

Weathering and Soils

Biogeochemistry Chapter 4: The Lithosphere

- Introduction: the context
- Rock Weathering
- Soil Chemical Reactions
- Soil Development (see text)
- Weathering Rates & Denudation

Introduction: The Context

- Throughout Earth's history, the atmosphere has interacted with Earth's crust:

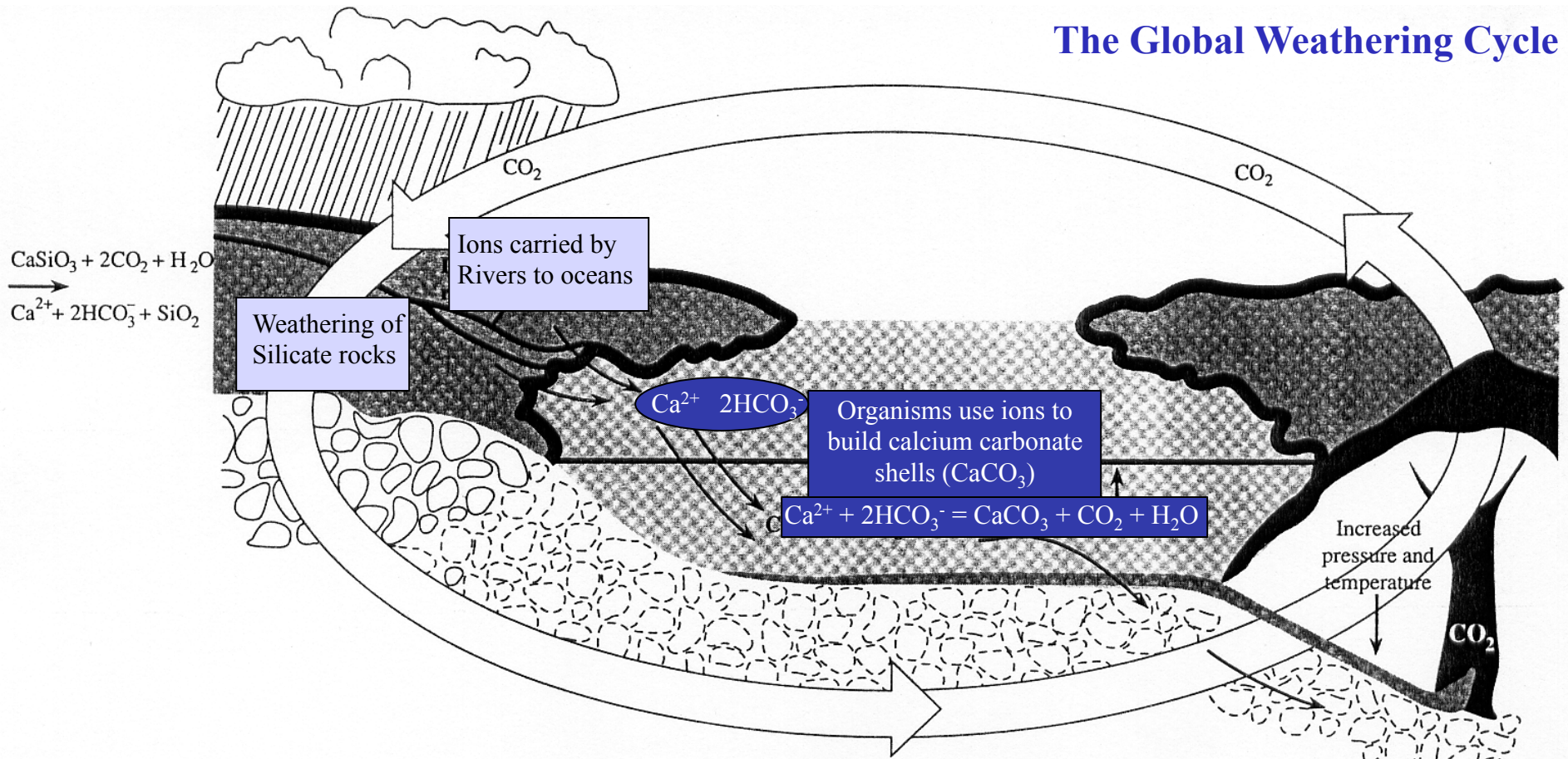
 rock weathering

- Basic Summary Equation (Siever 1974):

Igneous rocks + acid volatiles = salty oceans + sedimentary rocks

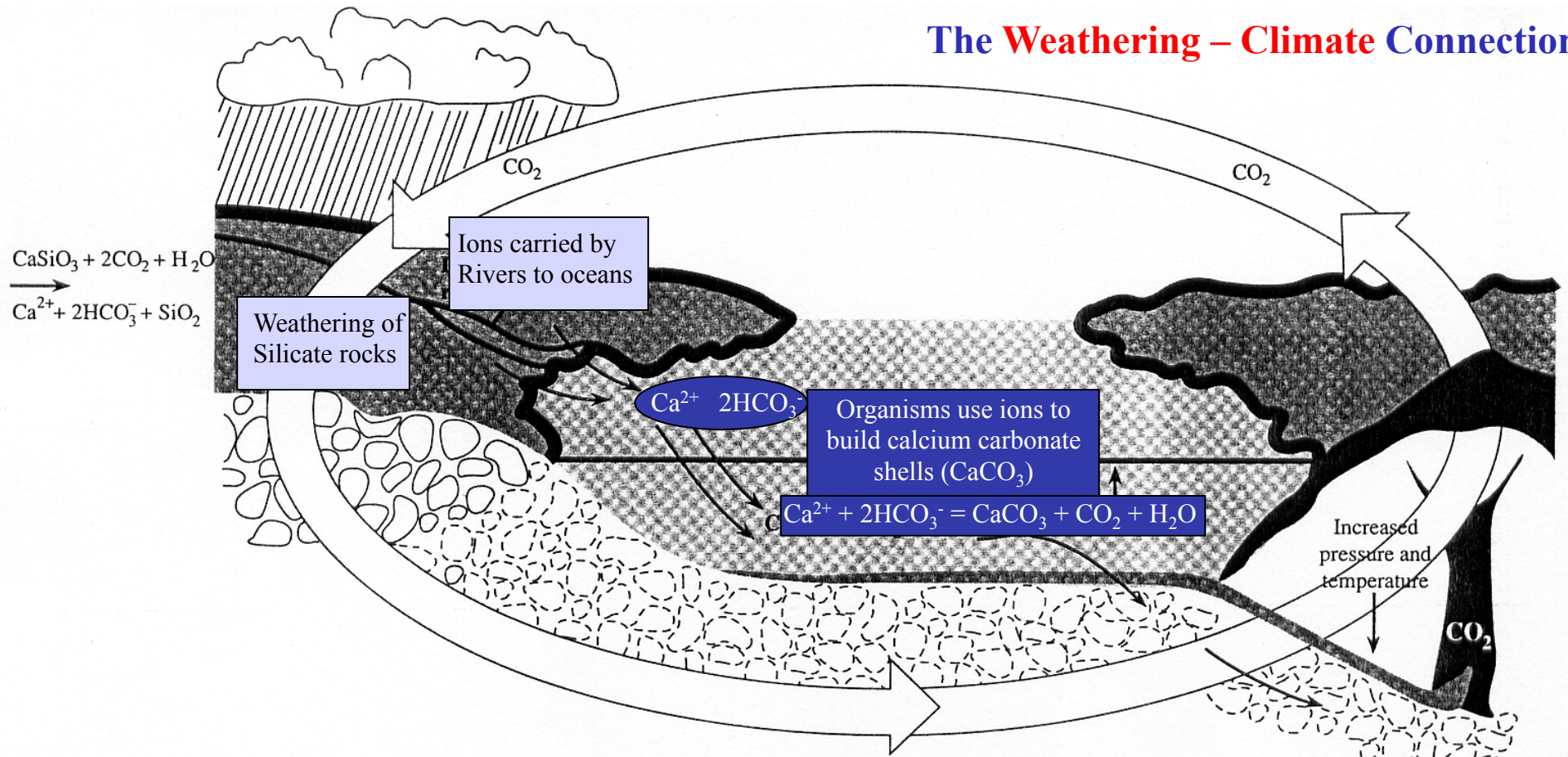
- Weathering through Geologic Time:
 - Early Earth: acidic volcanic gases
 - Later: atmospheric O₂, oxidation of reduced minerals
 - Advent of land plants: metabolic CO₂, H₂CO₃
 - Modern era: anthropogenic NO_x, SO_x, acid rain

The Global Weathering Cycle



- 1° minerals at Earth surface exposed to acid forms of C, N, S derived from the atmosphere
- Products of weathering reactions are carried to the ocean via rivers
- Weathering products accumulate as dissolved salts or sediments
- Subduction carries sediments back into the deep earth
 - CO_2 released
 - 1° minerals re-formed at high T and P
 - once uplifted, these are subject to a renewed cycle of weathering
 - 75% of rocks on Earth's surface today are sedimentary

The Weathering – Climate Connection



- The Global CO_2 Balance Links Weathering and Climate:
 - CO_2 is consumed in weathering
 - CO_2 is released in volcanism
 - HCO_3^- produced in weathering reactions is carried to the oceans via rivers
 - Biogenic carbonate [$2\text{HCO}_3^- + \text{Ca}^{2+} = \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$] is buried in sediments
- The balance between weathering rate and seafloor spreading (subduction) exerts control on atmospheric P_{CO_2}
- Climate is impacted because CO_2 is an important greenhouse gas

Why is weathering important?

- Climate regulation through CO₂ balance
- Weathering - *Bioactivity Feedback* (Biogeochemistry):
 - Land plants and soil microbes affect rock weathering and soil development
 - Biological processes are affected by weathering
 - Controls bioavailability of elements that have no gaseous form
 - Impacts soil fertility, biological diversity, agricultural productivity
- Weathering plays a critical role in global element cycles:
 - Global rate of rock weathering impacts atmospheric chemistry
 - Global rate of delivery of weathering products to the sea
 - Global cycles of bioactive elements – biogeochemical cycles

Table 4.1 Approximate Mean Composition of the Earth's Continental Crust^a

^a Data from Wedepohl (1995).

Constituent	Percentage composition
★ Si	28.8
Al	7.96
★ Fe	4.32
★ Ca	3.85
Na	2.36
★ Mg	2.20
★ K	2.14
Ti	0.40
★ P	0.076
Mn	0.072
S	0.070

★ Weathering particularly important for nutrient elements *that have no gaseous form*.

Conditions Required for Weathering:

- Rocks are exposed at the Earth surface by *uplift* or *extrusion*
- Weathering occurs at the Earth surface

Two Categories of Rock Weathering:

- **Mechanical** weathering
- **Chemical** weathering

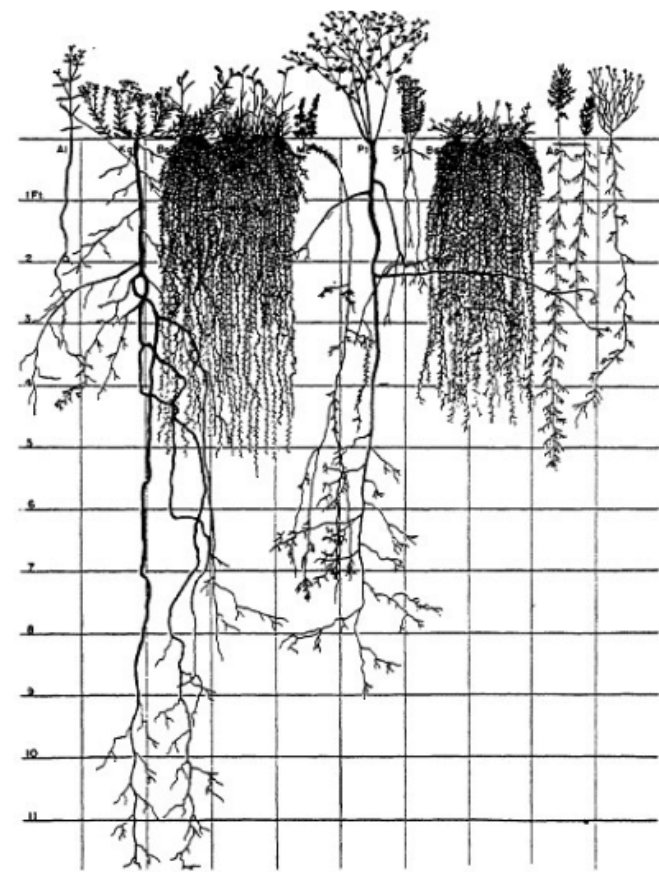
- **Mechanical** weathering: Fragmentation without chemical reaction: physical change
 - **Erosion** (water, wind)



- **Mechanical** weathering: Fragmentation without chemical reaction: physical change
 - Erosion (water, wind)
 - **Frost heaving**



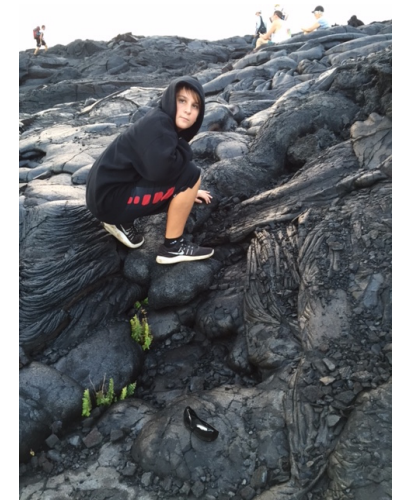
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 - **Plant root fragmentation**



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 - **Catastrophic events (e.g. landslides)**



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- Important in extreme climate regimes
- Transport-limited systems develop thick soil layers
- *Creation of surface area*

Chemical weathering

- Reaction of minerals in soils and rocks with acidic or oxidizing solutions
- Production of soluble elements, making them available for plant uptake
- Chemical weathering rates:
 - often depend upon rate of mechanical weathering
 - depend upon *mineral composition of rocks*
 - More labile minerals are attacked first, sometimes leaving more refractory minerals behind, intact
 - depend upon *climate*

Order of Formation of 1° Silicate Minerals from Molten Rock

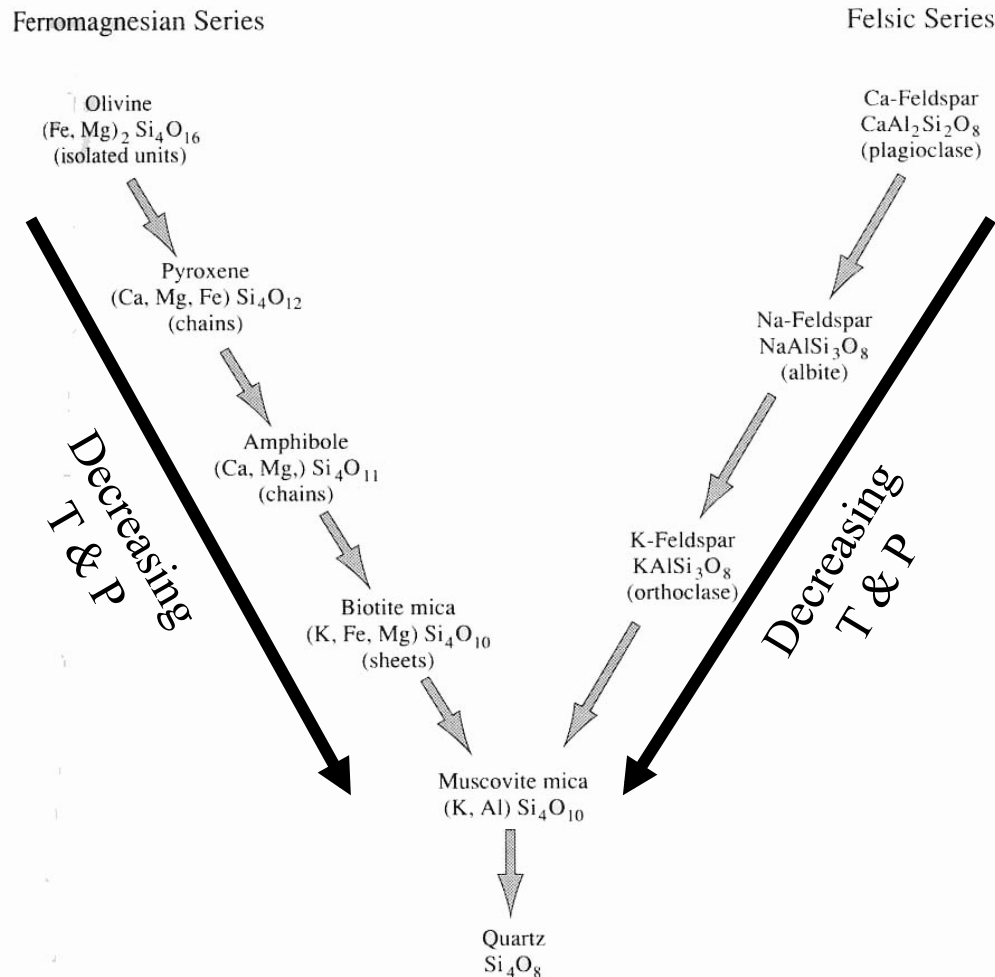


Fig. 4.1. Bowen Reaction Series

- Two classes of 1° silicate minerals:
 - ferromagnesian series (Mg)
 - felsic series (Al)
- Series reflects the order of mineral crystallization from a cooling magma.
- T & P decrease as magma cools & ascends, mineral crystal structure & composition changes:
 - Olivine: isolated units
 - Feldspar: chains
 - Micas: sheets
 - Highest O:Si ratio in Olivine
 - O:Si ratio decreases as sequence progresses

The Inverse of Crystallization Sequence: Weathering Reactivity Sequence

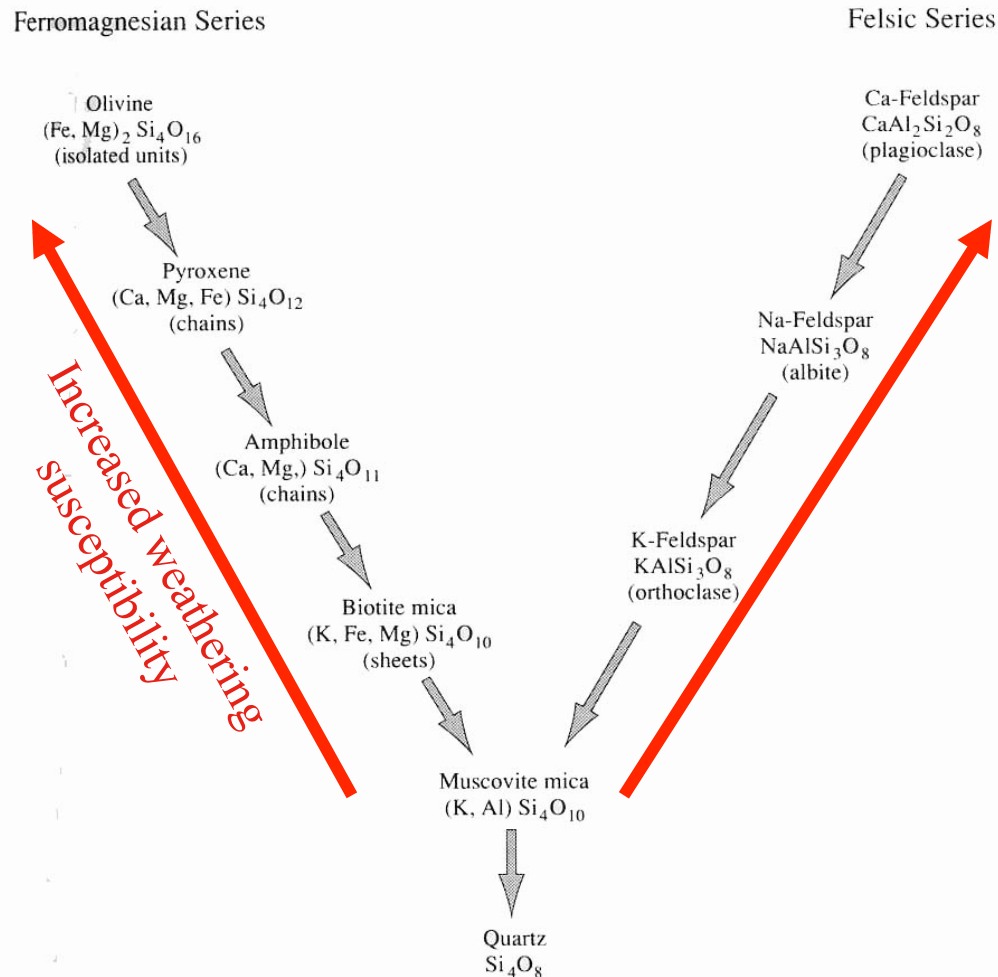


Fig. 4.1. Bowen Reaction Series

- Susceptibility to weathering is affected by crystal structure:
 - isolated units more reactive than chains or sheets
- Susceptibility to weathering is affected by crystal chemistry:
 - lower O:Si ratio minerals are more resistant
- Minerals formed at high T & P are more susceptible to weathering because:
 - thermodynamically less stable at Earth surface conditions
 - fewer bonds that link their crystal structure
 - cation (Ca, Na, K) substitutions distort crystal shape

End Products of Chemical Weathering: Soils

- Two ‘end-member’ soils produced:
 - **Saprolites:** reduction of density due to weathering loss of *some* constituents, without collapse of initial rock volume (isovolumetric weathering): “*rotten rock*” (SE-US).
Transport-limited conditions required.
 - **Bauxites, Laterites:** more extensive removal of constituents accompanied by collapse of soil profile, with *apparent* increase in concentration of remaining elements (e.g., Zr, Ti, Fe, Al, etc.)

Carbonic Acid Weathering

- The dominant form of chemical weathering
 - Carbonic acid forms in soil solution

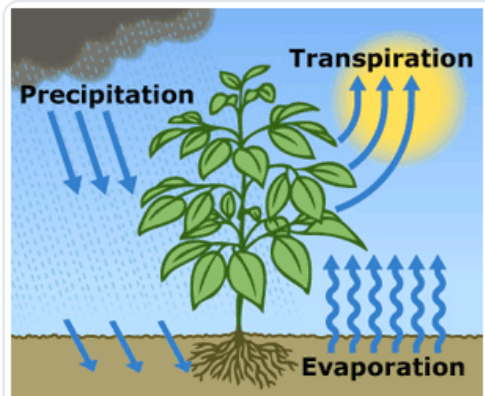


- Soil $[\text{H}_2\text{CO}_3]$ often exceeds equilibrium with atmospheric CO_2 (400 ppm, or 0.04%)
 - Plant roots and microbes release $[\text{CO}_2]$ to soil
 - High CO_2 can extend to considerable depth in soil (1% @ 36 m), leading to weathering of underlying rock
 - High $[\text{CO}_2]$ under snow pack implies significant weathering during winter

Biogeochemical Feedback

- Plant growth is greatest in warm and wet climates
- Warm humid climates maintain the highest soil [CO₂], and greatest weathering rates
- By maintaining high soil [CO₂] plants and associated organisms exert biotic control over the geochemical process of rock weathering on land

Average soil [CO₂] scales with evapotranspiration



Evapotranspiration is the sum of evaporation from the land surface plus transpiration from plants. Precipitation is the source of all water. Credit: [Salinity Management Guide](#)

<http://water.usgs.gov/edu/watercycleevapotranspiration.html>

- Evapotranspiration is the sum of evaporation from the land surface plus transpiration from plants.
- Evapotranspiration scales with temperature and biological activity



After a plastic bag is wrapped around part of a plant, the inside of the bag becomes misty with transpired water vapor. Credit: [Ming Kei College, Hong Kong](#)

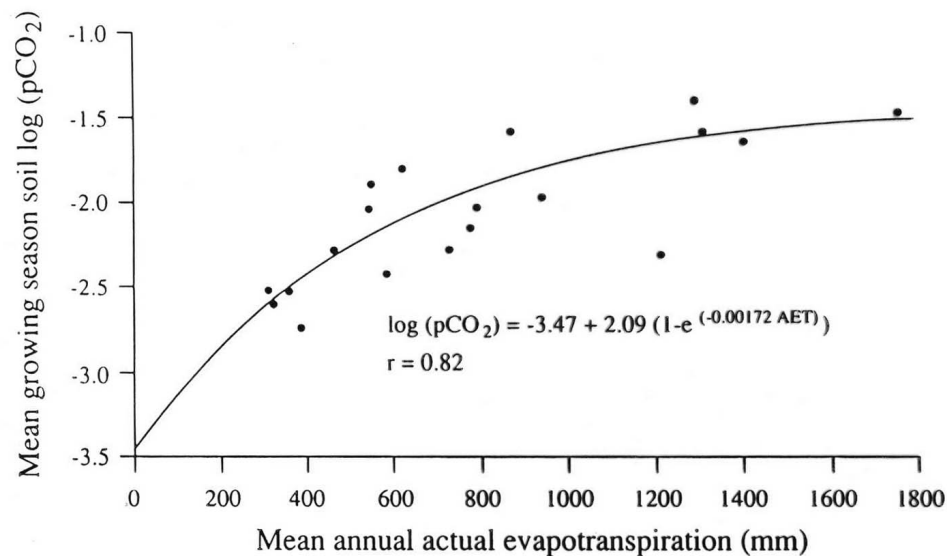


Figure 4.3 Relationship between mean CO₂ concentration in soil pore space and actual evapotranspiration at the site for various ecosystems of the world (Brook et al. 1983).

Impact of Climate on Chemical Weathering

Chemical weathering reactions are most rapid at high T and high rainfall

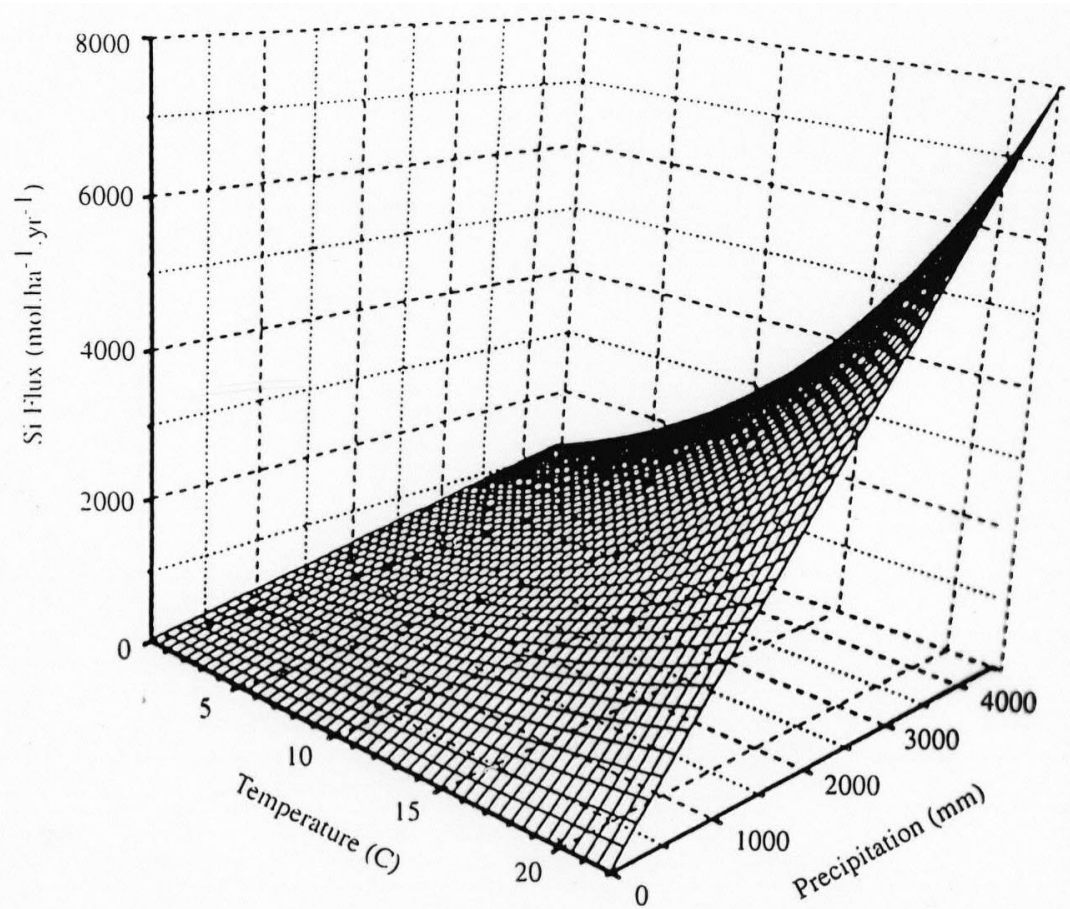
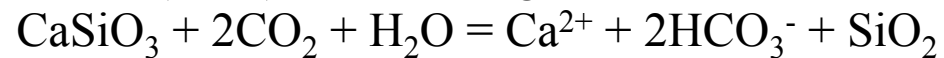


Figure 4.2 Loss of silicon (SiO_2) in runoff is directly related to mean annual temperature and precipitation in various areas of the world. Modified from White and Blum (1995). Silica is a good indicator of chemical weathering.



Discussion of Weathering Figures

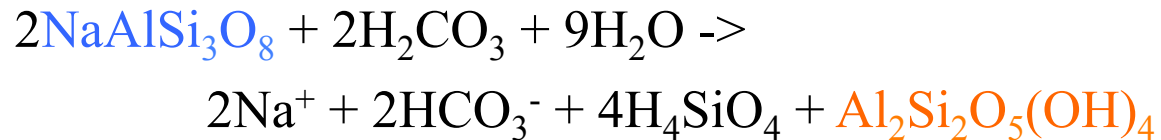
Two Categories of Mineral Dissolution

- **Incongruent Dissolution**
- **Congruent Dissolution**

Incongruent Mineral Dissolution

- Definition: Only some constituents of the 1° mineral are solubilized.

– Example: plagioclase → kaolinite:

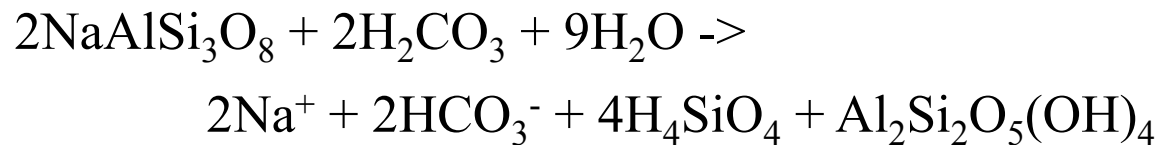


– Results in formation of 2° minerals

Incongruent Mineral Dissolution

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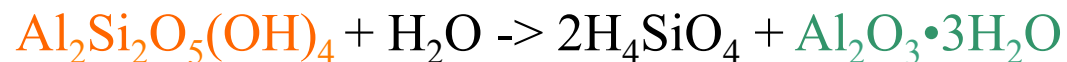
– Example: plagioclase → kaolinite:



– **Results in formation of 2° minerals**

- Solubilization of Na and Si
- Production of HCO_3^- indicates this is carbonic acid weathering
- 2° mineral has lower Si:Al ratio

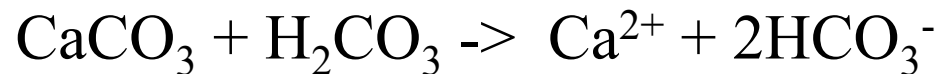
– **Kaolinite** can weather incongruently to form **Gibbsite**



Congruent Mineral Dissolution

- Complete dissolution: solubilization of all mineral constituents.

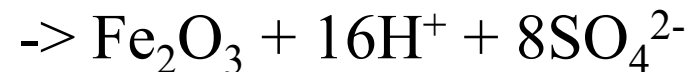
– Example: calcium carbonate \rightarrow constituent ions:



– Other examples: olivine (FeMgSiO_4), pyrite (FeS_2)

- Mg^{2+} , H_4SiO_4 , SO_4 lost from soil to runoff waters
- Fe is retained in oxidized forms, e.g. Fe_2O_3 ; often a microbially mediated reaction (*Thiobacillus ferrooxidans*)

– Acid mine drainage produced from weathering of pyrite:

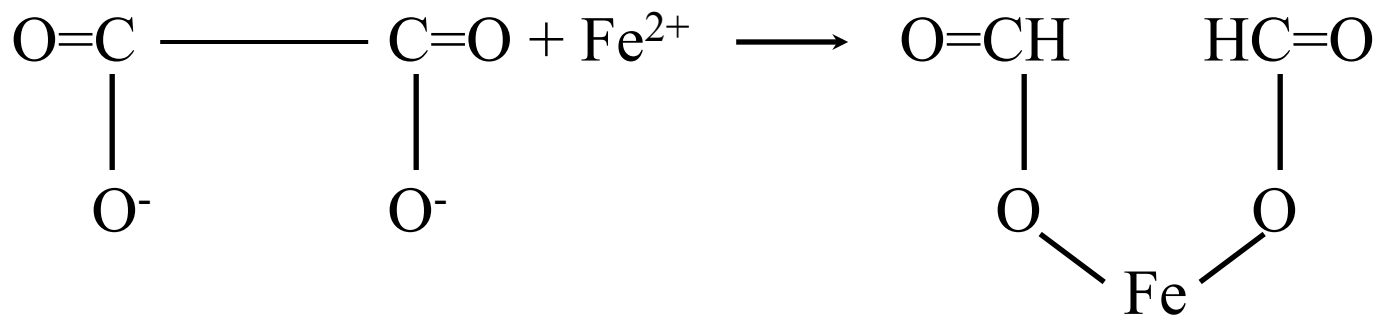


Organic Acids

- Released by soil organisms to soil solution
 - Plant roots: acetic acid, citric acid
 - Soil microbes: fulvic and humic acids, phenolic acids (tannins)
 - Fungi: oxalic acid
- Affect weathering in two ways:
 - Contribute to total acidity of soil
 - These are *chelators*: any of a class of coordination or complexing compounds that can bind to metal atoms
 - Metals are complexed to the *ligand* in a cyclic or ring structure.

Organic Acids are Chelators

- Oxalic Acid: HOOC-COOH, or H₂C₂O₄



- When insoluble metals bind with *chelators*, they become mobile
 - They can move lower in soil profile or be washed out
 - Their presence increases weathering rate by 10-100 x
- Organic acids often dominate the upper soil, carbonic acid becomes more important at depth in soil profiles

Secondary Minerals

- Produced by weathering of 1° minerals
- May initiate as coatings on surfaces of 1° minerals
- Clays dominate 2° minerals in temperate forest soils
 - control structural and chemical properties of the soil
- Crystalline oxides and hydrous oxides of Fe and Al dominate tropical soils

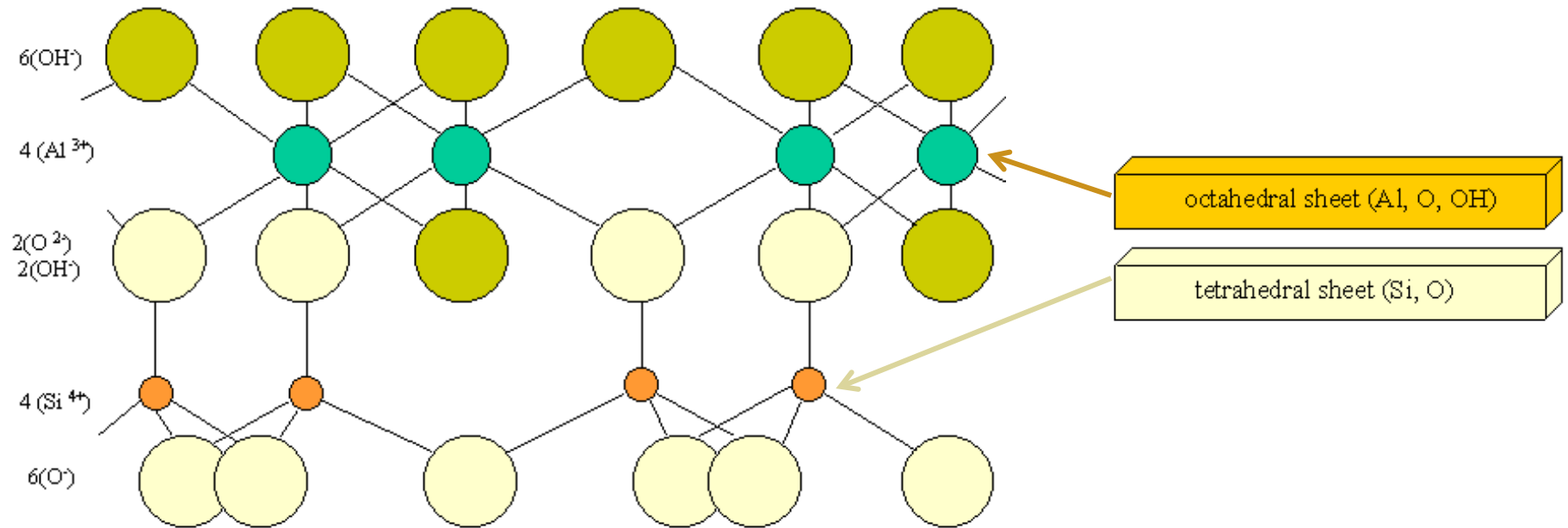
Clay Minerals

- Layered aluminosilicates, $< 2 \mu\text{m}$ in size
- Two types of layers
 - Si layers
 - Al layers
 - Layers are held together by shared O atoms
 - Different clays are classified on the basis of the #, order, ratio of these layers
 - Moderately weathered clays (montmorillonite, illite)
 - 2:1 ratio of Si:Al
 - More weathered clays (kaolinite)
 - 1:1 ratio of Si:Al, reflecting a greater Si-loss.

1:1 Clay Mineral Structure: Kaolinite



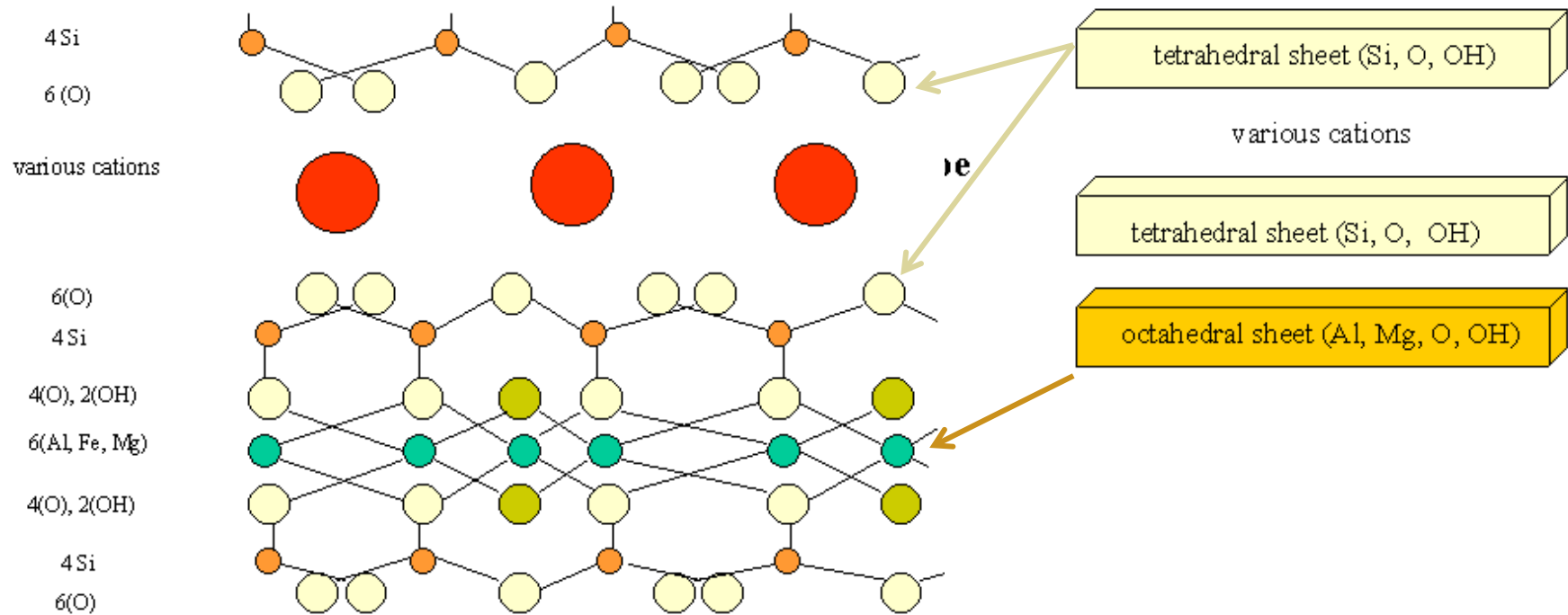
Diagrammatic Representation of Kaolinite



2:1 Clay Mineral Structure: Montmorillonite



Diagrammatic Representation of Montmorillonite



2° Mineral Formation Impacts Bioavailability

- Ions released from 1° minerals removed from solution to 2° minerals
 - Mg^{2+} often fixed in *montmorillonite* (temperate)
 - K^+ often fixed in *illite* (temperate)
 - NH_4^+ often fixed in 2:1 clay minerals (can be >10% of total N in soils)
 - *Implications for N-limitation of soils*
 - *Fe-* and *Al-oxides* and *hydroxides* are insoluble unless chelated
 - *Can sequester PO_4^{3-}*
 - *Implications for P-limitation of soils*

Tropical soils

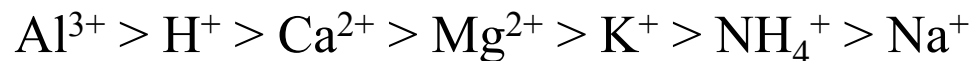
- Crystalline oxides and hydrous oxides of Fe and Al
 - Fe: goethite (FeOOH), hematite (Fe_2O_3)
 - Al: gibbsite [$\text{Al}(\text{OH})_3$], boehmite
- High T and ppt cause rapid decomposition of plant debris in soils, few chelators available, Fe and Al immobilized as 2° minerals
 - 2° clays lose all Si^{4+} , Ca^{2+} , K^+ to runoff
 - Leave behind Fe and Al oxides and hydrous oxides (laterites, bauxites)

Soil Chemical Reactions

- Release essential biochemical elements
- Bioavailability is controlled by K_{eq} between soluble and insoluble forms
- Soil exchange reactions occur more rapidly than weathering reactions

Cation Exchange Reactions

- Clays have net negative charge, attract cations
 - Internal/Structural (*permanent*): e.g., if Mg^{2+} subs for Al^{3+}
 - Edges (*reversible*): Un-protonated OH^- groups exposed on edges of clays (pH dependent) attract cations
- Cation Exchange Capacity (CEC) = total negative charge in a soil:
= (mEq/100g of soil)
 - Cations are held on exchange sites and displace one another in sequence:



Cation Exchange Capacity Changes During Soil Formation

- CEC increases during initial soil formation on newly exposed parent rock, then subsequently declines as soil ages
- CEC of temperate soils (2:1 clays dominate)
>> CEC of tropical (1:1 clays dominate) soils
- Highly weathered tropical soils (laterites, bauxites) have no CEC

Soil Buffering

- CEC can buffer acidity of temperate soils
 - Added H^+ are exchanged for cations on clays and organic matter, especially Ca, which when solubilized forms a base, e.g., $Ca(OH)_2$
 - Buffering effect can be described by the following eqn:

$$pH - \frac{1}{2}(pCa) = k \quad (4.8)$$

- Explains why pH of many temperate soils is unaltered by acid rain
- Strongly acid tropical soils have little CEC to buffer acidity, but:
 - Reactions involving Al buffer acidity
 - When Al^{3+} precipitates as Al-hydroxide, soil acidity increases :
 - 1) $Al^{3+} + H_2O = Al(OH)^{2+} + H^+$
 - 2) $Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+$
 - 3) $Al(OH)_2^+ + H_2O = Al(OH)_3 + H^+$
 - Because these reactions are reversible, they buffer against H^+ additions

Anion Adsorption Capacity

- Tropical soils show variable charge depending on soil pH
 - Under acid conditions (low pH) they have a “+” charge, adsorb anions
 - At high pH they develop CEC
 - As pH increases from acid to alkaline, the soils pass through a zero point of charge (ZPC), where # of cation exchange sites = # anion exchange sites
 - The pH of the ZPC is different for different soil compositions

Anion Adsorption Capacity: Some Details

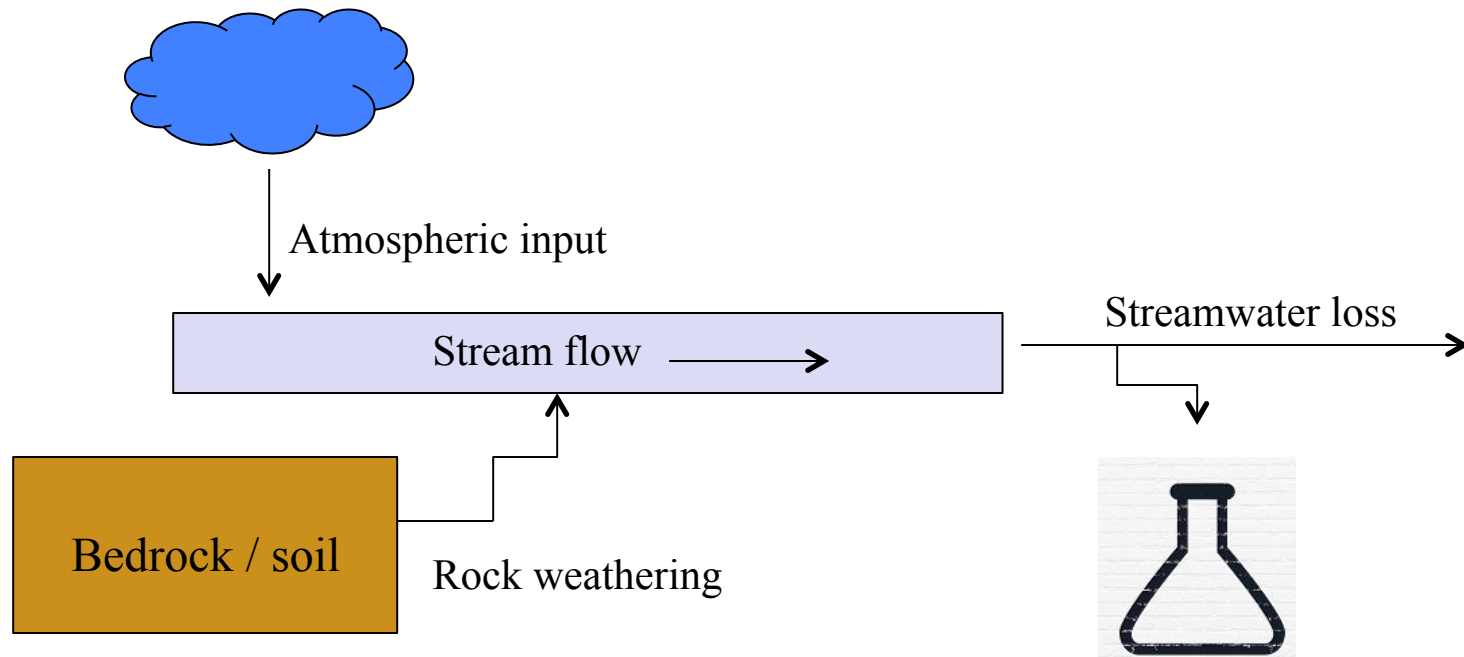
- Anion Adsorption Capacity (AAC) is greatest when Fe and Al oxyhydroxides are present and amorphous (greater surface area)
- Anion adsorption follows the sequence:
$$\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$$
- Strong PO_4^{3-} adsorption explains why P frequently is limiting in tropical soils

Weathering Rates

- Estimates of weathering rates allow us to relate the biogeochemistry of watersheds to global element cycling (*primary source of many nutrients*)
- Rates difficult to evaluate because processes occur slowly and are difficult to isolate
- Classical Approach:
 - Infer rates from residuum in soil profile and/or
 - Infer rates from losses in stream water
- Global weathering rates are inferred from dissolved and suspended load of rivers

The Hubbard Brook Forest

- Several comparable watersheds
- Underlain by impermeable bedrock (no flow to groundwater)
- $(\text{Stream water loss}) - (\text{atm input}) = (\text{release from rocks})$



The Hubbard Brook Forest

- (Stream water loss) - (atm input) = (release from rocks)

$$\text{Weathering rate} = (\text{Ca}_{\text{stream}}) - (\text{Ca}_{\text{ppt}}) / (\text{Ca}_{\text{rx}}) - (\text{Ca}_{\text{soil}})$$

- Solution to this equation varies for different ions due to different propensities for:
 - Biological uptake
 - Formation of 2° minerals

Table 4.4 Calculation of the Rate of Primary Mineral Weathering, Using the Stream Water Losses and Mineral Concentrations of Cationic Elements^a

$$\text{Weathering rate} = (X_{\text{stream}}) - (X_{\text{ppt}}) / (X_{\text{rx}}) - (X_{\text{soil}})$$

Element	Annual net loss (kg ha ⁻¹ yr ⁻¹)	Concentration in rock (kg/kg of rock)	Concentration in soil (kg/kg of soil)	Calculated rock weathering (kg ha ⁻¹ yr ⁻¹)
Ca	8.0	0.014	0.004	800
Na	4.6	0.016	0.010	770
K	0.1	0.029	0.024	20
Mg	1.8	0.011	0.001	180

^a Data from Johnson et al. (1968).

- Different elements show different weathering rates
- Slower rates imply secondary removal processes

**Table 4.5 Inputs and Outputs of Elements
from the Hubbard Brook^a**

	Inputs (%)		Output as a percent of input
	Atmosphere	Weathering	
Ca	9	91	59
Mg	15	85	78
K	11	89	24 ★
Fe	0	100	25
P	1	99	1 ★
S	96	4	90
N	100	0	19 ★
Na	22	78	98
Cl	100	0	74

★ Nutrient elements are retained!

^a Data from Likens et al. (1981).

Chemical Weathering Rates

- Cl and Si are key ions to derive weathering rates:
 - Si source is bedrock, atmospheric inputs negligible: a good index of chemical weathering
 - Cl content in rocks low, atmospheric input dominates
 - Because Cl⁻ is unreactive (inert), it is a good metric for evaluating hydrologic budget
- Loss of dissolved constituents during chemical weathering is defined as *chemical denudation* of the landscape
- In most areas with silicate bedrock, loss to stream water relative to concentration in bedrock:

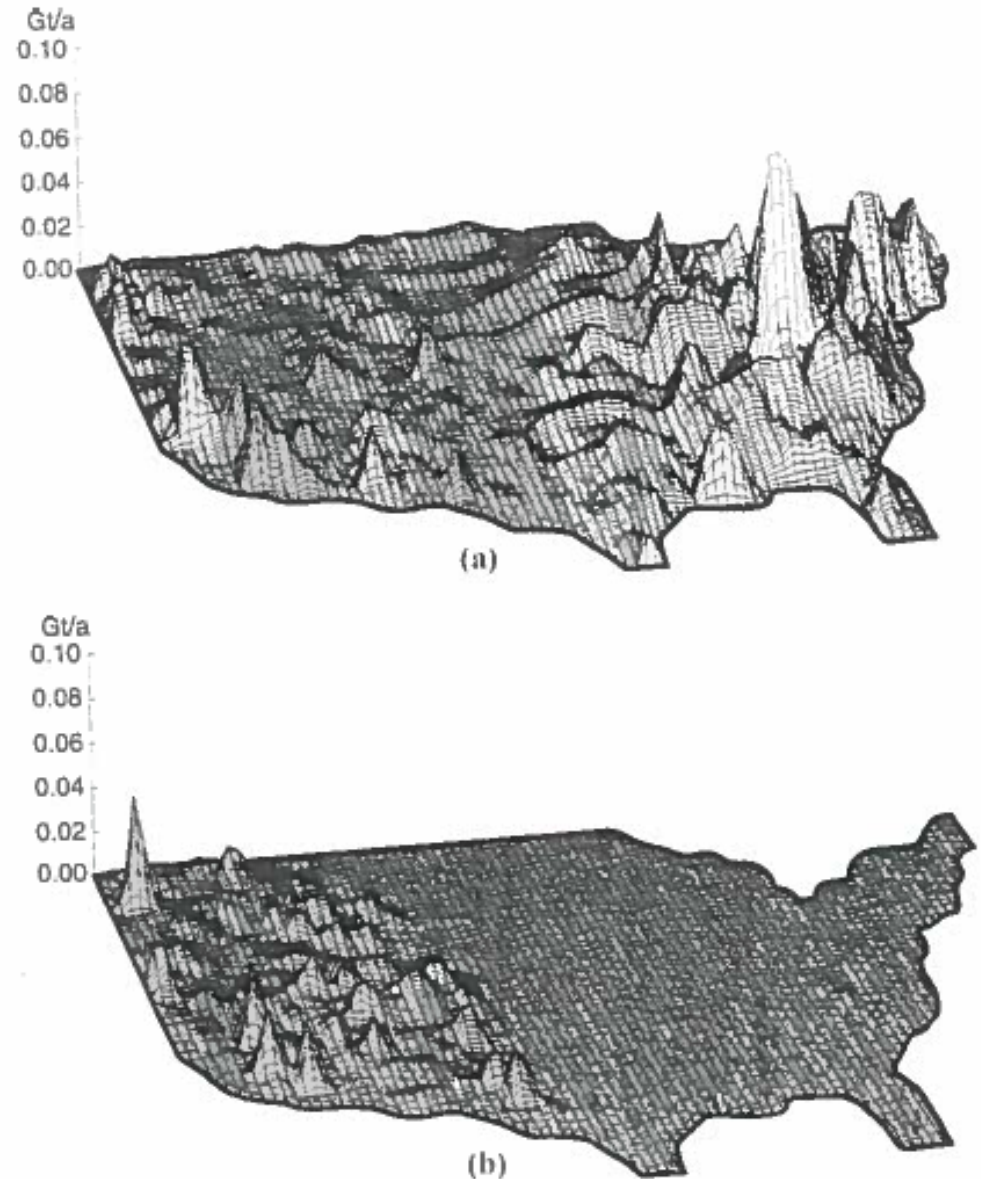


Total Denudation

- Total Denudation = Chemical + Mechanical Denudation
- Mechanical Denudation (vs. chemical) has been studied less because products are not bioavailable
 - 3 to 4 x > chemical denudation world wide
 - $\approx 75\%$ carried as suspended sediments in rivers
 - Today's rates higher due to land use
 - Importance increases with elevation
 - Transports insoluble elements to the sea (Fe, Al, Si, P)
 - Toxic metal (Cu, Zn) fluxes have increased due to human activities

Anthropogenic vs. Riverine Denudation

Fig. 4.21. Denudation rate by (a) humans, and (b) rivers. Surface mining for coal is largely responsible for the massive mobilization of crustal material in the eastern US.



Brief Lecture Summary

- Rates of mechanical weathering impact rates of chemical weathering via production of surface area
- Rates of weathering and soil development are strongly affected by biota
 - Carbonic acid weathering
 - Production of organic acids
- Both chemical and mechanical weathering are impacted by climate (temperature, rainfall, CO₂)
- Chemical weathering produces essential nutrients
 - Congruent vs. incongruent weathering
 - Impact of 2° mineral formation on bioavailability
- The weathering – climate connection is modulated by production and consumption of CO₂ and impacts global element cycles