Soil science – Scavenging for scrap metal

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SOIL SCIENCE

Scavenging for scrap metal

All organisms require elements to live, grow and reproduce, but some of these are hard to find or take up. Nitrogen-fixing bacteria solve the problem by secreting compounds that allow them to acquire the metals they need.

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Organisms acquire some elements from the environment with ease. Diffusion alone often provides enough carbon dioxide, oxygen and water. But getting other elements requires more effort, spurring unique evolutionary adaptations: instead of taking up nutrients from the soil, some plants in acidic bogs trap insects to obtain nitrogen and phosphorus[1]; geophagy — or eating dirt — may sometimes be important for acquiring iron by primates[2]; plants and microorganisms secrete compounds that liberate phosphorus from unavailable forms in soil[3]; and many bacteria secrete metal-scavenging compounds called siderophores to capture iron and copper[4,5]. Evidence has mounted that molybdenum is also specifically targeted[6]. On page 243 of this issue, Bellenger and colleagues[7] confirm this, showing that siderophores produced by the nitrogen-fixing bacterium *Azotobacter vinelandii* bind with molybdenum and vanadium in the laboratory, promoting uptake of these metals.

Metals are vital for enzymes and are often required in relatively high concentrations[8], so it makes sense that organisms mine them from the environment. The enzyme nitrogenase requires iron, molybdenum or vanadium to catalyse nitrogen fixation[9]. This converts atmospheric N_2 gas, which is unavailable to most organisms, to a bio-available form of nitrogen. In soils, however, aluminium oxides, iron oxides and clay minerals can bind Mo and V in unavailable forms. Organic compounds, too, can complex with these elements and make them unavailable, such that reservoirs of these elements in inorganic forms may be too low to meet the requirements of nitrogen-fixing bacteria[10].

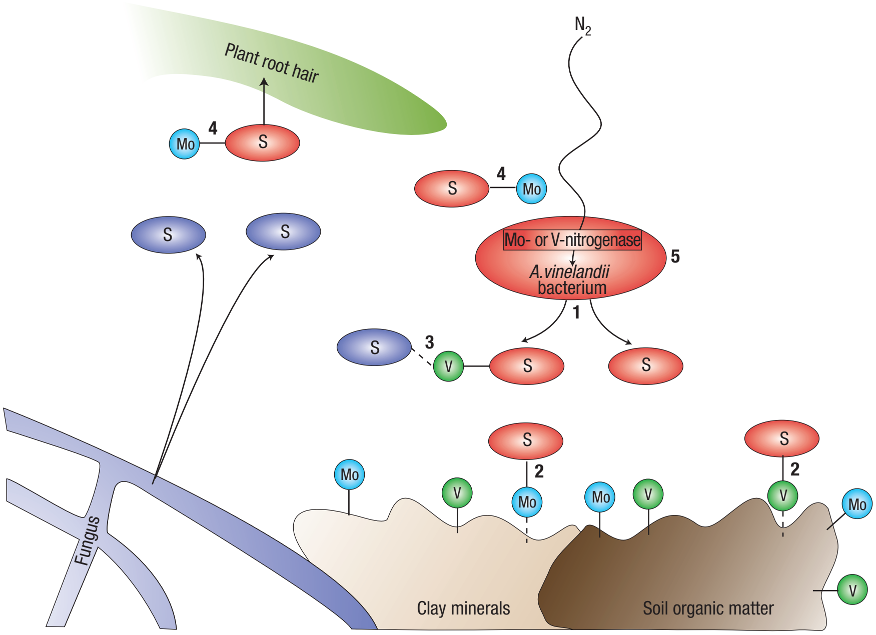

Figure 1 The long road to nitrogen fixation. Under metal-limiting conditions, the bacterium *A. vinelandii* secretes metal-scavenging compounds (siderophores; S) (**1**). These siderophores scavenge the metals molybdenum and vanadium from unavailable complexes with clay, soil organic matter or other elements (**2**). The siderophores compete with siderophores produced by other organisms such as fungi for these metals (**3**). The bacterium or plant roots readily take up the siderophore-metal complexes (**4**). Within the bacterium, the metal is incorporated into the enzyme nitrogenase (**5**), to allow the fixation of atmospheric nitrogen (N_2) that would otherwise be unusable to the bacterium.

Bellenger and colleagues[7] show that *A. vinelandii* produces siderophores that target Mo and V, especially when Mo and V are limiting, helping explain how the bacteria acquire these key elements. One of the siderophores produced by *A. vinelandii* — protochelin — is able to bind several metals, Mo, V and Fe. Such flexibility suggests that under conditions where Fe is abundant, but Mo and V are scarce, Fe could preferentially complex protochelin, making it ineffective at scavenging Mo and V. High Fe concentrations in soils could thus limit Mo and V uptake by microbes and plants[10]. But Bellenger *et al.* found that, even though Fe availability was high in their experiments, most of the Mo and V in culture were recovered bound to protochelin, whereas only a small fraction of the Fe was found to be complexed with the siderophore. This siderophore thus appears to enable efficient Mo and V uptake, even when Fe availability is high.

This metal-scavenging system appears to be tuned to promote uptake of only those elements the organism actually needs. For example, tungstate has chemically analogous properties to molybdate and vanadate, but is toxic to N_2-fixing organisms because its substitution in nitrogenase renders the enzyme inoperable[11]. Although the siderophores produced by *A. vinelandii* formed complexes with tungstate, the cells did not take them up in the experiments by Bellenger and colleagues. Furthermore, cells with low V concentrations rapidly took up siderophore–V complexes, but only if they also had low Mo concentrations. The Mo–nitrogenase is the most efficient version of the enzyme, explaining why uptake of the siderophore–V complex is suppressed when Mo is sufficiently available.

The strategy of producing siderophores to generate bioavailable metal complexes may be ancient, potentially having evolved under pressure from a low Mo environment in the Earth's early oceans[12]. Plants, too, may rely on such strategies. Extractable pools of Mo in soil may be too low to supply plants with the Mo they need. Plants are known to facilitate their own uptake of Fe, manganese, and zinc by producing phytosiderophores[13], though whether these influence Mo availability is not known. How important are siderophores for providing elements to nitrogen-fixing bacteria in natural systems, as opposed to the laboratory as in the study by Bellenger and colleagues? Might phytosiderophores promote Mo availability to plants?

The production of extracellular metal-scavenging compounds raises interesting ecological and evolutionary questions (Fig. 1). For example, Bellenger *et al.* found that excretion of azotochelin out-competes another siderophore — desferioxamine B — which is produced by a fungus. This is important because the complex of desferioxamine B and vanadium cannot be taken up by *A. vinelandii*, so by sending its more effective scavenger protein into the environment, *A. vinelandii* helps promote its own uptake of V, and potentially reduces V uptake by the fungus. In this way, metal-scavenging compounds could mediate resource competition outside the cell, modulating the availability of limiting elements to competing organisms.

On the other hand, some siderophores form complexes that are available to numerous bacteria in the environment, such that 'cheaters' can evolve that take up the metal complexes without expending the resources to produce the siderophores themselves. As described earlier, plants produce their own phytosiderophores[3], but plants can also cheat, taking up the siderophore–Fe complexes where the siderophore was produced by bacteria[13]. Because these metal-scavenging compounds are extracellular, they may or may not end up benefiting the organism that produced them. Production of siderophores thus provides an excellent model system for exploring competition and cooperation among microorganisms, and possibly even between plants and microorganisms[14].

Nitrogen fixation is the major natural pathway for converting nitrogen into available forms, and is important because of widespread nitrogen limitation of plant growth[15]. Limitation of nitrogen fixation by other elements, including Mo, has been empirically demonstrated[16] and raises the possibility that terrestrial productivity is ultimately limited by one or several 'master' elements[15].

As shown by Bellenger and colleagues, organisms engineer element cycling by secreting compounds into the environment to scavenge for rare metals, manipulating their geochemical environment, and providing yet another example of the footprint of biology on the earth system.

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OCEANOGRAPHY

Knock-on effect

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Between the lush islands of Indonesia lies one of the bottlenecks of the global ocean circulation — the Indonesian throughflow, which connects the Pacific and Indian oceans. Over 80% of the water flowing from the Pacific to the Indian Ocean in the low latitudes passes through a tiny 45-km-wide channel in the Makassar Strait, which separates the islands of Borneo and Sulawesi. Through this narrow passage, comparatively warm and fresh Pacific waters are delivered into the Indian Ocean and transported further westward, towards Africa.

In 1976–1977, the characteristics of the tropical Pacific background climate changed distinctly, first noticed because the large-scale climatic seesaw of the El Niño/Southern Oscillation became biased towards more El Niño-like conditions. The equatorial Pacific sea surface temperatures rose sharply, beyond expectations from global warming. At the same time, the easterly trade winds weakened.

Lana Wainwright at the University of Tasmania, Australia, and colleagues suggest that these changes in the Pacific Ocean affected the Indian Ocean. According to their data analysis, the strength of the Indonesian throughflow was about 23% weaker after the 1976–1977 climate shift (*Geophys. Res. Lett*. **35,** L03604; 2008). As a result, the thermocline became shallower and cooler on the Indian Ocean side of the passage.

The origin of the Pacific climate shift in 1976–1977 is still a matter of debate, with natural variability and human-induced global warming both being considered as possible contributors. It is clear, however, that the change in the Pacific Ocean had an effect on the waters around it.

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