

WITH LOW ENVIRONMENTAL IMPACT?

MM-FREE NERC SOS-MINERALS CATALYST GRANT CONSORTIUM

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Bioprocessing used as an economical mining technology is currently mainly limited to the recovery from low grade ores of copper, cobalt, nickel, uranium and precious metals (gold), and use acidophilic prokaryotes (bacteria and archaea) to degrade reduced minerals (sulphides) by oxidative dissolution [1]. Recent research has also shown that bioleaching could be used to process oxidized ores (lateritic nickel ores) [2]. Mechanism and rates of microbially induced sulphide oxidation reactions have been extensively investigated and process-based models have been developed to aid in the optimisation of the bioleaching process at industrial scale [3]. This knowledge base does not exist for the REE minerals, though it is essential for the development of biotechnologies for REE recovery.

In this review, part of the work carried out by the UK NERC-funded MMFREE project, we discuss the microbial potential to accelerate dissolution and fractionation of REEs from source minerals using evidence from studies of rock weathering processes, and how the natural selectivity of mineral and microbial surfaces as ligands for adsorption and biomineralisation of REE dissolved species could be exploited in the recovery of REE.

MICROBIAL PROCESSES LEADING TO EITHER MOBILISATION OR IMMOBILISATION OF METALS

Several metabolically-driven metal transformations may occur when microorganisms are in contact with mineral particles. Microorganisms are able to mobilise metals through the formation of organic and inorganic acids, by oxidation and reduction reactions, and through the excretion of complexing agents, based on three main mechanisms - acidolysis, complexolysis, and redoxolysis (See Table 1). These microbial activities may be applied in industry for the recovery of metals from solid materials.

Current **biomining** is mostly based on the oxidization of reduced sulphide minerals by chemolithotrophic acidophilic bacteria (**autotrophic bioleaching**) which fix carbon dioxide and obtain energy from the oxidation of reduced sulphur compounds or ferrous iron, yielding H₂SO₄ or Fe(III) as the respective end-products. Meanwhile, **heterotrophic bioleaching** is much less developed. Heterotrophic microorganisms with leaching capabilities are mostly filamentous fungi and bacteria. Metal leaching generally involves indirect as well as direct processes with microbial production of organic acids, amino acids and other metabolites. These microbial metabolites dissolve metals by displacement of the metal ions from the ore matrix by hydrogen ions or by the formation of soluble metal complexes and chelates. Furthermore, **biosorption** has a long tradition in bioremediation (i.e. removal of metals) and has only recently been suggested for the recovery of critical raw materials [7, 16].

Table 1: Major microbial metal interactions [4,5,6]

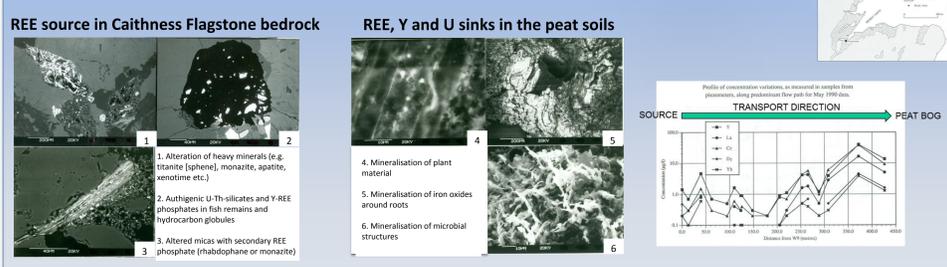
Process	Mechanism	Description of the reaction
Mobilisation	Redoxolysis	Metals are microbially oxidised or reduced during oxidation-reduction processes. As a result, metal mobility is increased depending on the type of metal and its oxidation state.
	Acidolysis	Also termed proton-induced metal solubilisation. Microbial secretion of protons results in changes of the metal mobility. Under these conditions protons are bound to the surface resulting in the weakening of critical bonds as well as in the replacement of metal ions leaving the solid surface.
	Complexolysis	Also termed ligand-induced metal solubilisation. Microbial formation of complexing or chelating agents leads to an increase of metal mobility. Complexes are formed on metal surfaces by ligand exchange polarising critical bonds and facilitating the detachment of metals species from the surface. Organic ligands of bi- or multi-dentate nature are particularly effective.
Immobilisation	Alkylation	Alkyl groups are enzymatically transferred to the metal and covalently bound. The process is often described as "metal volatilisation", because alkylated metals display an enhanced volatility as compared to their elemental or ionic forms. Methylation is the best known alkylation process.
	Biosorption	Defined as a passive process of metal sequestering and concentration by chemical sites (functional groups such as carboxyl, sulphonate, phosphate, hydroxyl, or amino acid residues) naturally present on the surface of microbial biomass. Metal sorption may be more or less selective depending on the organisms used and environmental conditions (e.g., pH, salinity).
	Bioaccumulation	Soluble metals are actively transported through the cell membrane and accumulated within the cells as solid particles or in vacuoles.
	Redox reaction	Metals are microbially oxidised or reduced during oxidation-reduction processes. As a result, metal mobility is decreased depending on the type of metal and its oxidation state.
	Extracellular precipitation	Extracellular formed minerals and metals are often product of a bioinduced process, i.e. the result of the metabolic (by)products causing chemical precipitation, for example sulphate reducing bacteria play a crucial role in metal mobility in the environment by precipitating metals through their metabolic end product, sulphide. Additionally, the bacterial activities can result in a reduction of the acidity in an environment leading to the precipitation of metals as hydroxides.

EVIDENCE OF REE MOBILISATION DURING WEATHERING

Many studies have shown that during weathering processes the concentration and fractionation of REE in the weathering profile depends on complex processes and interactions between chemistry, geology and microbiology, and especially the nature of the host rock- accessory mineral associations. Several factors such as redox, pH, solution composition, the presence of organic and inorganic ligands will affect the REE solubility and speciation, and the geochemical and biogeochemical processes of metal sorption-desorption, precipitation, ion-exchange, and uptake by biota. An understanding of these mechanisms of REE behaviour in low-temperature alteration processes is crucial for the formation of REE ore deposits as well as for industrial processing.

Figure 1 - Transport of REE in natural systems: Broubster site, Caithness, Scotland, UK- Milodowski et al. 1989 [8] observed the presence of REE mineralised structures in a peat bog, attributable to the activity of microorganisms.

- Naturally radioactive (U, Th, REE diagenetic mineralized) Devonian lacustrine strata (including phosphatic fish beds)
- Later polymetallic (Ba-Pb-Zn-U-carbonate) fracture-hosted mineralization (faults)
- Upwelling water through fault feeding mineralized water into an overlying peat bog with secondary U accumulation in peat and Mn oxide alteration products
- Y and REEs are transported in both surface drainage waters and groundwater feeding the peat bog
- Groundwaters REE concentration increases within the peat bog



ROLE OF BIOWEATHERING TO INFORM BIOMINING OF REE ORES

While a biomining strategy has not yet been applied to the recovery of REE, it is known that microbes play a role in the accumulation or fractionation of REE. The study of bioweathering in natural environments has often informed the selection of highly efficient microbial inoculate for the recovery of metals in biomining processes.

Although REE phosphates are highly insoluble (K_{ps} 10⁻²⁴ to 10⁻²⁶ [9]) colonisation of their surfaces by microbial communities can lead to their mineral dissolution, due to the combined effects of complexation of REE by organic ligands and microbial uptake of phosphorous [10]. Microbial-induced fractionation of the REE towards a heavy REE enrichment has been reported in several studies, for example during bacterial dissolution of fluorapatite [11], granodiorite [12], hornblende [13] and in natural waters [14].

Several studies have shown that REE have exceptionally high stability constants with siderophores (see e.g. [15]). Siderophores are ubiquitous, low-molecular weight organic molecules secreted by bacteria and plants to cope with iron deficiency. A well-studied example of such a chelator is the biogenic siderophore desferrioxamin-B (DFOB). Results by [15] demonstrated that siderophores not only enhanced the release of iron, but also promoted the mobilization of REE from volcanic ash, producing a characteristic type of fractionation within the dissolved REE pool (LREE-depletion and a convex patterns between La and Sm and selective enrichment of Ce, due to the formation of dissolved Ce(IV)-DFOB complexes).

A wide range of microorganisms have demonstrated the ability to take up or adsorb REE to cell walls, extracellular polymers or biominerals ([16] and references within, see Table 2). It has also been shown that bacteria can selectively adsorb REE [14] with an enrichment in heavy REE. Results by [17] suggest that the REE-binding sites of bacteria are phosphate and carboxyl groups.

Table 2: Summary of microorganisms reported to be involved in REE sorption [16]

Mechanism	Microorganism	Reference
Adsorption on cell wall	<i>Bacillus subtilis</i> , <i>Halobacterium salinarum</i> , <i>Pseudomonas fluorescens</i> , <i>Arthobacter nicotianae</i> , <i>Streptomyces albus</i> , <i>S. acidiscabies</i> W-12, <i>Micrococcus luteus</i> W-20, <i>Bacillus</i> sp W-28, <i>Acremonium</i> sp. KR 21-2, <i>Escherichia coli</i> , <i>Alcaligenes faecalis</i> , <i>Shewanella putrefaciens</i> , <i>Pseudomonas fluorescens</i>	14, 18; 19; 20; 22; 23
	Adsorption to extracellular biopolymer and cell wall	<i>Myxococcus xanthus</i>
Adsorption to extracellular minerals (Fe oxides)	<i>Gallionella ferruginea</i>	12

CONCLUSIONS

The existing literature data on REE mineral-microbe interactions clearly indicate the role of microbes in the mobilisation and fractionation of REE and the potential of biotechnologies to recover REE from ores. The biological processes occurring in near-surface environments have the potential to assist in the development of such biotechnologies. Weathering profiles can act as natural analogues of biomining.

Increasing future need to use low-grade primary metal ores and to reprocess mine wastes, which are economically more amenable to bioprocessing than conventional approaches, suggests that biomining might become more extensively used in the future. However, a step change in understanding is needed for key mobilisation, concentration and fractionation processes such as bioleaching, biosorption and biomineralisation and how they can 1) be harnessed to recover REE in situ from low grade ores or secondary deposits, and 2) be quantified for reactive transport in environmental risk assessment and management of mining operations.

Development of biotechnologies should be based on a mechanistic understanding of microbial processes to generate conditions for accelerated mass transfer of REE from minerals to aqueous solutions (acid/base and pH buffering, oxidative/reductive, chelating, physiological requirements), and how to fractionate and concentrate selected target elements from solution.

Mechanistic models represent a robust approach to ensure critical information and quantitative descriptions are delivered to adapt technologies from one resource to another in response to changing demand and supply, especially considering the complexity of REE mineralogy, REE fractionation and enrichment mechanisms.

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