3. charge transfer (e.g., ligand/donor sorption):
Sorption involves a number of related processes that all result in dissolved aqueous solutes being "stuck" to particles by Lewis acid-Lewis base interactions similar to those in complexes.

The sorption of organics is particularly important for:
- changing ionic equilibria in aqueous solutions
- removing organic matter from aqueous solutions (such as in soils or waste water treatment)
- helping microorganism communities to nucleate on inorganic substrates

The sorption of ortho P is particularly important for:
- the distribution of this photosynthetic nutrient between natural waters and sediments.

Let's examine some experimental determinations of the sorption characteristics of negatively charged organic acids, orthophosphate ions ($\text{PO}_4^{3-}$), and sulfate ($\text{SO}_4^{2-}$) on colloid particles (<0.2 $\mu$m for our purposes). Positively charged species behave similarly.
The sorption-desorption of materials is highly dependent on:

1. the acid-base behavior of solutes (their “speciation”)
2. the particle surface speciation of the sorbing species.

Here are some examples of adsorption of several organic acids bound to Al₂O₃, as a function of pH.

And here’s orthophosphate and sulfate bound to FeOOH.
Organic matter sorption on mineral surfaces can cause decomposition reactions of the mineral itself:

An example of the effect of soil DOC on silica dissolution rate, and a possible mechanism for the process:

How is charge distributed around particle surfaces?

This is a complex occurrence that can be modeled in a number of ways for different ions and surface types. These models involve different arrangements of anions and cations from the solution around the charged surface that stabilize the charged particle.
Gouy layers involve a preferential distribution of oppositely charged particles near a charge surface.

"Double Layer" models are the most realistic for most situations. They involve a layer of ions in close proximity to the charged surface which are strongly help in place (Stern or Helmholtz layers) and a more diffuse cloud of balancing ion charge in solution around them.

Why do we care?
▶ The size of ion clouds around surfaces affect aqueous solution composition because they expand and collapse depending on solution properties (e.g., pH, concentration and types of ions in solution)

▶ the interaction of one particle’s ion cloud clouds of another ion can also have significant effects. For instance:
  • in an open body of water, too much ion-cloud interaction destabilizes and thus desolvates solids, pulling solutes with them to the sediments.
  • in groundwater systems, close-packed charge surfaces can form "ion traps" that allow water but not ions through.

Soils
Soils … are one place where we see weathering in action and they form an important substrate and growth medium for the terrestrial biosphere. *They are susceptible to many anthropogenic effects.*

Soils are actually many materials in a gradient between organic rich surface deposits and deeper inorganic deposits called saprolite.

On a gentle slope, rock is altered in place, sometimes to form soil.

On a steep slope, weathered solids are whisked away by wind or water and deposited elsewhere, resulting in sediment accumulation elsewhere.

How do soils form?
Initially, physical and chemical breakdown of surficial rocks (“weathering”) produces secondary materials.
Weathering Reactions During Soil Formation:

Chemical reactions that occur in soils impact the chemistry of other surface reservoirs because they determine the mobility of many elements/compounds in the through-flowing groundwater.

Soils play a strong role in shallow ground water composition and form a critical link between the geosphere, atmosphere and biosphere.

In general, the more water moving through the system, the faster soil will accumulate and the deeper below the surface we find bedrock.

Soils can also be classified based upon the size fraction of mineral grains they contain, which controls porosity, drainage, wetting and rooting characteristics.
Soils are the combined products of rock breakdown and biological processes.

Soils are basically a stratified gradient between mostly organic, biological and resistive inorganic materials on the top and rock weathering products below.

*Ground water flow through soils is mostly vertical (top down), leading to distinctive layering.*

Soil horizons generally build from the bottom up; the further down one goes toward bedrock, the more similar the material gets to bedrock composition.

*Notice the relationship between the zones and tree roots.*

**Soil zone nomenclature** derives from physical and chemical properties reflecting these processes:

- **The A-zone** is the least like the rock from which it was originally produced.

- **The C-zone** is the most like the rock from which it was originally produced.

- **The B-zone** is intermediate. It contains solid residues of sparingly soluble materials mobilized and redeposited from the A-zone.
• Organic matter and porosity generally decrease with depth in a soil.
• Mineral grains in the very upper reaches of a soil are very resistive to weathering.
• Saprolite occurs at the base of the soil zone, so far removed from the organic zones of the soil that DOC plays little role in its formation.

Many soils, such as this one, show a classic “topsoil” horizon but this is not always the case.

“O” Horizon - decomposing organic matter

“A1” Horizon - brown humic-rich, some mineral matter.

“A2” Horizon - light grey, intensely leached; including loss of Fe & Al; mostly residual SiO₂

“B” horizon - brown horizon, accumulation of clays & Fe-oxides

<table>
<thead>
<tr>
<th>Soil Horizon</th>
<th>Description and Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>surface layer composed primarily of organic matter with only a small content of mineral materials; dark or dark brown in color</td>
</tr>
<tr>
<td>A</td>
<td>brown horizon; remains of weathering</td>
</tr>
<tr>
<td>E</td>
<td>primarily mineral grains that are too large to be translocated in colloidal suspension; low content of organic matter causes light grey color</td>
</tr>
<tr>
<td>B</td>
<td>enriched in clay minerals, oxides, and hydroxides of Fe, Al, Mg, etc., removed from underlying A and E horizons; may also contain calcite or gypsum that can precipitate from aqueous solution within this layer</td>
</tr>
<tr>
<td>C</td>
<td>saprolite or sediment that is largely weathered by sol-fraction processes; may be the product of chemical weathering of the underlying bedrock (saprolite) or have been transported and deposited by water (alluvium) or ice (glacial till)</td>
</tr>
<tr>
<td>R</td>
<td>unweathered bedrock underlying the C horizon</td>
</tr>
</tbody>
</table>
Soils of tropical and subtropical regions tend to be deeply weathered.

They are mixtures of quartz, kaolin, free oxides, and some organic matter. For the most part they lack well defined soil horizons.

Very extreme weathering can lead to soils that are largely just Al- and Fe-hydroxides and oxides.

http://soils.usda.gov/

In humid temperature regions relatively clay-rich and organic-rich zones can be found
Soils from very arid environments support limited plant growth.

Precipitation of minerals from simple salts are characteristic: calcium carbonate, gypsum.

These soils tend to have low organic content.

Caliche, a layer of calcium carbonate ppt.

This is common at shallow levels in soils from arid regions.

It is found in Hawaiian soils in leeward locales.
Wet “boggy” areas tend to have organic matter dominated soils.

Wet conditions favor plant growth and thus greater organic matter production.

Water logged soils quickly become very reducing. Why?

Cool to temperate conditions and reducing conditions both slow heterotrophic organic matter degradation.

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The Processes of Soil Formation are (from Wild, 1993):

Always occur
1. Weathering of parent material
2. Addition and partial decomposition of organic matter
3. Formation of structural units

Depend on Environmental Conditions
4. Leaching and acidification
5. Clay eluviation (washing of clay from upper horizons; deposition below)
6. Podzolization (transport of DOC complexed Fe and Al from upper horizons; deposition below in sharp horizons)
7. Desilication (Leaching of Si relative to Fe and Al)
8. Reduction (i.e., Fe$^{3+}$ → Fe$^{2+}$)
9. Salinization (accumulation of sulphate and chloride salts) and Alkalization (accumulation of Na on cation exchange sites)
10. Erosion and deposition of eroded soil.
Soil pH:

- Soils can be very acid (even to pH<4) to very basic (~ pH 10)
- Low pH accelerates cation leaching from soil and cation storage capacity decreases with decreasing pH
- CO₂ and organic acids produced from respiration of humus contribute to low pH
- H⁺ can displace exchangeable cations from clays.
- pH increases with depth into the B-zone, as fewer organic acids are left in the ground water and as more H⁺ is neutralized by CaCO₃ and/or other precipitate minerals (especially hydroxides of Al, Fe and Mg) in the soil column.
**Caliche (CaCO₃)**

is a precipitate mineral that forms near the base of the B-zone of many soils. The amount of caliche present depends in part on how much Ca there is initially in the bedrock. The CO₃²⁻ can include components from the bedrock, the atmosphere and from organic matter degradation.

Ca²⁺ and CO₃²⁻ that are dissolved in the A zone precipitates at deeper levels as soil water reaches CaCO₃ saturation, largely controlled by pH changes.

The depth to the caliche layer deepens with increasing surface rainfall.

The caliche layer is essentially a CaCO₃ "solubility front" and the more water we push through the soil zone, the farther down dissolved Ca²⁺ and CO₃²⁻ occur before CaCO₃ precipitates.

Thus the more water moving through the system, the faster the soil will accumulate and the deeper below the surface we find bedrock.

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Figure 7.4  Plot of the relation between rainfall and depth to the top of caliche mineral (caliche) accumulations in southern Nevada. H. Hetty and G. D. Larson, Soil Sci. 89, 377, (1960). Figur by Soil Science Society of America. Used by permission.