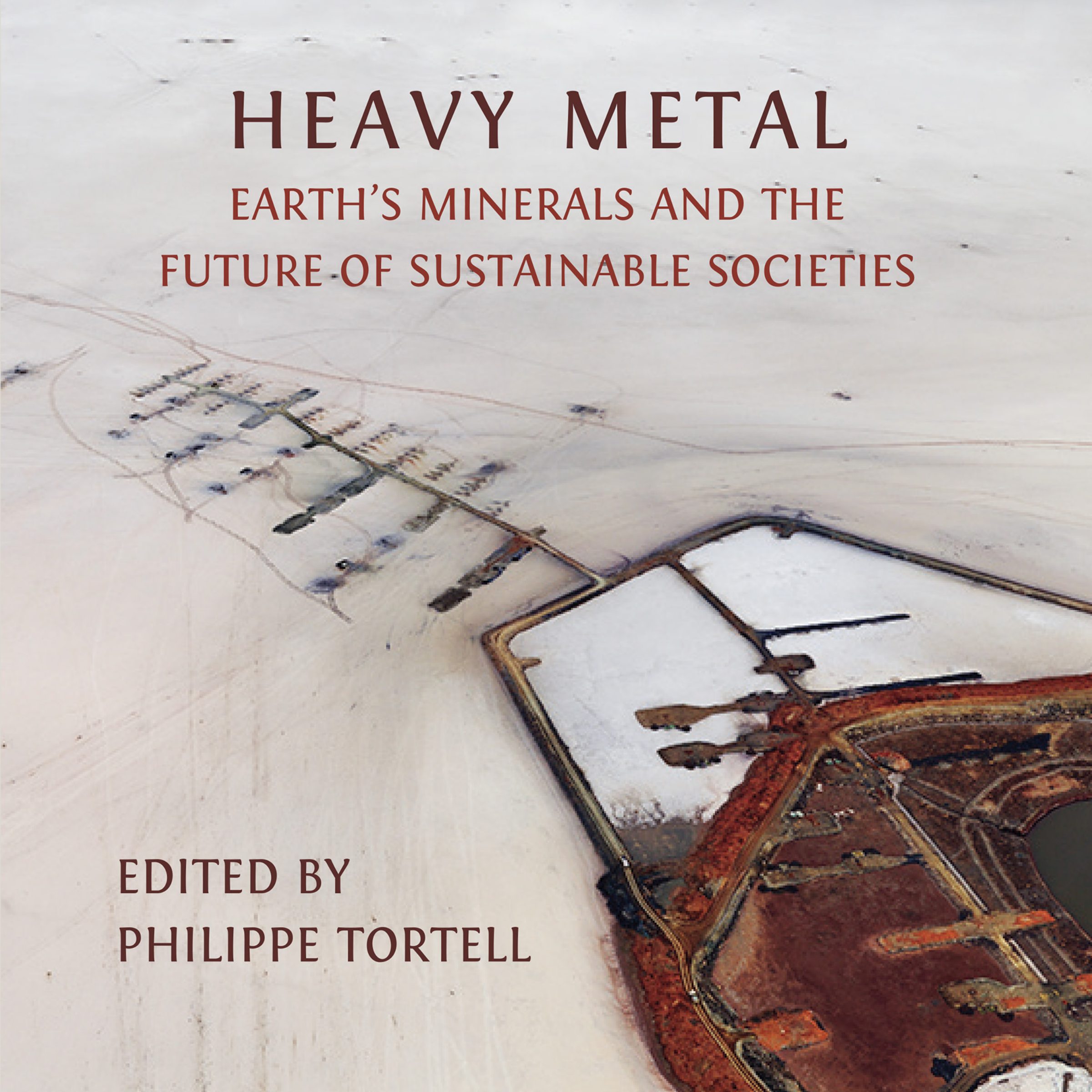
HEAVY METAL

EARTH'S MINERALS AND THE FUTURE OF SUSTAINABLE SOCIETIES



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Microbial Mining

Gordon Southam

The earliest forms of biotechnology can be traced back to the beginning of human civilization, with the domestication of plants and animals, and the discovery of fermentation. These early innovations sought to harness naturally occurring biological processes to provide useful products, such as food and wine. In the context of mining, biotechnology has also been used, though indirectly, for over a thousand years. The Romans used the 'colors of earths', in particular the intense red staining of iron oxide, to discover nearly all of the world-class metal ore bodies present across the Iberian Pyrite Belt in present-day Spain and Portugal. More than a millennium later, the German scholar Georgius Agricola published his 1556 book *On the Nature of Metals*, the fifth part of which discusses how various minerals and colors of earths can be used to give indications of the presence of metal ores.[1] Both Agricola, and the ancient Romans before him, had unwittingly discovered the signature of bacteria associated with metal-sulfide deposits. But it is only over the past few decades that we have come to better understand the potential for these microbes to identify significant mineral deposits and liberate metals from their host rocks.

Today, as we face the enormous challenge of provisioning massive quantities of minerals for the green energy transition, there is significant focus on innovation in the mining sector, including the application of biotechnology. With the advent of

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the molecular biology revolution, we can map the diversity and metabolic potential of microbes across the entire Earth system, from the deepest ocean trenches to the highest mountain glaciers. Microorganisms are ubiquitous in surface and subsurface environments, where they exhibit tremendous molecular and metabolic diversity, and exploit a wide range of chemical reactions to support their metabolism. By harnessing these microbial metabolic pathways, new biotechnology tools could eventually transform the mining industry, from the recovery and extraction of metals to the downstream treatment of wastes.

The first step in mining begins with the identification and characterization of an economically significant accumulation of metal(s) in an ore deposit. Historical mineral exploration focused on easily accessible ore body deposits contained in exposed rock outcrops on Earth's surface. As these 'easy' deposits have become scarcer, contemporary mineral exploration programs have increasingly employed geophysical surveys to target ever deeper subsurface geological materials. Once a potential exploration target is identified, surface geological measurements are used to improve confidence in the presence of subsurface metals. In many cases, these measurements are complicated by the presence of significant groundcover, including ancient marine sediments and glacial debris, which can mask underlying signatures of metal deposits. As a last step in exploration, drilling programs are used to extract rock samples for the analysis of chemical and mineralogical properties of potential ore deposits, and to identify potential harmful elements, such as arsenic, which could diminish the viability of a mining project. Coring (and the associated downstream laboratory analysis) is extremely expensive and time-consuming, accounting for a significant fraction of the total costs and personnel time associated with mineral exploration.

In many ways, the search for mineral deposits is like looking for needles in haystacks. But the search is guided by an underlying understanding of the geological processes that lead to metal enrichment in Earth's crust, and the 'footprint' these processes leave behind. Metal-rich materials are emplaced and concentrated in diverse geologic settings via high temperature, magmatic, hydrothermal, sedimentary and metamorphic processes.[2] Once emplaced and cooled, metal deposits can be subjected to chemical reactions, which spread out their subsurface and surface signatures. These anomalous geochemical signatures reflect the dispersion of metals from an ore body during weathering, and the enrichment of metals in near surface environments. Traditionally, these footprints have been mapped by measuring the concentration and isotopic composition of various elements across a defined sampling volume. With rocks in hand, geologists can measure the chemistry, mineralogy and geologic structures, targeting samples in three dimensions around the suspected location of an ore body. In practice, funding and time-constraints often limit the amount of sampling and chemical analysis that can be performed, and geologists typically use only a limited snapshot of data to point towards an ore body. At present, much less than 1% of mineral exploration projects lead to the development of a mine. Given this low probability of success, innovative approaches are needed to improve efficiency and reduce the costs of exploration.

Over the past decade, increasing focus has been placed on the potential use of bacteria to identify mineral deposits. This approach is based on the genetic information coded within bacterial cells, which provides clues about the concentration of metals in the rocks, soils and groundwaters that surround these tiny organisms. Soils typically contain thousands of different bacteria, each possessing hundreds to thousands of metal-specific metabolic pathways with distinctive molecular signatures. These molecular signatures, coded in genes and proteins, have been shaped by the evolutionary and ecological history of bacteria (i.e., exposure to metals over geologic time), and they can provide an integrated picture of metal availability in modern environments.

Many of the economically important metals, such as copper and zinc, are biologically toxic at the high concentrations found in ore systems. Exposure of microorganisms to these metals will select for metal-resistant microbes, which can persist down to several kilometers below Earth's surface. Some bacteria, for example, have pumps embedded into their plasma membranes that act to transport metals out of the cell. Other bacteria release metal-binding compounds (chelators) to reduce metal toxicity outside of the cell. Both these processes of metal detoxification are associated with genes that can be identified in natural samples. These metal-sensing genes 'respond' to many elements across the periodic table, providing a potential biological signature of high concentration metal deposits. The sum of all genes present in a bacterial population (the 'meta-genome') is thus akin to a genetic library, describing the collective metabolic pathways of all bacterial groups present in a sample. The more complex the bacterial population, the greater the genetic capacity of the 'library' that can be accessed through biotechnology. With up to hundreds of millions of bacteria per gram of soil, microbial metagenomes present a massive archive of metal-specific genetic elements that can be targeted for mineral exploration, providing information about the chemical environment surrounding the cells. Over geological time, the exposure of bacteria to weathered ore bodies has undoubtedly produced thousands of currently unknown biotechnological targets (such as chelators) that are waiting to be discovered.

Beyond the initial exploration phase, bacteria can also play a significant role in downstream aspects of the mining process. Once a mineral deposit has been identified, metals of interest must be economically extracted from the host rock in a way that minimizes energy consumption and the release of harmful wastes. At present, the mining industry is extremely energy and fossil fuel intensive, accounting for approximately 5% of global CO_2 emissions. Most of the energy used in mining is directed towards rock crushing and grinding, which is the typical first step in the extraction of metals. Over the past several decades, the industry has worked to improve energy efficiency and transition to renewable energy. These efforts have focused on improving conventional techniques; however, radically novel approaches, inspired by bacteria, could potentially offer even better results.

Naturally occurring bacteria play a significant role in the formation of certain mineral deposits, and could, in the future, be used to 'super-charge' these formation processes. So-called 'supergene' deposits provide a case in point. These metal enrichments form when bacterial metabolism helps break down minerals, allowing extracted metals to percolate down from upper rock horizons into an enriched subsurface 'blanket'. Targeting this enriched layer during mining can significantly reduce the amount of rock that needs to be crushed and ground, improving the efficiency of metal extraction. It is conceivable that bacteria could be used to 'grow' a supergene ore body, by introducing percolating fluids and nutrients to stimulate bacterial metabolism and speed up the dissolution of metal-containing minerals.

Even better than targeting metal-rich layers of host rock, what if metals could be extracted from ore without crushing any rocks? Such a process of in situ leaching occurs naturally when bacterial populations metabolize host minerals, releasing dissolved metals into the surrounding fluids. If such microbially mediated reactions could be controlled and scaled up, significant supplies of metals could be liberated into pore fluids, which could be accessed without the need to extract rock. This 'bioleaching' would massively decrease the energy requirements of metal extraction, leaving all the waste rock in the ground. It would also make it easier to selectively remove potential harmful metals from a solution. The underlying processes of bacterially mediated mineral weathering and dissolution are the same ones that account for the mineral-associated colors of Rio Tinto originally observed by the Romans thousands of years ago.

In recent years, bioleaching has come to play an increasingly important role in mining operations. As an example, approximately 15% of the world's copper is currently recovered using biohydrometallurgy, a process catalyzed by iron and sulfur-oxidizing bacteria that accelerates the extraction metals from rock. By artificially stimulating bacterial iron oxidation in an ore sample, the rate of bioleaching can be increased 100,000-fold. In addition, the same bacteria used to extract copper can help access gold from sulfide minerals, exposing interior mineral surfaces for more efficient chemical leaching. This greater efficiency significantly reduces the amount of cyanide needed for the chemical reaction, minimizing the production of hazardous waste.

The examples above serve to illustrate how bacteria could be used to target a range of metals from ore deposits. At present, most current mining operations are directed at the recovery of a primary metal (for example, copper), and perhaps a secondary target (for example, gold) that is amenable to economic extraction. There are no current mines that recover all the metals in a deposit, whether for potential economic benefit or to avoid environmental contamination. These abandoned metals often include low-grade deposits of critical minerals, such as cobalt, nickel and rare-earth elements (REEs), which are essential for our technologically advanced society. The recovery of abandoned metals in left-over mined rocks provides an opportunity to transform wastes into resources, with the goal of eventually accessing all the metals in a deposit.

With thousands of metal-specific metabolic pathways and metal-binding compounds, bacteria have an enormous potential to selectively remove metals from ore deposits. For example, the identification and use of metal-specific chelators holds significant promise to increase the recovery of a wide suite of metals from complex ore bodies. This would lead to improved economic benefits, in terms of valuable metals, while minimizing environmental impacts from harmful elements, such as arsenic, which remain behind in mine wastes. Such a biotechnology approach could effectively 're-mine' the waste from the ore, greatly improving the overall efficiency of metal extraction, and reducing the potential environmental impacts of waste storage.[3]

As noted elsewhere in this volume,[4] mining is essentially a waste management business. Massive quantities of metal-containing rocks and tailings are left behind after metal extraction, and these wastes pose the most significant environmental threat from mining activities. At present, it is estimated that there are currently thousands of major waste sites around the world. Of particular concern is the problem of acid mine drainage (AMD), which currently affects thousands of kilometers of rivers globally. AMD occurs when bacteria oxidize sulfide containing minerals to form sulfuric acid, which, in turn, releases a range of potentially toxic metals from an ore body and its host rock. The presence of AMD is often indicated by bright orange and red wastewaters, reflecting high concentrations of dissolved iron released from pyrite (an iron sulfide-containing mineral). If left untreated, metal precipitation from AMD can occur at significant distances (more than tens of kilometers) downstream from an acid-generating mine site. It can continue for hundreds or even thousands of years, well beyond the timescales of mine closure planning. The red-orange colors of Spain's Rio Tinto provide a particularly vivid example of this.

Current approaches to treating AMD focus on chemical methods aimed at preventing or limiting long-range impacts. These include the use of acid-neutralizing reagents such as calcium carbonate or caustic soda (sodium hydroxide), both of which have their own negative impacts. The use of calcium carbonate leads to significant CO_2 release (increasing the greenhouse gas emissions of mining), while the high pH of caustic soda can cause negative ecosystem impacts. Importantly, neither of these treatments address the underlying process that generates AMD. Rather, they produce treated mine waste reservoirs that are similar in size to the original mine waste site. Concentrations of metals in these reservoirs may be significantly lower than in untreated sites, but they often still exceed health and safety limits, affecting tens of thousands of kilometers of streams globally.

Biotechnology can offer some alternatives to address AMD. First, bacteria can be used to reverse the production of AMD. In the absence of oxygen, sulfate-reducing bacteria have the capability to convert sulfate ions into reduced sulfur (sulfide), which reacts with a wide range of metals to form highly insoluble metal sulfides. These minerals form a precipitate and sink out of solution, allowing them to be recovered and concentrated. This approach addresses the issue of environmental toxicity and provides a value-added economic benefit from metal recovery.

In addition to catalyzing reactions that cause metals to precipitate out of solution, bacteria can accumulate high concentrations of metals on their outer cell surfaces. Under normal conditions, negatively charged molecules on the bacterial membrane bind to a variety of positively charged ions, including calcium and magnesium, helping to stabilize the membrane. At high concentrations, positively charged metals, such as copper and zinc, can displace calcium and magnesium from the membrane binding sites, leading to the formation of mineral precipitates on the cell surface. The small size of bacteria makes them particularly efficient at stripping metals out of solution through cellular adsorption (as the size of a particle decreases, its relative surface area increases). A population of bacteria can thus present an extremely high effective surface area available to adsorb metals out of solution. Such 'bio-mineralization' holds significant promise as a means of metal recovery from mining waste materials, with both environmental and economic benefits.

Microbes have existed on Earth for billions of years and have evolved a wide variety of useful, biotechnological metabolic functions. These tiny organisms are partially responsible for the oxygen that we breathe and the food we eat. They also play a critical role in the natural cycling of elements, but it is only recently that we have begun to better understand their potential use in mining-related applications. Current biotechnological methods can offer a diverse range of approaches that could one day revolutionize the entire mining life cycle, from the discovery and extraction of economically important minerals, to the downstream recovery of metals from mine waste. In the face of diminishing ore grades, improved metal extraction efficiency is essential to our future material needs. As we look to the future, we may need to look also to the ancient past; it may be that the solution to our metal supply problems lies with some of the most ancient organisms on our planet.

Endnotes

1 Georgius Agricola, *De re metallica* (Basil: Hieronymus Froben and Nicolaus Episcopius, 1556).

2 See also 'Where We Find Metals' by Shaun Barker in this volume.

3 See also 'Mine Waste' by Roger Beckie in this volume.

4 Ibid.