Lecture 13

More Surface Reactions on Mineral Surfaces

& Intro to Soil Formation and Chemistry

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 detrimnations of the sorption characteristics of negatively charged organic acids, orthophosphate ions (PO_4^{-3}), and sulfate (SO_4^{-2}) on colloid particles (<0.2 μm for our purposes). Positively charged species behave similarly.

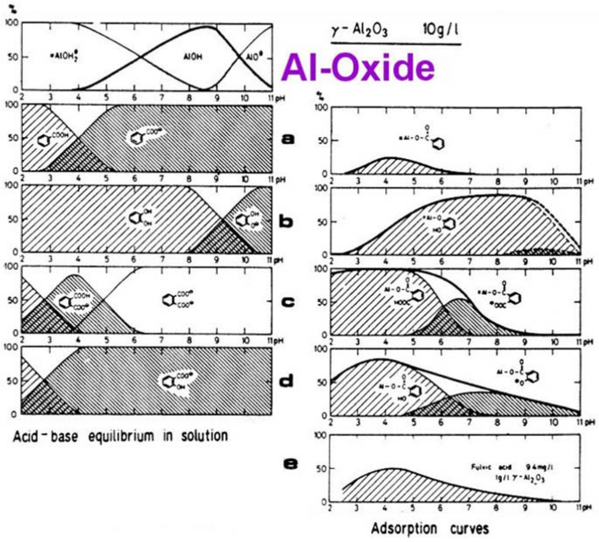


Figure 10.13 Adsorption of organic acids on γ-Al_2O_3 (*a–e*) and of anions on α-FeOOH (*f–h*). Curves (*a–d*) and (*f–h*) are calculated from experimentally derived stability constants (organic acids and anions 0.1 to 1 mmol liter^{-1}, 22°C, 0.1 *M* $NaClO_4$). Adsorption of fulvic acids (collected from lake sediments at high pH) (*e*) was experimentally determined. [Modified from Stumm, Kummert, and Sigg, *Croat. Chim. Acta* (1980).] *Strumm and Morgan, Aquatic Chemistry*

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 adsorbtion of several organic acids bound to Al_2O_3, as a function of pH.

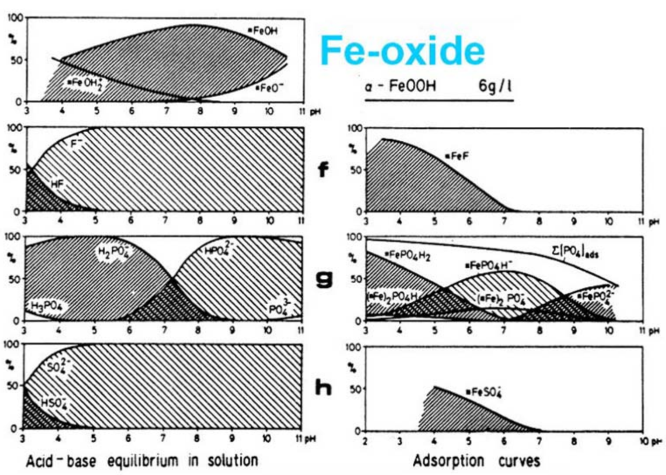


Figure 10.13 Adsorption of organic acids on γ-Al_2O_3 (*a–e*) and of anions on α-FeOOH (*f–h*). Curves (*a–d*) and (*f–h*) are calculated from experimentally derived stability constants (organic acids and anions 0.1 to 1 mmol liter^{-1}, 22°C, 0.1 *M* $NaClO_4$). Adsorption of fulvic acids (collected from lake sediments at high pH) (*e*) was experimentally determined. [Modified from Stumm, Kummert, and Sigg, *Croat. Chim. Acta* (1980).] *Strumm and Morgan, Aquatic Chemistry*

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:

FIGURE 4–12 Leaching of silica from quartz in 20 mmol/Kg solutions of various acids at pH = 7 compared to leaching of silica from quartz in water at pH = 6.6. Leaching is expressed as micromoles of silica per m² of quartz (reprinted from *Geochim. Cosmochim. Acta*, 52, Bennett, P. C., Melcer, M. E., Siegel, D. I., and Hassett, J. P., pp. 1521–1530, with permission from Elsevier Science).

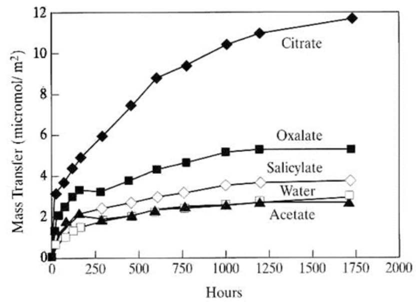
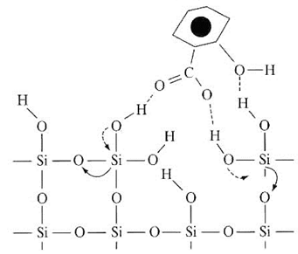


FIGURE 4–13 Dissolution model for hydroxylated silicate mineral. Organic-acid ligand forms complex with surface hydroxide, which polarizes and weakens internal bonds. Complex is then released into solution (reprinted from *Geochim. Cosmochim. Acta*, 52, Bennett, P. C., Melcer, M. E., Siegel, D. I., and Hassett, J. P., pp. 1521–1530, with permission from Elsevier Science).



From Kehew (2001) Applied Chemical Hydrogeology

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.

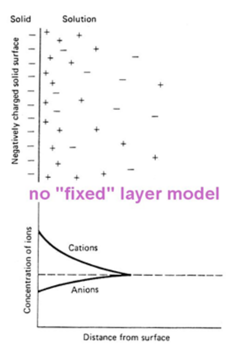


Figure 5-10 Simple picture of the electrical double layer, in which excess negative charge on a solid surface is balanced by an excess concentration of cations in solution near the solid–solution interface.

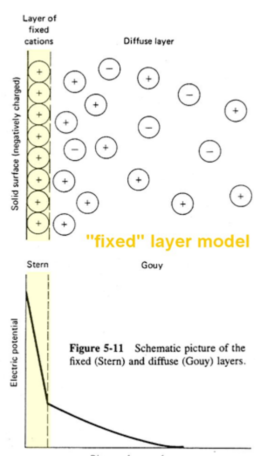


Figure 5-11 Schematic picture of the fixed (Stern) and diffuse (Gouy) layers.

Electric Double Layer Models

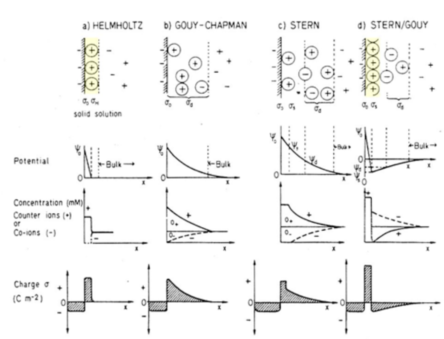


Figure 10.2 Distribution of charge, ions, and potential at a solid–solution interface.

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 Helmholz 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

deeper inorganic deposits called saprolite.

Saprolite with original rock textures preserved
http://www.nicholas.duke.edu/eos/geo41/

How do soils form?

Initially, physical and chemical breakdown of surficial rocks ("weathering") produces secondary materials.

- 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.

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.

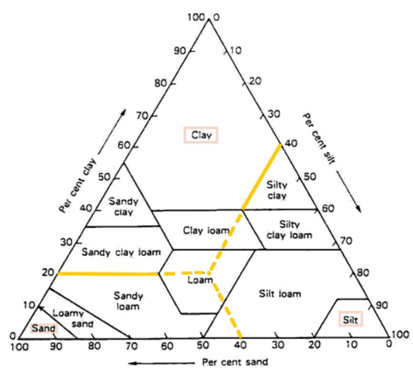


Figure 2.1 The composition of the textural classes of soils used by the United States Soil Survey. (Sand, 2–0.05 mm; silt, 0.05–0.002 mm; clay, less than 0.002 mm.) A soil with 40% sand, 40% silt and 20% clay is described as a loam, as shown by the broken line.

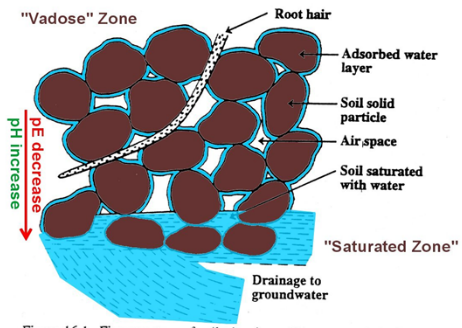


Figure 16.1. Fine structure of soil, showing solid, water, and air phases.

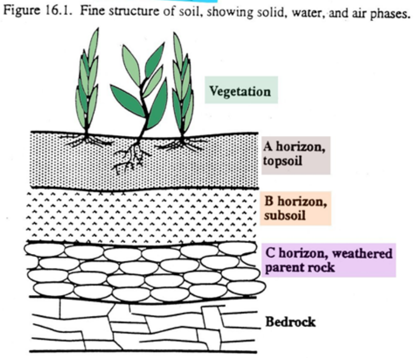


Figure 16.2. Soil profile showing soil horizons.

Manahan

A Soil Horizons Primer:

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.

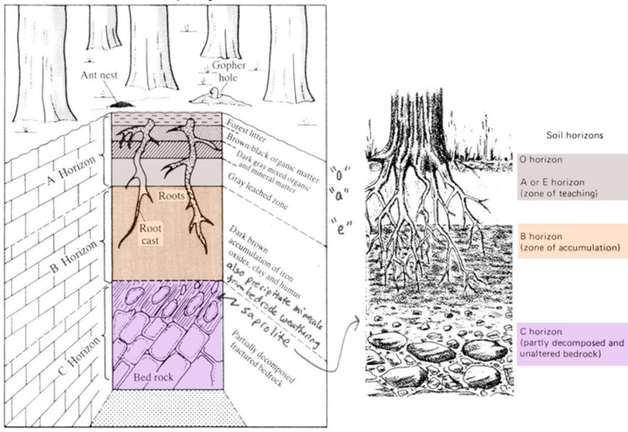


FIGURE 13-9
The best way to study soils is to dig a hole in the ground and square off the face to expose horizons of the soil profile. This is schematically illustrated here for a soil formed in humid temperate areas, a soil called podzol that displays sharp contrasts between the A, B, and C horizons. The uppermost horizon (A) consists of the forest litter, a zone of organic-rich debris in varying stages of decay, and a zone of extreme leaching of alkalies, alkaline-earth elements, and iron and aluminum. Iron, humus, and aluminum are deposited in the underlying dark brown middle horizon (B), which grades into the partially altered bedrock of the C horizon. Roots transect the profile, and upon their decay form open root casts that help in the downward transport of solutions and particulate matter. (Modified from Fig. 1-1 in FitzPatrick, 1980.)

Table 20.4 Description of Soil Horizons Starting at the Top

Soil horizon	*Properties and origin*
O	surface layer composed primarily of organic matter with only a small content of mineral material; black or dark brown in color
A	mineral particles mixed with finely divided organic matter that produces a dark grey color
E	primarily mineral grains that resist dissolution and are too large to be translocated in colloidal suspension, low content of organic matter causes light grey color
B	enriched in clay minerals, oxides, and hydroxides of Fe, Al, Mn, etc., removed from overlaying A and E horizons; may also contain calcite or gypsum that can precipitate from aqueous solution within this layer
C	saprolite or sediment that is largely unaffected by soil-forming processes; may be the product of chemical weathering of the underlying bedrock (saprolite) or have been transported and deposited by water (alluvium) or ice (till) or by volcanic activity (tuff) or an older soil.
R	unweathered bedrock underlying the C horizon

GG325 L13, F2013

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

"O" Horizon - decomposing organic matter

"A_1" Horizon - brown humic-rich, some mineral matter.

"A_2" Horizon - light grey, intensely leached; including loss of Fe & Al; mostly residual SiO_2.

"B" horizon -brown horizon, accumulation of clays & Fe-oxides

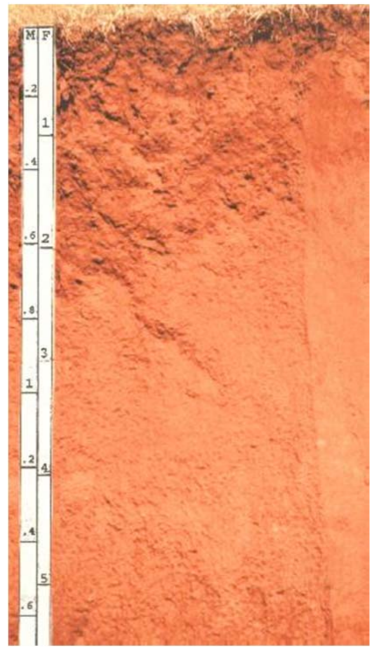
GG325 L13, F2013

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- amd 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 hetereotrophic organic matter degradation.

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., $Fe^{3+} \rightarrow Fe^{2+}$)
9. Salinization (accumulation of sulphate and chloride salts) and Alkaization (accumulation of Na on cation exchange sites)
10. Erosion and deposition of eroded soil.

Soil Evolution Reflects Time and Climate Factors:

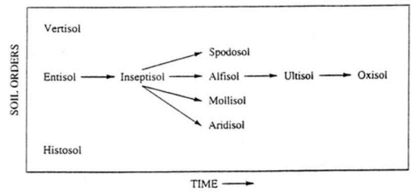
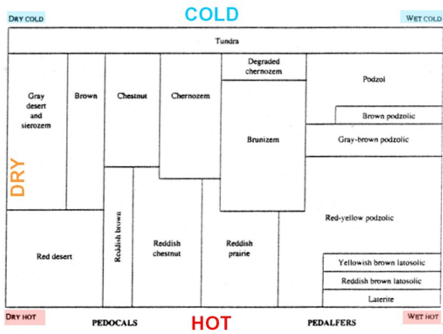


Figure 7.6 Approximate sequence of development of different soil orders. Entisols and inseptisols are early stages of soil development leading to spodosols, alfisols, mollisols, and aridisols, depending on the mineral composition of the parent material and climatic conditions. Utisols and oxisols occur in humid tropical regions as end stages of soil development enriched in oxides of Al and Fe. Vertisols develop only from parent material composed of swelling clay in regions with alternating wet and dry seasons. Histosols consist of partly decomposed plant material in places that are deprived of O_2, because they are waterlogged. From H. D. Foth. *Fundamentals of soil science*, 7th ed. Copyright © 1984 by John Wiley & Sons, Inc. Used by permission of John Wiley & Sons, Inc.

TABLE 7.4 A simplified description of the 10 soil orders as defined in the Comprehensive Soil Classification System (CSCS)

Order	Description
Soils with poorly developed horizons or no horizon and capable of further mineral alteration	
Entisols	Soils at an early stage of development and lacking horizons, due to short time available or location on slopes subject to constant removal by physical erosion.
Inseptisols	Young soils with poorly developed horizons. May have some leaching in the A horizon, but has only a weakly developed B horizon. Found in moderately humid upland areas.
Soils with a large proportion of organic matter	
Histosols	Organic-rich soils with thick, peaty horizons; formed in low-lying permanently water-logged areas. Typical of cool swamp environments.
Soils with well-developed horizons or with fully weathered minerals, resulting from long-continued adjustment to prevailing soil-temperature and soil-water regimes	
Alfisols	Forest soils of humid and subhumid climates with strongly leached acidic A horizon containing decomposing organic matter over a base-rich (smectitic) clayey and well-developed B horizon. High content of primary weatherable minerals (e.g., feldspars). One kind of pedalfer soil.
Spodosols	Highly acidic surface organic-rich layer over strongly leached and quartz-rich E horizon, on base-poor and Al and Fe-oxide/hydroxide rich B horizon. Typical under coniferous forests in temperate climates. Formerly called podzols.
Ultisols	Strongly-leached acidic A and E horizons over well-developed, kaolinite-rich (base-poor) B horizon. Low content of primary minerals due to extensive weathering. Midlatitude and warmer temperature deciduous forest soils, common in piedmont and coastal plain, southeastern United States.
Oxisols	Reddish soils of low latitudes, deeply weathered like ultisols. Strongly leached A horizon. Clays such as kaolinite largely leached from B horizon, where oxides of Al and Fe abundant. Almost no remaining primary minerals. Formerly called laterites.
Mollisols	Thick, well-developed and base-rich A horizon with much organic matter. B horizon clay-rich with abundant Ca^{2+} and Mg^{2+}. Clayey, calcareous or gypsiferous subsurface accumulations. Found under grassland and steppe vegetation in subhumid to semiarid climates.
Aridisols	Soils of dry climates and deserts. Often contain wind-blown dust. A and B horizons thin with little organic material. Calcium carbonate (caliche) accumulations generally present, sometimes with gypsiferous or saline horizons.
Vertisols	Old weathered soils with uniform, thick, clay-rich profiles. Deeply cracked and hummocky topography produced by intense seasonal drying of expandable clay minerals such as smectites. Soil profile poorly developed because of vertical mixing caused by the seasonal cracking. High in exchangeable cations (base-rich).

Note: Base-rich and base-poor clays are clays rich or poor in adsorbed Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}.
Source: Modified after Retallack (1990), Faure (1991), and Strahler and Strahler (1992).



Climate (Temperature and Water) are major controls on soil makeup

.... as is Time

Figure 7.5 Temperature-moisture (climate) relations favorable to the formation of some of the great soil groups. From *Fundamentals of Soil Science*, 3d ed. C. E. Millar, L. M. Turk, and H. D. Foth, Copyright © 1958 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

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

❖ CO_2 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 $CaCO_3$ and/or other precipitate minerals (especially hydroxides of Al, Fe and Mg) in the soil column.

Caliche ($CaCO_3$)

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 CO_3^{2-} can include components from the bedrock, the atmosphere and from organic matter degradation.

Ca^{2+} and CO_3^{2-} that are dissolved in the A zone precipitates at deeper levels as soil water reaches $CaCO_3$ saturation, largely controlled by pH changes.

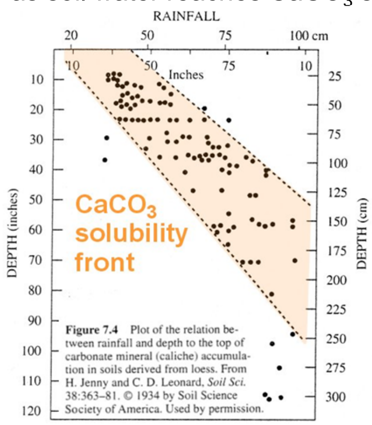


Figure 7.4 Plot of the relation between rainfall and depth to the top of carbonate mineral (caliche) accumulation in soils derived from loess. From H. Jenny and C. D. Leonard, *Soil Sci.* 38:363–81. © 1934 by Soil Science Society of America. Used by permission.

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

The caliche layer is essentially a $CaCO_3$ "solubility front" and the more water we push through the soil zone, the farther down dissolved Ca^{2+} and CO_3^{2-} occur before $CaCO_3$ precipitates.

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