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Cycling of biogenic elements drives biogeochemical gold cycling

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Abstract

Microorganisms are key-drivers of carbon-, nitrogen-, sulfur- and metal cycling on Earth. Through their metabolic activities they directly and indirectly link element cycles. This leads to the cycling of elements through the Earth's ecosystems from/to the atmosphere to/from the lithosphere. Gold (Au) is a rare, redox-active, noble transition metal, which is neither essential as a nutrient nor, reputedly, mobile in the environment. Therefore, observations published in recent decades, which have shown that gold is highly mobile and subject to biogeochemical cycling largely driven by microbiota, have surprised many. Questions concerning the fundamental biogeochemical processes mediating gold cycling, the organisms involved and the benefits they may gain have puzzled researchers. In this review we integrate the cycling of the major biogenic elements carbon, nitrogen and sulfur with that of gold. We identify key-processes that drive gold cycling and evaluate how different chemical Au(I/III)-species affect microbiota that form biofilms on gold-bearing minerals and placer gold particles. Additionally, we assess how the cycling of the gold-associated metal(loid)s silver, copper, iron, manganese, mercury and arsenic is linked to that of gold. Microbially produced compounds resulting from carbon, nitrogen, sulfur, iron and manganese cycling (*e.g.*, organic acids, cyanides, (thio)sulfates, ammonium, iron sulfides/oxy-hydroxides and managanese oxides) can each play important roles for the mobilization of gold. Highly toxic, mobile Au(I/III)-complexes affect the phylogenetic and functional composition of microbial communities resident on gold particles. This leads to gold detoxification coupled to active and passive biomineralization, and ultimately the aggregation and (trans)formation of metallic gold particles. The complex interplay between gold, microbiota and physicochemical conditions modified by these organisms (*e.g.*, redox or pH) has throughout the Earth's history led to the aggregation of gold particles (grains to nuggets), led to the

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formation of the largest known gold deposit (*i.e.*, Witwatersrand paleo-placer), and the largest gold reservoir in seawater. Today it opens up exciting biotechnological pathways for mineral exploration, processing and remediation.

Keywords: Biogeochemistry; element cycles; intercycle coupling; gold; carbon; nitrogen; sulfur; microorganisms; bacteria

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1. Introduction

Elements are transported through and between the Earth's compartments in different forms, including as gases, liquids, solids, organic or inorganic chemicals, and in their ionic, complexed or native forms. Although schematic models commonly depict cycles of individual elements, *e.g.*, the carbon cycle, processes affecting the cycling of one element commonly also affect the cycling of other elements (Jelen et al., 2016). By driving the biotransformation of elements *via* their highly diverse and complex enzymatic machineries, biota, especially prokaryotic microbiota, are central to element cycling on Earth (Banfield et al., 2005; Stahl et al., 2013; Paul, 2014). During their >3500 Ma evolution, prokaryotes have developed genetic, physiological, metabolic and ecological capabilities, which allow them to live anywhere where water is available and ambient temperatures are below 121 ºC (Gogarten et al., 2002; Ramette and Tiedje, 2007). Due to their metabolic capabilities ranging from photo-litho-autotrophy to chemo-organo-heterotrophy, they are able obtain metabolic energy from a wide variety of substrates and environments (Madigan et al., 2008). As a result of these capabilities and their high abundances (total bacterial biomass on Earth ~10^15 kg) they create the foundation of interconnected biogeochemical cycles of elements leading to cycling of elements from the atmosphere, hydrosphere into the pedosphere and lithosphere and *vice versa* (Falkowski et al., 2008).

Microorganisms acquire and metabolize essential macronutrients (C, Ca, K, Mg, N, Na, P and S) from many different environmental sources (Alexander, 1964). Diverse metabolic activities of microbes (*e.g.*, the excretion of organic acids and siderophores) ensure the bioavailability of essential micronutrients (*e.g.*, Co, Cu, Fe, Mn, Mo, Se, V, and Zn). These elements serve, for example, as co-factors for enzymes involved in photosynthesis, glycolysis, nitrogen-fixation and a wide range of other biochemical pathways (Moat et al., 2003; Gottschalk,

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2012). Metals and metalloids can also be directly and indirectly influenced by microbial activities. This includes the enzymatic bio-transformations of metals, the oxidation and reduction of metals to obtain energy, cell-mediated detoxification *via* active efflux or methylation, and the secretion of various metabolites to either obtain metals or avert their toxicity (Da Silva and Williams, 2001; Gadd, 2010). Consequently, the cycling of most major metals (Ca, Fe, K, Mg, Mn and Na), metalloids (As, Se and Te), trace- and ultra-trace metals (Ag, Cd, Cr, Cu, Hg, Mo, Ni, Pd, U, V, and Zn) in Earth's surface and many crustal environments is driven by biogeochemical processes (Gadd, 2010; Ehrlich et al., 2015).

In most environments, microorganisms exist as part of biofilm communities, rather than as free-living planktonic cells. This is attributed to the symbiotic potential and the protection conferred in biofilms (Donlan, 2002). Microbial biofilms commonly are multispecies, sessile aggregations of microbiota attached to abiotic or biotic surfaces by extracellular polymeric substances (EPS; Costerton et al., 1995). Collective activities of these biofilm communities (especially the dissolution and precipitation minerals and metals) play crucial roles for the weathering in the Earth's upper crust (Douglas and Beveridge, 1998; Banfield et al., 1999; Gadd, 2004).

An example of a biogeochemical cycle of a metal, which until recently was considered to be inert, immobile and not biologically active under Earth surface conditions is that of gold (Fig. 1). Gold is a rare, non-essential, transition metal, which occurs in Earth's surface environments as primary metallic gold-silver alloy (electrum), in a range gold-bearing minerals (especially sulfides and tellurides) within hardrock deposits and as metallic gold particles in placers (Fig. 2A, B). At the Earth's surface, gold cycling starts with the weathering of gold-bearing rocks and minerals, *e.g.*, the mobilization of gold from gold-hosting sulfide minerals (Southam et al., 2009;

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Reith et al., 2013). Geochemical and geobiological processes can stabilize Au(I/III)-ions in aqueous solutions, because free Au(I/III)-ions are unstable in aqueous solutions under standard conditions (Reith and McPhail, 2006; Pan et al., 2007; Fairbrother et al., 2009; Zou et al., 2015). For instance, many microorganisms excrete substances, which act as complexing ligands for Au-ions promoting gold mobilization. This, in combination with Ag-dissolution, can lead to the formation of a range of dissolution features commonly observed on placer gold particle surfaces (Fig. 2C).

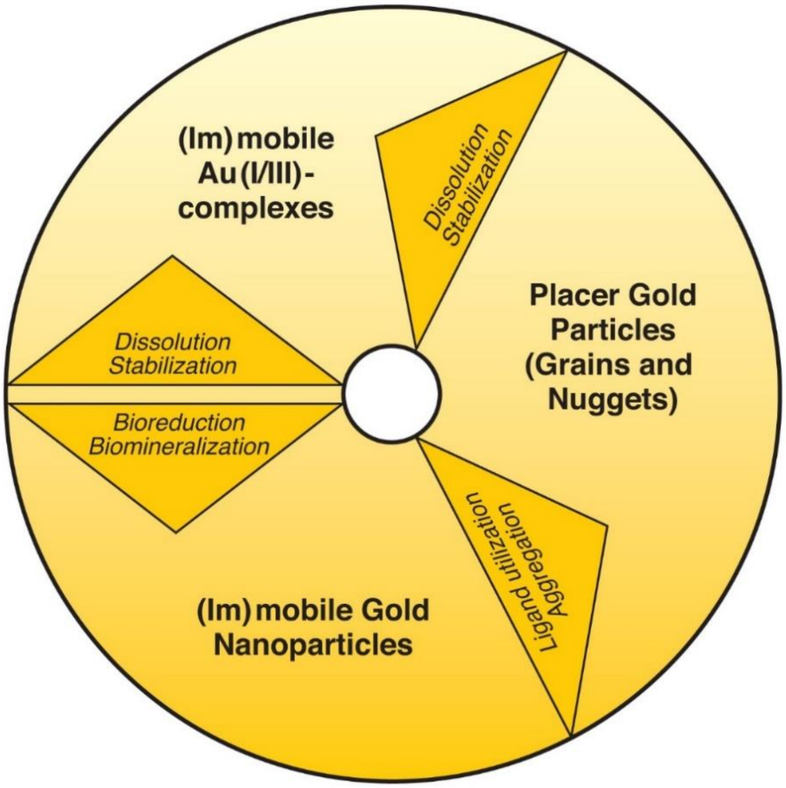

Figure 1 The biogeochemical cycle of gold in Earth's surface and near-surface environments comprises the solubilization, biomineralization and aggregation of gold. This leads to the formation of mobile or immobilized Au(I/III)-complexes

and metallic gold nanoparticles as well as the (trans)formation of placer gold particles.

Mobile Au(I/III)-complexes are highly cytotoxic by exerting oxidative and heavy metal stresses; note they display toxicity levels similar to those of Ag(I)- and Hg(II)-compounds (Nies, 1999; Wiesemann et al., 2013). Some bacteria living in biofilms on placer gold particle surfaces (Fig. 2 E, F) have developed biochemical responses to deal with the toxicity of Au(I/III)-complexes (Checa et al., 2007; Reith et al., 2009; Johnston et al., 2013; Wiesemann et al., 2013; Wiesemann et al., 2017). As a result they reductively precipitate Au(I/III)-complexes, which leads to the biomineralization of metallic gold nanoparticles (Reith et al., 2009; Johnston et al., 2013; Bütof et al., 2018). Aggregation and recrystallization of these nanoparticles contributes to the formation of pure (>99 wt.%) secondary gold overgrowths on placer gold (Fig. 2 B, D). The overgrowths exhibit a range of morphologies, including triangular, spherical, hexagonal and octahedral shapes (Fig. 2D). Microcrystals and bacteriomorphic gold as well as sheet and wire gold can also form (Southam and Beveridge, 1994; Kerrich et al., 2000; Shuster et al., 2017a). Ultimately, the above mentioned biogeochemical processes lead to: the (trans)formation of placer gold particles (*i.e.*, grains and nuggets, defined here following Hough et al. (2007) as gold masses weighing less or more than 1 g, respectively), the dispersion of gold in the world’s oceans, and the accumulation of gold in (sulfo-)organic sediments. The latter gave rise to the formation of a range of large gold deposits, such as shale-hosted- and quartz pebble conglomerate (QPC) deposits. The former has been the subject of scientific debate, especially in relation to the processes affecting the formation of gold nuggets (*e.g.*, discussed in Falconer et al., 2006). According to Hough et al. (2007), following on from the work on Australian nuggets by Liversidge (1893 and 1897), the formation of large gold nuggets is the result of hypogene

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processes, as demonstrated by internal structures of coarse grained and often twinned crystals of electrum. In contrast, Kamenov et al. (2013) and Rakovan et al. (2017), who have assessed lead isotope signatures and mineral inclusions of gold nuggets from the Rich Hill (Arizona, United States) and Bodaibo (Lena Goldfields, Russia), respectively, suggest that these have largely, and in some cases entirely, formed in surface environments.

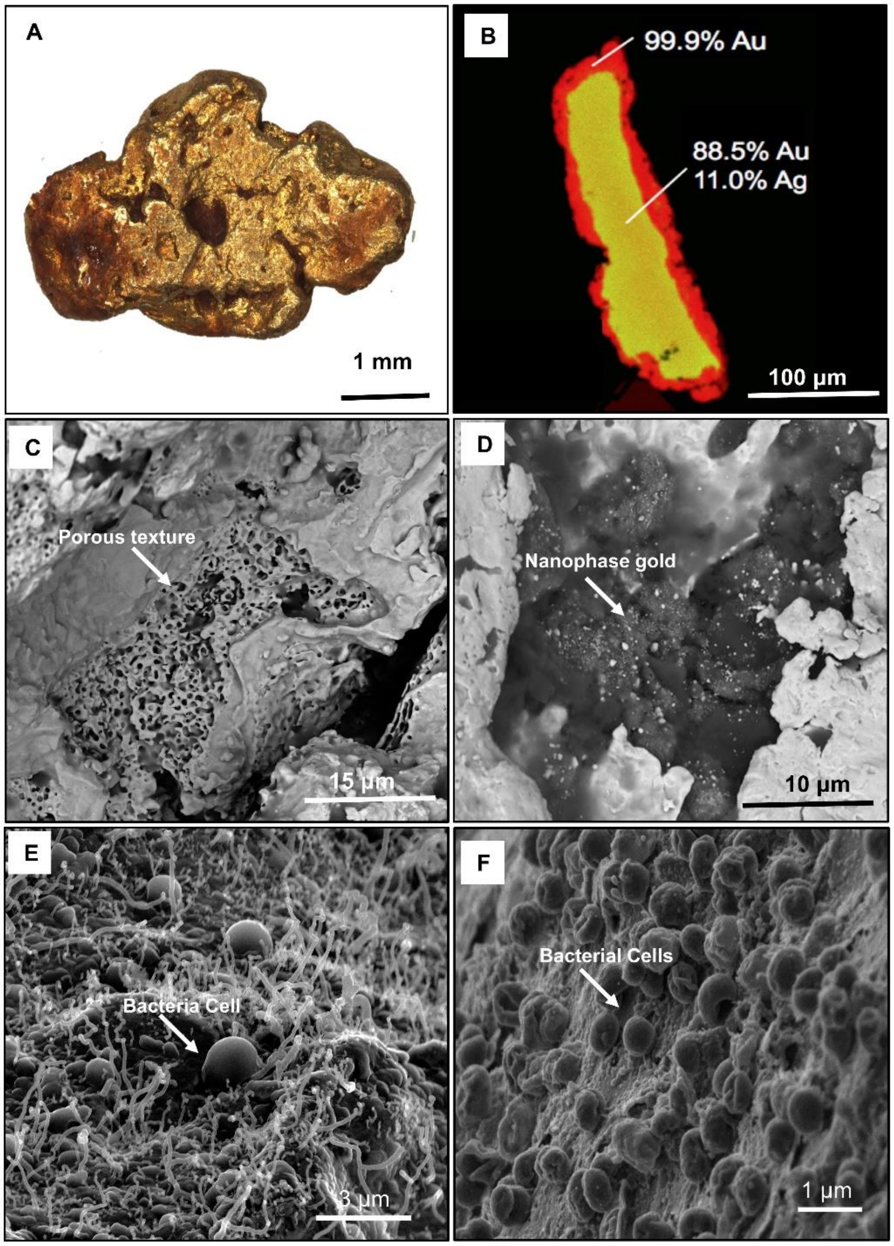

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Figure 2 **(A)** An optical micrograph of a placer gold particle. **(B)** Quantitative electron microprobe map of a polished whole-mount showing a transformed placer gold particle consisting of a primary core composed of electrum and a biotransformed rim of pure secondary gold (Rea et al., 2019). **(C)** Backscatter electron (BSE) SEM micrograph of a placer gold particle surface showing a porous network of gold dissolution morphotypes. **(D)** BSE SEM micrograph of a gold particle surface showing re-precipitation of secondary nanophase gold pseudo-spheres and euhedral crystals embedded in a clay-organic polymorphic layer. **(E, F)** Secondary electron (SE) SEM micrograph showing biofilms composed of bacterial cells and EPS on the surfaces of placer gold particles.

While we now understand a range of the processes that mediate gold cycling in the environment, a synthesis of knowledge in relation to integrating gold cycling with the major biologically-driven element cycles is urgently needed. The aim of this review is to enlighten the fundamental understanding of interconnected element cycles and assess how the cycling of biogenic elements drives the cycling of gold. The paper encompasses an in-depth review of critical microbial populations and processes that mediate carbon, nitrogen and sulfur cycling and how the cycling of these elements affects gold cycling in Earth's surface environments. In particular, the microorganisms driving major element and gold cycling in biofilms on placer gold particles are assessed. In addition, gold cycling in relation to the cycling of other metals with critical geochemical or biochemical links to gold is discussed.

2. Effect of biogenic element cycles on gold cycling

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2.1. Carbon and gold

If one element was nominated to signify life it has to be carbon, because the global carbon cycle exerts its dominance over all living things and the processes that affect them (Fig. 3; Fenchel et al., 2012; Ehrlich et al., 2015;). In the global carbon cycle, carbon is recycled through all Earth's major reservoirs, *i.e.*, from the atmosphere and hydrosphere through to the biosphere, pedosphere and lithosphere and *vice versa* (Janzen, 2004). A vast amount of carbon on Earth is stored in sedimentary rocks within the planet's crust. These rocks are produced by the sedimentation and diagenesis of organic carbon-rich mud and the formation of carbonate minerals, *e.g.*, calcite and dolomite, which is largely associated with marine systems (Altermann et al., 2006; Brumsack, 2006). Carbonaceous substances in sedimentary and metamorphic rocks are excellent sorbents of heavy metals (including gold) resulting in their diagenetic concentration and low-temperature metallogenesis (Razvozzhaeva et al., 2008; Large et al., 2011). This points to an important role of carbonaceous organic substances for the formation of large gold deposits (Fig. 3; Disnar and Sureau, 1990; Razvozzhaeva et al., 2008; Frimmel, 2014). Indeed, numerous reports have also shown highly elevated concentrations of gold in crude oil (Shah et al., 1970; Hulen and Collister, 1999; Yin et al., 2012). In some gold deposits ore bodies have been shown to contain elevated amounts of light hydrocarbons with C1 – C9 carbon chains (Hulen and Collister, 1999; Polito et al., 2002). In others, gold is finely dispersed in organic lenticular carbonaceous substances (Mossman and Dyer, 1985; Mossman et al., 2008; Wood and Popov, 2006). This is the case at the Sukhoi Log deposit, one of the largest gold deposits in Russia, where gold is associated with carbonaceous substances and sulfides in a black shale and siltstone sequence (Large et al., 2007). However, according to Frimmel (2014 and 2018) and Frimmel and Hennigh (2015) the largest concentrations of gold in the Earth's crust occur in laterally extensive carbonaceous seams.

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These are the result of gold accumulation in extensive mats of early photosynthetic bacteria (likely cyanobacteria) occurring in the oxygen-deficient environments more than 2900 Ma ago. Frimmel (2018) further suggests that reworking of gold from these mats by fluvial processes in ancient placer environments led to the formation of quartz-pebble conglomerate (QPC) deposits. Of these the super large Witwatersrand deposits in the Kaapvaal Craton in South Africa are the best persevered examples, other examples are found in the Pilbara Craton (Australia), as well as old cratons in Canada, China, Brazil and Fennoscandia (Frimmel, 2014). Frimmel (2014 and 2018) further argues that these gold-bearing bioorganic sediments also provided a source for large orogenic, porphyry-type, hydro- and epithermal gold deposits. The formation of the latter, so Frimmel (2014 and 2018), is a result of the onset of modern-style plate tectonics during the Neoarchaean, which led to the reworking of gold-rich sediments along active plate margins.

Arguably the first step in carbon cycling is the biological reduction of atmospheric, inorganic carbon, *i.e.*, carbon fixation (Fig. 3). It is one of the most important biogeochemical processes on Earth, because it creates a bridge between inorganic and organic/biological realms (Rothschild and Mancinelli, 1990). In modern and ancient ecosystems, the production of biomass through photosynthesis is the most widespread form of carbon fixation. Other forms of autotrophic carbon fixation have also been described, *e.g.*, by communities surrounding deep-sea hydrothermal vents (McKendry, 2002; Ver Eecke et al., 2012). Photosynthesis converts photo energy (sunlight) into chemical energy by converting atmospheric carbon dioxide to reduced, energy-rich, organic chemicals such as sugars. Eukaryotic phototrophy mediated by plants and algae dominates in current terrestrial environments (Smil, 2003; Raven, 2009; 3). Oxygenic photosynthesis by cyanobacteria is an important driver of carbon fixation in freshwater and marine environments and here provides organic carbon as a substrate for a heterotrophic

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succession (Stanier and Bazine, 1977; Huertas et al., 2014). Due to their ability to fix carbon phototrophically and their unique stress adaptation capabilities (including heavy metal resistance and salt tolerance) cyanobacteria are ubiquitous on Earth. They are found in fresh and saltwater environments, in top-soils, in sediments as well as in 'extreme' environments, including at metal-contaminated or hypersaline sites (Huertas et al., 2014)

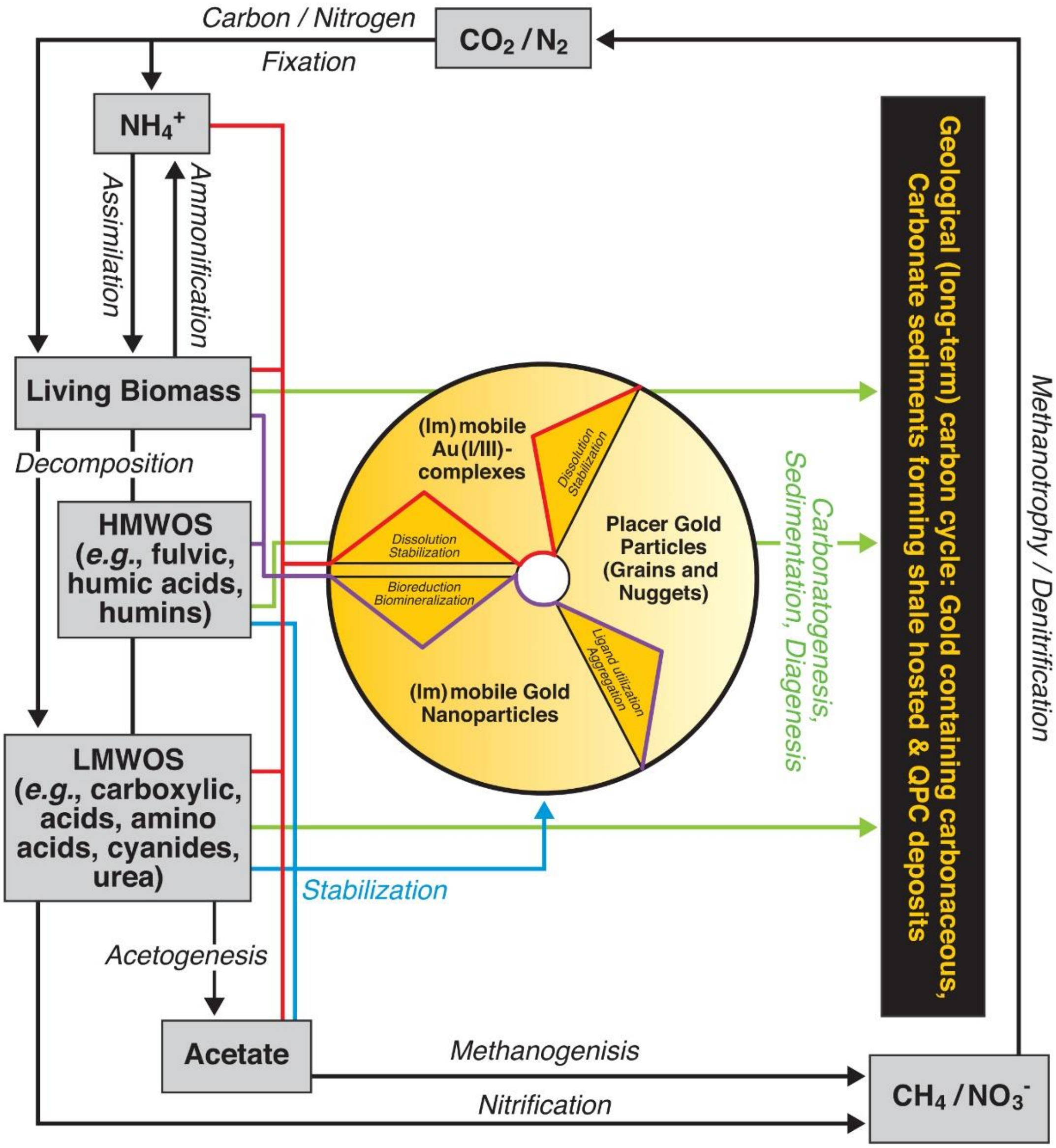

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Figure 3 Integration of the short- and long-term biogeochemical cycles of carbon and nitrogen with the biogeochemical cycle of gold.

In ancient (and modern anoxic) environments, prokaryotically-driven anoxygenic photosynthesis is thought to be the main pathway to fixing carbon. During this process cellular energy is produced without producing oxygen as a by-product (Blankenship, 2014). Therefore, anoxygenic photosynthesis is also considered to be an important link between the carbon cycle and the cycles of nitrogen, iron and sulfur, because electron donors other than water (*e.g.*, NO_2^-, H_2S, Fe^{2+}) are utilized (Burgin et al., 2011). Some modern cyanobacteria have the capability to grow by anoxygenic photosynthesis and morphological fossils of cyanobacteria have been recorded in Archean sediments (Nealson and Rye, 2003). For example, some communities forming Archean stromatolites (*e.g.*, in Pilbara Craton of Western Australia and in the Pongola Supergroup of South Africa) are thought to have been capable of driving anoxygenic photosynthesis; note: the occurrence of early oxygenic photosynthesis in the Archean has also been proposed (Allwood et al., 2006; Frimmel and Hennigh, 2015). Several other groups of obligate and facultatively anaerobic chemolithoautotrophs, *e.g.*, green sulfur bacteria, red and filamentous purple bacteria (*Chloroflexi*, some Acidobacteria and Heliobacteria) also use anoxygenic photosynthesis.

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A scenario where the importance of microbial carbon fixation on gold has been demonstrated, is formation of gold deposits in the Witwatersrand basin of South Africa (Frimmel, 2014; Heinrich, 2015). The Witwatersrand gold deposits host approximately 30 % of the world's gold resources (Frimmel, 2014). A large proportion of this gold, in some reef deposits as much as 70 % of all gold, is directly associated with organic carbon derived from

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microbial mats (Hallbauer and Joughin, 1973; Mossman et al., 2008; Frimmel, 2005 and 2018). These (cyanobacterial) mats grew in shallow lakes or river pools in an early anoxic Earth and accumulated mobile gold complexes from solution (Fig. 3; Frimmel, 2014, Heinrich, 2015). Geochemical modelling has shown that gold solubility in ancient waterbodies was much higher than today and that gold likely occurred as Au(I)-sulfide complexes (Heinrich, 2015). Different authors have suggested different precipitation mechanisms for these Au-complexes, including: i) adsorption (Mossman et al., 2008); ii) oxidative precipitation triggered by the release of oxygen on the surface of the microbial mats resulting from oxygenic photosynthesis (Frimmel, 2014; Frimmel and Hennigh, 2015); iii) precipitation *via* reduction by organic hydrocarbons (Heinrich, 2015); and iv) reductive precipitation as a result of bacterial activities (Horscroft et al., 2012). A laboratory study by Lengke et al. (2006) has shown that the cyanobacterium *Plectonema boryanum* can withstand high concentrations of mobile Au-complexes and has the ability to biomineralize them to metallic nano- and micro-phase gold. The study revealed that *P. boryanum* releases membrane vesicles, which are responsible for the reduction of Au-complexes and the precipitation of metallic gold nanoparticles outside of the cells and so prevent intracellular uptake of toxic mobile gold (Lengke et al., 2006).

Based on these results, Shuster and Southam (2015) have developed an experimental roller-bottle system, comprising cyanobacteria, iron-oxidizing- and sulfate-reducing bacteria (SRB), sand and fine-grained gravel, as well as nano- and microphase gold. The aim was to produce a simplified version of biogeochemical conditions in fluvial placer environments. Using this system the authors have successfully formed millimeter-scale gold particles in a range of experiments. These microbially produced gold particles are morphologically highly similar to particles from modern QPC deposits, *e.g.*, gold deposits in the Waimumu district, New Zealand

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(Falconer et al., 2006; Shuster and Southam, 2015). Gold from the Waimumu district, especially the Belle Brooke and Parker Road deposits, is commonly composed of sheet-like high purity secondary gold, resulting from the biogeochemical cycling of gold driven locally by the cycling of carbon and sulfur (Falconer et al., 2006). Similarities to gold particles from ancient Witwatersrand placer have also been made (*e.g.*, Hallbauer and Barton, 1987), but can be misleading due to the fact that here the microbially produced gold particles have been altered by post-depositional hydrothermal processes and metamorphism.

The next step of the carbon cycle is the decomposition of reduced organic carbon, which is important as it also regenerates other nutrients, *e.g.*, phosphorus and trace metals and hence links to the cycles of these elements (Fig. 3; Schimel, 1995). Under oxic conditions, aerobic respiration yields the most energy of any catabolic process. Here oxygen is the primary and ultimate oxidant for organic carbon. This results in the decomposition of carbohydrates and organic acids to the metabolic end-products CO_2, H_2O and mineral nutrients (Ehrlich et al., 2015). Under anoxic conditions, the decomposition of organic carbon involves a chain of activities mediated by a diverse group of facultative and obligate anaerobic heterotrophic bacteria and fungi. It starts with the hydrolysis of complex polymeric organic substances, *i.e.*, high molecular weight organic substances (HMWOS) to low molecular weight organic substances (LMWOS), and ends with the production of methane and carbon dioxide (Fig. 3; Madigan et al., 2008). A wide range of heterotrophic microorganisms play a role in producing metabolites, *e.g.*, low molecular weight organic acids (LMWOA) as metabolic by-products or through formation/degradation of HMWOS (Uroz et al., 2009). Many of these organic intermediates can act as lixiviants and/or reducers of Au(I/III)-complexes. They are therefore important determinants of gold mobility (Fig. 3). A number of experimental studies have shown

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that amino acids, *e.g*., aspartic acid, alanine, histidine, serine, and glycine, can solubilize gold *via* the formation of Au(I)-amino-acid-complexes (Korobushkina et al., 1976; Saxby, 2012). Bacteria such as *Chromobacterium violaceum*, *Bacillus* spp., *Pseudomonas aeruginosa* and *P. fluorescens* are known to contribute to gold solubilization *via* amino acid formation and cyanidation (Reith and McPhail, 2006; Fairbrother et al., 2009). Microcosm studies by Reith and McPhail (2006) and Fairbrother et al. (2009) have shown that bacterial consortia in soils can solubilize gold by producing Au-complexes with amino acids and cyanide. During the later stages of the experiments (after 40–50 days of incubation) bacterial consortia metabolized Au-complexing ligands and thus destabilized gold in solution, leading to its precipitation. Under anoxic conditions, LMWOAs are degraded to acetate by acetogenic bacteria (Fig. 3). Acetogens are a specialized, yet ubiquitous, group of anaerobic bacteria that produce acetate (Drake et al., 2008). Gold has been shown to readily form complexes with acetate increasing its mobility (Shock and Koretsky, 1993; Bakrania et al., 2009). As a result of the anoxic carbon decomposition in soils and sediment, organo-Au-complexes and organically stabilized nanoparticulate gold colloids may be transported in the soil solution and groundwater as part of the dissolved organic matter (DOM; Reith et al., 2007).

Together with acetogens, methanogenic archaea constitute the last limbs of the anaerobic carbon decomposition (Fig. 3; Liu and Whitman, 2008). Under anoxic conditions, acetoclastic methanogens convert acetate to CH_4 and CO_2 (Horn et al., 2003). Methanogens typically thrive in environments in which all electron acceptors, other than CO_2, have been exhausted (Horn et al., 2003). A study by Takai et al. (2001) has shown high abundances of methanogenic archaeal communities in modern gold mine waters from mines in the Witwatersrand (South Africa). Therefore, the presence of hydrocarbon seeps in gold deposits containing light hydrocarbons

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may be attributed to the biochemical activity of methanogenic archaea. Methanogenesis and sulfate reduction are thought to be the dominant anaerobic microbial processes in the deep subsurface marine environment. In the immediate vicinity of deep sea hot (~350 °C), reducing, metal-rich hydrothermal systems, *i.e*., 'black smoker' and 'white smoker' chimneys, where H_2, CH_4, H_2S gases are abundant, active chemolithoautotrophic thermophilic sulfate reducers and methanogens were detected (Ver Eecke et al., 2012). This suggest that these microbial communities might play an important role in subsurface metal deposit formation (Jannasch and Mottl, 1985; Tivey, 2007). However, further research is required to establish the role of methanogens on gold biogeochemistry, especially close to hydrothermal systems.

Methanotrophic bacteria are a group of bacteria, which metabolize methane as their only source of carbon and energy, have been detected on secondary gold particles (Rea et al., 2016). A study by Levchenko et al. (2002) has shown that a methanotrophic strain of *Micrococcus luteus* isolated from a gold mine site has a unique Au-binding protein, which forms a Au-protein complex that enhances the methane oxidation rate.

Complex biogeochemical processes produce recalcitrant carbonaceous substances, *e.g*., humic and fulvic acids as well as humins. These substances are not readily biodegradable and find their way into the pedosphere and finally into the lithosphere (Fig. 3; Atlas, 1998). As an element of group IB in the periodic table gold has a strong affinity for complex organic matter (Vlassopoulos et al., 1990). Due to the complexity and diversity of DOM researchers have found contradicting results in their solubilization/precipitation experiments (*e.g*., Freise, 1931; Baker, 1978; Varshal et al., 1984; Bowell et al., 1993). For example, metallic gold has been mobilized into solution by waters containing high amounts of organic matter derived from lignite in the absence of oxygen (Freise, 1931). Ong and Swanson (1969) have found that organic acids did

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not dissolve, complex or oxidize gold, but reduced auric chloride solution to Au(0) and formed stable gold colloids in aqueous solutions with a high DOM content. Overall, the interactions of Au-complexes with organic matter seem to be predominantly linked to nitrogen- and sulfur-containing functional groups, which constitute important reactive sites in many HMWOS (Housecroft, 1993).

Carbon is taken out of the fast biogeochemical cycle and moved into slow, geological cycle through burial of refractory organic material (*i.e.*, coal and oil) as well as through precipitation as carbonate minerals (*e.g.*, calcite, dolomite, vaterite and aragonite; Fig. 3; Schlesinger, 1995; Jiao et al., 2010). For example, calcrete is a type of pedogenic calcium-carbonate covering many arid environments around the world (Lintern, 2001). Calcrete is considered an important sampling medium for geochemical gold exploration, because in calcrete, calcium displays a strong positive correlation with gold, but not with base metals (Lintern et al., 2006; Reith et al., 2011). A comprehensive biogeochemical model for gold-anomalous calcrete formation has been proposed, which is based on microbial metabolic processes that combine biogenic calcium carbonatogenesis with gold co-precipitation (Schmidt-Mumm and Reith, 2007; Reith et al., 2011). The process involves the destabilization of Au-amino-acid-complexes through degradation to urea and suggests that nitrogen-containing compounds formed by microbes are also strongly involved in gold cycling (Schmidt-Mumm and Reith, 2007).

2.2. Nitrogen and gold

Nitrogen comprises most of Earth's atmosphere and is the fourth most abundant element in cellular biomass (Stein and Klotz, 2016). Several studies have shown that reactive nitrogen-

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containing compounds, such as proteins, their building blocks (*i.e.*, peptides and amino acids) and decomposition products (*e.g.*, cyanides and ammonium) can react with metallic gold in the presence of a strong oxidants (*e.g.*, some manganese oxides or bioorganic manganese compounds; Ta et al., 2014 and 2015) to form soluble Au-complexes (*e.g.*, Au(I)-cyanide $[Au(CN)_2]^-$, Au(I)-diammine $[Au(NH_3)_2]^+$; Campbell et al., 2001; Vicente et al., 1997). Therefore, it is likely that the biogeochemical cycling of nitrogen plays an important role for gold mobility and cycling. The global biogeochemical nitrogen cycle is closely linked to that of carbon and largely dependent on the activities of microbiota (Fig. 3; Godfrey and Glass, 2011). Steps of the nitrogen cycle are nitrogen fixation, anammox, ammonification, nitrification and denitrification (Fig. 3). All of the processes are highly dependent on the activities of a diverse assemblage of microorganisms (*e.g.*, Gutknecht et al., 2006; Madigan et al., 2008).

Atmospheric nitrogen fixation is the starting point and most essential part of the nitrogen cycle (Fig. 3). Nitrogen fixation is an energy-requiring process, in which two moles of ammonia are produced from one mole of nitrogen gas using the enzyme complex nitrogenase (Canfield et al., 2010). Only relatively few species of microorganisms are capable of fixing atmospheric nitrogen, all of which are prokaryotes. Important groups of prokaryotes that catalyze nitrogen fixation in terrestrial ecosystems are symbiotic, nitrogen-fixing bacteria belonging to the genera *Rhizobium*, *Bradyrhizobium*, and *Frankia*, which live in root nodules of legumes (Canfield et al., 2010). A number of free-living soil bacteria (e.g., some *Clostridium spp.*, *Bacillus spp. and Azotobacter spp*.) are also able to fix atmospheric nitrogen (Gutknecht et al., 2006). In aquatic environments, cyanobacteria (in addition to their role in carbon fixation) are the dominant drivers of nitrogen fixation, hereby fueling aquatic primary production (Geider et al., 2001).

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Reduced nitrogen in the form of NH_4^+ can be assimilated into biomass, such as amino acids, which are then incorporated into other nitrogen-containing biomolecules, *e.g.*, nucleotides and proteins (Fig. 3). Amino acids are abundant in geological bodies and have the ability to form mobile Au-complexes (Vlassopoulos et al., 1990; Reith and McPhail, 2006). Ambient temperature and acidity as well as type and concentration of amino acids in solution are important factors for Au-amino-acid complex formation. A study by Jingrong et al. (1996) indicates that organic acids in waters at moderate to shallow depths, *i.e.*, in meso-epithermal solutions, are capable of forming soluble Au-complexes, and thus enhance the gold mobility. This suggests that these processes may play an important role in metallogenesis of gold deposits by enabling migration of gold from source rocks (Jingrong et al., 1996). Amino acids, such as glycine, function as metabolic precursors for cyanide production in bacteria, including *Chromobacterium spp. and Pseudomonas spp.*, which have been shown to solubilize of gold *via* cyanidation (Knowles, 1976; Blumer and Haas, 2000; Campbell et al., 2001; Faramarzi and Brandl, 2006). In some ecosystems, *e.g.*, in rhizosphere soils, cyanide-producing microorganisms can constitute up to 50 % of the microbial community (Kremer and Souissi, 2001). Eksteen and Oraby (2015) have developed a gold extraction process using a glycine-hydrogen peroxide system, which may provide a cheap, environmentally friendly alternative to conventional extraction methods. Moreover, they suggest that this method has the potential to turn Western Australia's low-grade copper-gold deposits into commercially viable operations by enabling the *in situ* recovery of the metals.

Ammonification involves the conversion of organic nitrogen to ammonia *via* deamination, *i.e.*, the metabolic break-down of amino acids and other organic acids by heterotrophic microorganisms (Fig 3; Mancinelli, 1996). The ammonia generated dissolves in

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water to form ammonium ions (NH_4^+). Interestingly, Klyakhin and Levitskiy (1969) suggest that NH_4^+ in hydrothermal solutions enhances the solubility of heavy metals by acting as a transporting agent, and therefore may play a crucial role in formation of metalliferous ore deposits. Studies on ammonium-rich minerals present in gold deposits indicate that ammonium contributes to ore-forming processes by enhancing the mobility of gold in hydrothermal solutions (Klyakhin and Levitskiy, 1969; Bottrell and Miller, 1990). In addition, a fluid inclusion study by Bottrell (1986) on an ammonium-mineral-rich black shale-hosted quartz-vein gold deposit in northern Wales has revealed a close association between nitrogen levels in the fluids and the grade of gold deposit.

Urea is a common intermediate product of microbial ammonification in soils. Several studies have demonstrated that the formation of gold anomalies in calcrete (*i.e.*, accumulations of calcium carbonate forming in soil and regolith environments) is driven by ureolytic microbes (Schmidt-Mumm and Reith, 2007; Reith et al., 2011). These studies have shown that resident ureolytic bacterial communities are capable of utilizing amino acids, including L-aspartic acid and urea. This leads to the destabilization of the Au-amino-acid-complexes and concomitant co-precipitation of gold with calcium carbonates (Reith et al., 2009 and 2011). Here the formation of ammonium and carbon dioxide from urea creates suitable physicochemical conditions required for calcium-carbonatogenesis.

Nitrification is the next step of nitrogen cycle, where microbial ammonium is converted to nitrate *via* nitrite (Fig. 3; Gutknecht et al., 2006). Nitrification is an aerobic process performed by nitrifying bacteria. Nitrification contributes to soil acidification, which can result in increasing the mobility of heavy metals, such as gold, particularly in poorly buffered soils (Prosser, 2005). Gold nitrate complexes have been reported from the laboratory, but evidence for their existence

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in nature is lacking (Manfait et al., 1981). The final step of the nitrogen cycle is denitrification (Fig. 3). Dentrification is a microbially facilitated process in which nitrate is reduced and ultimately atmospheric nitrogen is produced through a series of intermediate nitrogen oxide products. Again an important link exists here between nitrogen cycling and the cycles of other biogenic elements, because reduced carbon or sulfur compounds serve as electron donors for this process. In relation to gold mobility, autotrophic denitrifying bacteria have reported to destabilize Au-complexes by utilizing sulfur-containing ligands such as thiocyanate and thiosulfate (Broman et al., 2017). This suggests that denitrifying bacteria may play a role in gold cycling. Overall, one can conclude that reactive nitrogen-containing compounds formed during biogeochemical cycling of nitrogen likely have a strong impact on gold mobility, gold biomineralization and ore forming processes.

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2.3. Sulfur and gold

Sulfur is an essential nutrient for all organisms and geochemically very important due to its ability to form a wide range of metal sulfide minerals. Indeed, most of the Earth's sulfur is tied up in primary rocks as metal sulfides (*e.g.*, pyrite, galena, sphalerite, millerite, bornite or covellite), in sediments and weathered materials as sulfate minerals (*e.g.*, gypsum, jarosite, and barite) and in secondary (biogenic) sulfides (*e.g.*, pyrite, marcasite; Ivanov and Freney, 1983; Hedges, 1992). Microorganisms especially sulfate-reducing bacteria (SRB) are a major contributors to the formation of biogenic sulfides and facilitate sulfide and gold co-precipitation by creating localized reducing conditions through their metabolic activities (Fortin and Beveridge, 1997). Some of these are products of microbial processes from earlier periods of the Earth’s history, *e.g.*, sulfides and sulfates in sedimentary Precambrian rocks (Farquhar et al.,

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2000). Like nitrogen and carbon, microbiota cycle sulfur and thereby transform it from its most oxidized- (sulfatic) to its most reduced (sulfidic) form (Fig. 4; Fike et al., 2016). The individual processes involved in sulfur cycling are dissimilative and assimilative sulfur- and sulfate reduction as well as sulphide- and elemental sulfur oxidation (Fig. 4; Kellogg et al., 1972; Nordstrom and Southam, 1997).

Gold has a unique relationship with sulfur, because it is incorporated in solid solution and as nanophase gold in (biogenic) sulfide minerals (*e.g.*, pyrite, chalcopyrite, arsenopyrite and marcasite; Arehart et al., 1993; Groves et al., 1998). In hydrothermal fluids, gold exists as sulfide- and bisulfide-complexes, *e.g.*, $[Au(HS)^0]$, $[Au(HS_2)^-]$, $[Au_2S_2{}^{2-}]$ (Renders and Seward, 1989; Gammons and Williams-Jones, 1997). Changes in ambient pressure and/or temperature can lead to the precipitation of quartz. During this processes, Au-complexes are co-precipitated as metallic gold or in gold-hosting sulfide minerals leading to the formation of gold-bearing, hydrothermal quartz-veins (Knight, 1999). In these sulfides gold is either finely dispersed in crystal lattices or occurs as metallic nano-inclusions (Boyle, 1979; Hough et al., 2011).

In Earth's surface environments sulfur-bearing minerals and compounds are readily transformed as a result of biogeochemical oxidation-reduction reactions (Ehrlich et al., 2015). Generally, the oxidative dissolution of sulfide minerals involves a complex interplay between microorganisms, solutions and mineral surfaces that leads to the formation of sulfuric acid, fuelling for example acid mine drainage (Edwards et al., 2000). Here acidophilic chemolithotrophic iron-sulfur-oxidizing bacteria (*e.g.*, *Acidithiobacillus thiooxidans, A. ferrooxidans, A. caldus, Leptospirilium ferrooxidans*) play a critical role in the dissolution of sulfides and in regulating the mobility of sulfur compounds and associated metals (Nordstrom and Southam, 1997). Under acidic weathering conditions these bacteria can dissolve gold-

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hosting sulfide minerals. This releases the gold trapped within minerals *via* the formation of mobile Au-complexes (Fig. 4; Lindström et al., 1992). Specifically, the oxidation of metal-sulfides produces thiosulfate as a metastable intermediate, which can act as ligand for the formation of soluble Au(I)-thiosulfate complexes (Lengke and Southam, 2005; Nordstrom and Southam, 1997).

A study by Schippers and Sand (1999) has shown that iron- and sulfur-oxidizing bacteria drive the biogeochemical oxidation of metal sulfides *via* the t thiosulfate-leaching- or the polysulfide-leaching mechanism, depending on the mineralogy of the metal sulfides. For acid-insoluble metal sulfides, oxidation *via* the thiosulfate-leaching mechanism' is commonly used. Hereby Fe-S_2 is cleaved. This followed by bacterial oxidation of Fe(II) to Fe(III)-hexahydrate, which drives the oxidation of inorganic sulfide to thiosulfate and ultimately produces sulfuric acid (Schippers and Sand, 1999). For acid-soluble metal sulfides, a polysulfide-leaching mechanism has been proposed. Hereby sulfides are attacked by both Fe(III)-ions and protons, resulting in the formation of intermediate polysulfides, elemental sulfur and ultimately sulfate (Friedrich, 1997;

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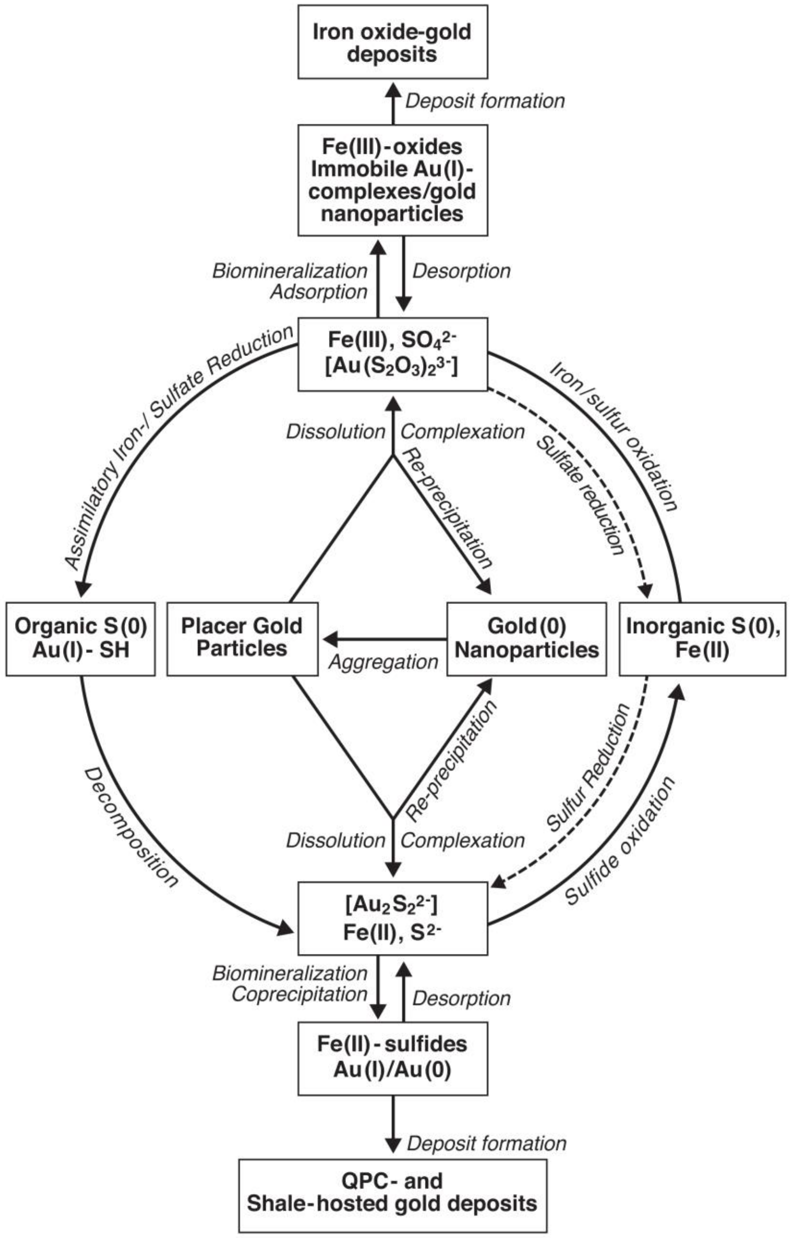

Figure 4 Integration of the biogeochemical cycles of sulfur and iron with the biogeochemical cycle of gold.

Nordstrom and Southam, 1997; Schippers and Sand, 1999). On the basis of these biogeochemical mechanisms an industrial scale bioleaching process for refractory gold ores named BIOX® has

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been developed (Van Aswegen et al., 2007). In this process, consortia of iron- and sulfur-oxidizing bacteria oxidize gold-containing sulfidic ores. This reduces the quantity of toxic lixiviants (*i.e.*, cyanide) required in downstream leaching steps and ultimately increases gold yields (Van Aswegen et al., 2007). The process has been used in gold mines in South Africa (Fairview mine), in Australia (Fosterville, Harbour Lights and Wiluna mines), in Ghana (Ashanti-Shansu and Bogoso mines), in China (Jinfeng mine), in Brazil (Sao Bento mine), in Peru (Tamboraque mine), in Kazakhstan (Suzdal mine) and in Uzbekistan (Kokpatas mine; Kaksonen et al., 2014).

The next step of the sulfur cycle is the assimilative reduction of sulfate (Fig. 4). The process involves the uptake of SO_4^{2-} by organisms, which is intracellularly reduced to sulfhydryl groups (R–SH). These are incorporated as active functional groups in a range of organic metabolites, *e.g.*, into the sulfur-bearing amino acids cysteine and methionine (Madigan et al., 2008). These amino acids constitute the key functional regions of peptides and proteins capable of gold-binding and intracellular Au-S-complex formation in bacteria (*e.g.*, in *C. metallidurans*; Reith et al., 2009). Hence, assimilative sulfate reduction can also lead to the biomineralization of gold and ultimately result in the formation metallic gold nanoparticles associated with the microbial cell or plant tissues (Anderson et al., 1999; Reith et al., 2009). Studies by Lintern et al. (1997) and Ryan et al. (2013) have shown that substantial amounts of gold can be detected in eucalypts and other plants growing in goldfields of southern Western Australia. In these plants gold appears to exist as metallic nanoparticles inside the cells (Ryan et al., 2013).

In the following steps of the sulfur cycle (*i.e.*, dissimilative sulfate and sulfur reduction) sulfate or elemental sulfur are reduced to hydrogen sulfide under anoxic condition (Fig. 4). The processes, where sulfate/sulfur act as terminal electron acceptors, are mediated by a diverse

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group of SRB, including members of the genera *Desulfovibrio Desulfomonas*, *Desulfurimonas* and *Desulfobacter* (Nealson and Stahl, 1997). Thereby, substantial amounts of hydrogen sulfide are produced, which react with available aqueous metal ions, *e.g.*, Fe^{2+}, to form metal-sulfides (*e.g.*, pyrite and marcasite; Fortin and Beveridge, 1997). A study by Boice (2002) assessed present-day microbial communities in the deep subsurface of the Witwatersrand Basin, and found a diverse SRB communities to be present. A laboratory study by Lengke and Southam (2006) has shown that SRB (*e.g.*, *Desulfovibrio* spp.) are capable of metabolizing thiosulfate from mobile Au(I)-thiosulfate complexes. This destabilizes the Au-complexes in solution, which leads to extracellular precipitation of gold nanoparticles and the production of hydrogen sulfide as a metabolic by-product (Lengke and Southam, 2006). A study by Tomkins (2013), assessing anoxic ancient oceanic and sedimentary systems, has theorized that bacterial sulfate reduction played a crucial role for the formation of sedimentary pyrite minerals and organic muds. Tomkins (2013) also suggests that bacterial sulfate reduction has led to a dramatic reduction in the solubility of gold in deep seawater environment and the subsequent formation of gold-bearing pyrite. Therefore, in early Earth's euxinic conditions, where waters were both anoxic and sulfidic, bacterial sulfate reduction likely played a crucial role in the formation of gold-bearing sedimentary sequences, which are ideal source rocks for gold deposits (Hutchinson, 1987). Walsh and Lowe (1985), who studied gold-bearing rocks the 3,500-Myr-old Onverwacht Group (Barberton Mountain Land, South Africa), suggested that SRB may have contributed in precipitation of gold. In the Witwatersrand basin in South Africa, the highest gold contents were detected in syn-sedimentary concentrically laminated pyrite, which are likely of microbial origin (Frimmel, 2018). Gold-bearing sulfide minerals, which bear strong textural resemblances to Witwatersrand precipitates, are found at the Bellebrook deposit in New Zealand. Here authigenic, secondary gold is abundant in quartz-pebble conglomerates, which are forming under present day conditions (Falconer et al., 2006). The sulfides at the Bellebrook deposit are framboidal anhedral marcasite as well as framboidal euhedral pyrite, which are common products of BSR (Falconer et al., 2006). Sulfur isotope data of marcasite from Bellebrooke corroborate that BSR is responsible for the formation of these iron sulfides (Falconer et al., 2006). Overall, this suggests that SRB and other sulfur transforming bacteria are likely to play a key role in formation economically valuable gold deposits, such as QPC-deposits.

3. Gold and other metals

In the environment the occurrence and behavior of gold is strongly intertwined with biogeochemical cycles of other metals, particularly: i) silver, through the gold-silver alloy (electrum) commonly constituting primary gold; ii) copper, through copper occurring in primary gold and soils/sediments overlying gold deposits; iii) iron, through gold-hosting, biogenic iron sulfides and sorption to iron oxides; iv) manganese, through sorption/oxidation of gold by reactive manganese oxides; v) arsenic, through arsenic-containing sulfides (*e.g.*, arsenopyrite) hosting gold in primary deposits; and vi) mercury, through natural and anthropogenic gold-mercury amalgamation. Therefore, the biogeochemical cycling of these elements in relation to gold mobility is briefly discussed.

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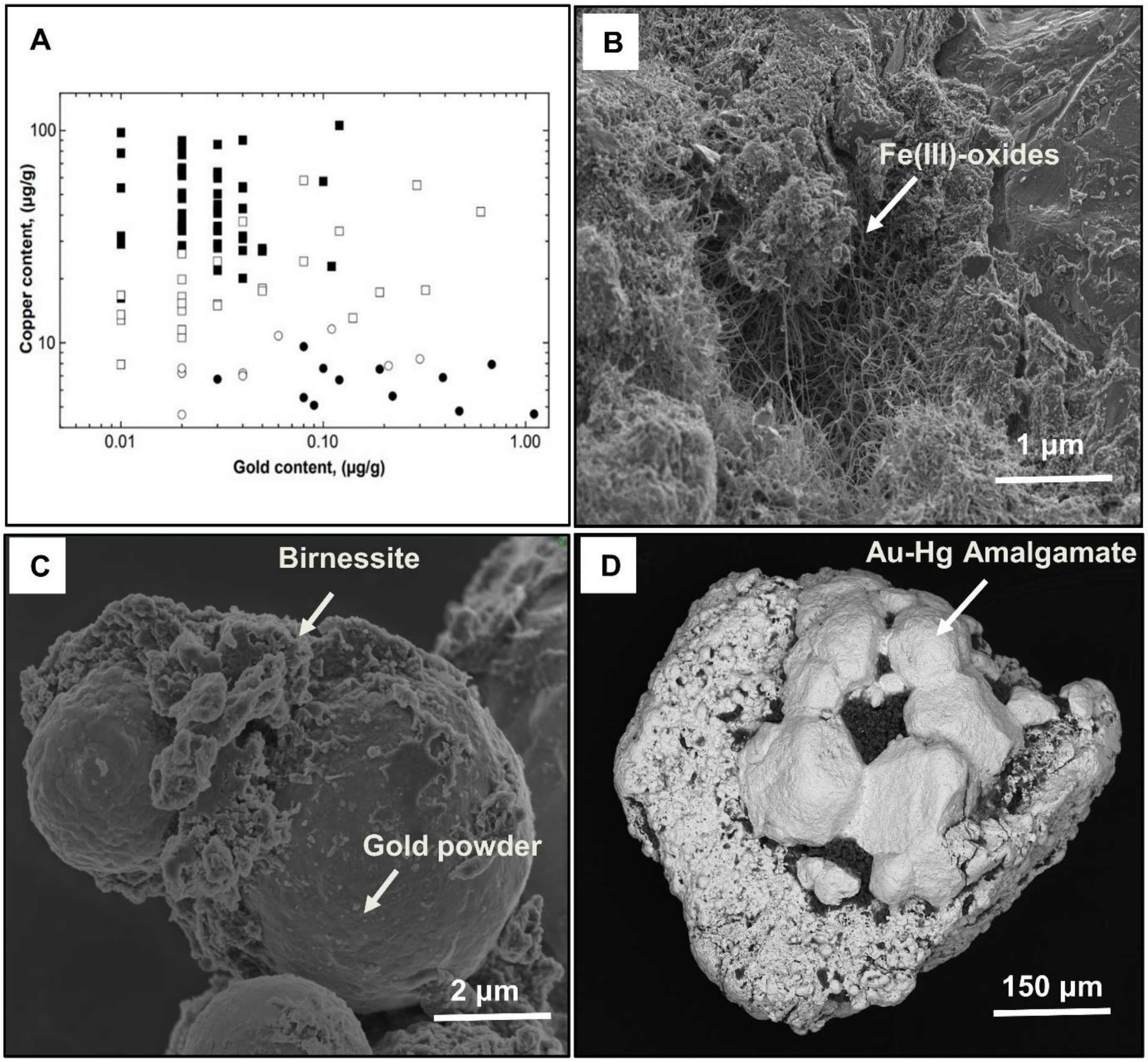

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Figure 5 Examples of the association of gold with copper, iron, manganese and mercury. **(A)** The plot shows copper and gold contents of Australian auriferous soils from four sites i) Old Pirate (○); Humpback (□); Wildcat (■); and Tomakin Park (●) (Wiesemann et al., 2017). **(B)** SE micrograph of acicular Fe(III)-oxides on the surface of a placer gold particle. **(C)** SE micrograph showing microbially formed birnessite on the surface of gold spheres. **(D)** A high resolution BSC micrograph of a gold particle affected by anthropogenic amalgamation with mercury.

3.1. Silver and gold

Silver (Ag) is a white, lustrous transition metal, which forms a natural alloy (electrum) with gold in primary gold deposits. In addition, silver occurs in silver-bearing sulfides, in mercury/gold-silver-alloys and as free native silver (nano)particles (Boyle, 1968). Because of its close association with gold and its mobility, silver is commonly used as a pathfinder element in geochemical exploration for gold (Boyle, 1979). Under surface conditions, especially in acidic and oxidizing environments, silver is more mobile than gold (Boyle, 1968). Therefore, it is depleted from primary gold-silver particles. This, in combination with the re-precipitation of mobilized gold, results in the formation of transformed secondary placer gold particles (grains as well as nuggets) that have silver-poor, gold-rich rims and silver-rich cores (Fig. 2B; Boyle, 1979). Leaching of silver from placer gold particles commonly occurs from the outside and can be seen as a continuous process. Generally, modern oxic environments seem to facilitate silver leaching from silver-bearing minerals and gold-silver alloyed particles, whereas the anoxic conditions in Precambrian environments may not have been conducive to silver mobilization (Hallbauer and Utter, 1977). Therefore, detrital gold particles in ancient conglomerates, *e.g.*, in the Pilbara Craton, and any diagenetically added gold may have remained silver-rich if the diagenesis of gold was abruptly halted and preserved (Falconer, 2018). However, care has to be taken during with interpreting gold/silver ratios in these particles, as they may be the result of later stage alteration. For instance the Witwatersrand gold particles have been compositionally altered by post-formation hydrothermal processes, so that no information about the original gold/silver distribution can be obtained (Frimmel and Gartz, 1997). Silver dissolution and complexation can be counteracted by re-precipitation of secondary, silver-

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bearing minerals or elemental silver in the environment, but this appears to be a rare phenomenon (Yin et al., 2012). Craw (1992) has shown that during the re-precipitation of gold-silver alloyed particles, only between 1 and 8 % of mobilized silver is re-precipitated. The reason behind this likely is the high environmental mobility of silver ions, which readily form water-dispersible complexes with sulfate and nitrate, as well as chloride (Levard et al., 2012; Shuster et al., 2017b). This suggests that in addition to gold toxicity the organisms also have to deal with mobile silver. Mobile Ag-complexes and nanoparticles are highly cytotoxic, because they detach cytoplasmic membranes from cell walls and affect a wide range of biochemical processes in cells (Ratte, 1999; Levard et al., 2012). A range microbes have evolved mechanisms to detoxify Ag-complexes through the silver-specific resistance genes expressing transmembrane efflux protein systems, *i.e.*, sil (silver resistance determinant) and cus (copper-sensing copper efflux system; Silver, 2003). These are found in metal-resistant and gold-cycling bacteria living on gold particle surface, such as *C. metallidurans*, *Geobacter metallireducens* and a range of other *Ralstonia* spp., *Shewanella* spp. and *Pseudomonas* spp. (Silver, 2003). Mobile Ag-complexes can also be extracellularly reduced to metallic silver nanoparticles, *e.g.*, in polysaccharide (EPS) layers, which are important components of microbial biofilms on placer gold particles (Miao et al., 2009; Gillan, 2016).

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3.2. Copper and gold

Copper has a unique geochemical relationship with gold, because it occurs as a component of primary gold particles, and is a main constituent of copper-gold-porphyry and iron-oxide-copper-gold (IOCG) deposits (Sillitoe, 1979; Groves et al., 2010). Here, it occurs as copper sulfides and sorbed to iron-oxides (Sillitoe, 1979; Groves et al., 2010). Analyses of copper contents in soils overlying gold deposits have shown elevated total copper and gold concentrations, although the gold/copper ratios can vary depending on site conditions (Fig. 5A; Wiesemann et al., 2017). Under the Earth's surface conditions, copper is more mobile and therefore more bioavailable than gold (Gadd, 2010). Notably, copper is an essential nutrient, which plays a central role in cellular biochemistry, but is toxic if present at high concentrations inside cells. Because of this copper concentrations in cells are tightly regulated *via* active biochemical import and efflux mechanisms (Pena et al., 1999). In gold-containing soils, microorganisms may commonly encounter elevated concentrations of toxic soluble Cu-ions and -complexes (Wiesemann et al., 2017). Therefore, organisms have developed sophisticated copper regulation and resistance systems, *e.g.*, the cop (copper-inducible copper resistance system) and cus systems. These are found in many bacteria living in metal-rich environments (Nies, 1999; Wiesemann et al., 2013). The toxicity of mobile Cu-ions and -complexes can, similar to silver and other metals, play an important role in gold-containing environments by exerting a continuous selective pressure on resident microorganisms, which drive the (trans)formation of placer gold particles. This is well reflected in genome of the metallophilic bacterium *C. metallidurans*, which can occur in high abundances in biofilms on gold particles (Reith et al., 2010). *Cupriavidus metallidurans* harbors a wide range of well-coordinated metal resistance systems and can co-utilize its copper resistance elements for the detoxification of toxic Au(I/III)-complexes (Wiesemann et al., 2017; Bütof et al., 2018). Biomolecular studies of this bacterium have shown that its periplasmic Cu(I)-oxidase (CopA) is involved in Au(I/III) detoxification (Wiesemann et al., 2017; Bütof et al., 2018). Here CopA functions as an oxygen-consuming Au(I)-oxidase, which converts Au(I) to Au(III). This prevents entry of Au(I) in the cytoplasm and the subsequent formation of Au(I)-S adducts, which create cellular oxidative stress (Bütof et al., 2018). The result is the direct

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reduction of Au(III) to Au(0) nanoparticles in the periplasm without the formation of toxic Au(I) intermediates (Bütof et al., 2018). Based on these results, Bütof et al. (2018) have concluded that synergistic gold-copper detoxification is the core of gold biomineralization in *C. metallidurans* CH34, and may also be important in other organisms living on gold particle surfaces.

3.3. Iron and gold

Iron (Fe) is the most abundant redox-active metal in the Earth's crust (Emerson et al., 2012). It occurs naturally as ferrous iron (Fe(II)), and ferric iron (Fe(III; Fig. 4). During the (bio)geochemical iron cycle, iron is oxidized and reduced *via* a range of abiotic and biotic processes. Microorganisms catalyze the oxidation of Fe(II) under oxic or anoxic conditions and the reduction of Fe(III) in anoxic habitats (Raiswell and Canfield, 2012). This leads to the formation of a range of iron-oxide and -sulfide minerals, *e.g.*, through bacterial biomineralization, which effect the mobility of trace elements including gold (Konhauser, 1998). The oxidation of Fe(II) to Fe(III) leads to the formation of Fe(III)-oxyhydroxides at neutral and alkaline pH, *e.g.*, goethite and ferrihydrite (Fig. 4 and 5B; Kappler et al., 2015). Chemolithoautotrophic acidophilic bacteria (*e.g.*, *A. ferrooxidans*, *Sulfobacillus acidophilus*, *Leptospirillum ferrooxidans*) as well as some heterotrophic acidophilic bacteria, play important roles in Fe(II)-sulfide oxidation in acidic conditions (Kappler et al., 2015). Under anoxic conditions, chemolithotrophic and heterotrophic bacteria and archaea can couple the reduction of Fe(III) with the conservation of energy (Kappler et al., 2015). This leads to the formation of Fe-sulfide minerals (*e.g.*, pyrite, arsenopyrite, chalcopyrite and marcasite; Miot and Etique, 2016). Microbial reduction of Fe(III)-minerals by dissimilatory Fe(III)-reducing prokaryotes has a

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strong influence on overall biogeochemical cycles of trace metals due their incorporation into resulting Fe(II)-sulfides (Emerson et al., 2012).

Gold has a close geochemical relationship with iron, because it is commonly incorporated in Fe-sulfides and adsorbed by Fe(III)-oxyhydroxides (Fig. 5B; Reith and Cornelis, 2017). The oxidation of Fe(II)-sulfides, such as gold-bearing pyrite, can lead to the mobilization of associated gold as soluble Au(I)-thiosulfate complexes (Southam and Saunders, 2005). Field and experimental studies have shown that Fe(III)-oxides possess a substantial capacity for the sorption of mobile Au(I/III)-complexes and gold nanoparticles (Gray and Lintern, 1998; Reith and Cornelis, 2017). In lateritic systems, gold is associated with Fe(III)-oxides at a range of mining sites, including at Kangaba (Mali), at Cassiporc (Brazil), at Ashanti (Ghana) and in the Yilgarn (Western Australia). It occurs as coatings on the surface of Fe(III)-oxides or interstratified within Fe(III)-minerals (Greffié et al., 1996). In samples from the Darling Ranges in Western Australia, gold has been found as micrometer-sized particles incorporated into Fe(III)-oxide pisoliths (Anand and Verrall, 2011). An experimental study by Cancès et al. (2007) on gold and goethite proposed the presence of gold interlocked in goethite. This, so the authors propose, is likely due to the strong inner-sphere sorption of Au(III) on the surface of goethite. In a study on the interactions of gold with magnetite (Fe_3O_4), Spiridis et al. (2014) have shown that atomic structure of the magnetite surface can act as a template for the ordered adsorption of gold. Recently, magnetic nanoparticles, such as magnetite nanoparticles, have been extensively studied as an industrial adsorbent for the recovery of Au(III)-complexes from aqueous or waste solutions (Sheel and Pant, 2018).

The biochemical activities of Fe(III)-reducing thermophilic bacteria and archaea provide a glimpse of the possible role of these organisms in the formation of Precambrian gold deposits.

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The reduction of Fe(III) to Fe(II) by thermophilic Fe(III)-reducers and subsequent bacterial sulfate reduction can lead to the formation of sedimentary pyrite (Tomkins, 2013). In an experimental study, enzymatically catalyzed precipitation of gold has been observed in dissimilatory Fe(III)-reducing hyperthermophilic bacteria (*Thermotoga maritime*) and archaea (*Pyrobaculum islandicum* and *Pyrocococcus furiosus*; Kashefi et al., 2001). With the aid of an unique membrane-enclosed hydrogenase enzyme these organisms can perform extracellular precipitation of metallic gold nanoparticles from Au(III)-chloride at 100 °C under anoxic conditions in a hydrogen-rich atmosphere (Kashefi et al., 2001). These results suggest that on early Earth, and today in the deep subsurface and hydrothermal systems, Fe(III)-reducing extremophiles along with SRB may have been involved in the formation of sedimentary metal sulfide deposits (*e.g.*, gold-bearing sulfide deposits; Southam and Saunders, 2005).

3.4. Manganese and gold

Manganese (Mn) is an essential trace element for living organisms and plays a crucial role in cellular metabolism (Ehrlich et al., 2015). In the natural environment, manganese is found as a major or minor component in more than 100 oxide, carbonate and silicate minerals (Das et al., 2011). Natural manganese oxide accumulations often consist of a range of manganese minerals including manganese dioxide (MnO_2), hausmannite (Mn_3O_4), ormanganite (MnOOH), and the biomineral birnessite ($(Mn^{4+},Mn^{3+})_2O_4$). Manganese-oxides are strong oxidants and scavengers of trace elements, whereas manganese-carbonates (*e.g.*, rhodochrosite, manganese-calcite and kutnahorite) are important long-term reservoirs for carbon (Tebo et al., 2004). In surface environments, the oxidation/biomineralization of Mn(II) to Mn(III/IV)-oxides is mediated directly or indirectly by a diverse group of microorganisms including cyanobacteria, heterotrophic and lithothrophic organisms (*e.g.*, *Hyphomicrobium* sp., *Pseudomonas* spp., *Leptothrix* sp., *Nitrosomonas europaea*, *Nitrobacter winogradskyi;* Nealson, 2006). Ultimately, these processes lead to the formation of reactive biogenic manganese-oxides, such as birnesitte (Fig. 5C; Webb et al., 2005).

In 1958 Goldschmidt first proposed a role of manganese oxides for the mobilization of gold (Goldschmidt, 1958). In a range of studies, Ta et al. (2014, 2015) have corroborated the role of manganese-oxides for the solubilization of gold. These studies revealed that under acidic conditions, birnesitte, can catalyze the oxidation of Au^0 and Au(I) to mobile Au(III)-complexes, which can persist in saline and hypersaline environments at neutral to alkaline pH and reducing conditions. In contrast, manganic oxide (Mn_2O_3) has also been shown to spontaneously reduce Au(III) to metallic gold with an ability of both anchoring and dispersing of gold nanoparticles in the absence of a specific reducing agent (Wang et al., 2008). The unique surface redox properties of Mn_2O_3 play a critical the role in this process (Wang et al., 2008; Yamashita et al., 2008). Due to their omnipresence in most weathering environments and their high reactivity and variable reactions with gold, manganese oxides minerals play an important role in gold mobility in Earth surface environments.

3.6. Mercury and gold

Mercury (Hg) is a highly cytotoxic heavy metal, which occurs naturally with gold as gold-(silver)-mercury amalgamate in a number of deposits, *e.g.*, OPC-deposits near Gore in New Zealand and the Prophet Gold Mine in Kilkivan, Australia (Fig. 5D; Falconer et al., 2006; Holley et al., 2010; Reith et al., 2010). Since Roman times mercury has been used in artisanal and small-

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scale gold mining in a process called mercury-gold amalgamation (De Lacerda and Salomons, 2012). In this process, mercury is mixed with gold-containing materials, which leads to the formation of a pasty mercury-gold amalgam. This is then heated and the mercury is vaporized leaving the gold behind (Adler Miserendino et al., 2017). Today, mercury amalgamation is widely used for the artisanal production of gold in many countries in South America (especially in the Amazon region), in Asia, (*e.g.*, in the Philippines and China) and throughout Africa (Lacerda, 1997). In Brazil more than 100 t of mercury are used annually for extraction of alluvial gold (Palheta and Taylor, 1995). Pacyna et al. (2010) have reported that South Africa contributes >10% of the global mercury emissions, which are derived mostly from artisanal gold mining. Mercury is highly persistent in the environment, and, partly due to microbial activities, is also highly dispersible and bioavailable. As a results, soils and waterways surrounding artisanal mining sites, in which mercury is used, are commonly highly contaminated with the metal. To combat mercury toxicity biota, especially prokaryotes, have developed a range of mercury-specific resistance mechanism (Parks et al., 2013). Mercury methylation and enzymatic reduction of Hg^{2+} to Hg^0 by members of the MerR (mercury resistance) family of proteins are the most common of the detoxification mechanisms. In some bacteria (*e.g.*, *C. metallidurans*, *Escherichia coli*, *Salmonella enterica*) MerR family regulatory proteins have also been shown to defend the cells against gold toxicity (Irawati et al., 2012; Jian et al., 2009; Pontel et al., 2007). For example, CupR/CueR or GolS, which selectively respond to toxic soluble Au(I/III)-stress, upregulate the expression of Au(I) or Cu(II) translocating ATPase proteins, which translocate toxic Au(I) from bacterial cell cytoplasm (Checa et al., 2007; Jian et al., 2009).

3.7. Arsenic and gold

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Arsenic (As) is a cytotoxic metalloid, which in the environments is transformed by a diverse group of bacteria (Sanyal et al., 2016). In arsenic-rich gold deposits, gold is often found incorporated in arsenic-bearing sulfide minerals, *e.g.*, arsenopyrite (FeAsS), realgar (As_2S_2) or orpiment (As_2S_3; Simon et al., 1999). Microcosm experiments with Australian soils have shown that resident microbial communities can solubilize gold and arsenic from these soils (Reith and McPhail, 2007). Due to the high mobility of As(III), compared to gold, it is readily dispersed in soils and groundwaters (Ehrlich et al., 2015). Therefore like silver and copper, arsenic is considered as an important pathfinder element for gold exploration (Reith and McPhail, 2007). As a result, microorganisms may encounter arsenic toxicity in the environment leading to the evolution of various genetic resistant mechanisms, including those regulated by the *ars* (arsenical resistance) operon and *arr (*arsenate reductase) and *aio* (arsenite oxidase) genes clusters (Sanyal et al., 2016). However, links between bacterial arsenic resistance and detoxification of soluble Au-complexes need to be further investigated.

4. Microbial biofilm communities on placer gold particles

Multispecies biofilms are commonly found on natural placer gold particles and are known to play a key-role in their biotransformation (Fig. 2; Reith et al., 2010; Reith et al., 2018; Reith et al., 2012b; Shuster et al., 2015; Rea et al., 2016; Rea et al., 2018). This next section will therefore briefly summarize our current understanding concerning the composition and the functional roles of the organisms constituting these biofilms. Biomolecular studies on bacterial biofilms present on gold particles have revealed that the biofilms create favorable micro-environments for the leaching of gold, silver and other metals and for re-precipitation of mobile Au-complexes as secondary gold (Reith et al., 2010; Rea et al., 2016). These biofilms have the

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ability to drive the biomineralization of gold *via* the formation of intra- and extracellular spherical nanoparticles. These can subsequently aggregate, which leads to the biotransformation of primary placer gold particles and may induce the neoformation of secondary gold particles (grains to nuggets) in Earth's surface environments (McCready et al., 2003; Reith et al., 2009; Reith et al., 2010; Kamenov et al., 2013; Shuster and Southam, 2015; Rakovan et al., 2017).

Taxonomic evaluation and studies of putative functional abilities have shown that bacterial groups capable of carbon, nitrogen and sulfur biotransformation (including carbon- and nitrogen fixation, nitrification, denitrification, sulfur oxidation, sulfate reduction) are present in these biofilms (Fig. 6; Rea et al., 2016; Rea et al., 2018; Reith et al., 2018). Carbon- and nitrogen fixation are essential for the initial bacterial colonization of the gold particles in many placer environments, because organic carbon concentrations are commonly so low that they alone are likely insufficient to support the growth and proliferation of heterotrophic bacteria. Initial colonization with autotrophic bacteria is assumed to generate the supply of bioavailable carbon and nitrogen, which provides the foundation for the subsequent colonization with heterotrophic bacteria (Fig. 6). The presence of the autotrophic bacteria *Rhodobacter* spp., *Rhodospirillium* spp. as well as cyanobacteria highlights the ability of the biofilm community for carbon and nitrogen fixation. Other bacteria capable of nitrogen fixation can also be abundant in the biofilm communities and include many Alpha-proteobacteria (*e.g.*, *Beijerinckia* spp. and *Rhizobium* spp.). Other nitrogen transformations occurring in the biofilms include nitrite oxidation, which is for example mediated by *Nitrobacter* spp. (Fig. 6).

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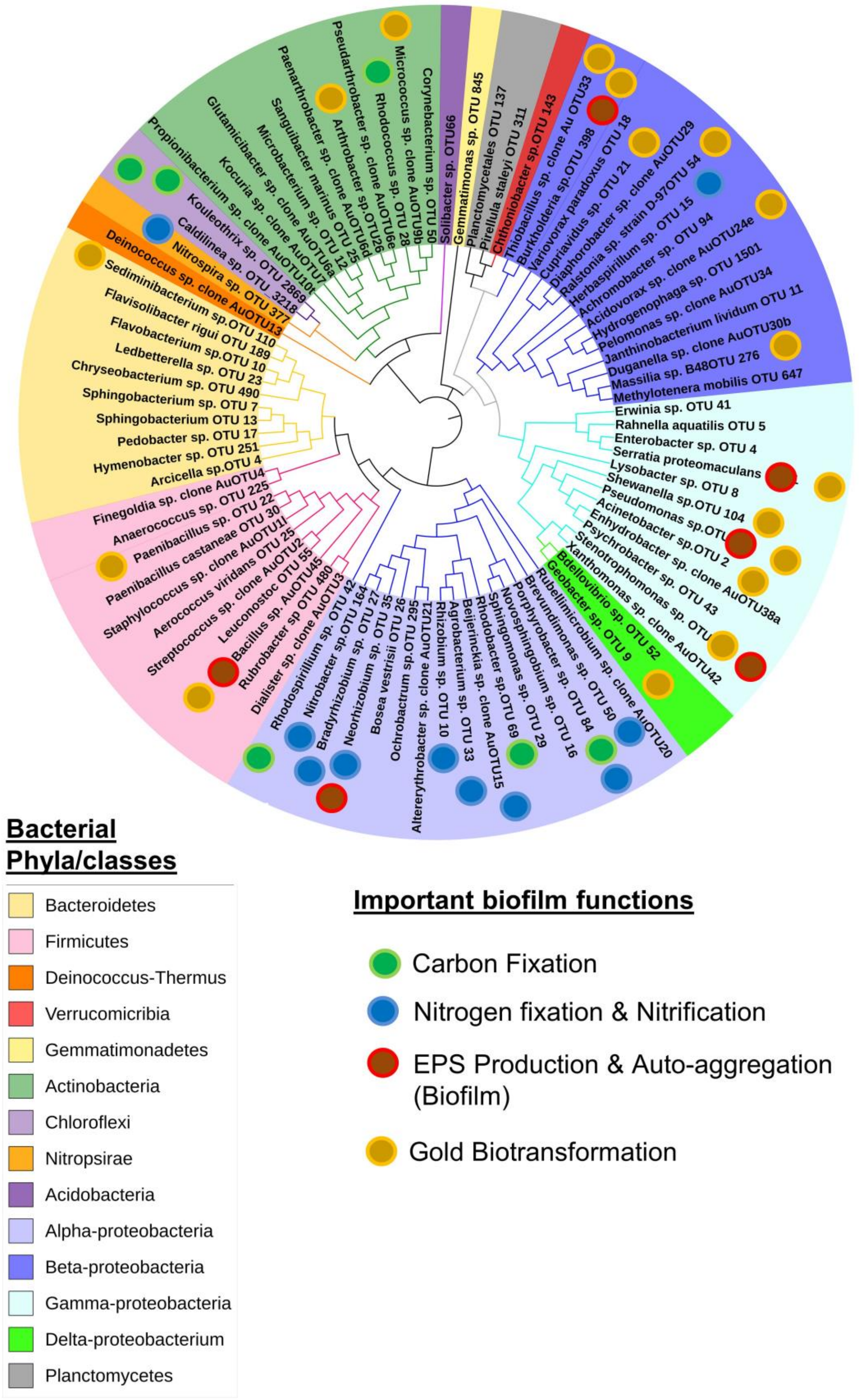

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Figure 6 A neighbor-joining circular phylogenetic tree of bacterial taxa detected on placer gold particles biofilms from sites in Australia, New Zealand, Brazil, Finland and the UK, demonstrating the diversity of bacterial species. The tree was generated using MEGA 5 and further analyzed using the Interactive Tree of Life (https://itol.embl.de/) online platform; colored circles indicate biochemical functions required for biofilm functioning on gold particles.

A diverse group of heterotrophic bacteria (from the phyla Proteobacteria, Firmicutes, Bacteriodetes and Actinobacteria) is likely to promote the solubilization of gold and other metals by producing ligands capable of mediating the formation of soluble Au-complexes (*e.g.*, amino- and carboxylic acids; Fig. 6; Rea et al. 2016). Resident cyanogenic bacteria, such as the resident *Pseudomonas* spp., *and Stenotrophomonas* spp,. can also promote gold solubility by excreting gold-complexing cyanide (Fig. 6; Fairbrother et al., 2009). Other bacteria (*e.g.*, *Diaphorobacter* spp., *Sphingomonas* spp., *Methylobacterium* spp.) harbor complete *sox* (sulfur-oxidizing) gene clusters. Expression of these permits the conversion of elemental sulfur to thiosulfate, which can from the water-soluble Au(I)-thiosulfate complexes at the biofilm/particle interface (Friedrich et al., 2005).

When taken up by cells, soluble Au(I/III)-complexes, are very toxic, because they create oxidative stress by stripping electrons from cell compounds. This leads to the disruption of both extracellular and intracellular structures as well as heavy metal stress, which can interrupt enzyme pathways (Reith et al., 2007). The presence of EPS-producing bacteria, such as some *Pseudomonas* spp., *Acinetobacter* spp., in the biofilm bacterial community is a safeguard for the structural integrity of the biofilm (Fig. 6; Karthikeyan and Beveridge, 2002; Teitzel and Parsek,

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2003). To reduce the biofilm's exposure to Au-complexes, EPS layers act as the first biological defense against gold toxicity. EPS layers immobilize Au-complexes extracellularly, which reduces the amount of soluble gold reaching the inside of cells constituting the biofilms (Harrison et al., 2007; Fairbrother et al., 2013; Johnston et al., 2013).

Other resident organisms have an even more targeted approach to dealing with gold toxicity. The extensively studied bacterium *Delftia acidovorans* produces a siderophore (delfibactin) in presence of Au(I/III)-complexes. Delftibactin reduces gold extracellularly to metallic gold nanoparticles and thus protects the biofilm from the toxicity of Au-complexes (Johnston et al., 2013). The metallophilic bacteria *C. metallidurans, Stenotrophomonas maltophilia*, *Achromobacter* spp., can detoxify Au(I/III)-complexes through a range of intracellular mechanisms, including excretion, reductive precipitation, nanoparticle formation and possibly also gold biomethylation (Rea et al., 2016). In *C. metallidurans* CH34, biomineralization of gold nanoparticles occurs *via* the reduction of mobile Au(I/III)-complexes in the periplasmic space by the copper- and gold-handling CopA (Zammit et al., 2016; Bütof et al., 2018). The resulting nanoparticulate gold can be highly mobile, susceptible to chemical dissolution and transport as well as uptake by macrobiota (trees), and hence drive the environmental dispersion of gold and the formation of secondary gold anomalies. Overall, the combination of the wide range of carbon, nitrogen and sulfur cycling capabilities coupled with metal-resistance and detoxification mechanisms enables the existence of a thriving biofilm community on gold particles despite the omnipresence of toxic mobile metals (*e.g*., gold, silver, copper and mercury). As a whole the community gains an ecological advantage by being able to live on the toxic mobile metal-rich microenvironments that are placer gold particles.

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5. The biogeochemical gold cycle – starting point for biotechnical applications

So far this review has shown that environmental gold cycling is highly complex and combines geochemical processes and microbial cycling of major elements. In combination, these processes control the nature and kinetics of gold dispersion and re-concentration in near surface- and surface environments (Boyle, 1979; Reith et al., 2007; Southam et al., 2009; Reith et al., 2013;). The fundamental knowledge of environmental gold cycling can now be used to develop efficient and cost-effective methods for gold exploration, processing and remediation. Using state-of-the-art (meta)genomic techniques allows us to characterize the microbiota and microbial functions important for gold cycling and biomineralization in key metallogenic environments, *e.g.*, in soils and deeper regolith materials, overlying different styles of gold deposits. An understanding of the distribution, diversity and function of microorganisms in soils overlying gold deposits can be used to develop bioindicator systems, which can assist with gold exploration (Fig. 7; Zammit et al., 2012). In combination with novel micro-analytical techniques, a probalistic link between microbial communities and physiochemical parameters occurring in metal anomalous soils can be established. In several recent Australian studies of soils overlying volcanogenic massive sulfide (VMS), gold-, platinum-, copper-gold-uranium and base metal deposits, microbial community compositions and abundances of metal-resistance genes were closely linked to the underlying deposits, demonstrating that pinpointing underlying ore bodies is feasible using these techniques (Reith et al., 2012a; Wakelin et al., 2012; Reith et al., 2015). To provide a dataset against which these microbial anomalies can be compared the Biomes of Australian Soil Environments (BASE) project is currently underway and to date contains phylogenetic and geochemical data of 1400 sites across the Australian continent (Bissett et al., 2016). From these databases a selection of OTUs and functional genes indicative of gold deposits can be combined

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on a low cost, high-throughput microarray, and a scoring system resulting in one number score per sample can be implemented (Fig. 7). Scores for soil samples on tenement and larger scales can then be imported into mapping software, and score maps can be produced. Importing the results into a mapping software will also enable to link these data to other datasets, *e.g.*, geological, geochemical and geophysical data.

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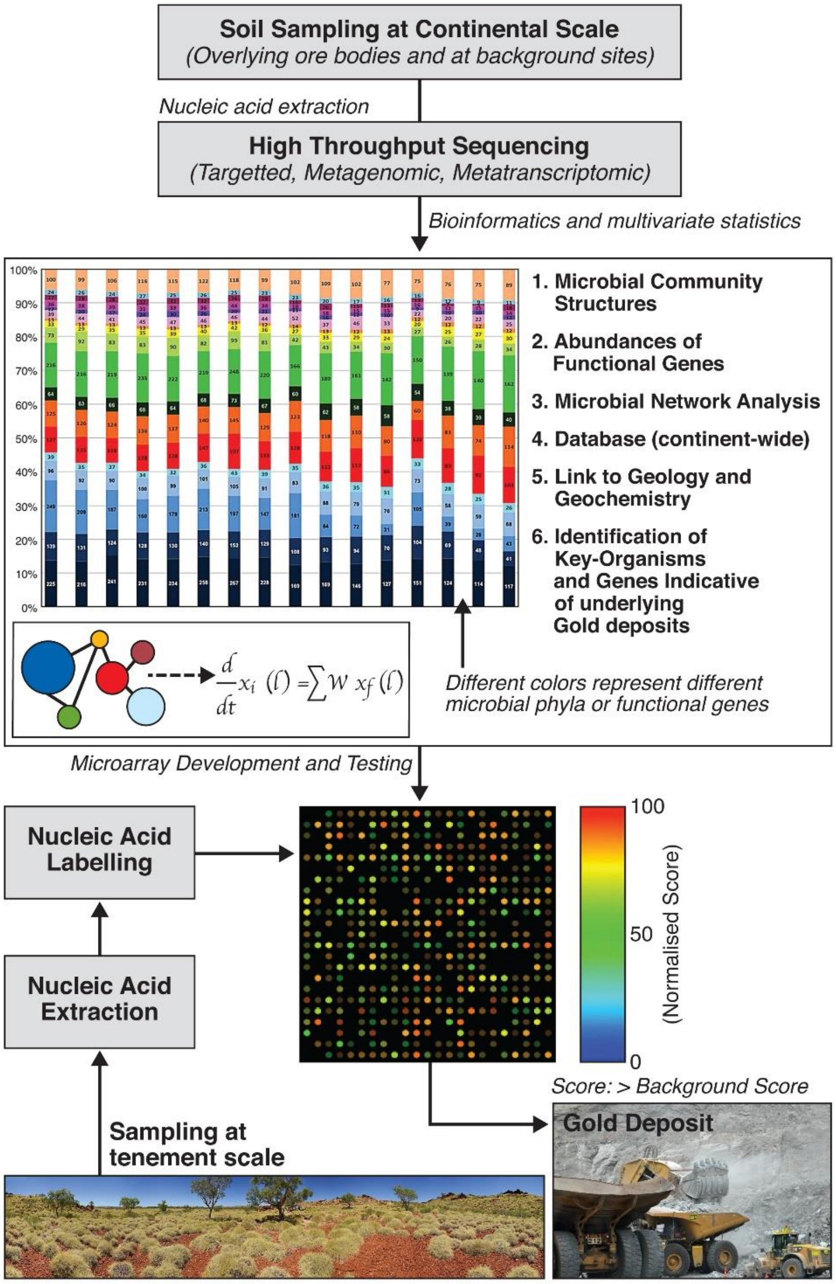

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Figure 7 Flow-diagram highlighting the development of a bioindicator scoring system for gold exploration that can be integrated with other spatially resolved data, *e.g.*, geophysical or geochemical exploration datasets.

Additionally, an in-depth knowledge of how microorganisms interact with Au-complexes can be used to develop biosensors, *e.g.*, using the gold detoxification mechanism observed in a strain of *Salmonella enterica* serovar Typhimurium. The organism harbors gold resistance *golT*SB gene cluster to alleviate gold toxicity through an active efflux system (Checa and Soncini, 2011). Based on this Zammit et al. (2013) have developed a whole cell biosensor containing the *golTSB* gene. The sensor was tested on soil samples and was able to measure the concentration of gold accurately down to a quantification limit of 20 ppb (0.1 µM) and a detection limit of 2 ppb (0.01 µM)(Zammit et al., 2013).

Gold processing technologies can also be improved based on advances in our understanding of the interactions between gold and microorganisms (Kaksonen et al., 2014). For example, thiosulfate- and cyanide-producing microorganisms can be used *in-situ* leaching of gold. Other metallophilic microbes, such as *C. metallidurans* and *D. acidovorans*, are being assessed for their ability to bioaccumulate mobile Au-complexes and nanoparticles to make them ameneable to conventional recovery (Johnston et al., 2013; Kaksonen et al., 2014). A recent study by Tay et al. (2013) has shown that metabolically engineered a strain of *Chromobacterium violaceum* enables the recovery gold from electronic (E-) waste. The organism has the ability to produce a large quantities cyanide lixiviants, which can efficiently dissolve gold from the E-waste (Tay et al., 2013). Another study by Sheel and Pant (2018) has proposed a chemical technique, assisted by microbial biosorption, for removal gold from electronic (E-) waste. The

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technique involves a combination of ammonium thiosulfate and a novel strain *Lactobacillus acidophilus* for gold recovery (Sheel and Pant, 2018). In future, the strains of *C. metallidurans* and *D. acidovorans* strain may also be used to efficiently recover gold from mining and electronic waste. Additionally, the range of application for gold nanoparticles is growing rapidly. A range of sizes and shapes of gold nanoparticles are now used in electronics as conductors, in diagnostics as biomarkers, in therapeutic drug delivery systems, in sensory devices and as industrial catalysts. Thereby, microbial processes may offer a cost-effective way of producing gold nanoparticles, of particular shapes and sizes.

6. Conclusion and outlook

This review reveals that a microbially driven interconnected web of element cycles affects gold mobility and governs gold cycling. The geobiological cycling of carbon, nitrogen, sulfur, iron and gold leads to the (trans)formation of placer gold particles, the dispersion of gold in the environment, and enabled the formation of large gold deposits, including QPC and shale-hosted deposits. Molecular profiling of gold particles and subsequent studies identifying the biochemical pathways of gold cycling have shown that a wide range of organisms are involved in driving biogeochemical cycle of gold. Therefore, now is a good the time to use this fundamental knowledge of gold biogeochemistry to develop biotechnological applications. These have the potential to revolutionize gold exploration, processing, as well as enabling gold recovery from mining and E-waste. In addition, a wide range of applications for organisms forming gold nanoparticles exist in the area of nanobiotechnology. Additional studies should therefore focus on metagenomic, (meta)transcriptomic and (meta)proteomic approaches to fully understand the functions that directly or indirectly affect the gold biotransformation in biofilms.

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Novel gold-transforming bacteria should be isolated and studied to uncover novel resistance pathways and associated proteins, which will enhance our understanding of the overall biochemistry of the microbial biofilm on gold particles and provide additional isolates for biotechnical applications.

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