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Review Article

From exploration to remediation: A microbial perspective for innovation in mining

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ABSTRACT

As society transitions to low-carbon, renewable energy resources, the demand for metals and minerals is set to increase. Massive quantities of base metals and mineral materials (for example, silica and concrete) along with smaller quantities of precious metals will be required for the construction of wind turbines, solar panels and battery storage facilities to meet the demands of the 'Electric Planet' of the future. Harnessing microbe-mineral-metal interactions may offer many opportunities to improve some mining practises and support the long-term sustainability of mining. As easily exploitable, high-grade deposits are becoming increasingly depleted there is a need for new technologies to improve exploration and mining strategies. Microorganisms are ubiquitous and diverse, surviving in almost all environments in the Earth's crust and recent advances in molecular techniques have enabled scientists to study these communities is extraordinary detail. Microorganisms also interact directly with their environment; both responding to and changing the environment around them. These responses and their influences on the surrounding environment are preserved within their genome (a complete set of the DNA of the microorganism). Here, we discuss using state-of-the-art sequencing techniques to identify key microbial genes that have been demonstrated to correlate with metal concentrations. These genetic-based bioindicators may provide additional tools to guide and improve the success rate of mineral exploration programmes. Advances in molecular techniques will also improve existing biohydrometallurgical techniques and expand the commodity range for which biohydrometallurgy are currently economically viable. Finally, microorganisms may be used in a number of strategies for mine remediation; specifically, we review in detail microbially accelerated carbon capture and storage strategies and mine waste stabilisation.

1. Mineral and metal cycles: potential roles for microorganisms

Metals are fundamental for almost all sectors of the economy and are required for infrastructure, technology and the transition to carbon neutral energy systems. The mineral resources these metals are sourced from are finite and non-renewable on human timescales. Therefore, by its very nature, mineral mining is not sustainable; however, initiatives in the mining sector can reduce the social and environmental impacts of mining. In this review, we explore potential innovations in the mining industry, with a focus on microbial biotechnologies.

Low-carbon technologies, including photovoltaics, wind turbines and batteries, require immense amounts of metal compared with fossil fuel energy generation. For example, Hertwich et al. (2015) modelled that for a unit of energy generation, the copper material requirements for photovoltaics is 11–40 times that of conventional fossil fuel energy generation. From 2025 to 2050, a 30% increase in demand for raw materials is expected (Valero et al., 2018). Cobalt and lithium for electric vehicles and magnesium, titanium and zinc for concentrated solar power and solar thermal energy production are all expected to undergo a six-fold increase in demand (Valero et al., 2018). Base and major metals, including iron, copper, lead, nickel and zinc, are also required for industrial and urban development. These base and major metals typically cannot be replaced by cheaper alternatives and have been modelled to be depleted within 350 years (Henckens et al., 2014), highlighting a need to expand exploration-based programmes to meet societal need while also improving metal recycling practices.

Furthermore, finding new, high grade, metal deposits at, or close to the Earth's surface has become more difficult through time (Calvo et al., 2016). Therefore, mineral exploration has to identify targets that may be 100 s of metres below the surface which requires the development of

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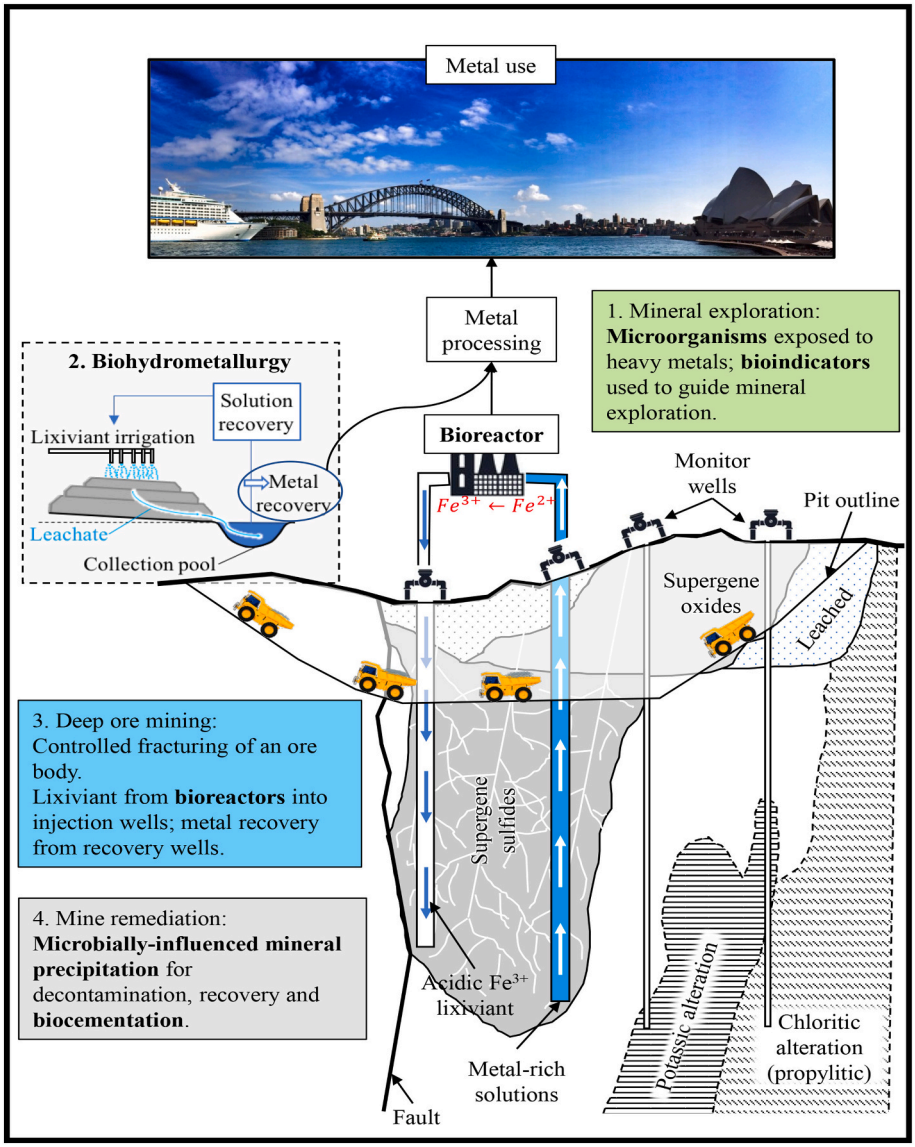


Fig. 1. Potential roles of microorganisms throughout the mining lifecycle, using a supergene style porphyry ore deposit as an example, simplified from Ossandón et al. (2001) (1.) Genetic information from microbial communities exposed to metals during supergene leaching may be used as an bioindicators for metal mineralisation. (2.) Biohydrometallurgy may be used to leach metals from ores for recovery by precipitation or electrowinning. (3.) Deep ore bodies may be mined *in situ* by treatment with an acidic ferric iron lixiviant generated in a bioreactor. (4.) Microorganisms may be used to accelerate mine tailings stabilisation and immobilise heavy metals in mine remediation.

new technologies to identify and extract minerals and metals using sustainable methods as well as improvements to water and waste management. Valenta et al. (2019) highlight the need for innovations in the mining industry by examining 308 of the world's largest undeveloped copper ore deposits. Their analysis highlighted that a significant proportion of these ore deposits are affected by a number of environmental, social and governance risks that cannot be overcome simply by an increase in the economic value of the resource.

Existing and emerging biotechnologies throughout the mining lifecycle are highlighted in Fig. 1, including potential uses in mineral exploration, metal extraction and recovery *via* biohydrometallurgy and remediation of tailings and mine sites. Geological, microbiological and engineering terms required to cover the broad range of topics discussed here are briefly described in Table 1.

All microbial-based mining biotechnologies are underpinned by the interactions between microorganisms with minerals and metals (Section 2). For exploration (Section 3), a potential road map is discussed for how studying the microorganisms associated with metal enriched regions may offer tools (bioindicators) to guide future drilling programmes (Fig. 1). Microorganisms have been widely employed for copper and gold recovery from sulphide minerals using biohydrometallurgy for many years (Johnson, 2014) and these processes may be implemented to extract metals during *in situ* mining (Fig. 1; see Section 4.2) (Johnson, 2015). Biohydrometallurgical practises are also increasingly being applied to oxidised ores under both acidic and circumneutral conditions (Johnson and du Plessis, 2015; Newsome et al., 2020). Finally, we detail geomicrobiological developments in mine remediation, including accelerated carbon capture and storage as well as biocement formation for mine waste stabilisation (Gagen et al., 2019a; Hamilton et al., 2020).

2. Metal-microbe interactions

The need to understand, and quantify, the interactions of microorganisms with metals is fundamental to using and developing biotechnologies for mining and industrial applications (Fig. 2). Some metals, most in very low concentrations, are required for microbial growth; therefore, all microorganisms contain metal-specific binding sites. Biologically essential metals (for example, sodium, magnesium, potassium, calcium, manganese, iron, cobalt, nickel, copper and zinc) are integral to a number of biological functions including stabilising cell wall and protein structures, the formation of metalloenzymes as well as the maintenance of membrane charge potentials and concentration gradients across cell membranes (Borst-Pauwels, 1981; Green and Berg, 1990; Jones and Gadd, 1990; Lanyi, 1979). Sodium, magnesium,

Table 1
List of geological, engineering and biological terms.

Term	Brief description
Physical science terms	
Ore resource	Concentration of naturally occurring materials in a form in which economic extraction may be feasible; currently or in the future
Ore reserve	Portion of a resource that a useable mineral or energy can be economically and legally extracted at the time of determination.
Secondary deposit	Weathering of primary rock leaches metals into solution, which re-precipitate at lower depths or laterally downstream
Biohydrometallurgy	Harnessing biochemical processes to extract and recover economically valuable metals
Mineral heap	Stock piling of low-grade ore and waste rock that can not processed economically using conventional methods
Lixiviant	Solutions used to selectively extract metals of interest
Bioleaching	Using microorganisms to accelerate selective mineral dissolution for metal recovery
Fracture filling	Infilling natural or artificially generated rock fractures
Metal foam	Manufactured, light weight, highly porous metal structure
Biological terms	
Genome	An entire copy of an organism's genetic material
Metagenome	All genetic material within an environment
Chromosome	Molecule containing most of an organism's DNA
Plasmid	Typically a small, extrachromosomal DNA molecule that can replicate independently
Transposon/Transposable element	Known as 'jumping genes' - mobile DNA sequences that can move and replicate throughout the genome
Transcription	Copying of DNA information into a messenger RNA (mRNA) molecule
Translation	Converting an mRNA molecule into an encoded protein
Vector	DNA molecule used to import foreign genetic material into a cell for replication/expression
qPCR	Quantitative polymerase chain reaction – using a fluorescent probe to quantify DNA generation of a target gene
FISH	Fluorescence *in situ* hybridization – a microscopy technique using fluorescent probes to localise specific genes
Homeostasis	Physiological processes that tend toward relatively stable equilibrium
Prophages/Phages	Bacterial/Archaeal virus that can insert a viral genome into a cell

potassium and calcium are major ions required for all life and halophilic microorganism have developed strategies to survive in extremely saline environments (Kushner et al., 1964; Silver and Phung, 2005), including brines well beyond supersaturation and up to a point where the only liquid water is due to deliquescence from hygroscopic salts (Schulze-Makuch et al., 2018). Similarly, some of the transition metals that have multiple environmentally-stable oxidation states (for example, iron and manganese) can facilitate redox-based processes, energy generation and carbon fixation, and microorganisms in acidic environments can survive relatively high aqueous iron concentrations (Nordstrom et al., 2000). Many of the other essential transition metals are typically only required in trace concentrations; for example, copper, nickel, chromium and cobalt play important roles in enzyme structure and formation but, at elevated concentrations, each of these metals become toxic (inhibitory to growth) to microbes that lack mechanisms to tolerate such metals (Silver and Phung, 2005). Other metals, for example, aluminium, silver, cadmium, mercury and lead, do not serve a known biological process and labile forms are always considered harmful (Gadd, 1992; Nies, 1999).

Microorganisms have developed many genetic-based metal resistance mechanisms that can be chromosomal or plasmid-based. Metal resistance genes can also be transposons, allowing for genetic mobility and gene duplication within microbial genomes (Nies, 1999). Generally, metal toxicity involves the displacement or outcompeting of essential metals from metal binding sites, resulting in disruptions to essential cell functions (transcription, cell division, DNA repair, enzyme structure and activity, cell membrane transport and structure) and inducing oxidative stresses on microbial cells (Asmuß et al., 2000; Gadd and Griffiths, 1977; Hartwig et al., 2002; Kluska et al., 2018; Macomber and Hausinger, 2011; Warnes et al., 2012).

There are many metal resistance mechanisms employed by microorganisms (Fig. 2). Metal resistance mechanisms have been reviewed specifically for lead (Naik and Dubey, 2013) and more generally for heavy metals (Bruins et al., 2000; Gadd and Griffiths, 1977). These mechanisms include (i) the widely distributed efflux metal pumps that actively relocate metals from intracellular regions back into the environment, (ii) detoxification of heavy metals (for example, catalysing the reduction of Hg^{2+} to Hg^{0}), (iii) protein-induced intracellular sequestration and bioaccumulation, (iv) the biosorption of metals onto extracellular cell surfaces and extracellular polymeric substances (EPS), (v) extracellular sequestration and microbially-promoted precipitation of metals as phosphates, sulphides or sulphates (Fig. 2) as well as (vi) adaption of cell membrane structures to reduce toxic metal binding and transport into the cell (Bruins et al., 2000; Naik and Dubey, 2013). From this list of mechanisms for heavy metal resistance, (i), (ii) and (iii) requires the expression of regulons (group of genes that are regulated together) that are specific for metal resistance; these offer potential genetic targets for mineral exploration (see Section 3). The genes responsible for the later three metal resistance mechanisms are generally non-metal specific; for example, metal-microbial interactions can be passive (iv and v) or controlled *via* the up- or down-regulation of non-metal specific and widely distributed genes (v and vi). Therefore, these non-metal specific microbial responses will be more difficult to link directly to increased metal exposure; however, biologically-induced or influenced precipitation of metals may preserve microorganisms and also offer insights into the roles of microorganisms in metal redox-transitions and element mobility (Levett et al., 2019; Pal and Paul, 2008).

By interacting with metals, microorganisms influence metal mobility in the environment. All microorganisms can induce or passively influence the precipitation of metals (Fig. 2). Of particular interest for mine remediation strategies, including heavy metal decontamination and accelerated mineral carbonation and biocement formation, is the precipitation of metals on cell surfaces and extracellular appendages (biosorption; Fig. 2). Microorganisms can also promote metal mobility, accelerating mineral dissolution and leaching metals into solution (Fig. 2). For example, as a by-product of carbon degradation, heterotrophic and fermentative microorganisms produce organic acids that can chelate metals or attack mineral bonds (Welch and Ullman, 1996). Redox-active metals can also be utilised as alternate electron acceptors during cell respiration in anoxic conditions, driving the reductive dissolution of minerals (for example, iron (III) oxides). Chemolithotrophic microorganisms can also oxidise reduced metals and sulphur compounds in acidic environments to gain electrons for carbon fixation, thereby, promoting mineral dissolution (Fig. 2).

2.1. The importance of environmental conditions

The environmental conditions play an important role in the interactions of metals and microbes. The major complexation sites for metals on bacterial surfaces are carboxyl, phosphoryl and hydroxyl groups; phosphoester sites and sulfanyl groups are less significant functional groups for metal-bacteria complexation (Burnett et al., 2006; Fein et al., 1997; Guiné et al., 2006; Moon and Peacock, 2011). At low pH values (less than pH 2), these reactive sites are typically protonated and metal-microbe binding is low (Fein et al., 1997). Therefore, at pH values less than 2, microbial binding and uptake of metals is likely to be limited, despite the increased mobility of metals in low pH environments. In environments above pH 3, these reactive sites sequentially

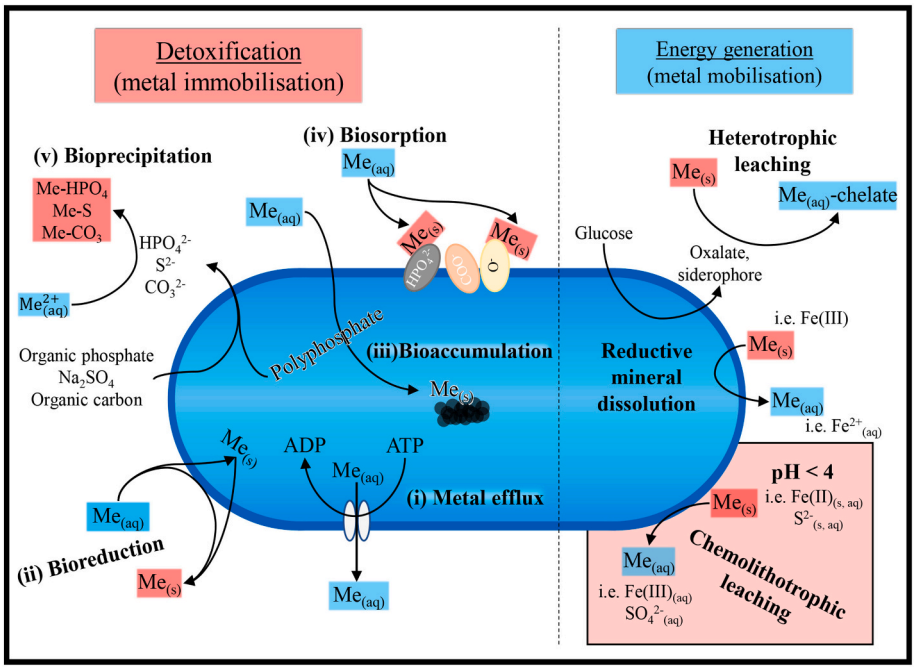


Fig. 2. Microbe-metal interactions highlighting mechanisms of metal immobilisation and mobilisation, modified from (Nancharaiah et al., 2016). Microbes employee a number of passive and active mechanisms to reduce metal toxicity including, (i) metal influx, (ii) bioreduction, (iii) bioaccumulation, (iv) induced bioprecipitation, often involving polyphosphates, and (v) biosorption, which may be detrimental to microorganisms. Microbes may also contribute to metal mobility *via* the production of organic acids during heterotrophy, reductive dissolution of oxides and autotrophic iron and sulphur oxidation in acidic environments. Abbreviation: Me, metal.

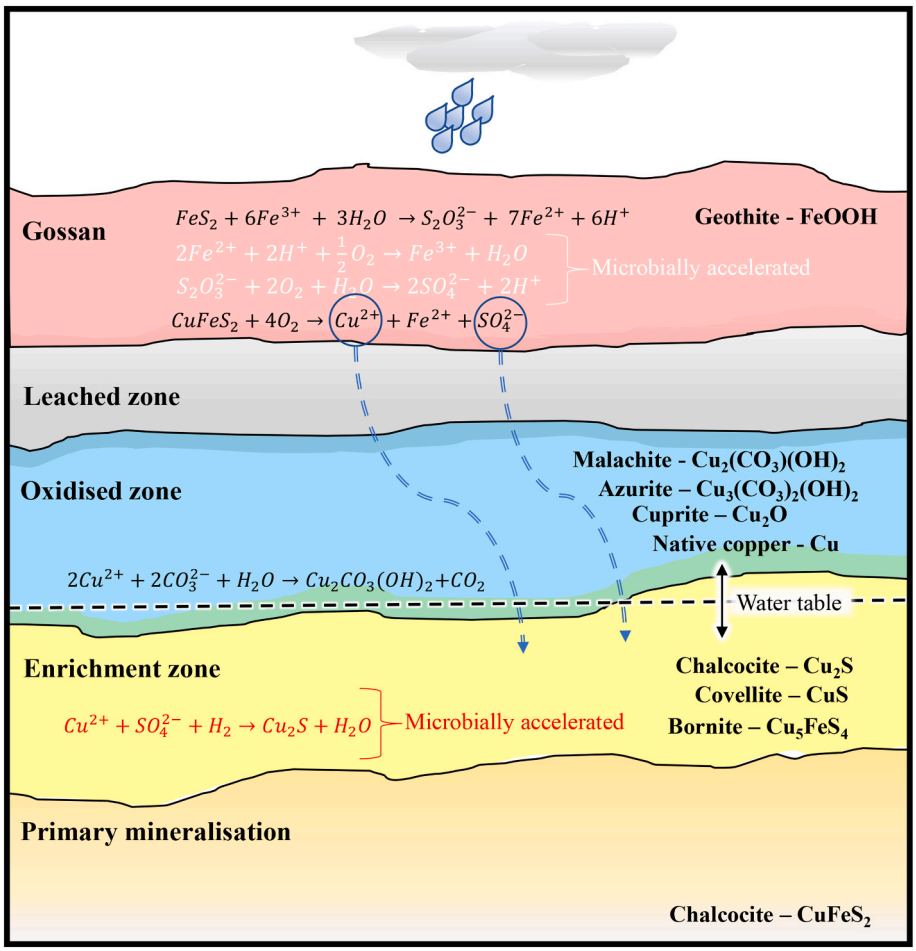


Fig. 3. Classical model of a supergene enrichment profile, highlighting insoluble iron and aluminium enriched in the gossan underlain by a leached zone. Metals mobilised at the surface are transported in solution, where they re-precipitate in reducing conditions below the water. Chalcopyrite dissolution at the surface and secondary copper sulphide precipitation below the water table are likely to be influenced by separate microbial processes.

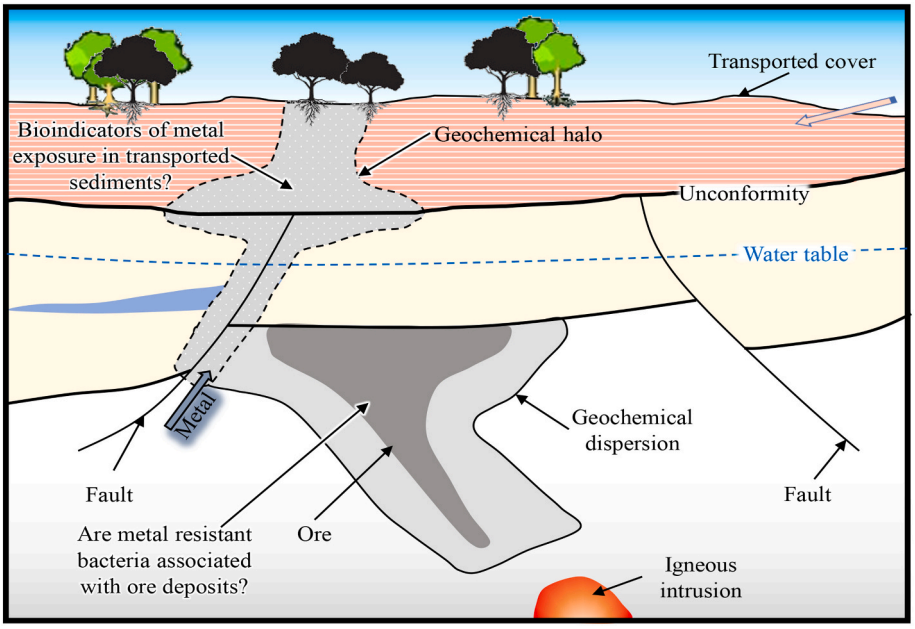


Fig. 4. Simplified schematic of an ore body modified from (Spinks et al., 2017), highlighting the need to study the genomic potential of microorganisms that exist within an ore body, within the metal enriched geochemical dispersion around an ore body and determine if genetic bioindicators can be correlated with geochemical haloes.

deprotonate (for example, $pK_{a(carboxyl)} \sim 4.8$; $pK_{a(phosphoryl)} \sim 6.9$ and $pK_{a(hydroxyl)} \sim 9.4$) allowing for passive microbial-metal interactions (Fein et al., 1997). Therefore, it is anticipated that microbial metal resistance genes may be most highly regulated in pH 3–6 environments, where metal mobility is relatively high and metal-binding sites on microbial cell surfaces are deprotonated.

2.2. Advances in molecular ecology

Metagenomics has revolutionised microbial ecology. Advances in molecular biology and DNA sequencing techniques provide environmental scientists with an extraordinary set of tools to understand the complexities of natural microbial communities. These techniques offer a range of potential biotechnological advances, including assessing the prevalence of important genes in bioremediation efforts for polluted environments (Bouhajja et al., 2016) and bioprospecting various environments for new antibiotics and enzymes that can used as biocatalysts to reduce the energy requirements of chemical engineering processes (Kakirde et al., 2010; Madhavan et al., 2017).

Metagenomics refers to the collective genomes of all microorganisms within an environmental sample. Typically, metagenomics takes advantage of two distinct sequencing techniques: direct (shotgun) sequencing and indirect (library-based) metagenomics. These techniques have been extensively reviewed elsewhere, along with the different sequencing technologies and associated costs, which are increasingly affordable (Bouhajja et al., 2016; Kakirde et al., 2010).

Briefly, for direct sequencing, DNA is essentially randomly fragmented before being sequenced and does not include a pre-cloning stage of genetic material, therefore, removes this as a basis. Direct sequencing has been most prominently used for environmental characterisation and is a technique that is increasingly available to environmental scientists. The second method involves library-based targeted metagenomics, whereby environmental or enrichment genomes are targeted using specific DNA extraction and purification methods. These are cloned into a suitable vector depending on fragment size and introduced into a host organism, commonly *Escherichia coli,* to produce a metagenomic library, which is screened for specific functional or genetic characteristics before sequencing of these specific clones.

Since the advent of second-generation sequencing (*circa* 2007), sequencing costs have dropped by approximately five orders of magnitude, making widespread environmental metagenomic studies possible. With the development of rapid, high-quality and affordable sequencing techniques, downstream sequence analysis is now a bottleneck in reconstructing genomes of individual species in complex environments. Computational and bioinformatic advancements aim to improve the recovery of (near)-complete genomes from increasingly large metagenomic datasets (Albertsen et al., 2013; Sangwan et al., 2016). At present, it is unfeasible for mineral exploration and mining companies to employ teams of bioinformaticians, therefore, using metagenomics as a novel strategy for mineral exploration (see Section 3) will ultimately involve the identification of reliable microbial-based indicators of previous metal exposure, which can be explicitly targeted either using quantitative PCR (qPCR) or imaging techniques that can be optimised for high throughput (for example, fluorescence *in situ* hybridisation; FISH).

3. Potential genetic-based exploration techniques

3.1. Developing bioindicators

Mineral exploration is expensive and has a low success rate, making it a high risk-investment. Even if an economic ore body can be identified, the lag-time between exploration and the first production from a mine requires significant, long-term investment. With near-surface deposits being depleted and ore grades within these deposits declining, new innovations are required in the mineral mining sector to aid in the discovery of new ore deposits and improve the efficiencies of current mining practises (Calvo et al., 2016; Prior et al., 2012).

One of the greatest challenges for mineral exploration are the surface duricrusts (Fig. 3) and the transported cover (Fig. 4) that form or are deposited over potential ore deposits. Many technologies are currently being developed to complement the existing geochemical and geophysical exploration strategies used to guide expensive (up to millions of dollars) drilling programmes. These developing techniques include the identification of indicator minerals and pathfinder-elements, the use of partial-leaches and selective-extractions, isotope

geochemistry and biogeochemistry (Anand et al., 2007; Kelley et al., 2006; Winterburn et al., 2019). The development of a diverse array of potential exploration techniques is important to determine which technique or combination of techniques can be used to produce the most reliable sampling strategies, dependent on various land uses and ore deposit systems. Developing bioindicators of metal exposure and mobility may provide information to help guide mineral exploration programmes in the future.

The idea to use microbial responses to heavy metals as a potential bioindicator for mineral exploration was suggested over a decade ago (Reith et al., 2009) but these techniques remain underdeveloped and are typically focused on precious metals (primarily, gold). Reith et al. (2013) highlight that there are three major advantages for developing genetic-based exploration techniques (bioindicators). Firstly, microorganisms can respond and adapt to extremely low concentrations of metals; secondly, these techniques can be easily adapted for many metals and polymetallic deposits and, finally, bioindicators represent a holistic probe, providing evidence of elemental cycling (sulphur, iron, manganese, *etc.*) and volatile fluxes. With advances in sequencing and 'omics'-related technologies, scientists have the capacity to determine the exact genetic and microbial community-based responses that occur in a changing environment, for example, changes in pH, metal exposure or oxygen concentrations. These microbial responses may be community-based responses where specific microorganisms with adaptions to survive in the altered environment form a larger portion of the microbial community. For example, continental-scale studies have attributed changes in microbial community structures to soil pH (Fierer and Jackson, 2006; Lauber et al., 2009). By accounting for the community variation that can be assigned to physiochemical characteristics (for example, pH, electric conductivity, oxidation potential, soil organic matter, *etc.*) may allow for any remaining variation to be assigned to heavy metal concentrations in soils (Gans et al., 2005). Attempting to assign community variation to heavy metal concentrations represents a largely indirect method to develop bioindicators of metal mineralisation. However, this method can take advantage of the massive databases hosting 16S amplicon and geochemical datasets, such the Biomes of Australian Soil Environments (Bissett et al., 2016). Alternatively, these responses could be solely genetic-based without changing the community structure, for example, an alteration in gene copy numbers or gene frequencies (Gillan, 2016; Gillan et al., 2015). Here, we focus on microbial responses to heavy metal exposure; however, it should be noted that these environmental changes seldom occur in isolation. For example, oxidation of a sulfidic mineral may release heavy metals into solution, while also producing sulphate ($SO_4^{2-}{}_{(aq)}$) with acid-generating capacity as well as releasing redox-active elements such as ferrous iron, which can consume available oxygen or reduce other available electron acceptors. Therefore, changes in the microbial community structures and specific genetic responses within those populations are both likely to occur in naturally metal-rich environments (as opposed to anthropogenically metal-only contaminated environments, for example, (Gillan et al., 2015)).

For secondary copper deposits, microorganisms have been demonstrated to significantly accelerate iron oxidation within iron sulphide minerals, generating acid and ferric iron-rich solutions (Enders et al., 2006). Acid and ferric iron promotes the dissolution of chalcopyrite [$CuFeS_2$], leaching the copper into solution, which subsequently re-precipitates at depth, typically below the water table (Fig. 3). These processes enrich the ore deposit in copper at depth (Dill, 2010). The leaching of metals from sulphide minerals also releases heavy metals into solution; for example, elevated copper (2 ppm), selenium (0.8 ppm), molybdenum (0.5 ppm) arsenic (0.3 ppm) and rhenium (0.03 ppm) have been detected in the groundwaters of an undisturbed (natural) porphyry copper deposit (Leybourne and Cameron, 2008). Therefore, as microorganisms naturally accelerate the weathering of these minerals, those microbes that survive at the fluid-rock interface are subjected to potentially toxic concentrations of heavy metals. During periods of metal heavy exposure, microorganisms containing metal resistance genes will be able to survive. The acidophilic, metal-tolerant *Acidithiobacillus ferrooxidans* has been identified in many active and abandoned mine sites and successfully used in biomining projects to actively leach metals from mineral heaps (Orell et al., 2010; Rawlings and Johnson, 2007; Valenzuela et al., 2006). It is, therefore, unsurprising that genomic analysis of *A. ferrooxidans* revealed several heavy metal resistance genes (Valdés et al., 2008). Metatranscriptomic studies of acid mine drainage systems have revealed that prokaryotes in these environments express heavy metal resistance genes, particularly cadmium, cobalt and zinc efflux pumps. Regulation of these metal exporter systems have been linked with higher toxic metal concentrations (Chen et al., 2015; Hua et al., 2015; Tan et al., 2019).

There is increasing evidence that microorganisms also control the re-precipitation of metals in secondary ore deposits. Sulphate-reducing microorganisms at depth promote the precipitation of metal sulphides producing metal enriched cementation zones (Tornos et al., 2019). These microorganisms that promote the reprecipitation of metals at depths will also likely contain metal resistance genes. With microorganisms playing such significant roles in metal cycling, it likely that their genetic material holds information that can used as an indicator for metal exposure. Determining the functionality of key microbial species that contain these indicator genes (for example, metal resistance genes) will also provide information on the relative metal mobility and, when combined with hydrogeology data, can be used to guide drilling exploration. Additional research is required to reveal the genetic capabilities of subsurface microbiomes associated with mineral deposits and potentially linking these with microbial communities at the surface in the transported covers (Fig. 4).

3.2. Microbial responses to heavy metals

Many microorganisms, including *A. ferrooxidans* as well as *Cupriavidus Metallidurans* CH34, are commonly identified in metal contaminated sites. These microorganisms have served as model species to study the mechanisms and genes involved in metal resistance (Monsieurs et al., 2011; Valdés et al., 2008); however, heavy metal resistance is widely distributed throughout microbial phylogenies and has likely existed for billions of years since the beginning of life on Earth (Baker-Austin et al., 2006; Silver and Phung, 2005; Voica et al., 2016). Further, microbial communities that are subjected to heavy metals are able to rapidly adapt *via* horizontal gene transfer, allowing resistance to specific heavy metals to be distributed throughout all bacterial phylogenies (Mijnendonckx et al., 2011; Top et al., 1990; Van Houdt et al., 2009). For example, Klerks and Levinton (1989) demonstrated that microbial communities may adapt to heavy metal exposure within 1–4 generations. Metal-resistant genes are energy-dependent and their expression is tightly regulated. Therefore, after heavy metal exposure has passed, these genes will not continue to be expressed but, given the high mobility of metal resistance genes (see below), these genetic components may be maintained at higher than expected copy numbers per cell by the residual and ensuing microbial community.

The exploration of new mineral deposits using metagenomic techniques is likely to benefit greatly from the bounty of research investigating microbial responses to heavy metal contamination [see reviews by Bruins et al., 2000, Nies, 1999 and Silver and Phung, 2005]. When comparing river sediments that had long-term exposure to high heavy metal concentrations with upstream 'control' sediments, bacterial community structures were demonstrated to remain resilient to metal contamination, with only minor changes in the relative abundance of a few species (Gillan et al., 2015; Jacquiod et al., 2018). Interestingly, these studies did record significant genetic and functional changes between the metal-contaminated and uncontaminated sites, including the upregulation of cobalt-zinc-cadmium resistance proteins (CzcA and CzcD) and alterations to cell wall properties as a mechanism for metal resistance (Gillan et al., 2015).

Table 2
Potential genetic targets of metal resistance genes that may be used as bioindicators to guide mineral exploration.

Metal (atomic #)	Target gene	Publicly available primer: forward[a]	Publicly available primer: reverse[a]	Ref.
Vanadium (23)	VAN2	ACGCTGCCAAGCCTATTT	CGAAAGGTACTGTGTGGTTAGT	Fierros-Romero et al. (2017)
Chromium (24)	chrB	GTCGTTAGCTTGCCAACATC	CGG AAAGCAAGATGTCGATCG	Nies et al. (1990)
Cobalt (27), Zinc (30)	czcD	TTTAGATCTTTTACCACCATGGGCGCAGGTCACTCACACGACC	TTTCAGCTGAACATCATACCCTAGTTTCCTCTGCAGCAAGCGACTT	Nies et al. (1989)
Nickel (28)	nccA	ACGCCGGACATCACGAACAAG	CCAGCGCACCGAGACTCATCA	Abou-Shanab et al. (2007)
Copper (29)	copA	GGTGCTGAT CATCGCCTG	GGGCGTCGTTGA TACCGT	Besaury et al. (2013)
Arsenic (33)	arsA	TCCTGGATTGTCGGCTCTTG	ATCTGTCAGTAATCCGGTAA	Saltikov and Olson (2002)
Silver (47)	silE	AGGGGAAACGGTCTGACTTC	ATATCCATGAGCGGGTCAAC	Woods et al. (2009)
Cadmium (48)	cadC	GCGCGCTCATGAAAAAGAAAGATAC	CCCCGGATCCAAGCTTCAGACATTGACCTTCAC	Endo and Silver (1995)
Gold (79)	golS	CTGCGCCGTTTCCGGGCGCCGATGGCAACCCCATCCGACACATCCACGACGTGTAGGCTGGAGCTGCTTCG	TTAACATCAGCCTGGGTATAGGCCCGATAGCCGGAATCCGTCCGACTTGCCATATGAATATCCTCCTTA	Checa et al. (2007)
Mercury (80)	merA	GAGATCTAAAGCACGCTAAGGC	GGAATCTTGACTGTGATCGGG	Misra et al. (1984)
Lead (82)	pbrA	CCCTCACCTTGTGCYCTGG	GGAGCATCGTTAATDCCRTCDCC	Coombs and Barkay (2004)

A preference is given for heavy metal resistance gene targets with publicly available primers.
[a] All primers are listed 5′ to 3′.

Although low gene numbers with higher expression rates would also promote heavy metal resistance, long-term exposure of elevated heavy metal concentrations is commonly associated with increased heavy metal resistance gene frequencies. For example, quantitative PCR has demonstrated that metal resistance gene copy numbers (*czcA* and *czcD*) were 4.2 greater per microorganism in metal contaminated sites compared with control sites (Roosa et al., 2014). Similarly, when normalised to assumed 16S rRNA values, *cusA* and *copA* copper-resistant gene copy numbers were significantly greater in marine sediment drill core samples that had been exposed to copper contamination for decades (Besaury et al., 2013). Therefore, over for long periods of heavy metal exposure during mineral weathering, the frequency of metal resistance genes within the exposed microbiome would be expected to increase.

Increased numbers of phages, prophages, and transposable elements have also been recorded associated with heavy metal exposure and are likely to contribute to the mobility of heavy metal resistance genes (Gillan et al., 2015). However, these indicators of horizontal gene transfer are unlikely to be preserved in the environment over geological timescales. Therefore, a focus on gene copy numbers per cell, rather than community structure or indicators of horizontal gene transfer, may provide a more robust method for the development of microbially-based exploration techniques (Reith et al., 2013). Focusing on specific genes rather than alterations to microbial community structures will also reduce the bioinformatic workload for mining companies, removing the need to assemble complete or partial genomes to determine individual species proportions. Once reliable genetic targets have been identified by studying the genetic capabilities of microorganisms directly associated with ore deposits, mining companies will be likely to develop or optimise the available group-specific genetic primers to select for reliable genetic marker, for example, genes associated with specific heavy metal resistance (Table 2). These genetic targets may be quantified in individual samples using qPCR. Reith et al. (2013) advocated for the development of 200–300 probes for gold-specific microbial species and functional genes to improve multivariate statistical analysis in gold exploration, although only a few key genes were responsible for the greatest difference between auriferous and non-auriferous soil samples, including *chr*A, *cop*A, *czc*A and *czc*D (metal de-toxification genes for chromium, copper, cadmium-zinc, respectively) (Reith et al., 2012).

Molecular characterisation of several metal resistance gene clusters have demonstrated these genes are typically high conserved between species with more than 92% identity (Behlau et al., 2011) and often inherited by horizontal gene transfer (Behlau et al., 2013). The lateral transfer of genes between microorganisms growing in heavy metal-influenced environments is further corroborated by a recent study investigating microorganisms growing on gold grains, which contained various genomic islands and mobile genetic elements (Sanyal et al., 2020). Within their study, Sanyal et al. (2020) isolated gold-tolerant *Serratia* sp. and *Stenotrophomonas* sp., with the majority of metal resistance genes in the isolates orthologous to metal resistance genes in *C. metallidurans* CH34 (see Fig. 6 in Sanyal et al. (2020) for an annotated comparison of metal resistance gene clusters). These studies highlight the relatively highly conserved nature of metal resistance gene clusters between various microbial lineages and lends confidence to the hypothesis of targeting metal resistance genes as bioindicators of anomalously high metal exposure in rocks/soils.

The commodity in question (for example, zinc, copper, lead, gold, *etc.*) will dictate which gene assemblages (regulons) are likely to have been previously upregulated and likely to have higher gene copy numbers in cells (Table 2). Highly toxic heavy metals in trace concentrations (for example, arsenic) that are commonly associated with specific ore deposits may also provide additional genetic targets as well as the metal of economic interest. It should be noted, a database (BacMet) has been assembled for metal resistance as well as other antibacterial biocides genes (Pal et al., 2013). It is anticipated that future databases will aim to spatially correlate these metal resistance genes with differing geological units across a variety of geographical locations.

3.3. Linking bioindicators with ore deposit geochemical haloes

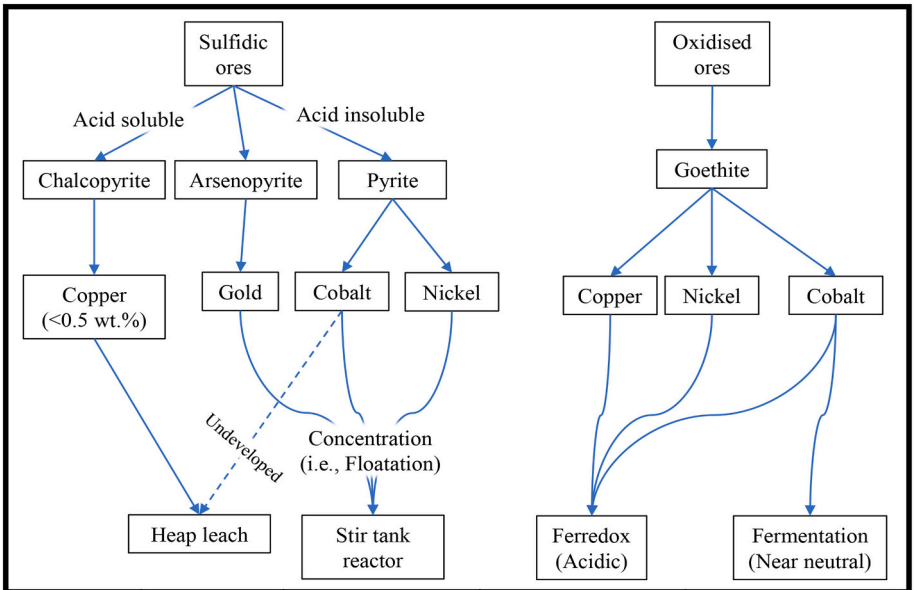
The key questions for the use of bioindicators include: (i) are metal resistant microorganisms associated with ore deposits and (ii) are these metal resistance genes distributed and elevated throughout nearby microbial populations, for example, in transported surface sediments and geochemical haloes associated with ore deposits (Fig. 4)? Gene amplification can occur up to 100 times when an evolutionary advantage is selected for, such as resistance to antibiotics (Darmon and Leach, 2014). Given the high genetic mobility of metal resistance genes as transposons and plasmids, transported microorganisms that co-exist with metal exposed microbial populations may also uptake these genes, even in the absence of a selective pressure. Alternatively, a gene can be deleted or mutated and consequently lost from an individual cell's genome may also be lost from all subsequent daughter cells, as the missing or defective gene would no longer offer an advantage.

Many other questions will also need investigating, including, how long are genetic markers of heavy metal exposure maintained in the microbial communities under environmental conditions that are no longer selective for metal resistance? Microorganisms employee a number of mechanisms, including postsegregation killing systems and the CRISPR-Cas system, to maintain genetic stability (Darmon and Leach, 2014). Similarly, plasmids containing metal resistance genes are likely to be well maintained in microbial populations. For example, under non-selective conditions, the probability of plasmid loss from bacteria is typically modelled by the equation $P_0 = 2^{1-n}$, where n is the number of plasmid copies (Bahl et al., 2004). Therefore, it is estimated that a plasmid present 31 times would be lost by 1 in 1,000,000,000 cell copies. Gene copy numbers can also be affected by a number of genetic mechanisms, including tandem-repeat deletions or amplifications (Darmon and Leach, 2014). Therefore, after a microbial community has been subjected to potentially toxic metal concentrations, metal resistance gene copy numbers may be maintained in higher gene copy numbers over extended periods of time, as well as naturally share these mobile genetic components with transported microbial communities.

3.4. Challenges for using metagenomics as a mineral exploration tool and opportunities for development

The transported alluvium, soil and sediments that cover some ore deposits will contain microbial genetic material from microorganisms that have not previously been exposed to heavy metals (Fig. 4). Previous human intervention and contamination at many of these sites may also pose limitations for using bioindicators in mineral exploration. Therefore, initially, it may be important to target soils and sediments that have formed *in situ* to determine changes in heavy metal resistance frequencies within microbial communities exposed to heavy metals to develop robust bioindicators. At the proof of concept stage, the development of bioindicators for mineral exploration may therefore require shallow drill cores to sample the uppermost rock units known to have previously contained elevated metal concentrations and are unaffected by anthropogenic disturbances. In subsequent development stages, correlating genetic changes with geochemical haloes within transported materials (Fig. 4) may expand the use of genetic bioindicators of metal mineralisation during exploration to include analysis of the transported cover.

Assessing the changes in metal resistance gene frequencies also requires developing an appropriate standard for 'background' metal resistance gene frequencies that are present in all microbial populations. To date, studies have aimed to characterise a suitable uncontaminated background site that acts as a control for the regions with elevated metals (Besaury et al., 2013; Gillan et al., 2015). These methods may be affected by an unintentional bias and have statistical limitations, particularly when extrapolating these results over long time periods,



Example reference	Watling, 2006	Moring and d'Hugues (2007)	Marrero et al. (2015)	Newsome et al. (2020)
Reported Recovery	~75% Cu from Chalcopyrite	~80 – 90% Co in pyrite	~50% Cu and ~70% Ni from goethite	~60% Co associated with goethite
Recovery time frame (residence time)	~200 days	~6-10 days	~7 days	~100 days
Key microorganisms	Acidophilic sulphur and iron oxidisers	Acidophilic sulphur and iron oxidisers	Acidophilic sulphur and iron oxidisers	Heterotrophic and fermentative
Metal mobilisation mechanism	Acid dissolution (Reaction a)	Iron and sulphur oxidation (Reactions b and c)	Iron and Sulphur oxidation (see Fig. x)	Organic acid metal complexation (Reaction d)
Commercial scale?	Yes	Yes	No	No

Fig. 5. Generalised flow diagram highlighting the potential biohydrometallurgical techniques that can potentially be used to extract metals from sulfidic and oxidised ores (Morin and d'Hugues, 2007; Watling, 2006).

with a less-well constrained environmental history. A more robust alternative for assessing background metal resistance gene frequencies may be required. Big data projects such as Terrestrial Metagenome database (Corrêa et al., 2019) may provide a valuable repository for assessing the distribution and prevalence of metal resistance genes throughout different lithologies and environmental conditions; however, these databases require careful curation and standardisation for effective statistical comparisons.

4. Microbial-induced mineral dissolution for biomining

Biomining is a generic term used broadly to describe metal recovery using microorganisms. Substrates include unprocessed primary ores that are naturally porous (*in situ*) or actively fractured (in place), low-grade ores or waste products that have been mined and crushed, metallurgical waste products (for example, smelter slags and residues) and the increasing quantities of electronic-wastes (e-wastes). Extractive metallurgical processing involves the selective separation of distinct phases based on their chemical, physical and electrical properties to enrich metals of economic interest. Pyrometallurgical metal recovery remains the predominant technology for metal recovery but high energy costs have promoted the use of (bio)hydrometallurgy, which is considered a moderately benign option for metal recovery. In biohydrometallurgy, a biologically catalysed lixiviant (leaching solution) is produced to leach metals into solution, which may then be selectively recovered to obtain relatively pure phases of a commodity, typically by precipitation or electrowinning.

The evolution of bioleaching processes over the past half century has been dramatic. Originating as poorly controlled dump piles, some of which were irrigated with sulfuric acid to promote the growth of native acidophilic sulphur- and iron-oxidising microorganisms, bioleaching practises are now highly controlled and engineered to optimise metal recoveries. At a commercial-scale, bioleaching is almost exclusively used for metal recovery form reduced ore types (for example, leaching copper from chalcopyrite) and the bio-oxidation of recalcitrant matrix minerals in which valuable metals (primarily gold) are embedded. These techniques have been reviewed extensively (Brierley and Brierley, 2013; Johnson, 2014; Kaksonen et al., 2018; Kaksonen et al., 2020; Vera et al., 2013). Therefore, the bioleaching of reduced ores (Section 4.1.) is only briefly discussed here as they form the basis for the evolution of biomining and it's applicability in different mining contexts including, the development of *in situ* biologically accelerated recovery of metals (Section 4.2.) and the bio-reductive processing of metals in oxidised ores (Section 4.3.). Mineralogy differences between potential ores are critical to the successful economic recovery of metals; Fig. 5 provides a generalised flowchart summarising potential biohydrometallurgical processing for different ore types.

Genetic modifications to microorganisms to improve bioleaching the efficiency of metal leaching and survival of microorganisms in adverse conditions, for example, exposure to high metals, increased temperature tolerances or highly saline solutions from re-cycled mine waters may seem attractive. Johnson (2014) highlight that engineering constraints,

even within closed systems such as stir tank reactors, pose an unacceptable risk of releasing genetically modified organisms into the environment. Therefore, artificial genetic modifications of microorganisms is not a technique applied to biomining organisms. Genetic modifications are typically restricted to selective culturing processes (Kaksonen et al., 2018).

4.1. Biomining by mineral oxidation

Biohydrometallurgy has been effectively used at a commercial-scale to process and extract metals from reduced ore-types, including copper and gold, for many years. It is estimated that approximately 15% of copper and 5% of gold are currently recovered using these processes (Brierley and Brierley, 2013; Roberto, 2017). Microbially-induced oxidative weathering of minerals can provide a relatively low-cost method for metal extraction and recovery, particularly for refractory and low-grade ores (Kaksonen et al., 2018). Increasingly, by-products from mining practises, goods for recycling and contaminated wastes are considered as important metal-bearing material sources; however, low-grade ores remain the primary substrates for biohydrometallurgical processing. Once the ore has been removed and crushed, biohydrometallurgical leaching of ores may take place in stirred-tank reactors, vats, ponds or heaps/dumps (Kaksonen et al., 2018). Technological developments to these systems, including improvements in the bioreactor configurations to promote efficient mixing and oxidation of ores and the need to promote the adaptive evolution of microorganisms involved in biomining have been extensively reviewed (Brierley and Brierley, 2013; Johnson, 2014; Rawlings, 2013; Schippers et al., 2013; Vera et al., 2013). The infrastructure requirements and capital costs associated with reactors and vats means these technologies are primarily used for gold recovery, whereas heap and dump leaches are more commonly used for low-grade copper ores (Kaksonen et al., 2018).

The lixiviant to solubilise minerals from reduced sulphide ores is an acidic ferric iron-rich solution. In these processes, acid-insoluble pyrite is attacked by ferric iron (Reaction 1; (Vera et al., 2013)). At low pH values and temperatures below 60 °C, the abiotic oxidation of ferrous iron is extremely slow, therefore microorganisms are required to catalyse Reaction 2, re-generating ferric iron and the continued oxidation of pyrite. The dissolution of pyrite is an acid-producing reaction, which in turn promotes the dissolution acid-susceptible minerals, including chalcopyrite (Sand et al., 2001; Schippers and Sand, 1999). The thiosulfate moiety produced during pyrite oxidation can provide a substrate for acidophilic sulphur-oxidising bacteria (Reaction 2) or can be abiotically oxidised (Reaction 3) to sulphate.

$$FeS_2 + 6Fe^{3+}_{(aq)} + 3H_2O_{(l)} \rightarrow S_2O^{2-}_{3\ (aq)} + 7Fe^{2+}_{(aq)} + 6H^{+}_{(aq)} \quad (1)$$

$$2Fe^{2+}_{(aq)} + 2H^{+}_{(aq)} + \frac{1}{2}O_{2\ (g)} \rightarrow 2Fe^{3+}_{(aq)} + H_2O_{(l)} \quad (2)$$

$$S_2O^{2-}_{3\ (aq)} + 2O_2 + H_2O_{(l)} \rightarrow 2SO^{2-}_{4} + 2H^{+}_{(aq)} \quad (3)$$

$$S_2O^{2-}_{3\ (aq)} + 4Fe^{3+}_{(aq)} + 5H_2O_{(l)} \rightarrow 2SO^{2-}_{4} + 4Fe^{2+}_{(aq)} + 10H^{+}_{(aq)} \quad (4)$$

Currently, biohydrometallurgical recovery of metals is typically restricted to use for low-grade or polymetallic ores. Similarly, ore-types with a deleterious element (typically arsenic) that cannot be treated at high temperatures are currently processed using (bio)hydrometallurgy (Neale et al., 2017), which can produce a stable arsenic waste product for impoundment (Reactions 5). Neutralising the arsenic-bearing solutions to pH 5 produces an $FeAsO_4$ precipitate for disposal (Rawlings, 2004).

$$FeAsS + 13Fe^{3+}_{(aq)} + H_2O_{(l)} \rightarrow 14Fe^{2+}_{(aq)} + AsO^{3-}_{4} + SO^{2-}_{4} + 16H^{+}_{(aq)} \quad (5)$$

Bio-oxidative recovery of gold typically utilises similar chemical processes to the bioleaching recovery of copper, with the difference being the mobilisation of the target metals. For bio-oxidative gold recovery, the sulfidic minerals that contain the gold are solubilised by the microorganisms, exposing the gold and making it available for secondary chemical processing (cyanide or thiosulfate leaches).

4.2. Biologically accelerated metal recovery of in situ mining operations

As world class near-surface deposits are depleted, mining companies must begin to target either (i) low-grade near-surface deposits, (ii) small, high-grade deposits or (iii) deep (>1 km) ore deposits. Each of these scenarios will require innovations to reduce the costs associated with mineral extraction and metallurgical processing. Here, we use the term '*in situ*' mining to generically described metal recovery from both in place (actively fractured ore bodies) and *in situ* (unfractured ore bodies) mining practises. *In situ* mining may represent the next frontier in the mining industry, providing a relatively low infrastructure setup and reducing energy requirements for mining with the trade-off that residence times for metal extraction are likely to increase (Batterham and Robinson, 2019; Vargas et al., 2020).

Increasing focus is being placed on developing effective engineering strategies for the *in situ* leaching of metals from low-grade and deep ores, not able to be mined economically using conventional techniques (Johnson, 2015). For an *in situ*-based mining program, the local structural geology and hydrogeology, mineralogy and hydraulic function of the region must be completely assessed.

The renewed attention for *in situ* mining practices is in direct response to the increasing costs associated with mining lower grade or less accessible deposits. Mines operating underground, would not expect to achieve the extraction and recovery rates of metals currently achieved with conventional mining but mineral processing and waste management costs would be significantly less. Similarly, the surface disruption of *in situ* mining is minimised, reducing the impact of mining on surface ecosystems. Compared with crushing of ores, which is estimated to consume 80–90% the energy usage of a mine (Jeswiet and Szekeres, 2016), *in situ* fracking or blasting of ores is likely to greatly reduce the energy expenditure associated with *in situ* mining. These benefits do not come without complications; engineering systems must be developed to prevent aquifer contamination (Mudd, 1998). In future, safeguards such as underground chemical precipitant traps may be used to prevent metal-containing solutions contaminating groundwaters. With a focused and collaborative effort, Batterham and Robinson (2019) guesstimate that *in situ* mining will revolutionise the mining industry, potentially within 20 years.

4.2.1. An example of in situ mining: Uranium

In situ mining of uranium was developed in the 1960s to extend the lives of uranium mines. Today, *in situ* mining is widely used for the economic extraction of uranium, accounting for approximately 50% of global production since 2015 (Seredkin et al., 2016). Rawlings (2004) reported that an additional 300 million tonnes of uranium was mined using *in situ* techniques from a single mine in Canada in 1988 by the biooxidation of iron to generate ferric iron, which subsequently oxidised the uranium in uraninite for recovery (Reaction 6). Today, any role of microorganisms associated with *in situ* mining of uranium is small, if at all (Mudd, 1998).

$$2Fe^{3+}_{(aq)} + UO_{2\ (s)} \rightarrow UO^{2+}_{2\ (aq)} + 2Fe^{2+}_{(aq)} \quad (6)$$

For *in situ* mining processes, the porous uranium-bearing ore bodies are periodically flooded to introduce an acidic or alkaline lixiviant to oxidise the uranite minerals and promote mineral dissolution (Mudd, 1998). Based on the local lithology and hydrogeology, carefully designed and highly engineered solution flow pathways are modelled for *in situ* mining to limit solution excursion (leaking) from the ore body into surrounding aquifers. To control the flow of injection solutions,

extraction volumes exceed injection volumes to prevent subsurface overpressure. Injection wells are typically surrounded by four or six extraction wells (Mudd, 1998). Injection and extraction well patterns are designed to maximise lixiviant-rock interactions and prevent the loss of solutions into aquifers, which contain toxic concentrations of valuable metals. Similarly, the mineralogy of the host rocks must be accounted for to ensure solutions remain acidic to maintain metals in solution. Calcareous-bearing rock types that buffer acidic lixiviants or promote the precipitation of minerals (gypsum) must be accounted for.

4.2.2. Applying in situ mining for a deep ore deposit

Conventionally, *in situ* mining was restricted to porous rock units (sandstones) situated below the water table that were confined above and below impermeable rock units (typically clays or shales) with artesian water pressures relative to the capping impermeable rock unit (Mudd, 1998). Other ore deposits require alternative treatments for *in situ* mining. For example, non-porous, hard-rock ores will need to be fractured and exposed to lixiviants by gravity-feeding before drainage solutions are collected and returned for processing (Fig. 1).

A joint research and industry program recently completed a 3-year *in situ* mineral extraction and metal recovery trial from a deep and complex black shale and sandstone ore body that would otherwise be uneconomical to mine (Filippov et al., 2017; Johnson, 2015). In these scenarios, the fractured ore body is treated with ferric iron-rich, acidic lixiviant generated within a bioreactor containing a consortium of acidophilic iron- and sulphur-oxidising bacteria. As these fluids percolate through the fractured ore body, the acidic, ferric iron-rich solutions attack and dissolve the reduced ore minerals (for example, chalcopyrite). These solutions are maintained at a low pH to keep metals in solution and are then collected in recovery wells and processed. Metals of economic importance can then be recovered by sulphide precipitation or solvent extraction and electrowinning and the remaining ferrous iron in solution is returned to the bioreactors for re-oxidation.

The potential benefits of *in situ* mining are unlikely to be realised without important collaborations between governments, researchers and industry. A number of government-supported trial mines will be essential to further develop *in situ* mining techniques to make informed decisions for the future of mining. Namely, can the theoretical environmental benefits of *in situ* mining be realised and can current business models adapt to changes in metal production timeframes? Ideal sites to optimise these *in situ* metal recovery techniques could be existing block mines, which are required to leave approximately 30% of the ore body in the ground. After the completion of conventional block mining, the remaining ore could be safely collapsed to fracture the remaining ore body and subsequently be treated with a lixiviant to leach the remaining metals into solution before being recovered *(*Schippers et al., 2013*)*.

4.3. Biomining by mineral reduction

Alternative bioleaching processes are now being applied to oxidised ore types, which can account for significant volumes of the global ore reserves (Dalvi et al., 2004). Supergene weathering environments are responsible for the secondary enrichment of many valuable metals (for example, Fig. 3). During supergene weathering, immobile elements including aluminium and iron are enriched at the surface and form chemically resistant oxide and hydroxide minerals. In particular, goethite [FeOOH] can form an array of mineral morphologies and can incorporate a number of metals, including cobalt, copper, chromium, manganese, nickel and zinc (Manceau et al., 2000). When the initial concentrations of valuable metals (copper, nickel, *etc.*) are relatively high within the unweathered protolith, economically valuable concentrations of metals can be associated with recalcitrant goethite minerals. Therefore, many researchers have worked at acidic (Section 4.3.1) and now circumneutral (Section 4.3.2) pH values to accelerate the reductive dissolution of iron oxide minerals.

The high chemical stability of goethite has resulted in many of these ore types being treated using pyrometallurgical processes and aggressive chemical extractants, which are energetically demanding and pose environmental risks. The microbiologically accelerated reduction (bioreduction) of crystalline iron oxide minerals, particularly goethite, provides a viable option to exact these ores at low temperatures. In anoxic environments, ferric iron [Fe(III)] can provide an alternative electron acceptor for cell respiration (Fig. 2). Typical electron donors for this reaction include a variety of organic compounds, reduced-sulphur moieties and hydrogen.

4.3.1. Iron reduction in acidic conditions

The Ferredox process (Fig. 5) was proposed as 'classical biomining in reverse-gear' (du Plessis et al., 2011; Johnson and du Plessis, 2015). The process aims to drive iron reduction, while maintaining a low pH to ensure metal ions stay in solution. *Acidithiobacillus* species are supplemented with elemental sulphur (S^0), which it oxidises to sulphate *via* thiosulfate species. These oxidised sulphur species subsequently drive the reduction of iron oxide minerals, placing ferrous iron along with the valuable metals of interest into solution (Fig. 5). Overall, these (bio) chemical reactions consume acid, therefore these systems have to be supplemented with additional sulfuric acid to maintain a low pH (Johnson and du Plessis, 2015). Laboratory-scale experiments have reported reasonable recoveries of metals from oxidised, lateritic ore types. For example, metal recoveries in experimental-scale operations are 80% nickel and 50% cobalt (Hallberg et al., 2011), 78% copper (Ñancucheo et al., 2014) and 55% nickel and 57% cobalt (Marrero et al., 2015), with residence times <3 weeks. Kaksonen et al. (2018) notes that experiments are often optimised beyond what can be achieved realistically at industrial scales and may overestimate potential metal recoveries. Once in solution, elements of economic interest can be separated from the ferrous iron in solution (Willis, 2007), which can be precipitated out as jarosite (Kaksonen et al., 2014).

4.3.2. Iron reduction in circumneutral conditions

Dissimilatory neutrophilic iron-reducing microorganisms also offer a possible pre-treatment for oxidised iron types in which valuable metals are associated with crystalline iron oxide phases. These microorganisms are phylogenetically diverse and are likely to exist within anoxic microscale niches, even within broadly oxidising environments (Levett et al., 2020a; Weber et al., 2006). Dissimilatory neutrophilic iron-reducing microorganisms in cultures are typically only able to reduce small proportions of the crystalline iron oxide phases, typically less than 5 wt% of the available ferric iron (Hansel et al., 2004).

Metagenomic studies are increasing our understanding of the microbiological mechanisms that contribute to the coupled carbon, iron and sulphur cycling within surface and subsurface environments. Extraordinarily, Wrighton et al. (2014) demonstrated that the majority of iron reduction within an aquifer environment was driven by fermentative breakdown of carbon products. In the search for effective iron-reducing microorganisms, Gagen et al. (2019b) enriched a fermentation-driven microbial consortia from the iron ore provinces in the Carajás, Pará, Brazil, that was capable of reducing up to 12% of the crystalline iron oxides (goethite) available. Applying this to biohydrometallurgy, Newsome et al. (2020) increased the amount of easily recoverable cobalt from an oxidised ore from less than 1% in controls to 64% in treatments, simply by inducing reducing conditions by addition of glucose, which promoted the growth of fermentative and heterotrophic microorganisms and production of organic acids.

These advances in the efficiency of iron-reduction for crystalline iron oxides at circumneutral conditions also provide future opportunities for the pre-treatment of oxidised ore types to release valuable metals, including rare earth elements associated with recalcitrant minerals in laterites (Nancucheo et al., 2019). For fermentation-driven iron reduction, a carbon source must be supplied, which will create anoxic conditions below a thick biofilm. This carbon source may simply be added to the oxidised ore types to stimulate a native population of

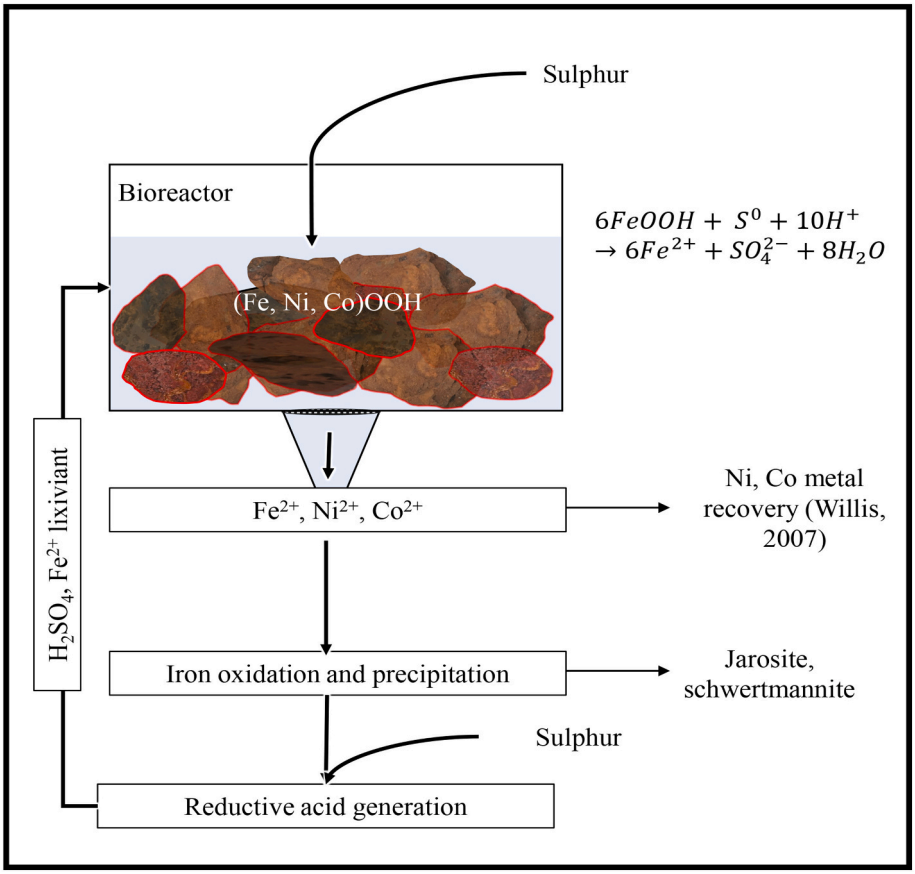


Fig. 6. Simplified schematic of the 'Ferredox' process (du Plessis et al., 2011) used to extract metals (typically, cobalt, copper, nickel) from oxidised ores.

microorganisms capable of iron reduction, or a consortium of microbes capable of iron reduction may be enriched and used to inoculate reactors. Carbon sources may take advantage of agricultural waste; for example, in tropical environments where laterites commonly occur, this may include banana and sugarcane wastes. Ferrous iron potentially generated during bioreduction of goethite may also be used for mine remediation and tailings stabilisation (see Section 5.2).

5. Microbially-induced mineral precipitation for bioremediation

As discussed in Section 2, there are number of passive and active mechanisms microorganisms employee to precipitate metals from solution and these can be utilised to de-contaminate polluted environments with the potential for metal recovery. Several review papers have recently discussed the advances in these fields (Dixit et al., 2015; Guo et al., 2010), along with the use of phytoremediation (Mani and Kumar, 2014). This section, therefore, will focus on microbiologically influenced mineral precipitation to promote carbon capture and the formation of biocements for mine remediation.

5.1. Microbial carbonation

To date, most research in the field of biocementation has focused on accelerating microbially enhanced carbonate precipitation, with calcium or magnesium being the common cations. Microbial carbonate precipitation has potential applications for fracturing filling in the oil, gas and construction industries, stabilisation of mine tailings, decontamination of polluted environments (by sorption of metals into the carbonate lattice) and large-scale carbon sequestration strategies (Mitchell et al., 2010; Phillips et al., 2016; Zhu and Dittrich, 2016). Microbial carbonate precipitation can occur as a by-product of a variety of microbial metabolic activities, with photosynthesis and ureolysis being the most commonly adapted for industry applications (Zhu and Dittrich, 2016). Extracellular polymeric substances (EPS) and cell envelopes provide templates to induce mineral nucleation (Dupraz et al., 2009). As well as the concentrations of the reagents (Ca, Mg, HCO_3^-), the environmental pH plays a critical role in promoting carbonate precipitation and subsequent mineral stability.

Expediting mineral carbonation processes has been proposed as an effective method for mining companies to offset their carbon footprints (Power et al., 2011; Wilson et al., 2009). These processes occur naturally in the environment; however, they are enhanced in ultramafic tailings that have been crushed and milled, increasing the reactive surface area of minerals (Wilson et al., 2014). The higher portions of reactive surfaces accelerates the weathering of ultramafic minerals, therefore increases the leaching of magnesium cations into solution. Weathering of ultramafic minerals has been identified as the rate limiting step to promote carbonation processes (Wilson et al., 2009).

Wilson et al. (2014) estimated that 11% of the CO_2 emissions from a nickel mine (Mount Keith in Western Australia) are offset by passive mineral carbonation processes. Optimising carbonation of more than 11% of the mines total mineral waste would provide the mining company with potentially valuable carbon credits, improving the economic output of the mine (Power et al., 2014; Wilson et al., 2014). This potential is now being realised at increasingly large scales with pilot *ex situ* reactors aiming to upscale these processes (Kemache et al., 2017; Mouedhen et al., 2017). In these *ex situ* reactors, magnesium extraction from serpentine polymorphs [$Mg_3Si_2O_5(OH)_4$] is achieved by heating the serpentine (400–500 °C) in the presence of ammonium sulphate to produce magnesium sulphate (Reaction 7), which is subsequently converted to brucite [$Mg(OH)_2$] (Reaction 8). Brucite is amenable to carbonation, forming magnesium carbonates (for example, magnesite;

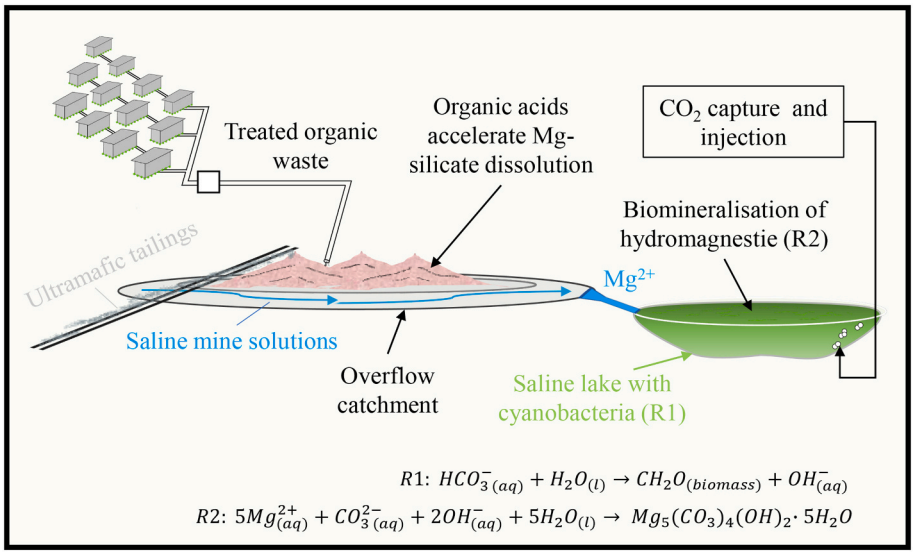


Fig. 7. Schematic of an ultramafic mine tailings based on Mount Keith Nickel Mine tailings (Wilson et al., 2014). Magnesium leaching from serpentine minerals could be accelerated by the addition of organic waste, which would be degraded anaerobically when covered by crushed ore to produce organic acids. Magnesium in solution would flow into a biomineralisation pond, where cyanobacterial growth would be promoted to neutralise solutions and their cell envelopes would provide a site for hydromagnesite nucleation to promote carbon capture. Carbon dioxide from onsite processing plants could be captured and bubbled through the pond to increase bicarbonate concentrations in the pond.

Reaction 9) (Fagerlund et al., 2012). For mining companies that are not able to invest in active mineral dissolution infrastructure to promote mineral carbonation, microorganisms may offer a more passive, long-term option for enhancing mineral weathering and providing nucleation sites for mineral precipitation.

$$Mg_3Si_2O_5(OH)_{4(s)} + 3(NH_4)_2SO_{4(s)} \rightarrow 3MgSO_{4(s)} + 2SiO_{2(s)} + 5H_2O_{(g)} + 6NH_{3(g)} \quad (7)$$

$$MgSO_{4\,(aq)} + 2NH_4OH_{(aq)} \rightarrow 2(NH_4)SO_{4\,(aq)} + Mg(OH)_{2\,(s)} \quad (8)$$

$$Mg(OH)_{2\,(s)} + CO_{2(g)} \rightarrow Mg(CO)_{3\,(s)} + H_2O_{(g)} \quad (9)$$

Accelerating mineral dissolution to leach magnesium from mining wastes remains a challenge to enhance carbonation processes (Hamilton et al., 2020). Standard sulphate-generating bioleaching or sulfuric acid can be used accelerate magnesium release into solution; however, requires further processing to remove and impound the sulphate in solution, which scavenges the released magnesium and precipitates as magnesium sulphate minerals (Hamilton et al., 2020). Therefore, alternative leaching processes are required. Organic acids, generated by microbial degradation of treated waste organic matter, may provide an alternate solution to accelerate mineral weathering. To achieve this, waste organic matter may be interspersed and covered with the crushed and milled waste rock (Fig. 6). Once covered, the waste organic matter will be degraded by the native microbial populations, producing organic acids (for example, acetic, citric, gluconic, oxalic and pyruvic acids) that accelerate the dissolution of silicates and leaching of magnesium from the waste rock, particularly at pH values below 5 (Welch and Ullman, 1996). In this scenario, oxygen would be consumed rapidly, therefore, limiting complete respiration of the organic matter and reducing the production of $CO_{2\,(g)}$. Minimising the production of $CO_{2\,(g)}$ phases in the mine waste is important to prevent mineral precipitation within the tailings that would restrict permeability of leaching solutions. Leached magnesium from the waste pile would subsequently flow to a carbonate mineralisation pond to undergo passive carbonation with atmospheric CO_2 with assistance from phototropic microorganisms (for example, cyanobacteria; Fig. 6) (Hamilton et al., 2020). Carbon dioxide released by onsite processing plants could be captured and bubbled through carbonation ponds to increase the soluble bicarbonate (HCO_3^-) concentration, further accelerating carbonate mineralisation (Fig. 6) (Power et al., 2014). As autotrophic microorganisms, the growth of cyanobacteria biofilms also contributes to carbon capture (R1; Fig. 6). After long periods of organic-based accelerated weathering, the mine tailings can be stabilised by direct injection of air to promote complete respiration of residual organics, producing CO_2 and the precipitation of magnesium carbonate minerals within the tailings dams. Adding organic waste matter to ultramafic tailings could accelerate mineral dissolution and subsequent mineral carbonation without major changes to current tailings storage processes, such as those used at Mount Keith Nickel Mine, Western Australia (Wilson et al., 2014). In general, carbonation processes hold immense carbon-capture potential to offset the carbon footprint of mining ultramafic minerals, including kimberlites, the world's primary source of diamonds (Mervine et al., 2018).

5.2. *Accelerating the biogeochemical cycling of iron for mine remediation*

There is strong geochronological, geochemical and paleomicrobiological (Fig. 7) evidence that microorganisms play important roles in the evolution of iron-rich duricrusts that cap supergene enriched deposits, including the giant iron ore deposits in Brazil (Gagen et al., 2018; Levett et al., 2016; Levett et al., 2020c; Monteiro et al., 2018; Monteiro et al., 2014; Spier et al., 2018). Learning from locations where these processes are naturally accentuated (Levett et al., 2020a) will allow for the accelerated remediation of mines that were originally capped by iron-rich duricrusts and may offer inspiration for the cost effective stabilisation of the massive tailings repositories created during mining.

The vast scale of iron ore mining creates huge tailings repositories, typically referred to as tailings dams, which can pose serious environmental risks and considerable financial liabilities for mining companies. In recent years, two massive iron ore tailings dam collapses highlight these risks, including the Samarco dam failure (2015) and the Brumadino dam failure (2019), both occurring in Brazil. Both of these disasters occurred at upstream dams, releasing millions of tonnes of an iron-rich sludge into the downstream valleys, causing fatalities and widespread environmental damage. Armstrong et al. (2019) reports a doubling of the number of dam failures in the past 20 years.

To stabilise the physical tailings or the tailings dams themselves, microorganisms may be used to create biocements (Fig. 7). Microorganisms naturally grow to produce biofilms and aggregate fragments. These microbial biofilms provide an organic framework that naturally aggregate crushed materials and their cell envelopes act as nucleation sites for the precipitation of chemically stable minerals. This is a result of the net negative cell envelopes of microorganisms attracting the positive metal cations in solution, promoting the nucleation of microbially influenced minerals at the cells' surface (biosorption; Fig. 2) (Ferris et al., 1988). Microbial growth could be promoted either at the surface

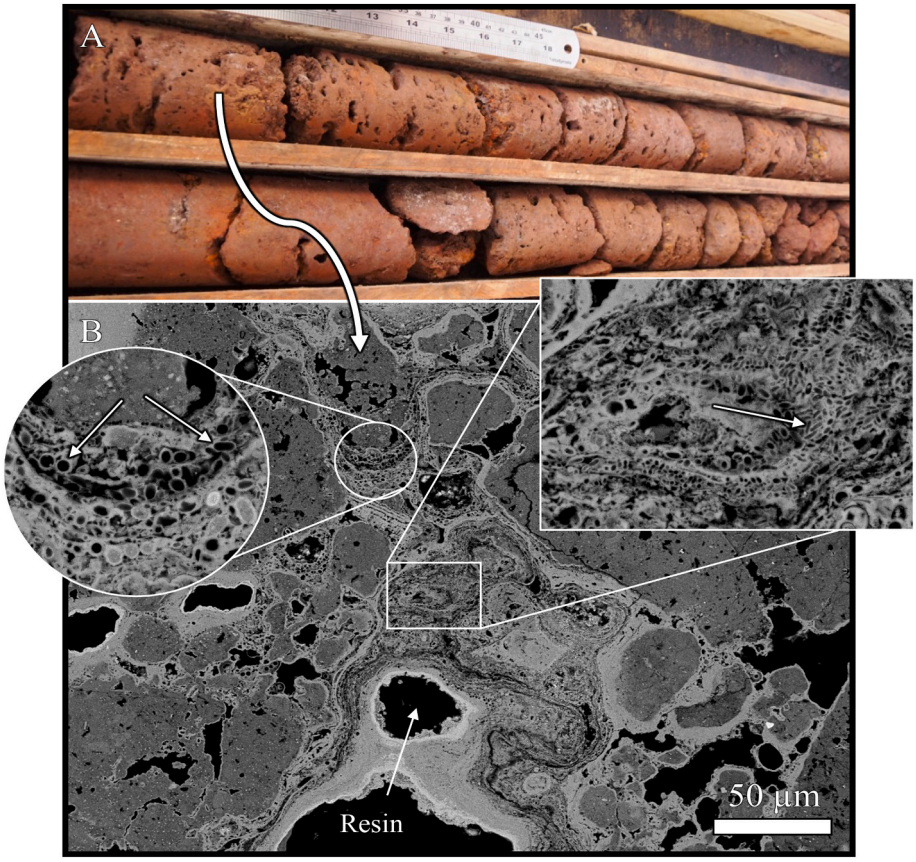


Fig. 8. (A) Photograph of a drill core of an iron-rich duricrust taken from the world's largest iron ore mine (S11D) in the Serra Sul, Carajás, Pará, Brazil. (B) Backscattered electron micrograph, highlighting microorganisms contribute to the ongoing formation of iron-rich cements, helping to make these duricrusts some of the most stable in the world and protecting the underlying ore from erosion (see Levett et al. (2020c) for details).

of a tailings dam or within the tailings themselves. Subsequently, these microorganisms could be subjected to metals in solution (for example, ferrous iron produced in a bioreactor). In the example of iron, the solution would then be oxygenated, promoting the nucleation of iron oxide minerals on microbial cell surfaces (Fig. 7).

There are several advantages for using microorganisms to promote stabilisation. Specifically, prokaryotic microorganisms are typically tiny (commonly 1–5 µm in length and less than 1 µm wide) and are able to maintain mobility in pore spaces only 30% larger them their own width (Männik et al., 2009), allowing them to continue to move and replicate throughout finely crushed mine tailings. Microbes are also able to grow in relatively harsh, metal-rich environments and, given the right conditions, can multiply relatively quickly at low cost. Finally, biocements produce a mineralised network with properties akin to metal foam, greatly reducing the amount of metal required to stabilise fragments. For example, Levett et al. (2020b) estimate that less than 1 wt% of ferrous iron is required to aggregate and stabilise the surface of crushed mine waste (Figs. 8 and 9).

This emerging biotechnology has potentially important structural implications, therefore, will require rigorous testing at the experimental stage, including determining the resistance to liquefaction and relative strength of biocement substrates. In addition, the relative water runoff and hydraulic functionality of surface crusts that may be established will require testing. The ultimate goal of these remediation projects will be to re-establish a relatively water impermeable layer to restore hydraulic functionality to the degraded landscape and physically stabilise easily erodible materials using chemically stabile biocements.

6. Conclusions

Microorganisms employee a number of strategies to survive in metal-rich environments and, as such, play important roles in metal mobilisation and immobilisation. Understanding mineral-metal-microbial interactions will continue to provide novel biotechnological tools to assist innovation in the mining industry. Studying the metabolic function and potential of microorganisms in environments containing metals may provide important insights into subsurface metal mobility to assist in the exploration for new mineral deposits. Many microbial-based mining strategies aim to optimise microbial metabolic function to accelerate mineral dissolution for (i) the recovery valuable metals, (ii) the release di-valent magnesium and calcium from silicate minerals into solution or (iii) generating metal-rich solutions for biocementation. Microbes may also provide active sites for metal immobilisation, which may be used to decontaminate heavy metal polluted environments, promote the precipitation of carbonate or iron oxide minerals for carbon capture and biocementation. Opportunities exist in the mining industry for these processes to have dual benefits. For example, fermentative bioreactors may use organic waste to promote the dissolution of iron oxide minerals to recover cobalt, copper and/or nickel from an oxidised ore. Subsequently, the reduced ferrous iron potentially produced during reductive dissolution may be used for mine remediation and mineral waste stabilisation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

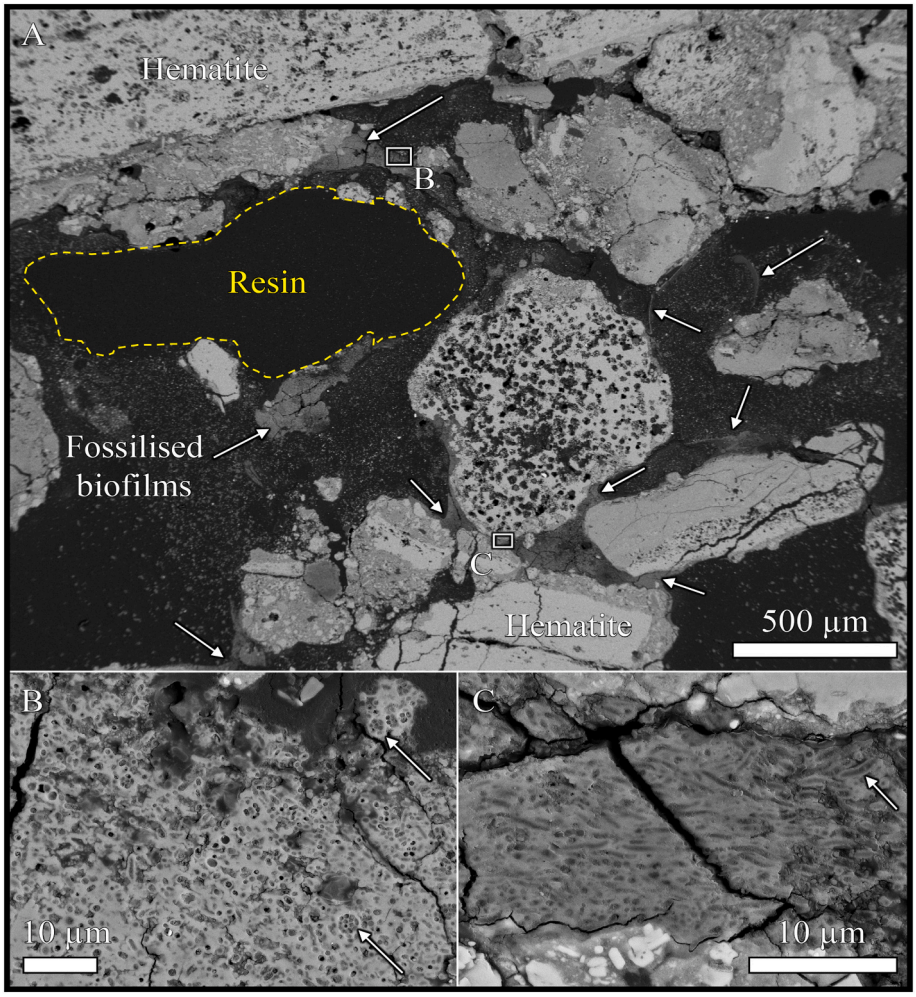


Fig. 9. Backscattered electron micrographs of microorganisms encrusted in iron oxide minerals by passive biosorption. (A) The growth of microbial biofilms naturally aggregates grains, after exposure to ferrous iron the microbial biofilms are fossilised (highlighted by arrows) to create biocements to stabilise mine tailings (Levett et al., 2020b). High magnification micrograph highlighting the fossilisation of (B) microbial cell clusters and (C) rod-shaped to filamentous microbial morphologies.

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