●	○	Pyrite	x	○	○	Orogenic gold	<1
Goiás Velho/ Fazenda Paraíso	Fazenda Cruceiro	>2400	●	?	?	Pyrite	●	○	○	Archaean basement	?
Jacobina	Serra do Corrego	>2400	●	●	○	Pyrite	●	○	○	Archaean basement	>5
Superior Province											
Huronian/ Elliot Lake	Matinenda	2450	○	○	x	Pyrite	●	x	○		>16

Table 1 (continued)

Supergroup/ group	Formation/reef	Age (Ma)	Metam. (low grade) overprint	Detrital gold	Gold nuggets >150 μ	Detrital Fe-phase	Detrital uraninite	Kerogen seams	Bitumen globules	Gold source	Gold endowment (t)[a]
Huronian/ Hough Lake	Mississagi	c. 2400	○	●	x	Pyrite	●	x	○	Archaean VHMS, orogenic gold Matinenda Fm.	
Hurwitz	Padlei	c. 2400 ?	○	?	?	Pyrite	?	?	?	?	?
West African Craton											
Tarkwa	Banket	2100	x	●	○	Haematite, magnetite	x	x	x	?	>830
Amazon-Sao Luis Craton											
Gurupi Belt	Igarape de Areia, Boa Esperanca and Viseu Congl.	c. 2100?	x	○	○	Haematite, magnetite	x	x	x	?	?
Roraima	several conglomerates above erosion surfaces	1900	x	●	○	Magnetite	x	x	x	Orogenic gold	<1
Congo Craton											
Muva/ Mporokoso	Mbala	c. 1800	●	?	?	Haematite, magnetite	x	x	x	?	?
Fennoscandian Shield											
Kumpu	Kaarestunturi	c. 1880	●	●	?	Haematite, magnetite	x	x	?	?	?

Black circle major, *dotted circle* minor, *letter 'x'* absent, *question mark* unknown

[a] Rough estimates based on reported production data and resources and extrapolated from company figures to stratigraphic allocation; note that, in many cases, a given company mines more than one stratigraphic unit

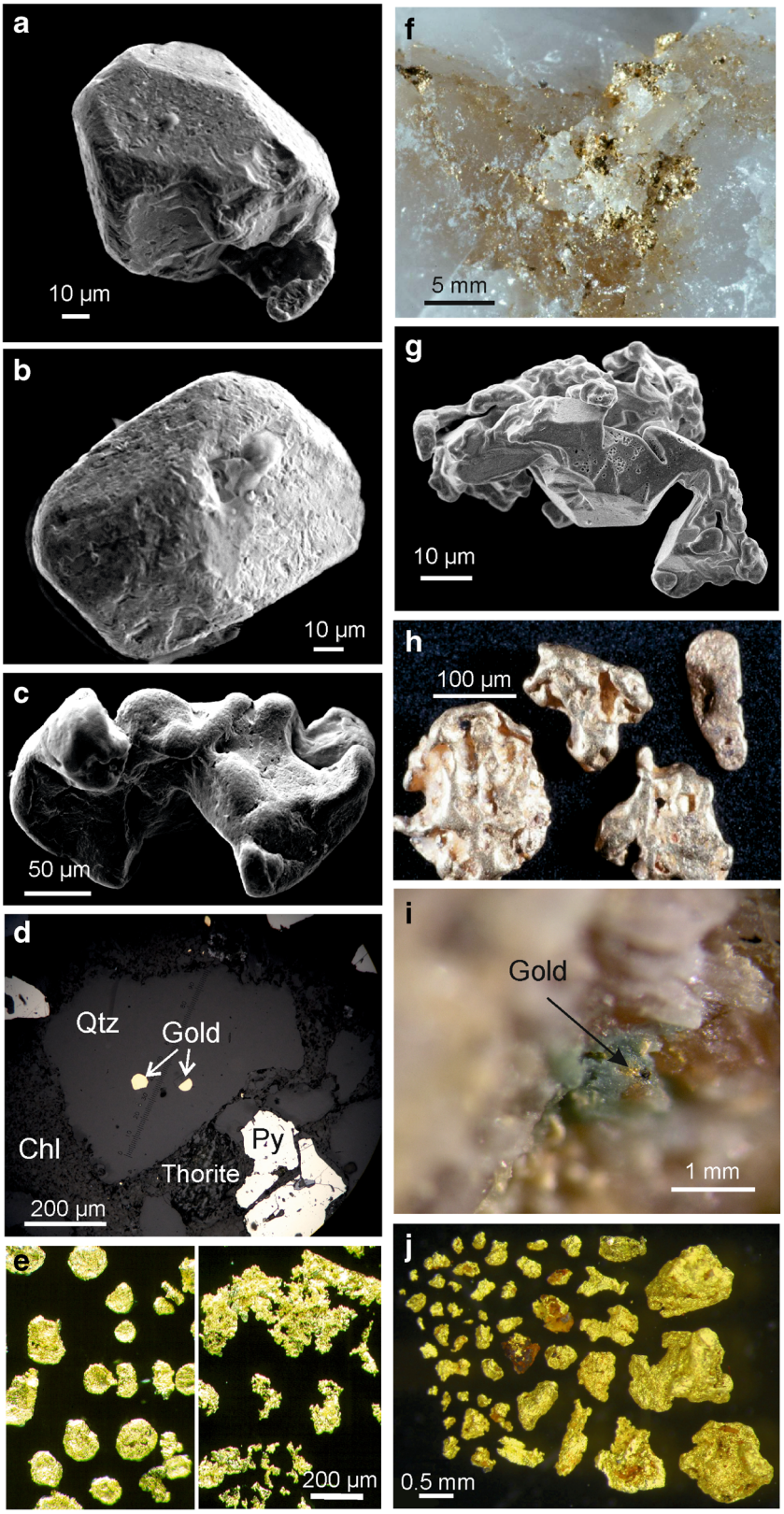


Fig. 2 Scanning electron microscope images and photographs of gold particles: **a**–**c** detrital gold from the Moeda Formation (Frimmel 2014), displaying a range from poorly rounded (**a**), intermediate (**b**) to well-rounded (**c**); **d** polished thin-section photo showing gold inclusions within detrital quartz (Qtz) in the Mississagi Formation conglomerate (Whymark 2014); **e** rounded and toroidal (*left*), primary and irregularly shaped, dendritic, secondary gold (*right*) particles from the Basal Reef, Welkom goldfield, Witwatersrand (Minter et al. 1993); **f** gold in quartz vein from the Omai deposit (Guyana greenstone belt); **g** poorly rounded, detrital gold from the proximal Roraima Supergroup; **h** well-rounded gold nuggets from the distal Roraima Supergroup, both derived from a source that was similar to the greenstone-hosted Omai orogenic-type deposit (**d**); **i** gold inclusion within clast of greenstone in Roraima conglomerate (courtesy of W.E.L. Minter); **j** gold nuggets from Beatons Creek Member conglomerate, Hardy Formation of the Fortescue Group at Beatons Creek, Nullagine, Western Australia

In short, three major differences exist between the richest Witwatersrand-type deposits, which occur in the Mesoarchaean conglomerates of the Witwatersrand-type gold province, and all the other, especially younger examples of this type of gold mineralization: (i) lack of proper gold nuggets and lack of specific point sources

(eroded gold deposits) in the hinterland, (ii) presence of carbon seams that tend to be particularly rich in gold and which are interpreted as representing some form of former microbial mats, and (iii) orders of magnitude larger gold endowment. It is suggested that these differences are not coincidental but the logical consequence of a gold-enrichment process that resulted from environmental conditions specific to this window of time in the Mesoarchaean world.

The role of hydrocarbons in the fixation of gold in Witwatersrand-type deposits

Hydrocarbons are, though usually very rare, a ubiquitous feature in many Witwatersrand-type deposits, especially in Archaean ones. Two principal types of textural appearance of such hydrocarbons can be distinguished: (i) bituminous globules (Fig. 3) and (ii) carbon seams (Fig. 4). Vitrinite reflectance and Rock-Eval pyrolysis data for both types

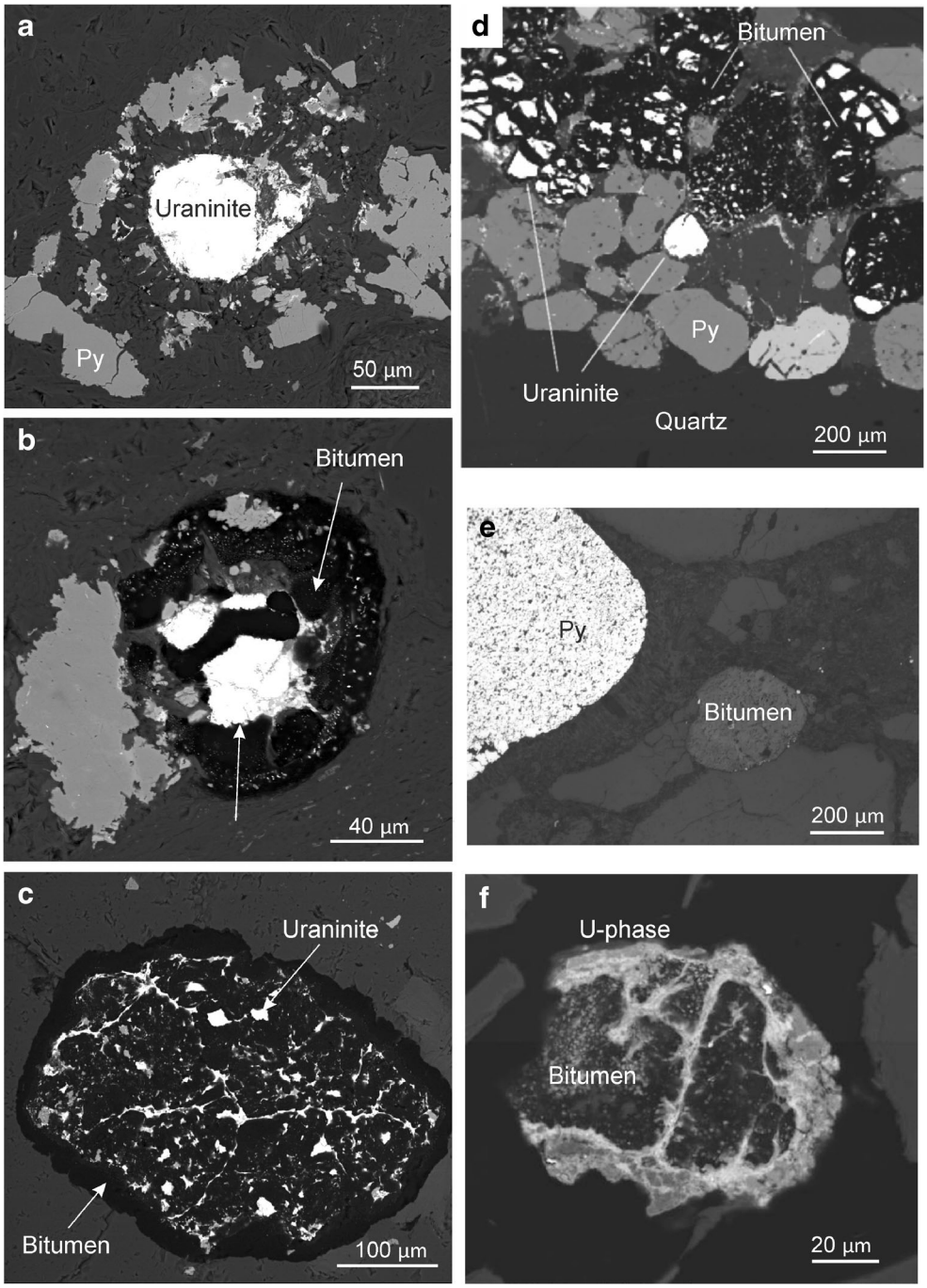
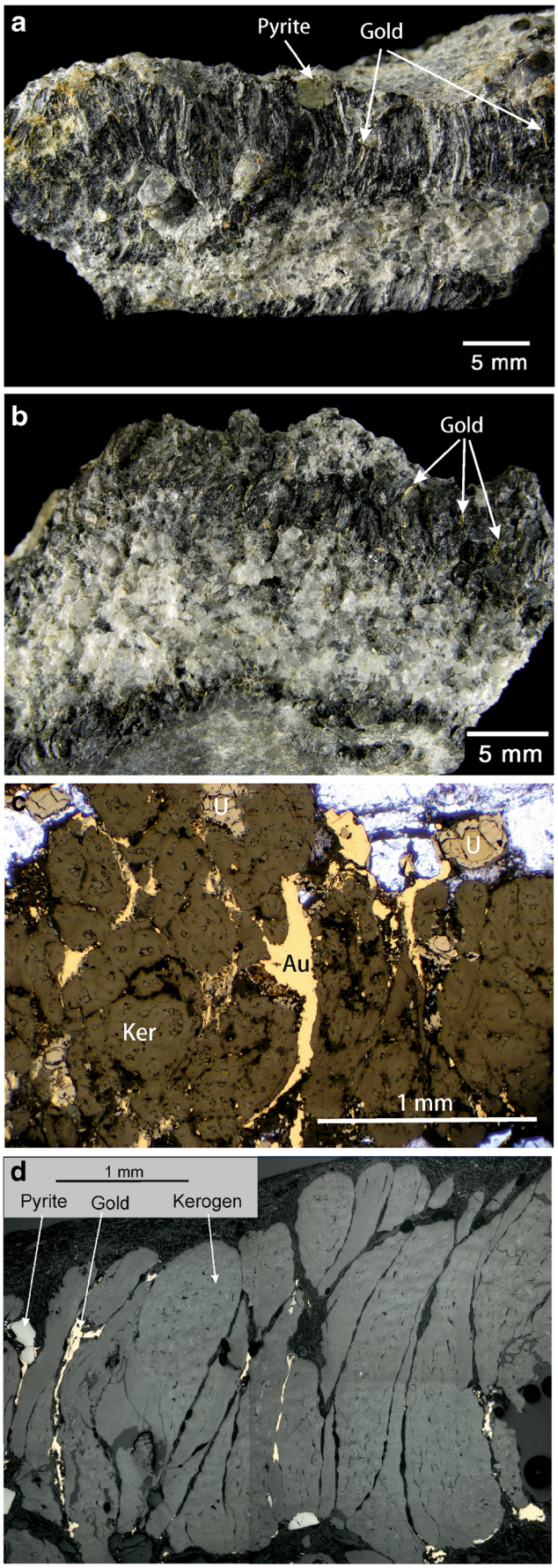


Fig. 3 BSE images showing textural relationships between uraninite and post-depositional pyrobitumen in Witwatersrand-type deposits: **a**–**c** 2.66 Ga Black Reef, base of Transvaal Supergroup: **a** rounded detrital uraninite grain without bitumen, surrounded by white mica, in pyrite-rich (Py) auriferous conglomerate; **b** pyrobitumen globule with fragments of detrital uraninite in its core; **c** pyrobitumen that almost completely replaced uraninite (partly altered to brannerite) (**a**–**c** courtesy G. Nwaila and A. McLoughlin); **d** pyrobitumen (*black*) enclosing broken-up detrital uraninite fragments (*white*) in quartz-pyrite pebble conglomerate, note that some uraninite (rounded grain in the middle) is not enclosed by pyrobitumen, Vaal Reef, Great Noligwa mine, Klerksdorp goldfield, Witwatesrand (from Depiné et al. 2013); **e** pyrobitumen globule in auriferous conglomerate of the Hardey Formation; **f** pyrobitumen globule (*dark*) surrounded by secondary U-phase (*light grey*) in conglomerate from the Beatons Creek Member of the Hardy Formation, Fortescue Group at Beatons Creek, Nullagine, Western Australia



◀ **Fig. 4** Gold-bearing kerogen (carbon) seams at the base of auriferous conglomerates in the lower Central Rand Group, Witwatersrand: **a**, **b** hand specimen, with interstitial heavy mineral (pyrite, uraninite) concentrate, base of Vaal Reef, Stilfontein mine, Klerksdorp goldfield; note thin gold platelets interstitially between kerogen columns; **c** microphotograph under combined transmitted and reflected light of a kerogen seam (Ker) that is rich in thin platy gold (Au), intercalated between heavy mineral concentrate, here uraninite (U), from the base of the B-Reef, Tshepong (previously Freddies) mine, Welkom goldfield; **d** reflected light microphotograph of kerogen seam, displaying columnar microstructure with gold platelets in between columns, base of Carbon Leader, West Driefontein mine, Carletonville goldfield

obtained on Witwatersrand samples reflect high thermal maturity that is in good agreement with the peak metamorphic temperature of 350±50 °C (Gray et al. 1998; Spangenberg and Frimmel 2001). Carbon isotopic data on both types attest to a biogenic origin of the C (Hoefs and Schidlowski 1967; Spangenberg and Frimmel 2001).

Pyrobitumen globules

Pyrobitumen globules occur preferentially within conglomerate, in which they are irregularly distributed, isolated or in clusters, or concentrated within cross-cutting veins, in which they are associated, in places, with galena, sphalerite, pyrite, pyrrhotite, chalcopyrite, gersdorffite and native gold, and in which they can reach centimetre size (Gartz and Frimmel 1999). Where present as isolated globules (colloquially referred to as 'flyspeck carbon') within the conglomerate, they enclose in many cases rounded, fragmented uraninite (Fig. 3b and d), which has led to the suggestion of their formation having been due to polymerization and cross-linking of liquid hydrocarbons around irradiating detrital uraninite (Schidlowski 1981; England et al. 2001). Their textural position leaves no doubt that they are related to migrating oils, which is further supported by the presence of oil-bearing fluid inclusions (Drennan and Robb 2006). It is noteworthy that even the secondary, hydrothermal gold generation in the Witwatersrand ores is exceptionally rich in Os (Frimmel et al. 2005a), which supports the concept of remobilization by oil-rich fluids because of the relatively high solubility of Os in organic solvents as opposed to its extremely low solubility in aqueous fluids (Xiong and Wood 2000). In the case of the Witwatersrand Basin, oil migration took place repeatedly from early diagenesis (England et al. 2002a) to epigenetic fluid circulation triggered by the giant 2020 Ma Vredefort impact event (Frimmel et al. 1999). These fluids were capable of transporting Au, thus contributing to the local remobilization of originally syngenetic gold, but without having a significant influence on the basin-wide distribution of the ore. Such pyrobitumen globules have been described from several Witwatersrand reefs, the Ventersdorp Contact Reef, the Black Reef, as well as the auriferous conglomerates in the Huronian

Supergroup and the Fortescue Group. Especially in the younger of these examples, there is also evidence of the pyrobitumen globules containing secondary U-minerals (Fig. 3f).

Carbon seams

The carbon seams form stratiform layers, a few millimetres to several centimetres in thickness, or thin films of hydrocarbons at the bottom of the auriferous conglomerate beds (Fig. 4). They occur on erosional unconformities, scour surfaces and bedding planes (Fig. 5a and b), where they show stromatolite-like columnar microstructures perpendicular to bedding. Where present, they tend to be particularly rich in gold. In some Witwatersrand reefs, such as the B-Reef in the Welkom goldfield, as much as 70 % of all the gold has been reported as attached to carbon seams (Hallbauer and Joughin 1973). Other estimates suggest that about 40 % of all the Witwatersrand gold is associated with carbon seams (Nagy 1993). While the epigenetic nature of the pyrobitumen globules is beyond doubt, the nature of the carbon seams has been controversial. Initially, the carbon seams were interpreted as remnants of former algal mats with the columnar morphology reflecting biological growth structures (Hallbauer 1975). Subsequently, this view was challenged and an epigenetic origin was favoured by several workers who interpreted the columnar structures as aggregates of bitumen globules that became plastically deformed in a post-depositional stress field (Gray et al. 1998; Parnell 1999; England et al. 2001). Such an epigenetic formation by solidification of migrating oils is, however, not tenable for reasons summarized by Mossman et al. (2008) and Frimmel (2014). Some of the arguments in favour of an indigenous origin in the form of microbial mats are the presence of clasts of (gold-mineralized) carbon seams in palaeoerosion channels that truncate in situ carbon seams and thin kerogen films that drape ripple surfaces or desiccation cracks. The latter is well displayed by Fig. 5c and d, which show desiccation cracks at the bottom of the Vaal Reef being filled with kerogen, thus clearly illustrating microbial growth within these desiccation cracks subsequent to exposure of the sediment surface.

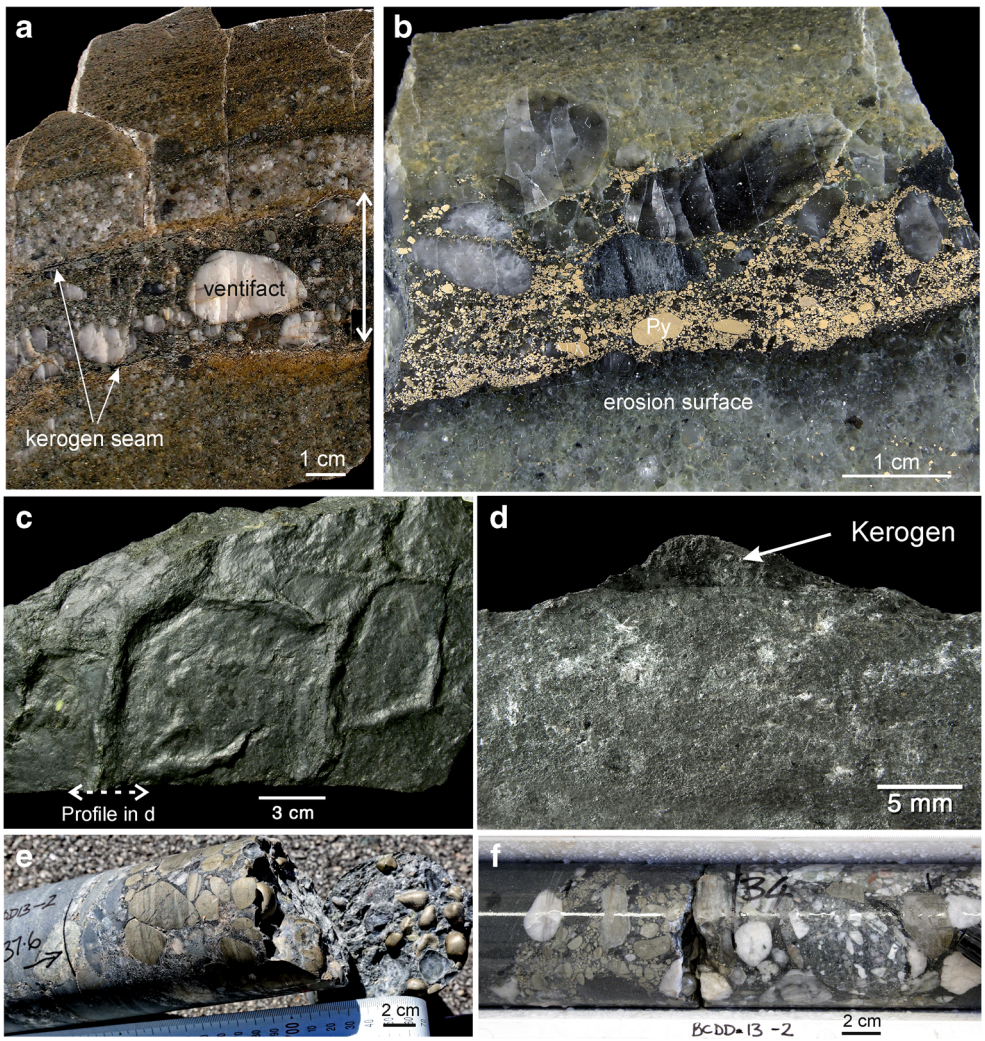


Fig. 5 **a** Pebble lags on multiple scour surfaces with thin kerogen seam at the bottom of each pebble lag, Steyn Reef, President Steyn mine, Welkom goldfield, Witwatersrand; aeolian deflation surface (*vertical double arrow*) with ventifact and kerogen seam at its bottom and top contact; **b** thin pebble lag with rounded pyrite (Py) clasts concentrated on top of erosional palaeosurface, Vaal Reef, Stilfontein mine, Klerksdorp goldfield, Witwatersrand; **c** dessication cracks at the bottom contact of the Vaal Reef, Stilfontein mine; **d** cross section through one of the dessication cracks (*upside down*) showing that the dessication crack is filled with kerogen; **e** *rounded*, detrital pyrite in conglomerate of the Beatons Creek Member, Hardey Formation, Fortescue Group, Nullagine, Western Australia; **f** polymictic, largely pyritic conglomerate with reworked conglomerate clast, Beatons Creek Member

The chemical and isotopic characteristics of the Witwatersrand carbon seams have been described by Spangenberg and Frimmel (2001). The dominant compounds that are resolvable in gas chromatograms are *n*-alkanes in the C_{15} to C_{27} range (without odd-even predominance) and the acyclic isoprenoids pristine and phytane, with minor amounts of mid-chain methyl- and dimethyl-branched alkanes and traces of *n*-alkylcyclohexanes and methyl-alkylcyclohexanes. The pristane/phytane ratio is generally <1, which points to reduction of phytol moieties and/or bacterial cell walls in an anoxic environment (Didyk et al. 1978). The $\delta^{13}C$ ratios of the *n*-alkanes and isoprenoids range from −28.5 to −34.8‰ (V-PDB) with very little variation between individual *n*-alkanes, which indicates a single local source of the *n*-alkanes and isoprenoids. Any longer range migration and/or mobilization of the hydrocarbons would have led to C isotope fractionation effects which are not seen in the samples investigated. Microstructural, textural as well as organic geochemical and isotopic evidence speaks for the carbon seams to represent in situ microbial mats. These should be referred to, therefore, as kerogen rather than as pyrobitumen. The strong spatial association of gold with this kerogen raises the question of the possibility of microbially mediated fixation of gold as suggested by Horscroft et al. (2011) and of the kind of microbes that existed at the time of Witwatersrand sediment deposition.

Kerogen seams as remnants of the first oxygenic photosynthesizing microbes

While agreement exists on the biogenic origin of the Witwatersrand carbon seams, the nature of this biomass remains poorly constrained. Critical here is the question whether some of the microbes that populated the flanks of braided rivers, fluvial deltas and coastal environments in the Mesoarchaean were O_2-producing. First forms of life in Earth's history most certainly evolved in anoxic environments in which geochemical energy gradients, supporting electron flow, enabled the formation of complex organic molecules from organic monomers. The availability of metals is considered a critical factor in the evolution of early life (Fedonkin 2003). The intracellular conditions in the first cells most likely corresponded to those of their surroundings because of the lack of an ion-impervious membrane in these cells. High concentrations of Zn and P as well as the K/Na ratio in modern cytoplasm are similar to those in hydrothermal fields but entirely different to those expected in the early ocean, which suggests that hydrothermal fields, such as black smokers on the ocean floor, played a prominent role as loci for the formation of first cells (Russell and Hall 1997). While the first microbes were most certainly anaerobic chemoautotrophic, they were followed by the emergence of anaerobic photoautotrophic forms for which photosynthesis provided the necessary energy. Amongst the latter, anaerobic anoxygenic forms, such as sulfur bacteria, are distinguished from anaerobic oxygenic forms, such as cyanobacteria. The timing of the first appearance of anaerobic oxygenic microbes remains uncertain but must have been long before the GOE at around 2.4 Ga. Microbes tend to live in complex communities and it is, therefore, most probable that both anoxygenic and oxygenic forms lived together with a gradual shift towards dominance of the latter. Prior to the GOE, O_2 produced by oxygenic photosynthesis was quickly consumed by oxidation reactions, mainly of sulfides and Fe^{2+} dissolved in the Archaean ocean. Only after these compounds in the ocean water had been oxidized could the concentration of atmospheric O_2 rise rapidly, which eventually led to the GOE. Over the last few years, an increasing number of independent studies have shown that first oxygenation of the Archaean atmosphere had occurred, however, long before (at least 600 Myr) the GOE; for a recent review of arguments, see Lyons et al. (2014).

Palaeosols have served as powerful source of information on early atmospheric evolution. Few examples of Archaean palaeosols have been documented on the Pilbara, Kaapvaal and Singhbhum cratons in Western Australia, South Africa and India, respectively. Based on Cr isotope ratios in the 2.98–2.96 Ga Nsuze palaeosol and overlying shallow-marine 2.96–2.92 Ga iron formation in the Pongola Supergroup, southeastern Kaapvaal Craton, Crowe et al. (2013) constrained the atmospheric O_2 concentration at a minimum of c. 10^{-4} PAL. This value exceeds the modelled maximum of O_2 produced by Archaean atmospheric photochemical reactions (Haqq-Misra et al. 2011), which led to the suggestion of at least some oxygenic photosynthesis having taken place already at around 3.0 Ga. More recently, this interpretation found independent support from a Mo isotope study on 2.95 Ga rocks from the same succession in the Pongola Supergroup, which indicates the oxidation of Mn in the water column at that time—a feature that requires elevated O_2 concentration (Planavsky et al. 2014). Other evidence of oxidizing conditions comes from negative Ce anomalies that have been reported for both shallow-marine and terrestrial environments, 2.8 Ga limestone in the Canadian Shield (Riding et al. 2014) and the 3.29–3.02 Ga Keonjhar palaeosol on the Singhbhum Craton in eastern India (Mukhopadhyay et al. 2014). First 'whiffs' of atmospheric oxygen are also suggested by secular changes in the trace element concentration in synsedimentary/early diagenetic pyrite, especially in Se-peaks in synsedimentary pyrite from 2.97 Ga Witwatersrand shales (Large et al. 2014).

Notwithstanding the fact that the Archaean atmosphere was reducing with O_2 levels of $<<10^{-5}$ PAL as indicated by the abundance of detrital uraninite and pyrite in Archaean fluvial and littoral sediments (Frimmel 2005) and by mass-

independent S isotope fractionation (Farquhar and Wing 2003; Farquhar et al. 2007), the above evidence suggests that, locally, oxygenic photosynthesis was already taking place from at least Mesoarchaean times. In that case, the stromatolitic and microbially induced sedimentary structures described from rocks as old as 3.2 Ga in the Kaapvaal Craton (Noffke et al. 2006, 2008) are most likely related to the growth of oxygenic photosynthesizing cyanobacteria or other mat-constructing microbes. Similarly, it is suggested that the kerogen seams along the bedding planes of some of the Witwatersrand reefs reflect the remnants of such cyanobacterial or other oxygenic photosynthesizing microbial mats.

This recognition opens up the possibility for a holistic genetic model that overcomes all of the previously existing problems with a palaeoplacer model for Witwatersrand gold. Critical for such a model is the emergence of first oxygenic photosynthesizing microbes around the time of maximum gold concentration into Meso- and Neoarchaean sediments because they provided an ideal and most effective trap for gold in the Archaean environments.

The big Archaean gold trap

The peculiarities of the Archaean environments provided sharp geochemical gradients within the Archaean surface systems, distinctly different to today's, which help to explain why so much gold was trapped in some Archaean sediments. The Mesoarchaean atmosphere was not only extremely low in O_2 ($<10^{-5}$ PAL, some authors would argue for even $<10^{-11}$ PAL, Kurzweil et al. 2013) but at the same time contained elevated CO_2 and CH_4 concentrations with a high CH_4/CO_2 ratio, thus off-setting the cooling effect of a faint early sun. Their concentrations, in combination with those of SO_2 and H_2S have been modelled on the basis of the observed pattern of mass-independent S isotope fractionation (Halevy et al. 2010; Kurzweil et al. 2013). High atmospheric CO_2 as well as SO_2 and H_2S concentrations are invariably a consequence of volcanic degassing in the Archaean, with the SO_2/H_2S ratio being essentially controlled by the proportion of submarine to subaerial volcanism (Gaillard et al. 2011). Contemporaneous rainwater was acidic, with a pH estimated at around 4 (Krupp et al. 1994), and consequently caused deep chemical weathering of the Archaean land surface. Evidence of such weathering is prevalent in geochemical profiles across Archaean erosion surfaces, which are marked by high chemical index of alteration (CIA) values in the respective footwalls (Frimmel and Minter 2002). The most important weathering reaction was the conversion of feldspars to clay minerals (mainly kaolinite), which explains the lack of detrital feldspar grains in most Archaean fluvial to fluvio-deltaic conglomerates. This reaction is acid-consuming and buffered the pH in river water to approximately 6 (Frimmel 2005). The stability of detrital pyrite and, more importantly, the growth of synsedimentary pyrite (concentrically laminated pyrite) in these waters indicate elevated H_2S contents. At lower atmospheric H_2S fugacity ($<10^{-5}$), siderite should be stable instead of pyrite. Detrital siderite has been reported, together with detrital pyrite, from the Fortescue Group in the Pilbara Craton (Rasmussen and Buick 1999), which is as young as 2.76 Ga. In all older fluvial and fluvio-deltaic siliciclastic deposits, detrital pyrite is omnipresent and thus elevated H_2S fugacity is postulated for the Palaeo- to Mesoarchaean environments. A shift towards higher SO_2/H_2S ratios in the Neoarchaean is also indicated by the S isotope record and has been explained by a corresponding shift from submarine to subaerial eruption in the formation of large igneous provinces (Halevy et al. 2010).

Under the given chemical conditions for Mesoarchaean meteoric waters, Au would be dissolved as $AuHS_{(aq)}$ or as $Au(HS)_2^-$, depending on the proportions of dissolved S^{2-} and Cl^- (Stefánsson and Seward 2004). Experimental data for the solubility of Au in aqueous sulfide solutions exist for elevated temperatures between 150 and 500 °C (Shenberger and Barnes 1989; Hayashi and Ohmoto 1991; Stefánsson and Seward 2004). Extrapolation of these data to lower temperatures does not change the overall topology of Au solubility contours in fO_2–pH space (as shown in Fig. A6) and suggests several orders of magnitude greater solubility of gold in Mesoarchaean meteoric waters compared to modern river water (Frimmel 2014). Thus, an extremely high fluvial Au flux from the Mesoarchaean land surface into fluvio-deltaic, coastal and eventually marine environments can be assumed.

Precipitation of gold from such Au-rich river waters is most easily achieved by oxidation as evident from the field with the narrowest spacing of the Au solubility contours in Fig. A6. Only a very small increase in fO_2 would lower Au solubility by orders of magnitude. This small increase in fO_2 in an overall O_2-deficient Archaean world could have been caused by the first photosynthesizing microbes. Wherever and whenever river water with a high dissolved Au load came into contact with the surface of the postulated (cyanobacterial) microbial mats (today's kerogen seams), gold would have precipitated according to the oxidation reaction:

$$4\,Au(HS)_2^- + 15\,O_2 + 2\,H_2O = 4\,Au + 8\,SO_4^{2-} + 12\,H^+.$$

Elevated gold concentrations in Mesoarchaean river waters are further supported by pyrite chemistry. It has been shown that amongst all the various morphological pyrite forms, the rounded, concentrically laminated pyrite has the highest concentrations of Au (Koglin et al. 2010). This pyrite type, which

is present in all of the coarser grained siliciclastic units of the Witwatersrand Supergroup, the Ventersdorp Contact Reef and even the much younger Black Reef, has long been suspected to be of synsedimentary origin (Barton and Hallbauer 1996; England et al. 2002b; Guy et al. 2010). The finding of anomalously high Au in this pyrite type has since been confirmed by further studies on pyrite chemistry by Large et al. (2013) and Agangi et al. (2013), and the interpretation of this pyrite to have formed by in situ growth in the wet sediment has found support from trace element, S and Fe isotope studies (England et al. 2002b; Hofmann et al. 2009; Guy et al. 2012; Agangi et al. 2015). The only plausible explanation for this observed accumulation of gold in syngenetic pyrite that has grown in fluvial to fluvial-deltaic environments is the trapping of Au from river water on the surface of the growing pyrite grains, whether by purely chemical processes or by microbial mediation.

From microbially mediated to placer gold

Precipitation of gold on the surface of oxygenic photosynthesizing microbial mats explains not only the observed very high concentration of gold in the kerogen seams along the contacts with Mesoarchaean conglomerates but it also explains the conspicuously fine grain size and the lack of proper gold nuggets in coeval palaeoplacers. The microbial mats, which had grown in low-energy environments, such as temporarily flooded river banks in braided river systems, estuaries, lagoons or shallow shelves, are delicate structures with little preservation potential. Any regressive stage in the littoral region or flooding event in the braided river system would invariably have led to fluvial reworking of the freshly deposited microbial mats into coarser grained fluvial deposits, such as the auriferous conglomerates. This is beautifully evidenced by the truncation of carbon seams, that developed on very gently dipping unconformities or disconformities, by fluvial erosion channels. The best examples have been recorded in the Carbon Leader reef, one of the richest reefs with particularly well-developed kerogen seams. This reef is cut in several places by up to 2.2 km wide and up to 100 m deep palaeochannels (Engelbrecht et al. 1986; Frimmel 2014), with reworked clasts of mineralized carbon seams present in the conglomeratic channel fill (Mossman et al. 2008). Platy and filamentous gold particles released from the carbon seams by fluvial reworking would have been rolled into micro-nuggets and redeposited downstream as heavy mineral concentrate. Many of the rounded micro-nuggets described from several reefs (Hallbauer and Joughin 1973; Minter et al. 1993) can be thus explained.

Elsewhere, on aeolian deflation surfaces, microbial mats would have dried up and become removed by wind. The delicate thin gold platelets on the growth surfaces of the microbial columns would have been released and blown away as flakes. A typical morphological expression of wind-blown gold particles is toroids with double-sided overfolded rims that result from peening by saltating sand grains (Filippov and Nikiforova 1986). Such forms have been described from the Basal Reef, where a concentrate of gold particles (together with other heavy minerals) defines the foresets and bottomset of a cross-bedded structure (Fig. 6), and they are astonishingly similar to the shapes of wind-blown gold on a Miocene deflation surface in Yakutia, Siberia, gold from recent stormy beaches of South Island, New Zealand, as well as gold particles produced experimentally in wind tunnels (Minter 1999). The relatively common occurrence of ventifacts in pebble lags and thin reefs that represent aeolian deflation surfaces throughout the Central Rand Group only adds to the evidence of strong winds in the depositional environments. Stormy environments were most likely the norm rather than the exception in the Archaean because of a higher rotation rate of Earth at that time, estimated to be 1.3 to 1.8 times higher than today (Williams 2000).

Derivation of the evidently detrital rounded to toroidal gold particles, for which a mean nominal diameter of 135 μm has been calculated (Minter et al. 1993), predominantly from similar-sized gold platelets and filaments within microbial mats (Fig. 6), solves the riddle of the lack of proper gold nuggets in the Witwatersrand deposits. It also solves the traditional source problem.

The source of the Mesoarchaean gold

Large-scale leaching of gold from the Palaeo- to Mesoarchaean land surface by meteoric waters removes the necessity for discrete gold deposits in the hinterland to have provided the bulk of the placer gold. Gold at background levels in the juvenile Archaean crust becomes the principal source instead. These background concentrations were most likely considerably elevated relative to post-Archaean crustal values for several reasons. Archaean crust formed when Earth's mantle was hotter (Labrosse and Jaupart 2007) and the degree of melting in the upper mantle correspondingly higher. Such conditions favour the production of S-undersaturated melts, which are known to be richer in Au than S-saturated ones. This is well reflected by elevated Au contents in Archaean komatiites (Pitcairn 2011). An ultimate source of the gold in the Archaean mantle is indicated by the fact that amongst all gold analyzed so far, Witwatersrand gold is characterized by Re/Os ratios that most closely approximate that of the mantle (Fig. 1), and also by its Os isotopic characteristics (Kirk et al. 2002; Frimmel et al. 2005a). Thus, the rate of gold extraction from the mantle into the crust is likely to correspond to the overall rate of juvenile crust formation, which was highest in the Archaean when probably >70 % of

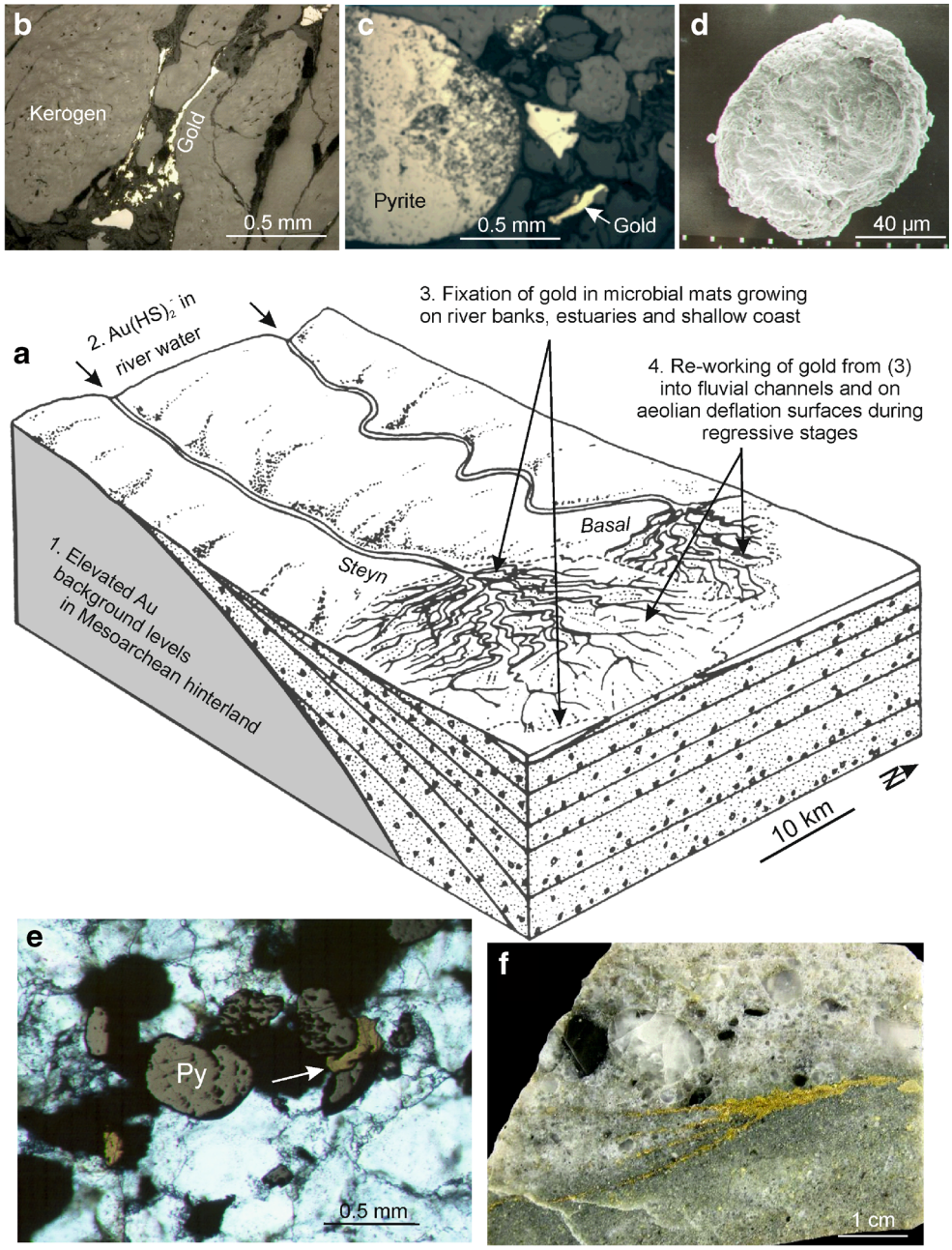


Fig. 6 **a** Schematic block diagram illustrating the likely depositional environments of a braid delta, using the Steyn and Basal reef palaeoplacers in the Welkom goldfield as example (after Minter et al. 1993), also highlighting the four principal stages involved in the formation of the gold deposits; **b**–**d** photographs illustrating different stages of reworking of microbial mat-hosted gold to placer gold: **b** gold platelets/filaments on surface of microbial columnar structures, Vaal Reef (see Fig. 4b); **c** gold toroid with overfolded rim in conglomerate next to kerogen seam shown in Figs. 4b and 7b; **d** SEM image of gold toroid with overfolded rim, Basal Reef; **e** in situ gold toroid with overfolded rim (*arrow*) between detrital pyrite grains (Py) in Basal Reef, under combined transmitted and reflected light; **f** gold concentrated along crossbeds in pebbly quartz arenite at base of Basal Reef, Free State Geduld mine, Welkom goldfield

the existing continental crust had originally formed (Belousova et al. 2010).

In addition to the higher degrees of melting in the Archaean mantle, mantle domains enriched in highly siderophile elements (HSE), such as Au, are expected to have contributed towards an overall higher Au background value in the Archaean crust. Such HSE-enriched domains in the mantle most likely formed due to largely Hadean endogeneous and/or exogeneous processes. The former includes incomplete core-mantle separation after formation of the planet, with some HSE-rich metal retained in the mantle; the latter are what is often explained by the 'late veneer hypothesis', that is the continued accretion to Earth of extraterrestrial material with chondritic abundances of HSE. Addition of asteroidal, HSE-rich material took place mainly in the Hadaean until c. 3.9 Ga (Zahnle et al. 2007) but would have been available for crust formation only several hundreds of millions of years later, depending on the mantle overturn rate at the time. Thus, it is likely that at least some domains of the mantle from which Archaean crust was extracted were enriched in HSE.

Archaean seawater as alternative gold source

While a strong case can be made for high Archaean Au flux off the Archaean land surface by meteoric waters,

contemporaneous seawater could have been an alternative source for microbially mediated gold formation (Horscroft et al. 2011). The Archaean ocean would have, of course, the huge advantage of being far more voluminous and thus a potentially much larger Au reservoir than any surface water.

Ultimately, the overall gold budget of Archaean seawater must have been dependent on (i) the supply of Au from the Archaean land surface, (ii) the supply of Au from submarine hydrothermal venting, (iii) the physico-chemical conditions of the ocean water, dictating the solubility of Au complexes and, possibly, (iv) the level of bio-productivity, influencing the fixation of Au onto organic matter, and (v) the sedimentation rate of carbonaceous muds.

While the underlying oceanic crust could have served as equally fertile source of the Au as the Archaean continents, it must be ascertained whether seawater at that time had a similarly suitable chemistry for dissolving/transporting large amounts of Au similar to coeval meteoric waters. Under the same reducing atmosphere, the pH of Mesoarchaean seawater would have also approached near neutral values based on the observation that many Algoma-type iron formations of Archaean age have coevally precipitated hydrothermal pyrite (sulfide facies) and magnetite (oxide facies) (Gross 1980), which are mutually stable at pH values of around 6–8 (Fig. A6). These same iron formations also commonly bear considerable siderite (carbonate facies), which is unstable under low pH conditions. Archaean Algoma-type iron formations of the Superior Province, Canada, commonly display elevated gold contents at levels of about an order of magnitude above crustal background (Gross 1988), a likely reflection of the presence of significant soluble Au in the seawater from which they formed. Submarine volcanism dominated the oceans, resulting in a high H_2S/SO_2 ratio in seawater, a concept that has found support from mass-independent S isotope fractionation patterns (Gaillard et al. 2011). Under these conditions, Au-sulfide complexes dominate.

From the temporal distribution of iron formations and bedded sulfate deposits, in combination with observed changes in $\delta^{34}S_{sulfate}$, three periods of different ocean water chemistry have been distinguished through the Archaean and Palaeoproterozoic eras (Huston and Logan 2004): (i) prior to c. 3.2 Ga, the ocean was S-poor and stratified with somewhat elevated S contents in the top waters, (ii) in Meso- and Neoarchaean times generally S-poor ocean chemistry prevailed and (iii) followed by a period of gradual increase in total S content of the oceans after the GOE, first in top, later in bottom waters. As illustrated by the existence of low-sulfidation epithermal gold deposits, the amount of total dissolved S necessary to transport Au as sulfide complex must be small. Consequently, even the Mesoarchaean ocean should have had a considerable capacity for high dissolved Au concentrations.

Geological evidence can be taken as suggestive of seawater having also played a critical role as supplier of Au only to be fixed by microbes in shallow-marine settings. For some of the microbial mats in the Witwatersrand strata, a distal, low-energy environment, such as an estuary or shallow shelf, is indicated. Tidal action would have supplied Au as well as Os, which occurs in such elevated concentrations in the Witwatersrand gold, in daily rhythms to the microbial mats and thus contributed to the microbially induced fixation of gold on these mats. During regressive stages, these microbial, gold-bearing mats would have been reworked first by retreating waves and then by fluvial channels that prograded over the exhumed estuary or shelf, thus generating the gold-bearing conglomerates.

In the Pilbara Craton, terrestrial conglomerates that were deposited far from the coast typically are low in gold whereas conglomerates that display evidence of contact with the oceanic environment commonly contain appreciable gold. At Beatons Creek near Nullagine, Western Australia, transgressive lag conglomerates within the Beatons Creek Member of the Hardy Formation contain significant amounts of gold as do conglomerates that are interbedded with marine black shales immediately beneath the Mt. Roe Basalt at the Tassie Queen Mine near Marble Bar, Western Australia.

Although gold-enrichment processes may have acted in the shallow-marine environment, evidence for gold enrichment in deep-marine siliciclastic sedimentary rocks from the Mesoarchaean is mixed. Marine metapelites in the Witwatersrand Supergroup do not show Au concentrations significantly above average crustal values (Phillips 1987). Only locally, in the immediate vicinity of auriferous conglomerates, elevated gold contents were noted in the same study and these can be ascribed to local remobilization of gold during post-depositional alteration. The lack of gold enrichment in deeper marine sediments of the Witwatersrand may be explained by a lack of planktonic photosynthesizing microbes at that time, thus no gold-precipitation mechanism was available to contribute gold to the sediment column, or perhaps, gold grades were diluted where sedimentation rates were higher. Unfortunately, Mesoarchaean marine turbidite sequences, the material with which the latter hypothesis could be tested, are only poorly represented in the geological record. One of the few well-preserved turbidite sequences from this time is the c. 2.93 Ga Mosquito Creek Formation near Nullagine in the Pilbara Craton. Pelites and psammites therein display high background Au concentrations, tens to hundreds of parts per billion, and conglomerate facies within the apex of the fan contain in places as much as 1.4 ppm Au (unpublished data; Novo Resources Corp.).

Evolution of the style of major crustal gold concentration through the Precambrian

A number of geochemical, geological and biological peculiarities, especially in the Precambrian, do not conform to

actualistic principles but reflect gradual changes in boundary conditions. It is well established that geological, biological and atmospheric evolution are closely linked with each other, which had profound effects on the concentration of metals in the crust, thus explaining temporal peaks in the distribution of certain types of mineral deposits (Kerrich et al. 2005), a prime example being iron formations (Bekker et al. 2010). We propose that similar to the secular changes in the concentration of metals, such as Fe and Mn, the interplay between Earth's evolving mantle, atmosphere and biology also dictated the concentration of gold into Earth's crust (Fig. 7).

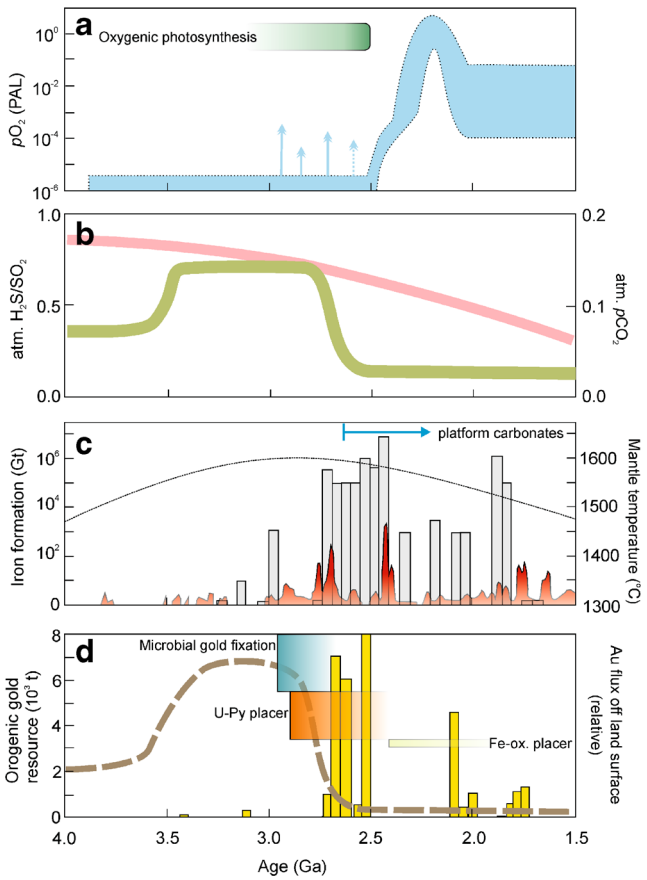


Fig. 7 Main stages of gold concentration styles in relation to the evolution of Earth's atmosphere and secular distribution of iron formations from Archaean to Palaeoproterozoic time: **a** evolution of atmospheric partial pressure of oxygen (pO_2) relative to present atmospheric level (PAL); *blue arrows* denote first "whiffs" of O_2 emanating from first emerging oxygenic photosynthesizing microbes (after Lyons et al. 2014); **b** evolution of atmospheric H_2S/SO_2 ratio and pCO_2 (after Halevy et al. 2010); **c** secular distribution of marine Fe deposits (banded and granular iron formations) compared with that of mantle plumes (*red*), after Bekker et al. (2010), also shown is the secular variation in mantle temperature (*stippled curve*) as calculated by Labrosse and Jaupart (2007); **d** secular variation in orogenic gold formation (from Goldfarb et al. 2001) and the main stages of surficial *gold* concentration on microbial mats, as uraninite-pyrite placers and as Fe-oxide-bearing placers; also shown (*brown stippled curve*) is the estimated secular variation in the Au flux off the ancient land surface (this study)

For a highly siderophile element, such as Au, sequestration into juvenile continental crust would have reached a maximum in Palaeo- to early Mesoarchaean times and been a function of crustal growth rate, degree of melting in the mantle and HSE availability in the source region within the mantle. Thus, elevated background concentrations of Au are to be expected in Archaean crustal rocks, with likely differences between better and less well-endowed cratons dependent on the HSE pre-enrichment in their respective source regions in the mantle. Considering the much higher amounts of Au and PGE in the Kaapvaal Craton with its exceptionally high amounts of gold (in the Witwatersrand Basin) and PGE (in the Bushveld Complex), that craton appears to represent crust that differentiated from a particularly well-endowed mantle domain (Frimmel 2014). Several processes, the effectiveness of which changed dramatically over geological time, brought about the concentration of this background gold into ore deposits. Depending on which of these processes dominated, several discrete time intervals can be distinguished, each of which is marked by specific styles of gold mineralization.

Mesoarchaean

For reasons explained above, Mesoarchaean environmental conditions were particularly conducive for releasing gold into surface waters as a result of chemical weathering of crustal rocks. Emerging oxygenic photosynthesizing microbes, probably cyanobacteria, provided the first traps for this gold. Precipitation of gold on the surface of cyanobacterial mats thriving in low-energy near-coastal environments led to the fixation of huge amounts of gold now preserved as the very gold-rich Carbon Leader (c. 2.90 Ga) and the Basal, Steyn and Vaal reefs (2.87 Ga) of the Witwatersrand Basin. Local and occasional reworking of this biogenically precipitated gold provided the source of gold in later Meso- to Neoarchaean palaeoplacer deposits. Gold also occurs in older conglomerates, but the overall gold endowment is an order of magnitude smaller (Table 1). No significant gold palaeoplacers older than 2.94 Ga are known. The Dominion reefs in the 3.07 Ga Dominion Group are rich in detrital uraninite, but their Au grade is comparatively miniscule. Thus, it may be reasoned that only by about 2.90 Ga had sufficiently large oxygenic photosynthesizing microbial communities developed that could scavenge large amounts of gold from the surrounding waters. This development had a profound effect as it triggered the onset of the crustal gold cycle (Fig. 7).

While repeated sediment reworking in fluvial to fluvio-deltaic environments caused further concentration of the initially microbially bound gold into placer deposits, with gold grade increasing with the extent of sediment reworking (as in the reefs of the upper Central Rand Group, e.g. Kimberley and Elsburg reefs), much of the Au flux off the Archaean continents resulted in progressively higher Au concentrations in the

ocean. Due to the high H_2S content of the Mesoarchaean ocean, much of that gold was probably dissolved as Au-sulfide complex. Some of that Au could be scavenged by progressively emerging oxygenic photosynthesizing microbes in some coastal and shallow shelf environments and/or became fixed by synsedimentary pyrite growth in muddy sediments in deeper marine facies.

Neoarchaean

The Neoarchaean Era is notable for the maximum amount of orogenic-type gold having formed in accretionary orogens, mainly in the Superior and Slave provinces and the Yilgarn and Zimbabwe cratons (Groves et al. 2005a). Evidently, this gold was transported by hydrothermal fluids and much of it was most likely sourced from the metamorphic mobilization of older Mesoarchaean Au-enriched sediments in the course of orogenic activity. This includes granite-related orogenic gold deposits, because even if the Au was derived from granitic magmas, the ultimate origin of these magmas would have been anatexis of pre-existing Au-enriched crustal rocks. The Neoarchaean peak in the secular distribution of orogenic gold deposits (Fig. 7d) most probably reflects higher Au concentrations in the orogenically recycled Archaean sedimentary rocks. Those fluids that formed older orogenic gold deposits, such as in the Barberton Mountain Land, could not have scavenged yet microbially mediated gold in tectonically reworked sediments but other forms of background gold (e.g. inclusions within sulfides) as in much younger, Phanerozoic examples. This difference in source availability would explain why there is so little Palaeo-/Mesoarchaean in comparison with Neoarchaean orogenic gold. At the same time, on the Neoarchaean land surface, the gold-enriched Archaean sediments became in places redeposited only to form further placer deposits in fluvial channels and erosion surfaces as exemplified by the Hardey Formation in the Pilbara Craton (2.76 Ga), the Ventersdorp Contact Reef (2.71 Ga) and the Black Reef (2.66 Ga), both in the Kaapvaal Craton, or the Moeda Formation (2.65 Ga) in the Sáo Francisco Craton (Table 1).

Concentration of gold in deeper marine environments was probably slowed down from Meso- to Neoarchaean times because of a change in seawater chemistry due to the transition from predominantly submarine to predominantly subaerial volcanism. This transition resulted in a shift towards higher SO_2/H_2S ratios and higher H_2 contents in volcanic gases (Gaillard et al. 2011). The increasing atmospheric SO_2 contents must have led to a higher seawater sulfate content, which in turn had an adverse effect on the solubility of Au-sulfide complexes. A further drastic change in seawater chemistry, affecting gold solubility, in the course of the Neoarchaean took place when the first large-scale platform carbonates (Lower Transvaal Supergroup) were deposited at around 2.6 Ga, taking up large volumes of CO_2 and thus increasing the seawater pH.

Palaeoproterozoic

The trends in chemical changes in the atmosphere and hydrosphere continued from the late Neoarchaean into Palaeoproterozoic times until the GOE, and the same style of superficial gold concentration processes as noted for the Neoarchaean continued to prevail into the early Palaeoproterozoic. By then, numerous orogenic-type gold deposits had already formed and became exposed to erosion. They provided new sources for placer gold accumulations, in addition to the reworking of older, Meso- to Neoarchaean placers. Examples of such palaeoplacers are those in the Huronian Supergroup, specifically in the 2.45 Ga Matinenda Formation and the c. 2.40 Ga Mississagi Formation.

As time progressed, more and more of the gold-rich Archaean sediments became recycled by orogenic or other tectonic overprints into metamorphic crustal terrains or via subducted slabs back into the upper mantle. Some of them melted partially to form potential reservoirs for later gold-mineralizing magmatic systems. Thus, a variety of gold sources for a range of magmatic and hydrothermal mineralizing systems evolved, giving rise to the variety of gold deposit types known. The role of palaeoplacer deposits as sites for large-scale gold concentration, however, began to diminish, as their most fertile sources, the Mesoarchaean microbial mats and resulting placers, had been either eroded, covered by younger sediments or tectonically reworked. Palaeoproterozoic placers are, therefore, mainly derived from point sources, i.e. discrete deposits in their former hinterland. With the drastic changes in atmospheric composition at around 2.4 Ga (GOE), the capacity of surface waters to take up Au from chemically weathered rocks diminished by orders of magnitude (Fig. 7). The Au flux from the land surface towards the ocean became effectively insignificant, and the Au concentration in Palaeoproterozoic seawater must have decreased dramatically. Further large-scale microbially mediated fixation of gold as postulated for the Archaean times, be it in fluvial or shallow-marine environments, became practically impossible.

As the preservation potential of the Archaean and possibly earliest, pre-GOE Palaeoproterozoic gold-rich microbial mats and placer deposits on the surface quickly decreased with time, they became less and less likely source candidates for younger placer gold accumulation. This might explain the lack of palaeoplacer deposits younger than 1.8 Ga. Instead, much of the crustal gold cycle took place by magmatic, hydrothermal and metamorphic processes within the lithosphere. Each of the numerous remobilization events would have caused a further loss of Os from the originally Os-rich Mesoarchaean gold because of the very low solubility of Os in aqueous fluids

(Fig. 1). Although some addition of juvenile gold also later in Earth history is indicated, such as for the giant Muruntau deposit in Late Palaeozoic times (Graupner et al. 2006), the overall contribution to the crustal gold budget was comparatively low.

Acknowledgments The ideas presented in this paper are based on more than 20 years of research by the first author on Witwatersrand deposits, which would have been impossible without the cooperation of and with numerous mining companies, most recently Sibanye Gold. W.E.L. Minter is thanked for providing many invaluable rock specimens and data from Witwatersrand operations that have long ceased to exist and from past exploration projects on the Moeda, Jacobina and Roraima occurrences/deposits. R. Murphy and W. Whymark from Ginguru Exploration kindly provided instructive samples from the Matinenda and Mississagi formations and the photograph for Fig. 2d. N. Koglin and S. Heinze are thanked for their assistance in the separation and documentation of gold particles. We thank G. Nwaila and A. McLoughlin for making the photographs of bitumen from the Black Reef available. P. Karpeta kindly provided unpublished information on hitherto very poorly known examples of Witwatersrand-type deposits in Brazil and Zambia. Both chief editors, B. Lehmann and G. Beaudoin, are thanked for their critical evaluation of the original manuscript. Some of this research was funded by the German Research Foundation (DFG grants FR2183/3 and KO4273/2).

References

Agangi A, Hofmann A, Wohlgemuth-Ueberwasser CC (2013) Pyrite zoning as a record of mineralization in the Ventersdorp Contact Reef, Witwatersrand Basin, South Africa. Econ Geol 108:1243–1272

Agangi A, Hofmann A, Rollion-Bard C, Marin-Carbonne J, Cavalazzi B, Large R, Meffre S (2015) Gold accumulation in the Archaean Witwatersrand Basin, South Africa—Evidence from concentrically laminated pyrite. Earth Science Reviews, 140:27–53

Barnicoat AC, Henderson IHC, Knipe RJ, Yardley BWD, Napier RW, Fox NPC, Kenyon AK, Muntingh DJ, Strydom D, Winkler KS, Lawrence SR, Cornford C (1997) Hydrothermal gold mineralization in the Witwatersrand basin. Nature 386:820–824

Barton ES, Hallbauer DK (1996) Trace-element and U-Pb isotope compositions of pyrite types in the Proterozoic Black Reef, Transvaal Sequence, South Africa: implications on genesis and age. Chem Geol 133:173–199

Bekker A, Slack JF, Planavsky N, Krapez B, Hofmann A, Konhauser KO, Rouxel OJ (2010) Iron formation: the sedimentary product of a complex interplay among mantle, tectonic, oceanic, and biospheric processes. Econ Geol 105:467–508

Belousova EA, Kostitsyn YA, Griffin WL, Begg GC, O'Reilly SY, Pearson NJ (2010) The growth of the continental crust: constraints from zircon Hf-isotope data. Lithos 119:457–466

Crowe SA, Døssing LN, Beukes NJ, Bau M, Kruger SJ, Frei R, Canfield DE (2013) Atmospheric oxygenation three billion years ago. Nature 501:535–539

Depiné M, Frimmel HE, Emsbo P, Koenig AE, Kern M (2013) Trace element distribution in uraninite from Mesoarchaean Witwatersrand conglomerates (South Africa) supports placer model and magmatogenic source. Mineral Deposita 48:423–435

Didyk BN, Simoneit BRT, Brassel SC, Eglinton G (1978) Organic geochemical indicators of paleoenvironmental conditions of sedimentation. Nature 272:216–222

Drennan GR, Robb LJ (2006) The nature of hydrocarbons and related fluids in the Witwatersrand Basin, South Africa: their role in metal redistribution. Geol Soc Am Spec Pap 405:353–385

Dziggel A, Poujol M, Otto A, Kisters AFM, Trieloff M, Schwarz WH, Meyer FM (2010) New U–Pb and $^{40}Ar/^{39}Ar$ ages from the northern margin of the Barberton greenstone belt, South Africa: implications for the formation of Mesoarchaean gold deposits. Precambrian Res 179:206–220

Engelbrecht CJ, Baumbach GWS, Maticen JL, Fletcher P (1986) The West Wits line. In: Anhaeusser CR, Maske S (eds) Mineral deposits of Southern Africa. Geological Society of South Africa, Johannesburg, pp 599–648

England GL, Rasmussen B, Krapez B, Groves DI (2001) The origin of uraninite, bitumen nodules and carbon seams in Witwatersrand gold-uranium-pyrite ore deposits, based on a Permo-Triassic analog. Econ Geol 96:1907–1920

England GL, Rasmussen B, Krapez B, Groves DI (2002a) Archaean oil migration in the Witwatersrand Basin of South Africa. J Geol Soc Lond 159:189–201

England GL, Rasmussen B, Krapez B, Groves DI (2002b) Palaeoenvironmental significance of rounded pyrite in siliciclastic sequences of the Late Archaean Witwatersrand Basin: oxygen-deficient atmosphere or hydrothermal evolution. Sedimentology 49:1122–1156

Farquhar J, Wing BA (2003) Multiple sulfur isotopes and the evolution of the atmosphere. Earth Planet Sci Lett 213:1–13

Farquhar J, Peters M, Johnston DT, Strauss H, Masterson A, Wiechert U, Kaufman AJ (2007) Isotopic evidence for Mesoarchaean anoxia and changing atmospheric sulphur chemistry. Nature 449:706–709

Fedonkin MA (2003) Geochemical impoverishment and eukaryotization of the biosphere: a causal link. Paleontol J 37:592–599

Filippov VE, Nikiforova ZS (1986) Transformation of particles of native gold in the process of eolian action. Institute of Geology of the Yakutia Branch, Siberia Division, USSR Academy of Sciences, Yakutsk

Frimmel HE (2005) Archaean atmospheric evolution: evidence from the Witwatersrand gold fields, South Africa. Earth Sci Rev 70:1–46

Frimmel HE (2008) Earth's continental crustal gold endowment. Earth Planet Sci Lett 267:45–55

Frimmel HE (2014) A giant Mesoarchean crustal gold-enrichment episode: possible causes and consequences for exploration In: Kelley K, Golden HC (eds). Society of Economic Geologists, Special Publication 18:209–234

Frimmel HE, Minter WEL (2002) Recent developments concerning the geological history and genesis of the Witwatersrand gold deposits, South Africa. In: Goldfarb RJ, Nielsen RL (eds) Integrated Methods for Discovery: Global Exploration in the Twenty-first Century. Society of Economic Geologists, Special Publication 9:17–45

Frimmel HE, Le Roex AP, Knight J, Minter WEL (1993) A case study of the postdepositional alteration of the Witwatersrand Basal reef gold placer. Econ Geol 88:249–265

Frimmel HE, Hallbauer DK, Gartz VH (1999) Gold mobilizing fluids in the Witwatersrand Basin: composition and possible sources. Mineral Petrol 66:55–81

Frimmel HE, Groves DI, Kirk J, Ruiz J, Chesley J, Minter WEL (2005a) The formation and preservation of the Witwatersrand goldfields, the largest gold province in the world. In: Hedenquist JW, Thompson JFH, Goldfarb RJ, Richards JP (eds) Economic Geology One Hundredth Anniversary Volume. Society of Economic Geologists, Littleton, pp 769–797

Frimmel HE, Minter WEL, Chesley J, Kirk J, Ruiz J (2005b) Short-range gold mobilisation in palaeoplacer deposits. In: Mao J, Bierlein FP (eds) Mineral Deposit Research: Meeting the Global Challenge, Proceedings of the 8th Biennial SGA Meeting, Beijing, 18–21 August 2005. Springer, Heidelberg, pp 953–956

Gaillard F, Scaillet B, Arndt NT (2011) Atmospheric oxygenation caused by a change in volcanic degassing pressure. Nature 478:229–232

Gartz VH, Frimmel HE (1999) Complex metasomatism of an Archean placer in the Witwatersrand basin, South Africa: the Ventersdorp Contact reef—a hydrothermal aquifer? Econ Geol 94:689–706

Goldfarb RJ, Groves DI, Gardoll S (2001) Orogenic gold and geologic time: a global synthesis. Ore Geol Rev 18:1–75

Graupner T, Niedermann S, Kempe U, Klemd R, Bechtel A (2006) Origin of ore fluids in the Muruntau gold system: constraints from noble gas, carbon isotope and halogen data. Geochim Cosmochim Acta 70:5356–5370

Gray GJ, Lawrence SR, Kenyon K, Cornford C (1998) Nature and origin of carbon in the Archean Witwatersrand Basin, South Africa. J Geol Soc Lond 155:39–59

Gross GA (1980) A classification of iron-formations based on depositional environments. Can Mineral 18:215–222

Gross GA (1988) Gold content and geochemistry of iron-formation in Canada. Pap geol Surv Canada 86–19:20 pp

Groves DI, Condie KC, Goldfarb RJ, Hronsky JMA, Vielreicher RM (2005a) Secular changes in global tectonic processes and their influence on the temporal distribution of gold-bearing mineral deposits. Econ Geol 100:203–224

Groves DI, Vielreicher RM, Goldfarb RJ, Condie KC (2005b) Controls on the heterogeneous distribution of mineral deposits through time. In: McDonald I, Boyce AJ, Butler IB, Herrington RJ, Polya DA (eds) Mineral Deposits and Earth Evolution. The Geological Society of London, Special Publication 248: 71–101

Guy BM, Beukes NJ, Gutzmer J (2010) Paleoenvironmental controls on the texture and chemical composition of pyrite from non-conglomeratic sedimentary rocks of the Mesoarchean Witwatersrand Supergroup, South Africa. S Afr J Geol 113:195–228

Guy BM, Ono S, Gutzmer J, Kaufman AJ, Lin Y, Fogel ML, Beukes NJ (2012) A multiple sulfur and organic carbon isotope record from non-conglomeratic sedimentary rocks of the Mesoarchean Witwatersrand Supergroup, South Africa. Precambrian Res 216–219:208–231

Halevy I, Johnston DT, Schrag DP (2010) Explaining the structure of the Archean mass-independent sulfur isotope record. Science 329:204–207

Hallbauer DK (1975) The plant origin of Witwatersrand carbon. Miner Sci Eng 7:111–131

Hallbauer DK, Barton JM (1987) The fossil gold placers of the Witwatersrand. Gold Bull 20:68–79

Hallbauer DK, Joughin NC (1973) The size distribution and morphology of gold particles in the Witwatersrand reefs and their crushed products. J S Afr Inst Min Metall 1973:395–405

Haqq-Misra J, Kasting JF, Lee S (2011) Availability of O_2 and H_2O_2 on pre-photosynthetic Earth. Astrobiology 11:293–302

Hayashi KI, Ohmoto H (1991) Solubility of gold in NaCl- and H_2S-bearing aqueous solutions at 250–350 °C. Geochim Cosmochim Acta 55:2111–2126

Hayward CL, Reimold WU, Gibson RL, Robb LJ (2005) Gold mineralization within the Witwatersrand basin, South Africa: evidence for a modified placer origin, and the role of the Vredefort impact event. In: MacDonald I, Boyce AJ, Butler IB, Herrington RJ, Polya DA (eds) Mineral Deposits and Earth Evolution. Geological Society of London, Special Publication, 248:31–58

Hoefs J, Schidlowski M (1967) Carbon isotope composition of carbonaceous matter from the Precambrian of the Witwatersrand system. Science 155:1096–1097

Hofmann A, Bekker A, Rouxel O, Rumble D, Master S (2009) Multiple sulphur and iron isotope composition of detrital pyrite in Archaean sedimentary rocks: a new tool for provenance analysis. Earth Planet Sci Lett 286:436–445

Horscroft FDM, Mossman DJ, Reimer TO, Hennigh Q (2011) Witwatersrand metallogenesis: the case for (modified) syngenesis. SEPM Spec Publ 101:75–95

Huston DL, Logan GA (2004) Barite, BIF's and bugs: evidence for the evolution of the Earth's early hydrosphere. Earth Planet Sci Lett 220:41–55

Hutchinson RW, Viljoen RP (1987) Re-evaluation of gold source in Witwatersrand ores. S Afr J Geol 91:157–173

Jaguin J, Poujol M, Boulvais P, Robb LJ (2012) Metallogeny of precious and base metal mineralization in the Murchison Greenstone Belt, South Africa: indications from U-Pb and Pb-Pb geochronology. Mineral Deposita 47:739–747

Kerrich R, Goldfarb RJ, Richards JP (2005) Metallogenic provinces in an evolving geodynamic framework. In: Hedenquist JW, Thompson JFH, Goldfarb RJ, Richards JP (eds) Economic Geology One Hundreth Anniversary Volume. Society of Economic Geologists, Littleton, pp 1097–1136

Kirk J, Ruiz J, Chesley J, Titley S, Walshe J (2001) A detrital model for the origin of gold and sulfides in the Witwatersrand basin based on Re-Os isotopes. Geochim Cosmochim Acta 65:2149–2159

Kirk J, Ruiz J, Chesley J, Walshe J, England G (2002) A major Archean gold and crust-forming event in the Kaapvaal Craton, South Africa. Science 297:1856–1858

Koglin N, Frimmel HE, Minter WEL, Brätz H (2010) Trace-element characteristics of different pyrite types in Mesoarchaean to Palaeoproterozoic placer deposits. Mineral Deposita 45:259–280

Koglin N, Cabral AR, Brunetto WJ, Vymazalová A (2012) Gold–tourmaline assemblage in a Witwatersrand-like gold deposit, Ouro Fino, Quadrilátero Ferrífero of Minas Gerais, Brazil: the composition of gold and metallogenic implications. Neues Jb Mineral Abh 189: 263–273

Krupp R, Oberthür T, Hirdes W (1994) The Early Precambrian atmosphere and hydrosphere: thermodynamic constraints from mineral deposits. Econ Geol 89:1581–1598

Kurzweil F, Claire M, Thomazo C, Peters M, Hannington M, Strauss H (2013) Atmospheric sulfur rearrangement 2.7 billion years ago: evidence for oxygenic photosynthesis. Earth Planet Sci Lett 366:17–26

Labrosse S, Jaupart C (2007) Thermal evolution of the Earth: secular changes and fluctuations of plate characteristics. Earth Planet Sci Lett 260:465–481

Large RR, Meffre S, Burnett R, Guy B, Bull S, Gilbert S, Goemann K, Danyushevsky L (2013) Evidence for an intrabasinal source and multiple concentration processes in the formation of the Carbon Leader Reef, Witwatersrand Supergroup, South Africa. Econ Geol 108:1215–1241

Large RR, Halpin JA, Danyushevsky LV, Maslennikov VV, Bull SW, Long JA, Gregory DD, Lounejeva E, Lyons TW, Sack PJ, McGoldrick PJ, Calver CR (2014) Trace element content of sedimentary pyrite as a new proxy for deep-time ocean–atmosphere evolution. Earth Planet Sci Lett 389:209–220

Lipson R (2014) The promise and perils of porphyry deposits in the future of gold production. SEG Newslett 98

Long DGF, Ulrich T, Kamber BS (2011) Laterally extensive modified placer gold deposits in the Paleoproterozoic Mississagi Formation, Clement and Pardo Townships, Ontario. Can J Earth Sci 48:779–792

Lyons TW, Reinhard CT, Planavsky NJ (2014) The rise of oxygen in Earth's early ocean and atmosphere. Nature 506:307–315

Malitch KN, Merkle RKW (2004) Ru-Os-Ir-Pt and Pt-Fe alloys from the Evander goldfield, Witwatersrand Basin, South Africa: detrital origin inferred from compositional and osmium-isotope data. Can Mineral 42:631–650

Milesi J-P, Ledru P, Marcoux E, Mougeot R, Johan V, Lerouge C, Sabaté P, Bailey L, Respaut JP, Skipwith P (2002) The Jacobina Paleoproterozoic gold-bearing conglomerates, Bahia, Brazil: a "hydrothermal shear-reservoir" model. Ore Geol Rev 19:95–136

Minter WEL (1991) Ancient placer gold deposits. In: Foster RP (ed) Gold Metallogeny and Exploration. Blackie, London, pp 283–308

Minter WEL (1999) Irrefutable detrital origin of Witwatersrand gold and evidence of eolian signatures. Econ Geol 94:665–670

Minter WEL, Goedhart ML, Knight J, Frimmel HE (1993) Morphology of Witwatersrand gold grains from the Basal Reef: evidence for their detrital origin. Econ Geol 88:237–248

Mossman DJ, Minter WEL, Dutkiewicz A, Hallbauer DK, George SC, Hennigh Q, Reimer TO, Horscroft FD (2008) The indigenous origin of Witwatersrand "carbon". Precambrian Res 164:173–186

Mukhopadhyay J, Crowley QG, Ghosh S, Ghosh G, Chakrabarti K, Misra B, Heron K, Bose S (2014) Oxygenation of the Archean atmosphere: new paleosol constraints from eastern India. Geology 42:923–926

Nagy B (1993) Kerogens and bitumens in Precambrian uraniferous ore deposits: Witwatersrand, South Africa, Elliot Lake, Canada and the natural fission track reactors, Oklo, Gabon. In: Parnell J (ed) Bitumens in Ore Deposits. Springer, Berlin, pp 287–333

Noffke N, Hazen RM, Eriksson K, Simpson E (2006) A new window into early life: microbial mats in a siliciclastic early Archean tidal flat (3.2 Ga Moodies Group, South Africa). Geology 34:253–256

Noffke N, Beukes N, Bower D, Hazen RM, Swift DJP (2008) An actualistic perspective into Archean worlds—(cyano-)bacterially induced sedimentary structures in the siliciclastic Nhlazatse Section, 2.9 Ga Pongola Supergroup, South Africa. Geobiology 6:5–20

Parnell J (1999) Petrographic evidence for emplacement of carbon into Witwatersrand conglomerates under high fluid pressure. J Sediment Res 69:164–170

Phillips GN (1987) Anomalous gold in Witwatersrand shales. Econ Geol 82:2179–2186

Phillips GN, Law JDM (2000) Witwatersrand gold fields: geology, genesis and exploration. SEG Rev 13:439–500

Pitcairn IK (2011) Background concentration of gold in different rock types. Appl Earth Sci 120:31–38

Planavsky NJ, Asael D, Hofmann A, Reinhard CT, Lalonde SV, Knudsen A, Wang X, Ossa Ossa FO, Pecoits E, Smith AJB, Beukes NJ, Andrey Bekker A, Johnson TM, Konhauser KO, Lyons TW, Rouxel OJ (2014) Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. Nat Geosci 7:283–286

Rasmussen B, Buick R (1999) Redox state of the Archean atmosphere: evidence from detrital heavy minerals in ca. 3250–2750 Ma sandstones from the Pilbara Craton, Australia. Geology 27:115–118

Riding R, Fralick P, Liang L (2014) Identification of an Archean marine oxygen oasis. Precambrian Res 251:232–237

Robb LJ, Meyer FM (1990) The nature of the Witwatersrand hinterland: conjectures on the source-area problem. Econ Geol 85:511–536

Robb LJ, Meyer FM (1991) A contribution to recent debate concerning epigenetic versus syngenetic mineralization processes in the Witwatersrand Basin. Econ Geol 86:396–401

Russell MJ, Hall AJ (1997) The emergence of life from iron monosulphide bubbles at a submarine hydrothermal redox and pH front. J Geol Soc Lond 154:377–402

Saunders JA, Kamenov GD, Hofstra AH, Unger DL, Creaser RA, Barra F (2011) "Forensic" geochemical approaches to constrain the source of Au-Ag in low-sulfidation epithermal ores. In: Steininger R, Pennell W (eds) Geological Society of Nevada 2010 Symposium, 14 May 2010. Geological Society of Nevada: Reno-Sparks, pp 693–700

Schidlowski M (1981) Uraniferous constituents of the Witwatersrand conglomerates: ore-microscopic observations and implications for Witwatersrand metallogeny. US Geol Surv Prof Pap 1161:N1–N29

Shenberger DM, Barnes HL (1989) Solubility of gold in aqueous sulfide solutions from 150 to 350 °C. Geochim Cosmochim Acta 53:269–278

Spangenberg J, Frimmel HE (2001) Basin-internal derivation of hydrocarbons in the Witwatersrand Basin, South Africa: evidence from bulk and molecular ^{13}C data. Chem Geol 173:339–355

Stefánsson A, Seward TM (2004) Gold (I) complexing in aqueous sulphide solutions to 500 °C at 500 bar. Geochim Cosmochim Acta 68: 4121–4143

Whymark W (2014) Gold bearing mineralization in conglomerates of the Mississagi Formation, southern Cobalt embayment, Ontario, Canada: mineral paragenesis, gold geochemistry and implications for exploration. Unpubl. BSc (Hons) thesis, Department of Earth Sciences. Laurentian University, Sudbury, p 25

Williams GE (2000) Geological constraints on the Precambrian history of Earth's rotation and the Moon's orbit. Rev Geophys 38: 37–59

Xiong Y, Wood SA (2000) Experimental quantification of hydrothermal solubility of platinum-group elements with special reference to porphyry copper environments. Mineral Petrol 68:1–28

Zahnle K, Arndt N, Cockell C, Halliday A, Nisbet E, Selsis F, Sleep N (2007) Emergence of a habitable planet. Space Sci Rev 129:35–78