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Episodic concentration of gold to ore grade through Earth's history

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Abstract

Concentration of gold to economic ore grades has been highly episodic through Earth's history with different sedimentary, magmatic and hydrothermal processes having operated as principal driving forces at different times. Comparison of the various types of gold deposits, their secular and spatial distribution and the amounts of gold contained in them, combined with thermodynamic considerations, reveals that the formation of gold deposits reflects fundamental changes in environmental conditions, biological evolution and styles of large-scale tectonism over the past four billion years. Here I suggest that most of the gold in the Earth's crust was first concentrated at around 2.9 billion years (Ga) ago by early photosynthesising microbes under an oxygen-deficient atmosphere. Sedimentary reworking of auriferous microbial mats provided the source for the richest known gold palaeoplacers between 2.9 and 2.7 Ga and an overall gold-enrichment of coeval marine sediments. Only after modern-style plate tectonics had begun to operate, sediments enriched in gold had been accreted along active plate margins, subducted and subcontinental lithospheric mantle had been correspondingly metasomatised, did the formation of larger orogenic, porphyry-type and epithermal, and to a lesser extent also other hydrothermal gold deposits become possible. Thus the principal secular peak in orogenic gold formation at 2.75 – 2.55 Ga can be explained.

Keywords: Gold; Archaean; microbes; plate tectonics; secular variations; Witwatersrand.

Declarations of interest: none.

1. Introduction

During the formation and early differentiation of our planet, all gold should have become concentrated in the Earth's core because of its high density and highly siderophile geochemical behaviour. Some 98 % of all the gold in our planet has been estimated to reside in the core (McDonough, 2005). Although being one of the rarest elements in the crust, the calculated average crustal gold content of some 1.5 ppb (Rudnick and Gao, 2005) is higher than expected from geochemical considerations and calls for an explanation. Locally, this background concentration has been upgraded to economic ore grade, which requires an enrichment by three to four orders of magnitude. A wide range of known gold deposit types are testimony to a large variety of geological processes that can lead to this enrichment. In terms of overall endowment (i.e. past production plus known resources) only three geological settings account for close to 90 % of all known gold that is (or has been) concentrated in gold deposits (Frimmel, 2008; Lipson, 2014): (i) syn-orogenic vein-type and disseminated deposits in collisional tectonic settings (c. 30 % of known gold), porphyry-related and epithermal gold deposits in supra-subduction settings (c. 28 %), and (iii) conglomerate-hosted deposits of the Witwatersrand-type (c. 30 %). The former two types typically form in accretionary orogens and above subduction zones, respectively, orogenic deposits at deeper crustal levels of c. 5-15 km from upwards migrating metamorphogenic fluids (Goldfarb et al., 2005) and porphyry as well as epithermal deposits at shallower crustal levels from magmatogenic hydrothermal fluids (Pokrovski et al., 2015; Sillitoe, 2010; Wilkinson, 2013). Active plate margins are by far the most productive areas, having contributed probably >80 % of hypogene gold in all known deposits (Frimmel, 2008).

The genesis of Witwatersrand-type deposits has been a matter of debate for more than a century. Most workers agree on sedimentary concentration of detrital gold particles by river water and wind (palaeoplacer model) with local remobilisation by post-depositional fluids to explain these deposits (for reviews of arguments for and against this model see Robb and Meyer, 1995; Frimmel, 2005, 2014; Frimmel et al., 2005; Tucker et al. 2016) but an entirely epigenetic formation with post-depositional introduction of gold into the host conglomerates by hydrothermal or metamorphic fluids has been suggested by others (Barnicoat et al., 1997; Phillips and Powell, 2011). Epigenetic models ignore, however, the fact that the first-order control on gold grade is stratigraphy and sedimentary facies. For some 130 years this control has been utilised highly successfully by the miners in their day-to-day delineation of reserves and the recovery of >52 000 t Au – far more than any other gold province has ever yielded. The ore bodies (reefs) are perfectly stratabound and stratiform, bound to specific conglomerate horizons that can be correlated across the entire basin over more than 300 km, independently of the extent, style and direction of post-depositional deformational and metamorphic overprint. Two sedimentary facies account for almost all the Witwatersrand gold: thin pebble lags representing, at least in places aeolian, deflation surfaces that are largely covered by kerogen seams, and conglomeratic, high-energy fluvial channel deposits (Frimmel et al., 2005; Tucker et al., 2016). The richest ore bodies (largely mined out) were only decimetre-thin sheet-like conglomerates that have been mined for more than 40 km along strike at grades of 20 - 40 g/t. Clearly, such a geometry of the ore bodies cannot be reconciled by post-depositional mineralisation through ascending fluids of whatever origin. A further conspicuous and extremely important control on mineralisation is the presence of erosional unconformities. Mineralised conglomerates rest, without exception, on such erosional palaeosurfaces, most of which are angular unconformities with some of the respective bedrock having been tilted prior to sedimentation and thus exposing parts of the immediately underlying stratigraphy, including older reefs, to erosion. Numerous studies conducted on a microscopic scale revealed that much of the gold occurs in late paragenetic positions (hence the idea of a possibly epigenetic formation). These observations, combined with the strong macroscopic to regional sedimentological control and the finding of gold micro-nuggets that are overgrown by secondary gold crystals (Minter et al., 1993) led to the model of palaeoplacer deposits in which post-depositional fluids remobilised some of the ore components, including gold, on a small scale within the host conglomerates. Cross-cutting structures, such as faults, veins and dykes are typically barren. Those that are mineralised are spatially limited to the immediate vicinity of gold-rich conglomerate reefs, evidence of cross-cutting feeder channels for ascending hydrothermal ore fluids is conspicuously absent. Note that in the long history of Witwatersrand mining, application of a hydrothermal model has not led to the discovery of a single cross-cutting ore body. Irrespective of the preferred genetic model, the question arises as to the source of all the gold in the c. 2.93 – 2.73 Ga auriferous conglomerates in the Witwatersrand Basin of South Africa (estimated to be >90 000 t of gold; Frimmel, 2014). This very question shall be at the fore of the present paper.

Major gold deposits older than 2.9 Ga are conspicuously lacking. The oldest known orogenic-type gold deposits are hosted by Palaeo- to Mesoarchaean greenstone belts, such as the c. 3.2 Ga Talga Talga deposit in the Pilbara Craton, Western Australia, the 3.08 – 3.04 Ga Barberton deposits (Dziggel et al., 2010) in the Kaapvaal Craton, South Africa. Their total gold endowment is, however, comparatively insignificant (only some 385 t Au mined so far in Barberton). Thus no discrete source in the sense of eroded older deposits is evident to explain the huge amount of Witwatersrand gold – a major argument that has been used against a palaeoplacer model for the latter. At the core of this contribution is, therefore, the question whether the observed paucity in gold deposits >3.0 Ga is an artefact of poor preservation of such old rocks or a primary feature of Eo- to Mesoarchaean geological processes in the mantle and the crust. To answer this question, I analysed the secular and spatial variation in the formation of the most important gold deposit types over the past 4 billion years, together with temporal changes in the mode of occurrence of conglomerate-hosted gold deposits.

2. Secular variation in gold endowment

Good correlation between the timing of mesozonal shear zone-hosted vein-type gold deposits and times of widespread orogeny (Fig. 1) has long been recognised and formed the base for their classification as “orogenic-type” (Goldfarb et al., 2005; Goldfarb et al., 2001). Notably, the largest peak in the age distribution of orogenic gold production (in terms of tonnage) is also the oldest, that is, at c. 2.75 - 2.55 Ga. In contrast, the vast majority of porphyry and epithermal deposits are younger than 0.1 Ga (Seedorf et al., 2005). This is easily explained by their low preservation potential because they typically form at very shallow continental crustal levels in topographic highs. More critical for this study is, however, the timing of first porphyry-type gold mineralisation. The oldest known porphyry-type deposits are in Palaeoarchaean greenstone belts of the Pilbara Craton, with the 3.317 Ga Spinnifex Ridge Cu-Mo deposit being the prime example (Huston et al., 2002), but they are poor in gold. One of the oldest gold-rich expressions of this type of mineralisation is the recently discovered 2.74 Ga Côté Gold Cu-Au deposit in the Abitibi greenstone belt, Canada (Katz, 2016), which indicates that the supra-subduction gold factory has been operating at least since Neoarchaean times.

Although some Mesoarchaean orogenic gold deposits exists, such as those in the Barberton Greenstone Belt (Dziggel et al., 2010) or in Greenland (Kolb et al., 2013), the total amount of gold in these, even when normalised to area of exposed rock, is comparatively very small. The examples from Greenland illustrate that future exploration might lead to a significant increase in the known reserves and resources of Mesoarchaean gold but much of this gold is <2.8 Ga in age (Kolb et al., 2013). Most probably it is not coincidental that first large-scale formation of orogenic deposits overlaps in time with the oldest subduction-related gold deposits at around 2.75 Ga. The paucity of hypogene porphyry/epithermal-type gold deposits older than 2.75 Ga can be explained by three critical factors that determine the extent of fertilisation of the subcontinental lithospheric mantle (SCLM): (i) timing of onset of (modern) plate tectonics, (ii) availability of gold in subducted rocks, and (iii) oxidation of the SCLM. An enriched SCLM has been regarded as principal source of gold (and other metals) in porphyry/epithermal systems (Sillitoe, 2010; Wilkinson, 2013; Pokrovski et al., 2015). Thus the question arises since when such fertilisation has been possible.

The exact nature and timing of the principal tectonic forces that shaped the overall hotter Hadaean to Archaean Earth remains a controversial topic but consensus is emerging on some form of plate tectonics having begun to operate from at least around 3 Ga (Dhuime et al., 2012) although some workers argue for subduction to have set in much later in Earth's history (for a recent example see Stern and Miller, 2018). Geochemical evidence of arc magmatism in Archaean igneous rocks, commonly used to argue for Archaean subduction, is equivocal (van Hunen and Moyen, 2012). More conclusive are seismic reflection profiles through old cratons that show shallow dipping reflectors interpreted as marking an orogenic wedge with imbricated thrust planes as expected in post-subduction continental collision zones. Such features are known from at least 2.7 Ga (Ludden and Hynes, 2000). The oldest paired metamorphic belt with low-*dT/dP* ($\sim$12–15∘C km^{-1}) and high-*dT/dP* domains, a typical result of subduction, has been documented in the Kaapvaal Craton at c. 3.2 Ga (van Hunen and Moyen, 2012). Diamonds that are >3.2 Ga old have been found to be peridotitic, those <3.0 Ga eclogitic (Shirey and Richardson, 2011). All of this points to plate tectonics to have commenced to operate sometime between 3.2 and 3.0 Ga. No major gold deposits are known that are older than 2.9 Ga. Thus it seems that up to that time, no significant reservoir was available from which gold could have been cycled into a SCLM by early subduction processes.

In order to fertilise the SCLM with regard to gold, oxidation of this source region for arc magmas is necessary. The overall oxygen fugacity of the mantle is believed to have not changed significantly since the Archaean (Nicklas et al., 2018), thus the issue of oxidation of the source region for Archaean arc magmas may follow an actualistic principle. It has long been recognised that magmas from which metal-rich aqueous phases emanate need to be H_2O-rich (>4 wt %) and oxidised (Sillitoe, 2010). If a high oxidation state is not attained, magmatic sulfides would precipitate, thus preventing chalcophile metals, such as gold and copper, to concentrate in the melt and eventually in the exsolving aqueous fluid. Oxidation of the SCLM can be achieved by the transfer of a number of components (Evans, 2012). These can be H_2O and/or CO_2. As the solubility of O_2 in water is very small, the redox budget of water is minimal. Furthermore, hydration of the Archaean oceanic crustal rocks would have been less effective than in post-Archaean times because of higher subduction rates that have been modelled for a hotter

Archaean mantle (van Hunen and Moyen, 2012). With less time available for the hydration of oceanic crust on the sea floor, less H_2O would have been released by metamorphism of the subducted slab into the overlying SCLM. Oxidised carbon would have been an equally insignificant transfer agent because of the lack of carbonate sediment available for potential subduction prior to 2.7 Ga. In younger subduction zones, transfer of ferric iron may play a role in the oxidation of the SCLM. This is, however, very unlikely to have been of any importance prior to the "Great Oxidation Event" (GOE: c. 2.45 – 2.2 Ga) for the low ferric iron content in sediments and oceanic crustal rocks at that time, the low solubility of Fe^{3+} in subduction zone fluids (Evans, 2012), and the above mentioned lower extent of hydration of oceanic crust because of higher subduction and spreading rates. This leaves oxidised sulfur species, such as SO_4^{2-}, HSO_4^- or S_3^-, as potential candidates, and modelling of the redox budget transfer to modern SCLM has led indeed to the recognition that S^{6+} could be the most effective transfer agent (Evans, 2012). Interestingly, the observed variation in mass-independent sulfur isotope fractionation in Archaean pyrite ($\Delta^{33}S_{Py}$) indicates a very low volcanic SO_2/H_2S ratio of c. 1.5 between 3.4 and 2.75 Ga only to rise to c. 8 towards the end of the Archaean (Halevy et al., 2010). Atmospheric SO_2 would have been invariably oxidised by Fe^{3+} in the top layer of the Archaean ocean according to the reaction

$$6\ SO_2 + 2\ Fe_3O_4 = 3\ FeS_2 + 8\ O_2$$

and, consequently, would not have been available for further cycling into the SCLM.

Similarly the question arises as to why orogenic-type gold deposits start to play a major role only from c. 2.8 Ga onwards. Orogenic gold deposits preferentially form in continental crustal sections that resulted from accretionary orogeny and that are underlain by young and thin SCLM (Bierlein et al., 2006). The source of this orogenic gold remains a matter of debate (Goldfarb and Groves, 2015), with most workers arguing for it to be located in the continental crust (e.g. Pitcairn et al., 2006; Large et al., 2011). This requires some process of pre-enrichment of the continental crust in gold prior to the first and major age peak in the secular distribution of orogenic gold deposits, i.e., before 2.75 Ga. Some of this pre-enrichment could be achieved by magmatic processes involved in the formation of juvenile crust, in which case the same constraints as discussed above for porphyry/epithermal deposits apply. Another pre-enrichment process is sedimentary through deposition of metalliferous black shale deposits. Carbonaceous shales (and especially pyrite therein) have been recognised as an important source of gold (and other elements) in epigenetic collision-related gold deposits such as orogenic and Carlin-type deposits (Large et al. 2011). This source was not available in the Archaean. Recently, Johnson et al. (2017) suggested, based on trace element data on black shales and on sedimentary pyrite, that formation of highly metalliferous black shales requires not only a euxinic depositional environment but also elevated oxygen levels in the contemporaneous atmosphere. Considering the lack of atmospheric O_2 prior to the GOE, gold-rich black shales as source of Au in crustal fluids in Achaean times can be effectively disregarded.

3. A 2.9 Ga mega gold-event by microbial fixation

The combination of all of the above explains the lack of large hypogene gold deposits prior to c. 2.75 Ga but raises the question as to the source of the largest known gold anomaly in the Earth's crust, i.e., in the Mesoarchaean Witwatersrand Basin. To find an answer to this, it is helpful to realise that Witwatersrand-type conglomerate-hosted gold mineralisation was by no means limited to the Witwatersrand Basin in the Kaapvaal Craton but affected many Mesoarchaean to Palaeoproterozoic fluvial conglomerates above major erosional unconformities in most old cratons worldwide. Examples from outside the Kaapvaal Craton are known from the Dharwar, Singhbhum, Pilbara, Sáo Francisco, Amazon-Sáo Luis, West African and Congo cratons, the Superior Province as well as the Baltic Shield in Fennoscandia (summarised by Frimmel, 2014). Comparison of all these deposits/occurrences reveals not only a very similar style of mineralisation but also systematic differences (Table 1). Their ore mineralogy is a function of depositional age, with those auriferous conglomerates older than the GOE typically containing abundant rounded pyrite and locally uraninite, which are, based on their mineral chemical and isotopic characteristics, without any doubt detrital (Hofmann et al., 2009; Koglin et al., 2010; Ulrich et al., 2011; Frimmel et al., 2014). In contrast, those conglomerates that are younger than the GOE contain magnetite and/or haematite instead and lack any detrital uraninite. Critical for the understanding of the genesis is the observation that the gold endowment in all of these conglomerates is independent of the extent of orogenic or metamorphic overprint and also independent of the chemistry of whatever post-depositional fluids that might have altered the host rocks (Frimmel et al., 2005; Frimmel, 2014).

It is not always straightforward to identify a given gold particle as being an allogenic nugget. The term "nugget" is typically applied to masses exceeding 1 g in weight or 4 mm in diameter, but many detrital gold particles in modern placers are much smaller (Hough et al., 2007). Detrital gold enters river systems either as free gold particles, usually <1 mm in size, or more commonly as inclusions in ore clasts. Comminuition of such clasts in the first few kilometres of a river leads to the release of gold particles from the clasts, some of which can reach several millimetres in size, only to be progressively reduced in size by mechanical abrasion further downstream (Youngson and Craw, 1999). Although many allogenic particles can be of very small size (<0.1 mm), gold particles that are larger than 0.1 mm and display morphological evidence of mechanical abrasion can be safely considered detrital. Proper gold nuggets with variable degrees of rounding, indicative of both proximal and distal point sources, have been observed in almost all of the above auriferous conglomerate occurrences that are younger than 2.76 Ga.

Features such as detrital gold-bearing greenstone fragments and detrital quartz grains with primary gold inclusions provide unequivocal evidence of derivation from greenstone-hosted auriferous quartz veins, and such a provenance can explain the variable degrees of rounding of unequivocally detrital gold particles with increasing distance from their point source in an Archaean or Palaeoproterozoic greenstone belt in the hinterland (Frimmel and Hennigh, 2015). There are two exceptions to this: (i) Rounded “macro-nuggets” in conglomerates of the 2.74 Ga Fortescue Group on the Pilbara Craton, which are much bigger than explicable by erosion and mechanical transport of orogenic-type gold particles; and (ii) the Witwatersrand gold deposits, most of which are in the 2.90 - 2.78 Ga Central Rand Group (upper Witwatersrand Supergroup, Fig. A1, online suppl. material), which differ by conspicuously lacking proper nuggets and any other evidence of derivation of the gold from erosion of discrete gold deposits in the hinterland. Nevertheless, the above mentioned strong sedimentological control on the distribution of gold throughout the entire Witwatersrand ore province, has been a major argument in favour of a palaeoplacer model. This finds support from the morphology of gold particles in the ores, which in places take the form of discrete, mechanically rounded and bent, predominantly disc- to toroidal shaped, evidently detrital micro-nuggets with diameters on the order of 0.1 mm (Minter et al., 1993; Fig. 2; see also Video 1 in online supplementary material).

Similar concentrations of very fine-grained detrital gold are prevalent especially in the younger conglomerates of the upper portion of the Central Rand Group (in the Turffontein Subgroup) and at the base of the overlying c. 2.73 Ga Ventersdorp Supergroup (Ventersdorp Contact Reef). Derivation of this detrital gold from reworking of underlying gold-bearing conglomerates becomes apparent from the overruling control sedimentary facies and existence of underlying unconformities have on gold grade across the Witwatersrand goldfields. The conglomerates are particularly rich in gold where they truncate older auriferous conglomerate beds on low-angle unconformities. This is also evident in the Ventersdorp Contact Reef and again in the c. 2.66 Ga basal conglomerate (Black Reef) of the next major megasequence in the Kaapvaal Craton, the Transvaal Supergroup (Frimmel, 2014). Such evidence of upgrading the detrital gold content by mechanical (in the case of the Black Reef also some chemical, see Fuchs et al. 2016b) reworking of underlying gold-bearing strata comes not only from the Kaapvaal Craton but also from other cratons. Prime examples are 2.45 – c. 2.40 Ga auriferous and uraniferous pyritic quartz pebble and cobble conglomerates in the lower Huronian Supergroup of the Superior Province and likely stratigraphic equivalents in the Wyoming, Hearne, and Karelia-Kola cratonic fragments, all of which were deposited probably in the same basin that had opened up during rifting of the Kenorland supercontinent (Whymark and Frimmel, 2017).

Detrital gold in conglomerates that are around 2.8 Ga in age or younger was mainly derived from mechanical reworking of pre-concentrated gold in older sediments, and from c. 2.65 Ga onwards, also from the erosion of discrete gold deposits, mainly of the orogenic type, as exemplified by the auriferous conglomerates at the base of Caraça Group in the São Francisco Craton, Brazil (Minter et al., 1990). The former source yielded the richer deposits but its significance diminished rapidly with time, whereas the latter became over time more and more the dominant source of younger placer gold deposits, such as the Cenozoic placers along the Yuba River in California, USA, those of Klondike in the Yukon Territory, Canada, and of the Otago goldfield in the Southern Alps, New Zealand. Total past production from these placer goldfields is on the order of 300 t for each and thus pales in relation to the roughly 52 000 t of Au produced so far by the Witwatersrand mines.

None of the above explains the source of gold in the oldest auriferous conglomerates at around 2.9 Ga, which constitute by far the richest ore bodies (reefs). As shown in Figure 3, the reefs at the base of the Central Rand Group have yielded about 55 % of total Witwatersrand gold production, followed by those in the middle Central Rand Group (29 %), upper Central Rand Group (8 %) and the Ventersdorp Contact Reef at the base of the Ventersdorp Supergroup (7 %). In comparison, gold production from conglomerates older than 2.90 Ga is insignificant. The exact gold endowment is difficult to quantify because of conflicting data on the remaining resources.

This gradient in gold endowment over time is also reflected by the corresponding ore grade. The richest reefs have been the Carbon Leader and Main Leader reefs (largely mined out) in the lower Central Rand Group with ore grades between 20 and 40 g/t gold, followed by the Basal and Steyn reefs in the middle Central Rand Group with 19 g/t, whereas those in the upper Central Rand Group and the Ventersdorp Contact Reef have been mined at 5 – 12 g/t. The even younger Black Reef contributed with <10 t a comparatively insignificant amount of gold and its grade is as low as 2 – 4 g/t. The exceptionally high grades in the older reefs can be explained by a different mode of gold occurrence. They contain, in places, stratiform accumulations of hydrocarbon-rich material (usually referred to as "carbon seams"), a few millimetres to several centimetres in thickness, draping old erosion surfaces, scour surfaces and bedding planes below conglomerate beds (Fig. 4). Locally, in some reefs, as much as 70 % of all the gold has been reported to occur within these "carbon seams" (Hallbauer and Joughin 1973). Their mode of occurrence, the presence of clasts of (gold-mineralised) carbon seams in palaeo-erosion channels that truncate in situ carbon seams, their chemical and isotopic composition, especially a lack of C isotope fractionation between *n*-alkanes, all point to a single organic source without any long-range mobilisation (Frimmel and Hennigh, 2015). These kerogen layers or seams must not be confused with pyrobitumen globules that occur locally dispersed in conglomerate (Figs. 4 E,F) or in quartz veins (Fig. 4D) therein. They are without doubt hydrothermal remnants of migrating oils. Some of them cover rounded, detrital uraninite grains (Fig. 4E) as a result of radioactivity-induced polymerisation and cross-linking of the oils and are intimately associated with a range of secondary sulfides, U-minerals and gold (Gartz and Frimmel, 1999; Fuchs et al. 2016b). Spatial correlation between the kerogen seams with uranium is, however, due to their occurrence on top of old erosion surfaces along which heavy minerals, including detrital uraninite, became concentrated. Thus the kerogen seams can be interpreted as remnants of microbial mats (Mossman et al. 2008), which, in turn, provides a possible solution to the enigma of an apparently missing gold source for the richest gold-anomaly known in the Earth's crust.

Overwhelming evidence exists, especially from mass-independent sulfur isotope signals, for the atmosphere having been rich in CO_2, and subordinately in CH_4 and sulfuric gases, but lacking O_2 throughout the Archaean until the onset of the GOE at c. 2.45 Ga (Farquhar et al., 2007; Kasting, 2014). Intense volcanic exhalation of SO_2 in the Archaean reacted with H_2O to produce sulfuric acid (H_2SO_4) and H_2S. The latter, together with primary H_2S in volcanic emissions, invariably led to acid rainwater. With land surface temperatures probably having been high because of the high concentration of greenhouse gases in the atmosphere (mainly CO_2 and CH_4) more than off-setting the effects of a weaker Sun in the Archaean, very high chemical weathering rates under such an atmosphere are predictable and have been documented in the rock record, at least for Central Rand Group times at around 2.9 Ga (Frimmel, 2005; Nwaila et al. 2017). Chemical reactions of such acid rain with feldspar-rich rocks must have shifted the pH to higher values, thermodynamically modelled as c. 6.2 (Frimmel, 2005; Hao et al., 2017). Although locally the partial pressure of atmospheric H_2S must have been below c.10^{-5} as constrained by the presence of detrital siderite in fluvial sandstone on the Pilbara Craton, Australia (Rasmussen and Buick, 1999), in most areas, detrital and syn-genetic pyrite are omnipresent in fluvial to fluvio-deltaic deposits of Meso- to Neoarchaean age (Table 1), indicating elevated H_2S contents. Under such conditions, the solubility of gold as sulfide complex is four orders of magnitude greater than in modern river and seawater (Frimmel, 2014; Heinrich, 2015).

Such high solubility of gold in Archaean river water implies not only the potential to leach huge amounts of gold from background concentrations present in rocks exposed on the Archaean land surface but also a very high run-off and correspondingly high transfer rate of gold into the Mesoarchaean ocean. Support for elevated Au concentrations in the ocean at that time comes independently from marine pyrite chemistry as well as marine shale chemistry. Syn-sedimentary marine pyrite from Mesoarchaean sediments has the highest Au content compared to any other marine pyrite from other periods, which led to the conclusion that the gold concentration in ocean water reached a peak between 3.0 and 2.7 Ga (Large et al., 2015). Non-carbonaceous, unmineralised marine shale should best reflect the average composition of the eroded source rocks in the hinterland. Recently acquired data on such shale units from the Kaapvaal Craton, covering the time span from 3.4 to 2.1 Ga, reveal systematic changes in their gold content (Nwaila, 2017; online suppl. material Table A1). They are all above today's continental crustal average concentration of 1.5 ppb but vary significantly: the highest values of 5 – 10 ppb were noted in shales of the Witwatersrand Supergroup. Rigorous sample selection from fresh drill core and avoidance of any kind of alteration zones, combined with a statistical treatment to eliminate above-average outliers, ensured that the noted elevated gold contents are not artefacts of a few samples that contain secondary, hydrothermal gold and thus yielded anomalous values but are realistic approximations of the true background gold concentrations. Thus, both the chemistry of marine pyrite and that of fine-grained marine sediment speak for elevated gold concentrations in the Mesoarchaean hydrosphere.

In order to achieve the uniquely high concentrations of gold in the 2.9 Ga fluvial to fluvio-deltaic conglomerates, an effective trap for at least some of the gold in the Mesoarchaean river water is called for. In particular the strong spatial association of much of the gold with locally preserved remnants of former microbial mats on top of old erosion surfaces provides a crucial clue in the search for this trap. Today, micrometre-thin films of gold drape millimetre-sized columnar structures of kerogen engulfing detrital pyrite and uraninite grains (Fig. 4, see Video 2 in online supplementary material). Some workers have regarded this assemblage as the product of diagenetic oil migration and conversion to pyrobitumen, followed by reduction-induced gold precipitation from post-depositional hydrothermal fluids on the pyrobitumen surface (Fuchs et al., 2016a). Such an interpretation defies, however, the above mentioned strong stratigraphic, sedimentological, structural and geochemical evidence of the "carbon seams" being kerogen that represents in-situ remnants of former microbial mats (Mossman et al., 2008; Frimmel and Hennigh, 2015;). Similarities between the shape of the columnar hydrocarbon and merged tubes of modern cyanobacteria (Bosak et al., 2010) are striking, but the possibility of post-depositional modification of the original hydrocarbon texture with short-range mobilisation of Au (and other metals) by post-depositional fluids (in the first instance by those triggered by the 2023 Ma Vredefort impact event) as evident throughout the Witwatersrand Basin (Frimmel et al., 2005) surely exists and would explain the data presented by Fuchs et al. (2016a). Such microbially fixed gold would then have been a most suitable proximal source of the observed micro-nuggets. Sedimentary reworking of the delicate, erosion-prone structures of microbial films on the sediment surface would have released the gold therein only to be transported either by streams or wind and then re-deposited in fluvial channels or on aeolian deflation surfaces (Frimmel, 2014; Frimmel and Hennigh, 2015).

Several trapping mechanisms have been suggested to explain the spatial relationship between gold and hydrocarbon seams: microbial adsorbtion of gold (Mossman et al., 2008), precipitation through abiotic chemical reduction by organic hydrocarbons (Heinrich, 2015), and precipitation by oxidation that was triggered by the release of O_2 bubbles on the surface of first oxygenic photosynthesing microbes (most likely cyanobacteria) into an overall O_2-deficient environment (Frimmel, 2014; Frimmel and Hennigh, 2015). Irrespective of which of these mechanisms applied (maybe all of them operated together), colonies of early photosynthesising microbes in quiet pools, on floodplains and maybe very shallow coastal environments are suggested to have been the sites of first large-scale concentration of gold on the Earth's surface.

4. Palaeoclimatic control on the gold mega-event?

Was the extraordinary fixation of gold in 2.9 Ga microbe-hosting sediments a unique global event or does it merely reflect exceptional local preservation of such easily erodible deposits? Conglomerates similar to those hosting the richest reefs in the lower Central Rand Group of the Witwatersrand Basin are known also from older successions, such as the 3.074 Ga Dominion Reef beneath the Witwatersrand Supergroup, various reefs with ages estimated to be around 2.93 Ga in the West Rand Group within the lower Witwatersrand Supergroup, but also outside of the Kaapvaal Craton, e.g. a c. 2.9 - 3.0 Ga conglomerate at the base of the Bababudan Group in the Dharwar Craton, India. They all have in common similar sedimentological characteristics, an abundance of detrital pyrite and variable enrichment in detrital uraninite, but they lack hydrocarbon seams and their gold tenor is orders of magnitude lower. This difference is likely due to palaeoclimatic differences. The gold-rich period from 2.90 to 2.73 Ga was marked by intense chemical weathering as indicated by deep weathering beneath palaeosurfaces and almost total destruction of detrital feldspar (Frimmel, 2005). In contrast, older sediment successions (3.07 – 2.90 Ga) are in places rich in detrital feldspar and contain several glaciogenic diamictite and thin iron formation beds (Smith et al., 2013), thus testifying to cold conditions that most probably hindered both microbial growth and leaching of background gold from the old land surface by chemical weathering.

Between 2.8 and 2.6 Ga, a fundamental change in global sediment lithology heralds a major change in ocean chemistry. By then the first thick successions of large microbial carbonate deposits appear in the rock record. Examples are the stromatolitic Mosher Carbonate Formation in NW Ontario, Canada (Fralick and Riding, 2015), and the Mushandike limestone in southern Zimbabwe (Moorbath et al., 1987). These are shallow marine deposits that indicate more alkaline and oxidising conditions in the hydrosphere. This major shift has been explained by a drastic increase in volcanic SO_2/H_2S, evidenced by mass-independent sulfur isotope trends and most likely related to a shift in large igneous province-volcanism from predominantly submarine to predominantly subaerial at that time (Halevy et al., 2010). Thermodynamic modelling predicts a significant decrease in gold solubility under such conditions (Heinrich, 2015). Thus the high fluvial gold run-off that marked the time around 2.9 Ga would have become ineffective by Neoarchaean times.

5. Post-Archaean crustal gold cycle

Some minor gold concentration took place locally by magmatogenic and metamorphogenic hydrothermal fluids already prior to 3.0 Ga (e.g. Barberton gold – see above) but was inconspicuous relative to the first major concentration of gold in the Earth’s crust, unparalleled by any other period in Earth’s history, in the short time span from 2.90 to 2.87 Ga. At that time ideal conditions in terms of intense source area leaching, as evidenced by studies on alteration and weathering indices for marine shales (Nwaila et al., 2017), maximum gold flux off the craton and first emergence of larger photosynthesising microbial colonies (Lyons et al., 2014) coincided. Some of the gold thus formed was preserved in the richest gold reefs of the Witwatersrand, much of it became reworked immediately after its initial deposition. Considering the fragile nature of microbial mats, regression of the coastline would have reworked those microbial mats that had grown in shallow marine settings, floods those that had grown on river banks. Such reworking invariably led to the release of very fine-grained gold particles only to be concentrated mechanically further downstream, or wind-blown on old erosion surfaces, as very fine-grained placer gold that is so typical of conglomerates of the Central Rand Group (see Fig. 2 and Video 1 in the online supplementary material). With time the primary source of all that placer gold became progressively diminished and buried under younger sediment, leading to lower gold grades and endowments in younger placer deposits (Fig. 3).

The Witwatersrand Basin is an exception in the sense that it survived for some 2.8 billion years thanks to its location in the middle of an old, buoyant, stable craton and thanks to a highly protective post-sedimentary cover in the form of a thick, erosion-resistant blanket of flood basalt of the 2.7 Ga Ventersdorp Supergroup and a likely impact melt sheet related to the 2.023 Ga Vredefort impact. Elsewhere, comparable Archaean sediment successions vanished as they became removed by erosion and tectonic processes. With the onset of plate tectonics in the Neoarchaean, first enrichment of SCLM became possible through subduction of by then gold-enriched sediments and accretion of gold-bearing sedimentary rocks onto old cratonic nuclei. Thus the first and main peak in orogenic gold formation between 2.75 and 2.55 Ga can be explained as the delay with respect to the 2.9 Ga microbially induced gold mega-event corresponds roughly to the period necessary for the recycling of sediments via accretion or subduction and rise of subduction-induced melts to upper crustal levels.

Once this new type of hypogene gold deposits, be it orogenic, porphyry, intrusion-related or epithermal, began to form above subduction zones and along accretionary orogens from c. 2.75 Ga onwards, new sources for placer gold became available and the style of gold palaeoplacers changed. Local point sources in the form of hypogene gold deposits became more and more important, while the significance of sedimentary reworking of auriferous microbial mats and older placers progressively diminished. Gold placer formation began to operate more and more like in Recent placer systems. Typical features of these are the presence of also larger gold nuggets, a transition from poorly to well-rounded nuggets reflecting variable proximity to the source, and the presence of detrital host rock clasts (predominantly vein quartz and greenstone fragments) containing primary gold inclusions.

It is proposed here to distinguish between three textural types of clastic sediment-hosted gold particles with regard to their size: (i) very fine-grained placer gold that might contain micro-nuggets (<1 mm in size) but lacks proper nuggets (>1 g in weight or >4 mm in diameter) as exemplified by the

Witwatersrand deposits, (ii) variably rounded detrital gold in the form of proper nuggets explicable from the erosion of primary gold deposits with macroscopically visible gold, as for example the bulk of Recent placer gold deposits; and (iii) gold nuggets that are too large to be explained by erosion and purely mechanical abrasion during transport. The latter type is typically found in geologically young lateritic soils and can reach weights of as much as allegedly 78 kg ("Welcome Stranger" nugget from Victoria, Australia). It is usually ascribed to supergene leaching followed by precipitation of gold, be it by purely inorganic processes (Freyssinet et al., 2005) or mediated by microbes (Reith et al., 2007). The oldest example of a palaeoplacer with large gold nuggets is known from the lower parts of the 2.766 – 2.752 Ga Hardey Formation in the Neoarchaean Fortescue Group of the Pilbara Craton, Western Australia (Frimmel and Hennigh, 2015). Recently, water-worn nuggets of as much as 4 cm diameter have been reported from there (http://novoresources.com/news-media/news/display/index.php?content_id=232_). By analogy this suggests that supergene growth of alluvial gold took place as early as in Neoarchaean times.

By 2 Ga, the potential Archaean to older Palaeoproterozoic gold sources had already disappeared to an extent that prevented the formation of any giant gold placer deposits. Gold endowment approached values typical of Phanerozoic placer goldfields: a few hundred tonnes of gold - two orders of magnitude less than in the rich Mesoarchaean placers (Fig. 3).

From the Proterozoic onwards, sedimentary processes have not been the main drivers for the concentration of gold to ore grade any more. Tectonic processes, including metamorphic devolatilisation, partial melting and metal transfer via melts and fluids took over as driving forces. Plate tectonics enabled the recycling of gold, initially concentrated in sediments, into accretionary orogens and the upper mantle from where it was returned to the crust by melts and hydrothermal fluids above subduction zones. This hypogene concentration of gold into ore deposits was as episodic as the growth of continental crust (Spencer et al., 2017). Such a model of repeated recycling of originally Mesoarchaean sediment-hosted gold finds support from gold chemistry. The Witwatersrand placer gold contains two to three orders of magnitude more Os than any younger gold analysed so far and this is not a "nugget effect" caused by potential contamination with osmiridium grains but a real feature of the gold (Frimmel et al., 2005; Frimmel and Hennigh, 2015). Any hydrothermally formed gold should be devoid of Os because of the low solubility of Os in aqueous fluids, and this is reflected by Os contents on the order of as little as 0.10 to 0.01 ppb in orogenic and epithermal gold. Although the exact trapping mechanism for Os (and a range of other metals) in the syn-sedimentary, microbially mediated gold in the Mesoarchaean deposits remains unclear, the exceptionally high Os contents on the order of 1 to 10 ppb therein suggests that this gold has not been part of a magmatic-hydrothermal cycle but represents the starting material for the global gold cycle.

The new concept presented here supports the growing recognition that many metals became concentrated to ore deposits episodically through Earth's history, with the initial, principal concentration having been controlled by changing chemical and biological conditions in the atmosphere and hydrosphere. Gold was no exception to this, and without the help of microbes, the Earth's crust might have never been sufficiently fertilised in gold in the first instance to produce the variety of deposits from which we can extract this most sought after noble metal.

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Table Captions

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

Figure Captions

Fig. 1. Temporal distribution of orogenic-type (grey, updated from Goldfarb et al., 2005) and conglomerate-hosted (yellow, this study) gold in comparison with number of modern river detrital zircon U-Pb ages as proxy of continental crustal growth (Spencer et al., 2017) and proportion of juvenile crust (Belousova et al., 2010).

Fig. 2. (A) Gold concentrated along crossbeds in pebbly quartz arenite at the base of the Basal Reef, Free State Geduld mine, Welkom goldfield; (B) Attenuation radioscopic X-ray image of gold particles along the crossbeds; (C) 3-D detail of the middle of radiograph shown in B; width of photo is 4 mm; from Hölzing et al. (2015).

Fig. 3. Amount of known conglomerate-hosted gold in dependence of time; also shown is the variation in gold grade. Note an exponential decrease both in amount of gold and ore grade from the postulated gold mega-event at 2.90 Ga toward younger ages. The richest deposit with ages between 2.90 and 2.86 Ga are distinguished by containing remnants of gold-rich microbial mats (see Fig. 4).

Fig. 4. Mode of hydrocarbon occurrence in Witwatersrand rocks: (A, B) Hand specimens of gold-rich kerogen seams with interstitial heavy minerals (pyrite) at the base of the Vaal Reef, Stilfontein mine, Klerksdorp goldfield; (C) reflected light microphotograph of columnar kerogen with gold platelets between columns from base of Carbon Leader, West Driefontein mine, Carletonville goldfield (from Frimmel and Hennigh, 2015); (D) Hand specimen of pyrobitumen globules (black) on drusy quartz vein, Ventersdorp Contact Reef, Tau Lekoa mine, Klerksdorp goldfield; (E) Back-scattered electron images of pyrobitumen globule with fragments of detrital uraninite in its core, and (F) pyrobitumen that almost completely replaced uraninite (partly altered to brannerite), both from c. 2.66 Ga Black Reef, base of Transvaal Supergroup; from Frimmel and Hennigh (2015).

Online Supplementary Material

Fig. A1. Stratigraphy of the Witwatersrand Supergroup, correlation between the various goldfields and stratigraphic position of the main gold-bearing conglomerate units (reefs); modified after McCarthy, T.S., 2006. The Witwatersrand Supergroup. In: M.R. Johnson, C.R. Anhaeusser and R.J. Thomas (Editors), The Geology of South Africa. Geological Society of South Africa, Johannesburg, pp. 155-186.

Table A1. Gold contents in marine non-carbonaceous shale units in the Kaapvaal Craton (from Nwaila, 2017)

Video 1: Attenuation radioscopic X-ray video of gold particles along the crossbeds in pebbly quartz arenite at the base of the Basal Reef, Free State Geduld mine, Welkom goldfield, shown in Figure 2; minerals with a density less than that of gold (mainly quartz) are not visible. Note the rounded, disk-like to toroidal shape of most of the gold particles and lack of an interconnected network of gold as would be expected if it were related to post-sedimentary fluid infiltration. The larger grains are evidently detrital micro-nuggets, the domain with very fine gold “dust” represents a zone of short-range gold mobilisation with crystallisation of secondary gold in secondary quartz and as overgrowths on detrital gold particles as documented by Frimmel, H.E., Le Roex, A.P., Knight, J. and Minter, W.E.L., 1993. A case study of the postdepositional alteration of the Witwatersrand Basal reef gold placer. Economic Geology, 88: 249-265.

Video 2: Attenuation radioscopic X-ray video of gold platelets draping columnar kerogen from base of Carbon Leader, West Driefontein mine, Carletonville goldfield, shown in Figure 4C; minerals with a density less than that of gold (mainly kerogen) are not visible. Erosion of this kerogen-bound gold is thought to have provided the source of the detrital micro-nuggets shown in Video 1.

Fig. 1

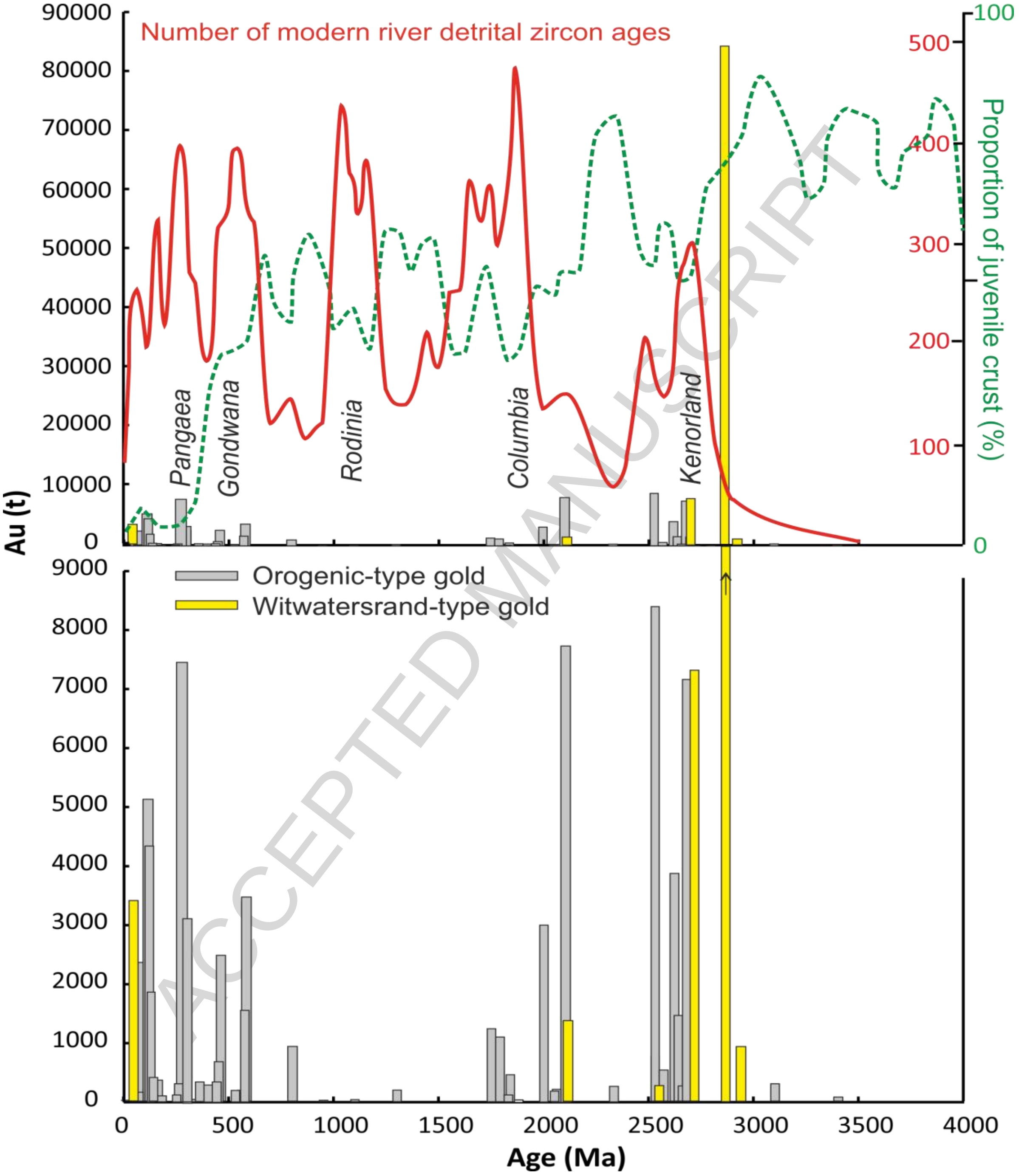
Number of modern river detrital zircon ages
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Au (t)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
500
400
300
200
100
0
100
Proportion of juvenile crust (%)
Pangaea
Gondwana
Rodinia
Columbia
Kenorland
Orogenic-type gold
Witwatersrand-type gold
0
500
1000
1500
2000
2500
3000
3500
4000
Age (Ma)

Fig. 2

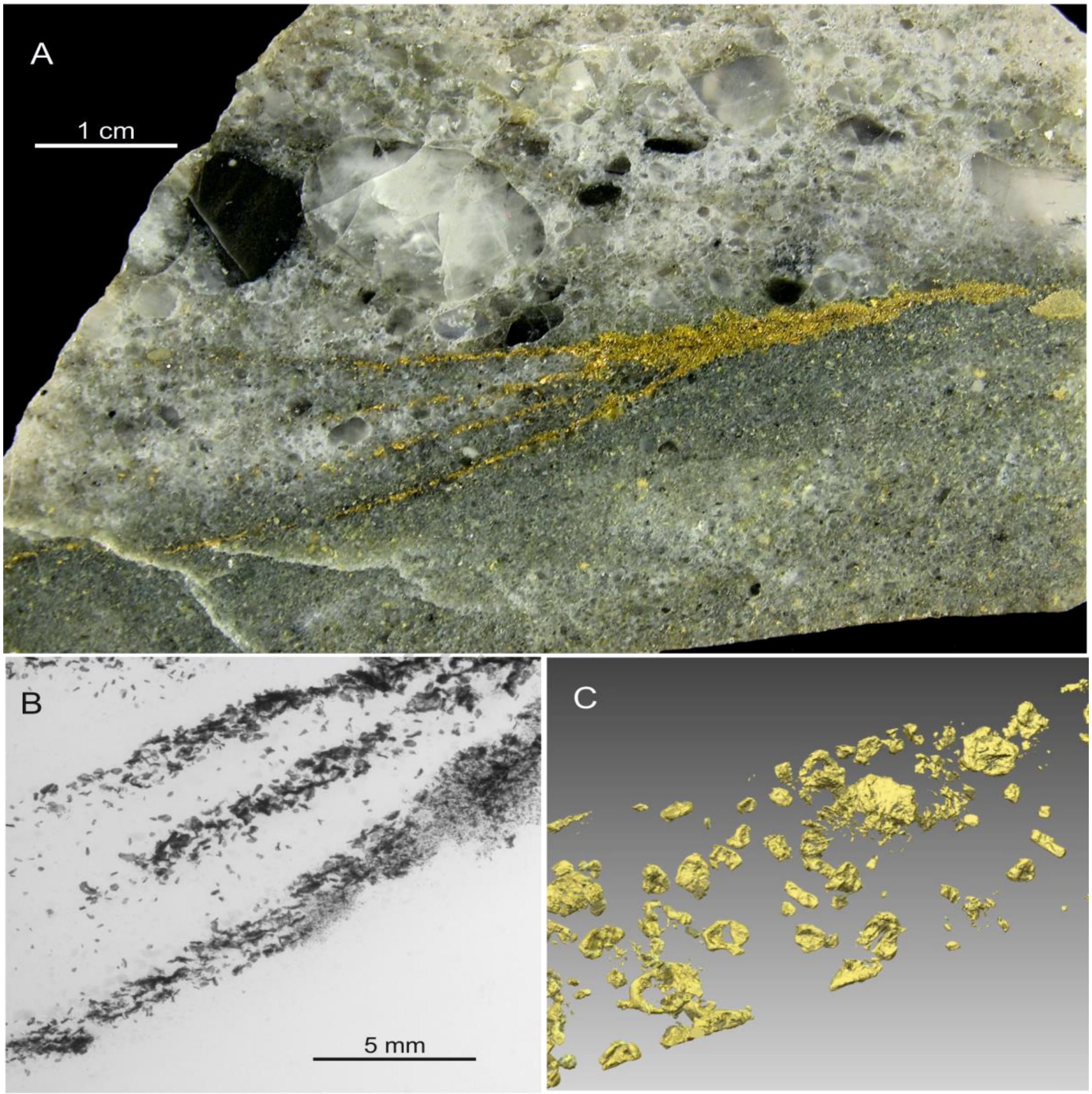

Fig. 3

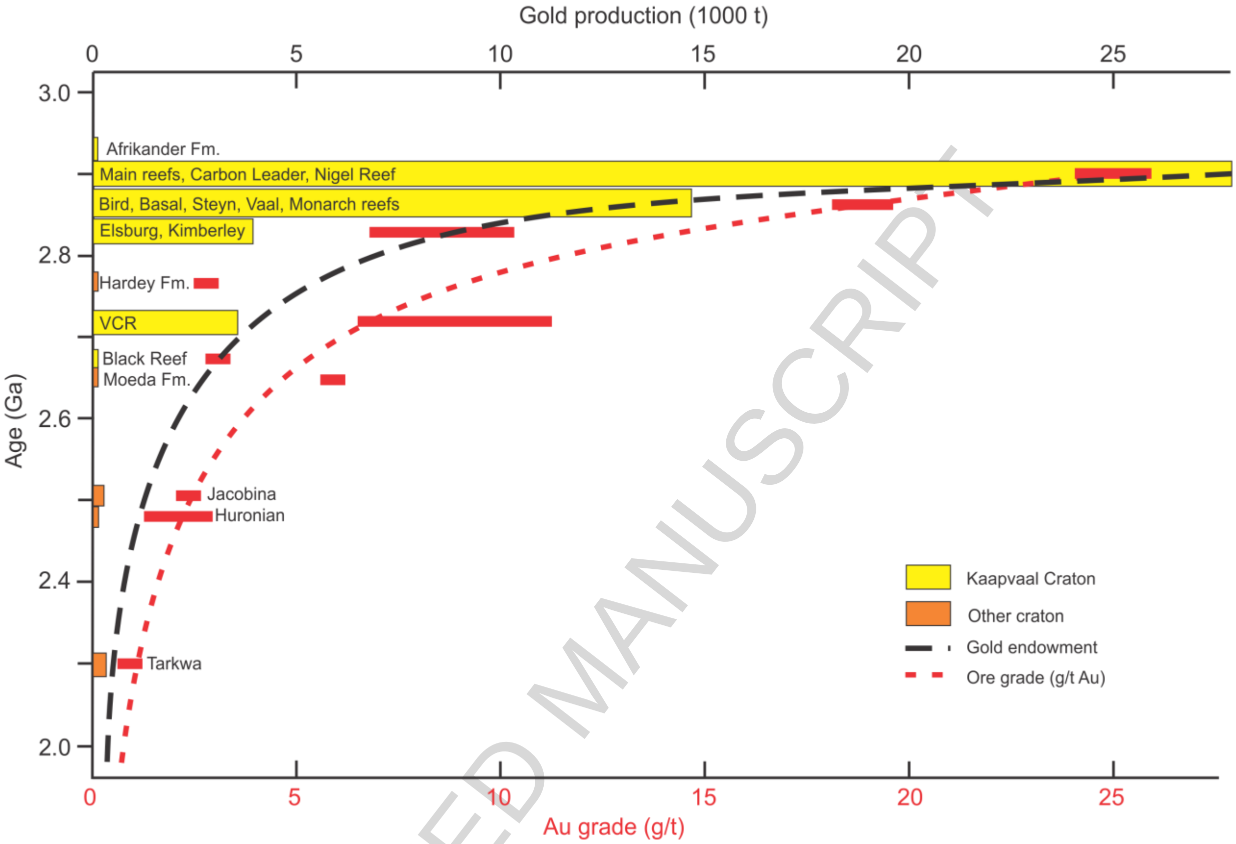
Gold production (1000 t)
0
5
10
15
20
25
3.0
2.8
2.6
2.4
2.0
Age (Ga)
Afrikander Fm.
Main reefs, Carbon Leader, Nigel Reef
Bird, Basal, Steyn, Vaal, Monarch reefs
Elsburg, Kimberley
Hardey Fm.
VCR
Black Reef
Moeda Fm.
Jacobina
Huronian
Tarkwa
Kaapvaal Craton
Other craton
Gold endowment
Ore grade (g/t Au)
0
5
10
15
20
25
Au grade (g/t)

Fig. 4

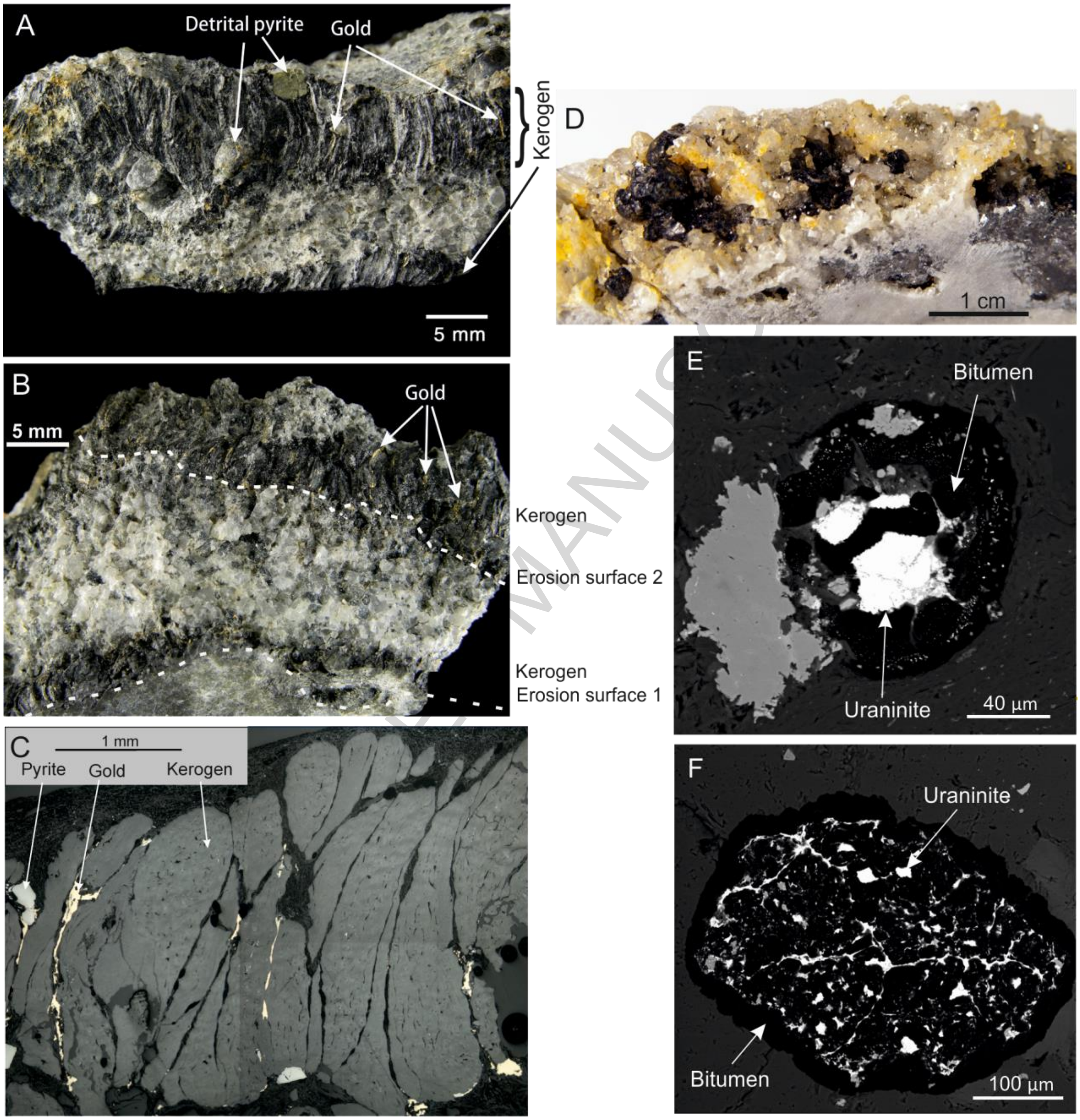
A
Detrital pyrite
Gold
Kerogen
5 mm
B
5 mm
Gold
Kerogen
Erosion surface 2
Kerogen
Erosion surface 1
C
1 mm
Pyrite
Gold
Kerogen
D
1 cm
E
Bitumen
Uraninite
40 µm
F
Uraninite
Bitumen
100 µm

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

Tectono-stratigraphic unit	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)*
Kaapvaal Craton											
Dominion Group	Dominion	3074	●	◌	x	pyrite	●	x	◌	no evidence of specific gold deposits as point source(s)	110[1]
Witwaters-rand Supergroup/West Rand Group	Bonanza	c. 2940	●	◌	x	pyrite	●	x	?		c. 10[2]
	Coronation/Rivas/Government	c. 2935	●	◌	x	pyrite	●	x	?		
	Buffelsdoorn	c. 2930	●	◌	x	pyrite	●	x	?		
	Veldskoen	c. 2920	●	◌	x	pyrite	●	x	?		
Witwatersrand Supergroup/Central Rand Group	Ada May, Beisa, North, Main, South, Carbon Leader, Commonage	2900	●	●	x	pyrite	●	●	●	mechanical reworking of gold-bearing microbial mats and older placers	41640[3]
	Middelvlei	c. 2890	●	●	x	pyrite	●	◌	◌		
	Livingstone	c. 2870	●	●	x	pyrite	●	◌	◌		21975[3]
	Basal, Steyn, Vaal, Saaiplaas, Leader, Monarch, Bird	2860	●	●	x	pyrite	●	●	●		
	Crystalkop, Kalkoenkrans, A, B, Kimberley	c. 2850	●	◌	x	pyrite	●	◌	◌		8600[3]
	Denny's, Beatrix, Composite, Elsburg, EA, Bastard	c. 2850	●	◌	x	pyrite	●	◌	◌	older Witwatersrand placers	

Ventersdorp Supergroup	Ventersdorp Contact	2714	●	◌	x	pyrite	◌	◌	●	Witwatersrand ore	8400[3]
Transvaal Supergroup	Black Reef	2664	x	●	◌	pyrite	●	x	●	Witwatersrand ore	170[4]
Pietersburg greenstone belt	Uitkyk	c. 2880-2670	●	◌	?	pyrite	?	x	◌	VMS in Pietersburg Greenstone Belt	?
Pilbara Craton											
Fortescue Group	Hardey	c. 2760	x	●	●	pyrite	●	x	◌	Archaean basement	>17[5]
Dharwar Craton											
Bababudan Group	Karthikere (basal congl.)	3050-2910	●	?	?	pyrite	●	?	?	Archaean basement	?
Chitradurga Group	basal conglomerate	>c. 2500	●	◌	?	pyrite	◌	?	?	Bababudan Gr./ Archaean basement ?	?
Singhbhum Craton											
Iron Ore Group	basal conglomerate	c. 3100 - 2900	●	◌	?	pyrite	●	?	?	?	?
Dhanjori Group	basal conglomerate	<2900, ?	●	◌	?	?	●	?	?	?	?
Sáo Francisco Craton											
Minas/Caraça Group	Moeda	2650	●	●	◌	pyrite	x	x	◌	orogenic gold	6[6]
Jacobina Group	Serra do Corrego	>2400	●	●	◌	pyrite	●	◌	◌	Archaean basement	220[7]
Superior Province											
Huronian Supergroup/ Elliot Lake Group	Matinenda	2450	◌	◌	x	pyrite	●	x	◌	Archaean VHMS, orogenic gold	>16[8]
Huronian Supergroup/ Hough Lake Group	Mississagi	c. 2400	◌	●	x	pyrite	●	x	◌	Matinenda Fm.	
Hurwitz Group	Padlei	c.	◌	?	?	pyrit	?	?	?	?	?

		2400 ?				e				
West African/Sao Luis Craton										
Boa Esperança Basin	Boa Esperança Reef	c. 2100	x	◌	◌	haematite	x	x	x	orogenic gold in Gurupi Belt	?
Tarkwa Group	Banket	2100	x	●	◌	haematite, magnetite	x	x	x	?	370[9]
Amazon Craton										
Roraima Supergroup	several conglomerates above palaeo-erosion surfaces	1900	x	●	◌	magnetite	x	x	x	orogenic gold	<1[10]
Fennoscandian Shield										
Kumpu Group	Kaarestunturi	c. 1880	●	●	?	haematite, magnetite	x	x	?	?	?
Bangweulu Block										
Mporokoso Group	Mbala Formation	<1800	◌	?	?	haematite	x	x	x	?	<<1[11]

● - abundant, ◌ - rare/low, x - absent, ? – unknown

* 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

[1] Rantzsch et al. (2011)
[2] estimate from Afrikander Lease and Buffelsdoorn mines prior to 1934 (Handley 2004)
[3] past production from SA chamber of mines statistics normalised by proportion (28.6) as given by Robb and Robb (1998), resource based on RMD (2015) data, normalised by estimate on rel. proportion of remaining resources (25 %)
[4] RMD 2015, Modderfontein - historic prod., Modder East mine - resource
[5] Novo Resources Technical Report (2015), http://www.novoresources.com
[6] Garayp and Frimmel (2016: presentation at 35th IGC, 27/08-04/09/2016, Cape Town)
[7] Yamana Gold Inc. company data
[8] estimate from Inventus Mining (pers. comm. 2017)
[9] RMG, 2015© Intierra Raw Materials Group, Stockholm
[10] W.E.L. Minter (Goldstone Resources, unpubl. report 2006)
[11] P. Karpeta (Bastillion Ltd. unpubl. report, 2001)