Lecture 14

More Soil chemistry and nutrients in soils

SOIL INORGANIC SOLIDS – saprolite development

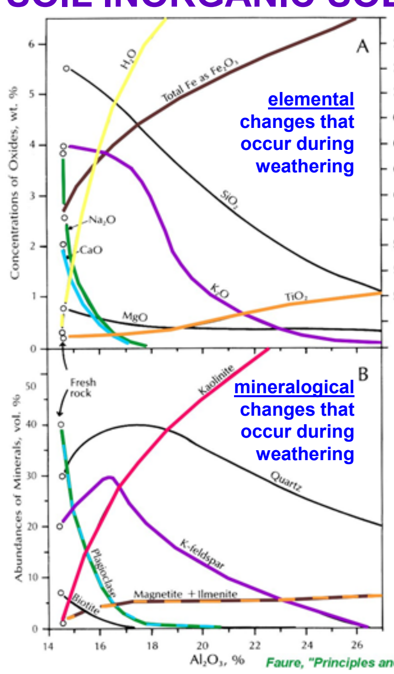


Figure 19.1 A. Variation of the chemical compositions of saprolites representing increasing intensities of chemical weathering of granitic gneisses in the Morton–Redwood Falls area of Minnesota (Goldich, 1938). Note that the concentrations of Na_2O, CaO, MgO, and SiO_2 decline continuously, whereas K_2O declines more slowly and the concentrations of total Fe as Fe_2O_3, Al_2O_3, and H_2O increase with increasing degree of weathering.

B. Variation of the measured abundances of minerals in the saprolites shown above. The rapid decrease in the abundance of plagioclase accounts for the loss of Na_2O and CaO shown in A. K-feldspar actually increases in abundance, as does quartz, but both ultimately decline. However, magnetite and ilmenite resist weathering and persist in the saprolite. Kaolinite is the principal weathering product and accumulates in the saprolite as the primary aluminosilicate minerals are decomposed (data from Goldich, 1938).

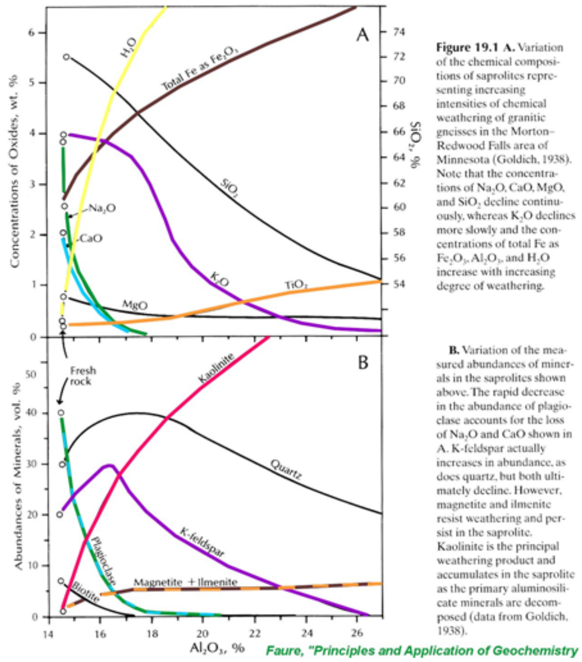
Faure, "Principles and Application of Geochemistry

The gain or loss of chemical constituents in saprolite records the progress of weathering/ soil formation … in the absence of significant DOC.

In practice, Al is the least soluble element during weathering followed by Ti and Fe.

Please note that % metal oxide is a way of expressing bulk composition of a rock. Many of these oxides are not actually present in the rock as oxides.

Elements removed from saprolites have high concentration in soil and ground waters.



Besides Ti and in some cases Fe, most other chemical species decrease as % Al_2O_3 increases.

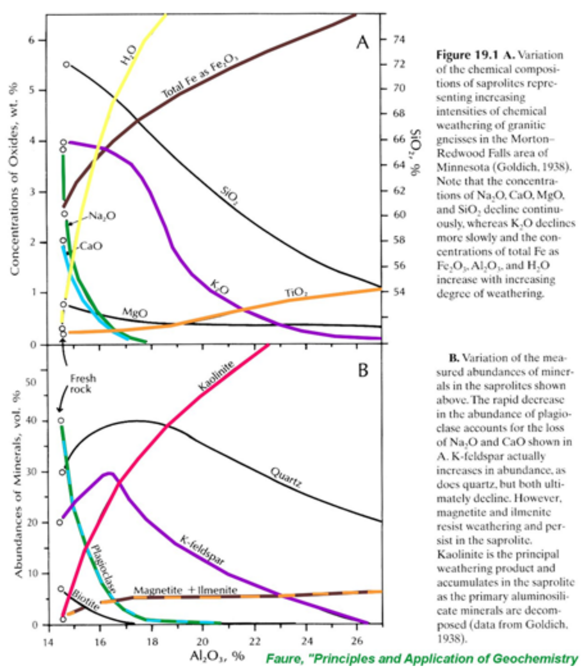
The faster the rate of decrease, the more mobile the element is.

Note that Ca and Na are removed very quickly (at relatively low Al_2O_3) and then K and Mg are removed.

Si is removed slower than Ca and Na, such that reduced but significant Si concentrations remain at high % Al.

The lower panel shows mineralogic changes that occur during weathering. It should be clear by comparison with panel A which phases contain which elements.

Fe and Ti, on the other hand, continually increase with Al.



This suggests that a totally weathered rock would be mostly Al, Fe, Ti plus Si

Note that the Si curve flattens out at higher Al content that is shown in these diagrams so long as some or all of the Al is found in Kaolinite, $Al_2Si_2O_5(OH)_4$.

But in a very intensely weathered rock, much of the Kaolinite can be leached of Si to produce gibbsite.

Remember that Fe^{2+} is soluble and Fe^{3+} is not. The typical accumulation of Fe in saprolites indicates that this process takes place at fairly high pe.

SOIL WATER

The common rock-forming chemical elements that are found in soil waters occur as a function of:

- ✓ inorganic solubility during saprolite formation
- ✓ solubility in the presence of DOC/POC higher up in the soil column.

Depth profiles of elemental concentrations in soil water, provide insight into geochemical processes during soil formation/ weathering and in bio-availability of some important nutrient elements.

It is important to examine the total amount of ion present and the relative proportions of “free” versus DOC-complexed ions.

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Al: Weathering-resistant. Conc. increases with depth. No significant DOC complexation.

Mg: Relatively constant and somewhat more DOC-complexed at depth. Mg enters soil waters fairly easily but since there are few reactions for its removal (e.g., incorporation in $CaCO_3$), it only diminishes slightly with depth.

Ca: Soluble element. Conc. decreases with depth due to $CaCO_3$ precipation at higher pH. No significant DOC complexation

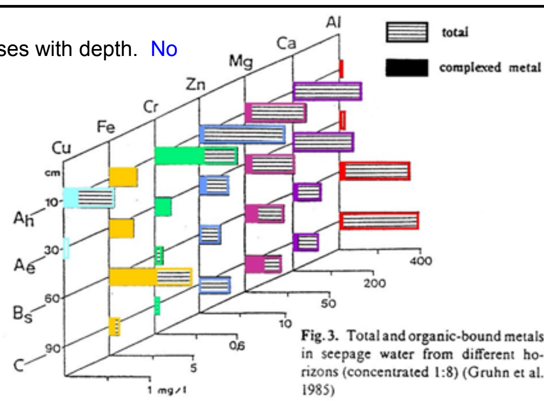

Fig. 3. Total and organic-bound metals in seepage water from different horizons (concentrated 1:8) (Gruhn et al. 1985)

Zn: Analogous to Ca. At high pe $ZnCO_3$ (pH 8-9) or $Zn(OH)_2$ (pH 9-12) forms. No significant DOC complexation.

Fe: Similar to Al except its peak concentration is somewhat higher up in the profile because of significant DOC complexation above the saprolites.

Cr: Generally soluble but even more so in the presence of DOC. It's profile looks similar to Ca except that in the upper layers, it is almost all DOC-complexed.

Cu: Moderately soluble but more so in the presence of DOC. Similar to Cr but found only in A zone.

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Organic Solids in Soils.

Organic solids typically make up <5% of a soil yet they largely determine the soil's productivity.

Organic matter:

✓ sets the availability of nutrients

✓ supports soil biota

✓ binds some organic contaminants (i.e., pesticides)

✓ helps determine soil pH (through DOC)

✓ mediates mineral dissolution (through DOC)

Table 16.1. Major Classes of Organic Compounds in Soil *from Manahan Ch16*

Compound Type	Composition	Significance
Humus	Degredation-resistent residue from plant decay, largely C, H, and O	Most abundant organic component, improves soil physical properties, exchanges nutrients, reservoir of fixed N
Fats, resins, and waxes	Lipids extractable by organic solvents	Generally, only several percent of soil organic matter may adversely affect soil properties by repelling water, perhaps phytotoxic
Saccharides	Cellulose, starches, hemi-cellulose, gums	Major food source for soil microorganisms, help to stabilize soil aggregates
N-containing organics	Nitrogen bound to humus, amino acids, amino sugars, other compounds	Provide nitrogen for soil fertility
Phosphorous compounds	Phosphate esters, inositol phosphates (phytic acids), phospholipids	Sources of plant phosphate

SOIL ACIDITY/ACIDIFICATION

Natural soil ph reflects bedrock and DOC content.

Most soils will naturally become more acidic with time in upper horizons because

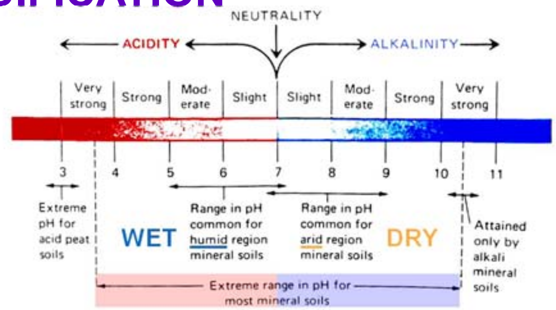

Figure 9.1 Soil pH ranges and soil reaction classes (From Brady, 1974).
Tan, "Principles of Soil Chemistry"

- ✓ Basic oxides and carbonates leach from the soil
- ✓ accumulation of humus
- ✓ Exchangeable Cations on clays are replaced by H^+
- ✓ Carbonic Acid is continually added by rainfall (so are anthropogenic acid compounds in acid rain).

The effects of increasing soil acidity can be slowed by $CaCO_3$ addition. But, acidification causes natural soils to eventually loose the ability to support normal plant communities.

Anthropogenic acid-rain production is dramatically speeding up this process.

These chemical processes affect elemental speciation and exchange with the biosphere by shifting the proportions of acid and base compounds exchanging between

▲ soil ▲ vegetation ▲ soil water ▲ atmosphere

Basification can occur at high inorganic weathering rates and low DOC/POC.

Sources of acidity and alkalinity in agricultural soils modified from Wild (1993)

Acidity

1. Addition of acids and acid-forming chemicals from the atmosphere
2. Removal of basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) by plant growth/harvesting and leaching
3. Oxidation processes such as nitrification
4. Microbial production of organic acids
5. Increase of soil organic matter content (including throughfall = washing of organic acids from leaves & litterfall = falling plant detritus)
6. Volatilization of amonia from ammonium compounds
7. Fertilization with ammonium salts (microbial oxidation produces HNO_3)

Alkalinity

1. Addition of atmospheric dust (carbonates and weatherable silicates)
2. Reduction processes
3. Weathering of primary minerals
4. Hydrolysis of exchangeable sodium ions, which may be present in high concentrations after irrigation with saline water

MAIN EFFECTS OF SOIL ACIDIFICATION ON PLANTS

- ✓ Increased concentrations of pH sensitive metals to potentially toxic levels for land plants, especially Al, but also Mn, Cr, Cu. Ni and Zn,
- ✓ Reduced nutrient supply (N, S and P remain immobilized in soil organic matter, which is not as efficiently degraded by soil microbes at low pH)

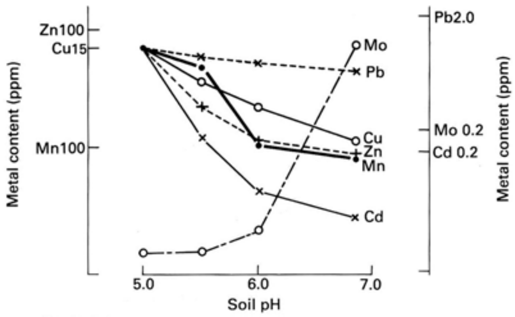

Figure 8.5 Relation between soil pH and the concentration of six metals in subterranean clover: pH did not affect yield. (From Williams, C.H., 1977, *Journal of the Australian Institute of Agricultural Science* **43,** 99; with permission, AIAS copyright.)

From Wild, 1993, Soils and the Environment

- ✓ Reduced Ca^{2+} and other cations supply lost to drainage water
- ✓ Reduced uptake of Phosphate and Molybdate by plants (Mo is essential for Nitrogenase enzymes)
- ✓ Nitrification (oxidation of ammonia to and nitrate) is inhibited
- ✓ Nitrogen fixation by legume hosted soil microbes is reduced unless acid-tolerant strains are present.

Soil nutrients

Besides H_2O, CO_2 and sunlight, terrestrial plants need:

- ✓ N & P
- ✓ Major cations - K, Mg & Ca. (also essential for marine photosynthetic organisms but are rarely in short supply there).
- ✓ Major Anions - S, Cl
- ✓ Micro Nutrients (Fe, Zn, Mn, B, Cu, Mo)

The CNP demands for terrestrial plants is (very roughly):

$$C_{1200}N_{35}P_2$$

N:P is similar to the Redfield Ratio but C:N and C:P are very different because much more C goes into "CH_2O", like cellulose

$$C_{106}N_{16}P$$

Photosynthesis and Nutrient elements

The concentrations of N, P, C and O in the hydrosphere are intricately related by the Redfield relationship, which closely describes phosynethesis and respiration in aquatic ecosystems.

Photosynthesis and Respiration

$$106\,CO_2 + 16\,NO_3^- + HPO_4^{2-} + 122\,H_2O + 18\,H^+$$

nutrients

(+ trace elements and energy)

P ↑↓ R

micro-nutrients

$$\{C_{106}H_{263}O_{110}N_{16}P_1\} + 138\,O_2$$

algal protoplasm

micro-nutrients don't show up in in this approximate molecular formula

Algal protoplasm may conveniently be also expressed as

$$\{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)\}$$

$\Delta N(+)/\Delta P(+) = 16$	$\Delta CO_2(+)/\Delta P(+) = 106$
$\Delta CO_2(+)/\Delta N(+) = 6.6$	$\Delta O_2(+)/\Delta P(-) = 138$
$\Delta O_2(+)/\Delta N(-) = 8.6$	$\Delta O_2(+)/\Delta CO_2(-) = 1.3$

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Important nutrients besides N and P:

macronutrients @ >0.1% in average plant tissue

micronutrients @ <0.01% = 100 ppm in average plant tissue

TABLE 4.1 Elements Essential for Nutrition of Plants

Element	Adequate Concentration (% dry wt. of Tissue)	
Carbon	45	
Oxygen	45	
Hydrogen	6	
Nitrogen	1.5	macro-nutrients
Potassium	1.0	macro-nutrients
Calcium	0.5	macro-nutrients
Phosphorus	0.2	macro-nutrients
Magnesium	0.2	macro-nutrients
Sulfur	0.1	macro-nutrients
Chlorine	0.01	micro-nutrients
Iron	0.01	micro-nutrients
Manganese	0.005	micro-nutrients
Zinc	0.002	micro-nutrients
Boron	0.002	micro-nutrients
Copper	0.0006	micro-nutrients
Molybdenum	0.00001	micro-nutrients

Source: Zinke, P.J. 1977. "Man's activities and their effect upon the limiting nutrients for primary productivity in marine and terrestrial ecosystems," In *Global Chemical Cycles and Their Alterations by Man*, ed. W. Stumm, p. 92. Berlin: Dahlem Konferenzen.

Table 7.5. Elements required by higher plants
(From Wild, 1993, Soils and the Environment)

From the atmosphere and water	carbon, hydrogen, oxygen
From the soil:	
Macronutrients	nitrogen, phosphorus, potassium, calcium, magnesium, sulphur
Micronutrients	iron, manganese, copper, zinc, boron, molybdenum, chlorine, nickel
Beneficial elements	cobalt[a] , sodium and silicon

[a]cobalt is essential for biological nitrogen fixation by bacteria, including Those species that have a symbiotic relationship with plants.
Note that nickel is included in this list. It is the most recent addition and appears to meet the required criteria for essentiality.

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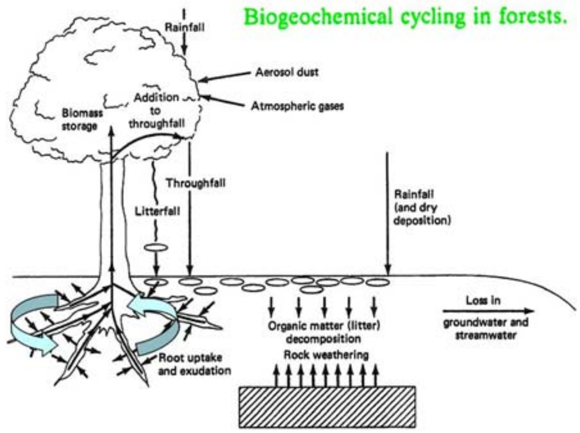
Nutrient Cycling

Terrestrial ecosystems cycle nutrients very efficiently:

N & P will cycle through plant tissues many times before being lost from a soil system.

Cultivated soils need continual fertilization because harvesting is a net flux out of the system.



In natural systems, heterotrophic bacteria and fungi remineralize OM and release nutrients: elements are "retained" in this order:
P >N > K > Ca > S > Mg > Na

Microbes and Material Transformation in Exogenic Cycles and Ecosystems

Microbes play numerous important roles in chemical transformations in Earth's surface reservoirs, particularly soils.

Microbes are responsible for:

a. "fixation" of the nutrient element N to biologically usable forms …

b. regeneration of nutrient elements from decaying organic matter (cycling nutrients through an ecosystem multiple times.

c. for releasing inorganic nutrients from minerals.

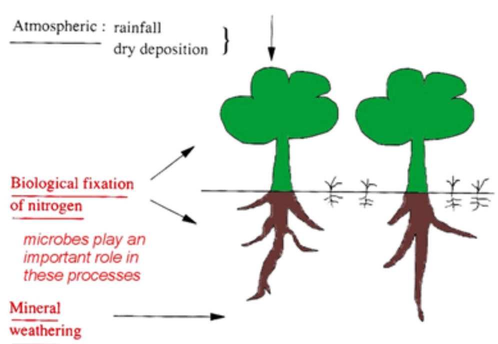


Figure 7.9 The three sources of nutrients for plants growing under natural conditions. Note that biological fixation of nitrogen by bacteria occurs in the nodules of plant roots, to a less extent in soil and probably occurs in the canopy of trees.

modified from Wild, "Soils and the Environment"

Nutrients are transferred to soil by this general scheme:

Mineral Matrix	Adsorption Surfaces	Soil Solution	Plant Root
Ca^{2+}, Mg^{2+} and other cations, also phosphate	→→→	→→→→→	→→→→
	Organic Matter N, P, S	↗ ↗ ↗	

Thus, a healthy soil not only has acceptable levels of nutrients in it's soil water,

... but it also has a *"reserve"* of exchangeable/desorpable nutrients associated with surfaces of soil solids,

...and a *"backup"* of nutrients stored in solid primary minerals and organic matter.

Microbes and organic matter cycling

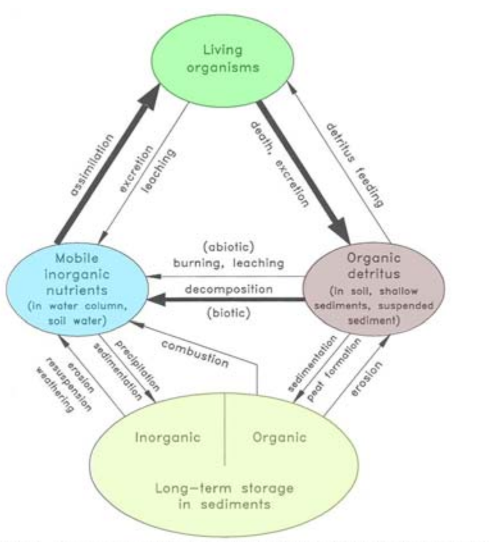


FIGURE 2-20 A generalized nutrient cycling diagram for an ecosystem. In contrast to energy, which flows through an ecosystem, nutrients are mostly recycled within the system. Inorganic forms are taken up by primary producers, converted to organic forms, passed up the food chain, and finally reconverted to inorganic forms by decomposers.

from Hemond and Fechner-Levy (2000) Chemical fate and transport in the environment

Microbes play an essential role in the cycling of organic matter in various sub-reservoirs of a healthy ecosystem by mediating reactions that degrade organic detritus.

Microbes and Elemental Cycling

The nitrogen cycle is particularly dependant upon microbes.

Nitrogen is very important in metabolic pathways and is an abundant element in Earth's exogenic environment, but the most common form (N_2) is not utilizable by most organisms.

Most biomolecules are based on Nitrogen in the -3 oxidation state (e.g., amines and amino acids).

More oxidized forms (e.g., N +5 in NO_3^-, which is the form that is easiest for plants to absorb from the environment) can be absorbed by organisms but must then be enzymatically reduced for use in synthesis.

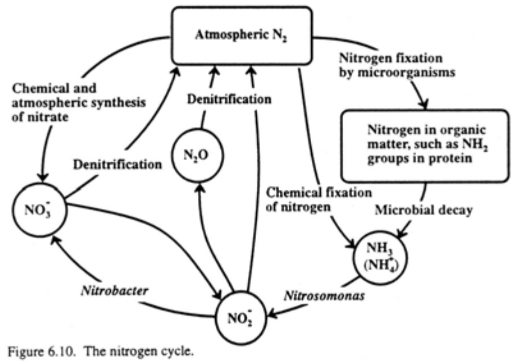


Figure 6.10. The nitrogen cycle.

Please don't memorize the names of specific organisms that fix or redox transform nitrogen, just know that they exist.

Biological nitrogen fixation

N_2 is converted into plant utilizable forms of nitrogen by a few genera of microorganisms, providing an important source of this nutrient to natural and agricultural ecosystems.

Nitrogen fixing bacteria take two main forms: free-living in soil and in symbiosis with plants, (see the table).

Table 5.4. *Biological nitrogen fixation by microorganisms*

	Main genera containing nitrogen-fixing species
1. Non-symbiotic	
Heterotrophic, aerobic	*Azotobacter, Azotococcus, Beijerinckia*
Heterotrophic, anaerobic	*Clostridium, Bacillus, Klebsiella, Enterobacter*
Autotrophic	*Nostoc, Anabaena, Calothrix*
2. Symbiotic	*Rhizobium, Bradyrhizobium, Frankia, Nostoc, Anabaena*

modified from Wild, "Soils and the Environment"

Nitrogen fixation occurs similarly in all organisms, by reduction to ammonia via the iron and molybdenum complexed enzyme nitrogenase.

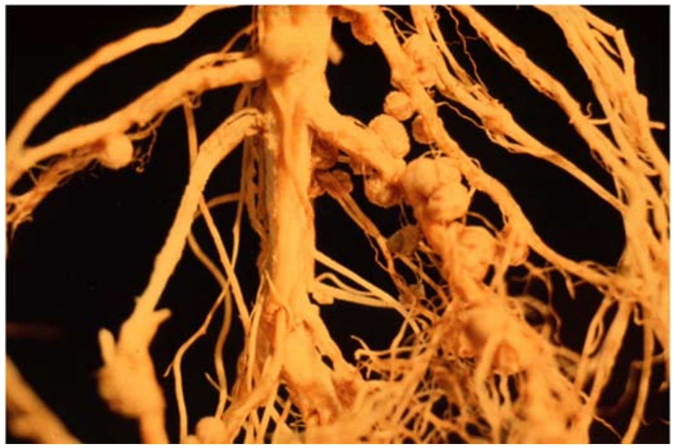
Microorganisms obtain the energy to fix nitrogen via nitrogenase reduction from the host plant, from soil organic matter, or from sunlight.

Nitrogenase is very sensitive to oxygen, so the organism or its host therefore adopts strategies to exclude oxygen from the sites of nitrogenase activity.

Nitrogen-fixing bacteria form symbiotic associations with the roots of legumes (e.g., clover and lupine) and trees (e.g., alder and locust).

Visible nodules are created where bacteria infect a growing root hair.

The plant supplies simple carbon compounds to the bacteria, and the bacteria convert N_2 into a form the plant host can use. When leaves or roots from the host plant decompose, soil nitrogen increases in the surrounding area.

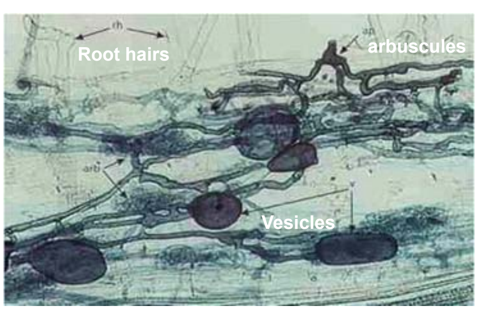


Nodules formed where Rhizobium bacteria infected soybean roots.
http://soils.usda.gov/sqi/concepts/soil_biology/bacteria.html

Fungal Microorganism and Phosphorous Cycling

Arbuscular mycorrhizas are an important type of fungus found on the vast majority of wild and crop plants, with an important role in mineral nutrient uptake (especially Phosphorous) and sometimes in protecting against drought or pathogenic attack.

The fungus obtains sugars from the plant, and the plant obtains mineral nutrients that the fungus absorbs from the soil.



The figure shows part of a clover root infected by an AM fungus. The site of penetration is shown at top right, where the fungus produced a pre-penetration swelling, (then it grew between the root cells and formed finely branched *arbuscules* (thought to be sites of nutrient exchange) and swollen *vesicles* (thought to be used for storage).

http://helios.bto.ed.ac.uk/bto/microbes/mycorrh.htm