OCN 401-16
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KCR

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:

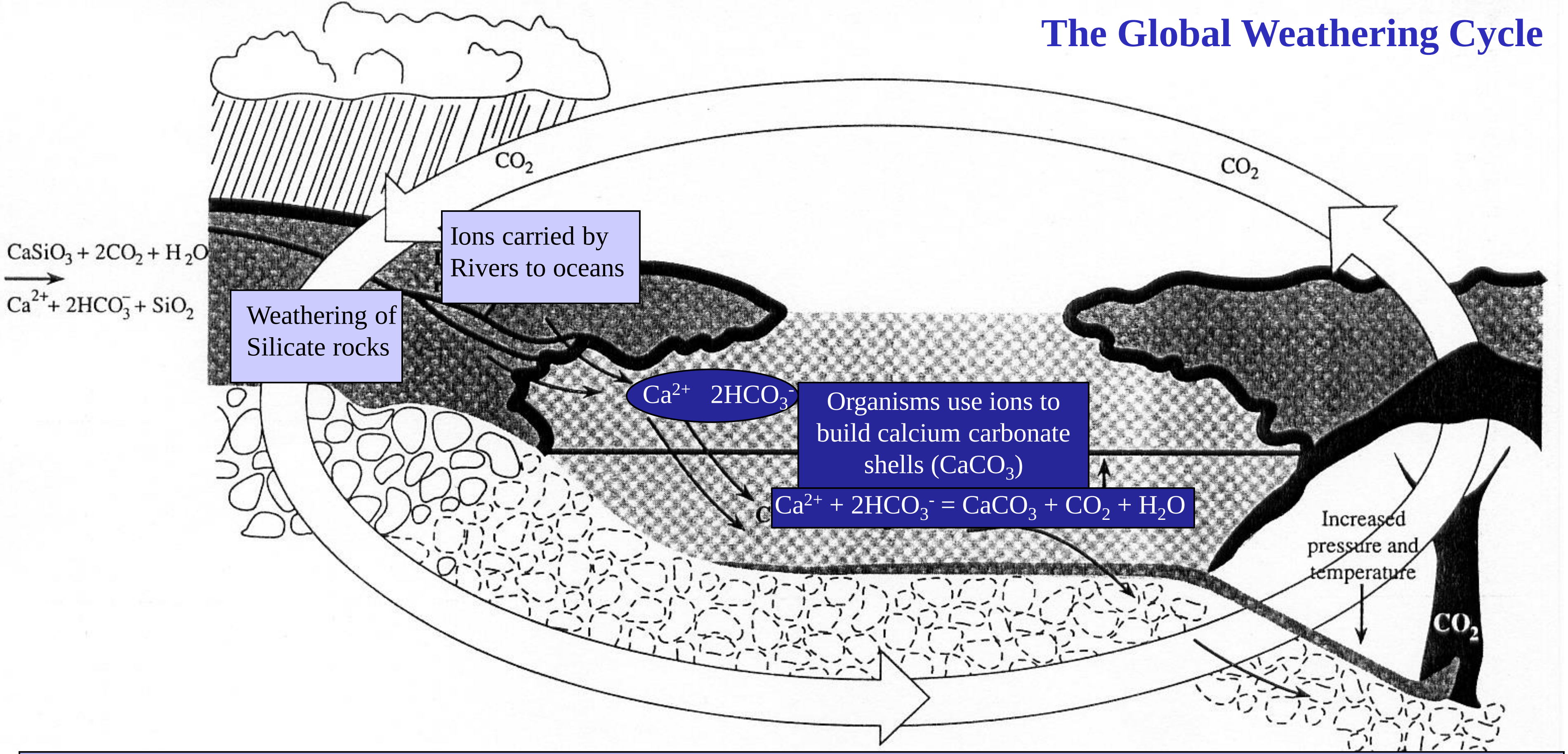
→ rock weathering

- Basic Summary Equation (Siever 1974):

Igneous rocks + acid volatiles = salty oceans + sedimentary rocks

- Weathering through Geologic Time:
  - Early Earth: acidic volcanic gases
  - Later: atmospheric O_2, oxidation of reduced minerals
  - Advent of land plants: metabolic CO_2, H_2CO_3
  - Modern era: anthropogenic NO_x, SO_x, acid rain

The Global Weathering Cycle



$CaSiO_3 + 2CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_2$

Weathering of Silicate rocks

Ions carried by Rivers to oceans

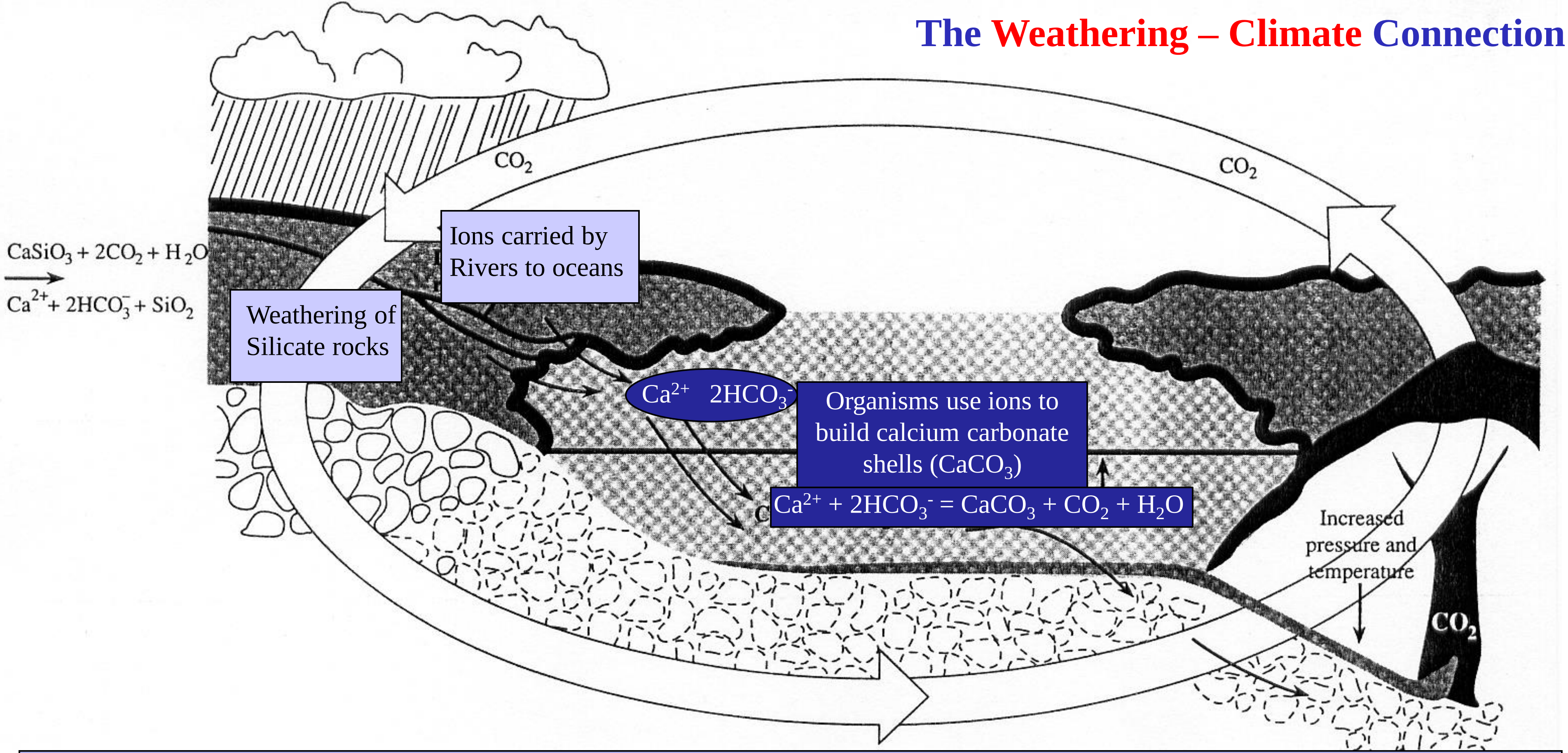
Ca^{2+} $2HCO_3^-$

Organisms use ions to build calcium carbonate shells ($CaCO_3$)

$Ca^{2+} + 2HCO_3^- = CaCO_3 + CO_2 + H_2O$

- 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



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- The Global CO_2 Balance Links Weathering and Climate:
  - CO_2 is released in volcanism
  - CO_2 is consumed in weathering
  - HCO_3^- produced in weathering reactions is carried to the oceans via rivers
  - Biogenic carbonate [$2HCO_3^- + Ca^{2+} = CaCO_3 + CO_2 + H_2O$] is buried in sediments
- The balance between weathering rate and seafloor spreading (subduction) exerts control on atmospheric P_{CO2}
- Climate is impacted because CO_2 is an important greenhouse gas

Why is weathering important?

- Climate regulation through CO_2 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***.

Two Categories of Rock Weathering

- Exposure at Earth surface, by *uplift* or *extrusion*

- **Mechanical** weathering
  - Fragmentation without chemical reaction: physical change
    - Erosion (water, wind)
    - Frost heaving
    - Plant root fragmentation
    - Catastrophic events (e.g. landslides)
  - Important in extreme climate regimes
  - Transport-limited systems develop thick soil layers
  - Important factor in large yield of small, mountainous regions
  - *Creation of surface area*

- **Chemical** weathering

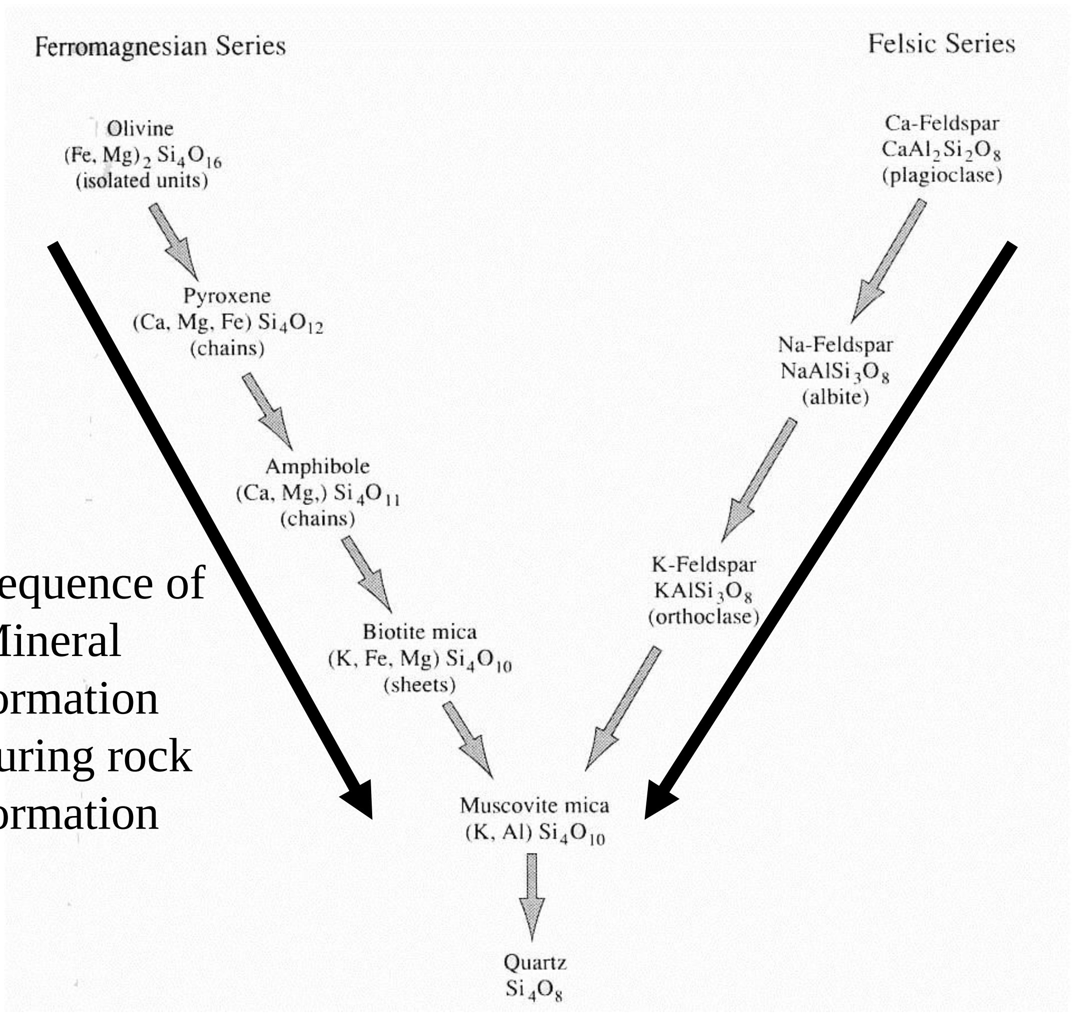
Chemical weathering

- 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



Sequence of Mineral formation during rock formation

Fig. 4.1. Bowen Reaction Series

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

Weathering Reactivity Sequence: the Inverse of Crystallization Sequence

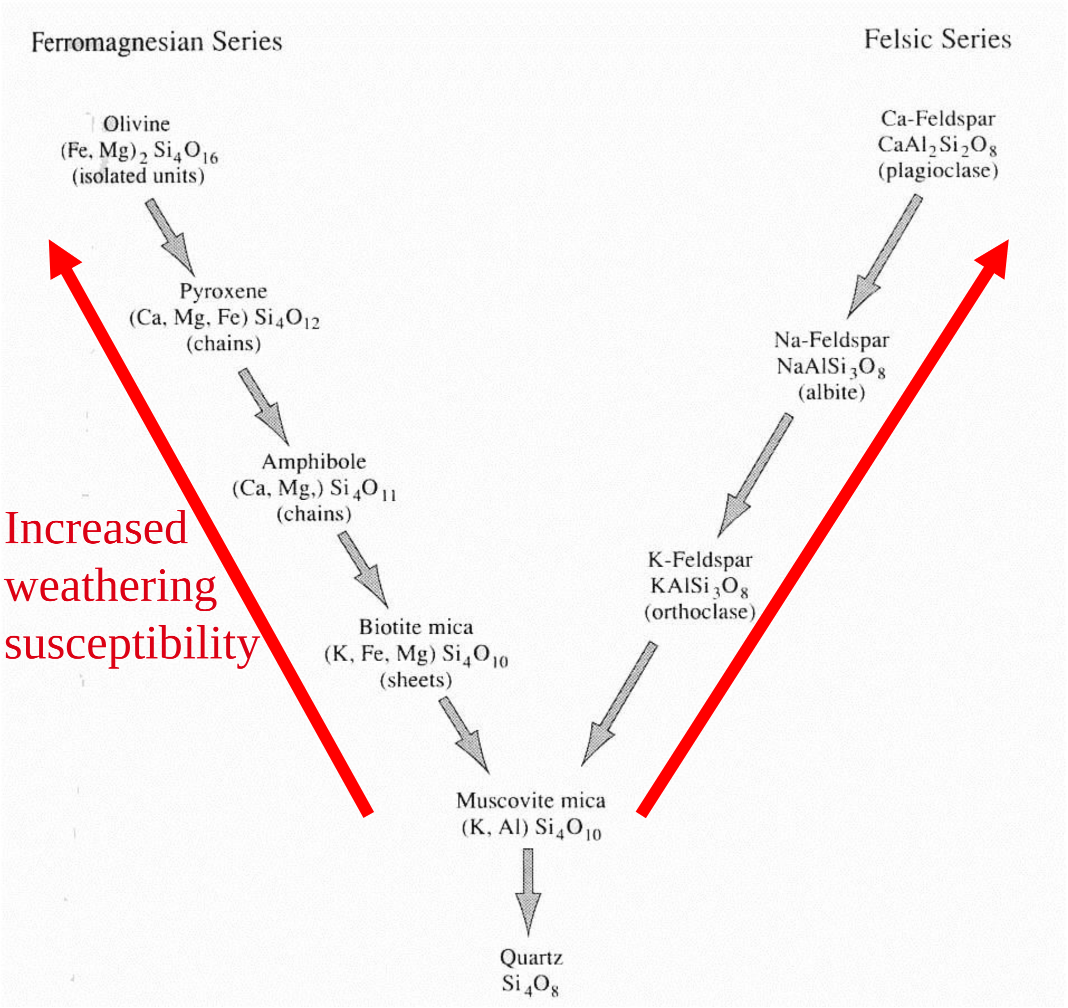


Fig. 4.1. Bowen Reaction Series

- Susceptibility to weathering is affected by crystal structure:
  - isolated units more reactive than chains or sheets
- Susceptibility to weathering is affected by crystal chemistry:
  - minerals with lower O:Si ratio are more resistant)
- Minerals formed at high T are more susceptible to weathering because:
  - they have fewer bonds that link their crystal structure
  - frequent 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.)

Impact of Climate on Chemical Weathering

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

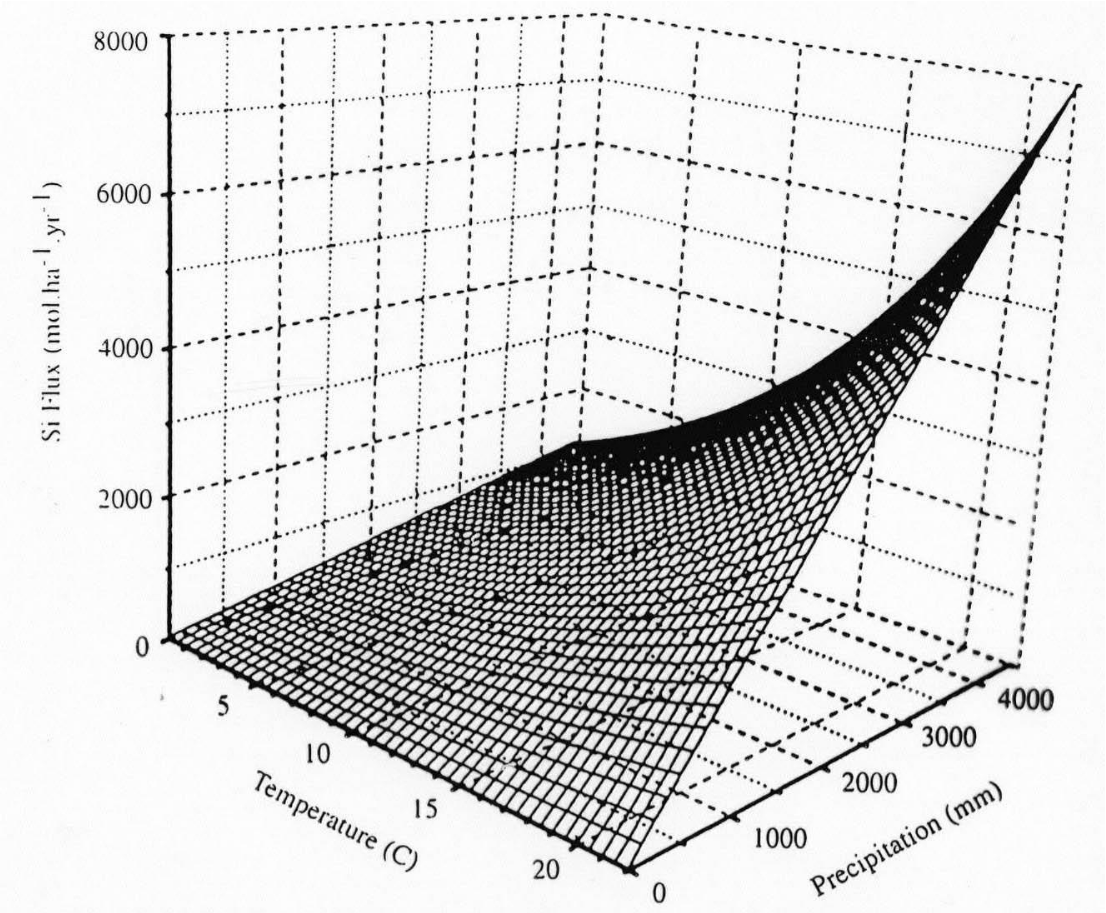


Figure 4.2 Loss of silicon (SiO_2) in runoff is directly related to mean annual temperature and precipitation in various areas of the world. Modified from White and Blum (1995). Silica is a good indicator of chemical weathering.

$CaSiO_3 + 2CO_2 + H_2O = Ca^{2+} + 2HCO_3^- + SiO_2$

Carbonic Acid Weathering

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

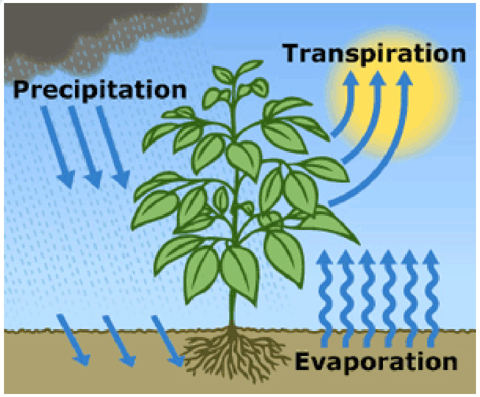
$$H_2O + CO_2 = H^+ + HCO_3^- = H_2CO_3 \qquad (4.2)$$

  - Soil [H_2CO_3] often exceeds equilibrium with atmospheric CO_2 (400 ppm, or 0.04%)
    - Plant roots and microbes release [CO_2] to soil
    - High CO_2 can extend to considerable depth in soil (1% @ 36 m), leading to weathering of underlying rock
    - High [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 [CO_2], and greatest weathering rates
- By maintaining high soil [CO_2] plants and associated organisms exert biotic control over the geochemical process of rock weathering on land

Average soil [CO_2] varies as a function of 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

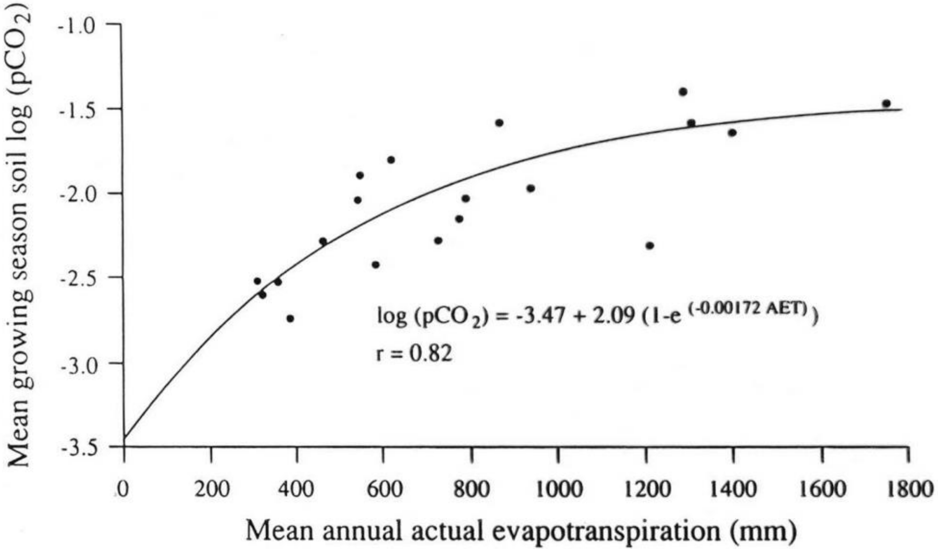


Figure 4.3 Relationship between mean CO_2 concentration in soil pore space and actual evapotranspiration at the site for various ecosystems of the world (Brook et al. 1983).

Incongruent Mineral Dissolution

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

– Example: plagioclase -> kaolinite:

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow$$
$$2Na^+ + 2HCO_3^- + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$$

– 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

$$Al_2Si_2O_5(OH)_4 + H_2O \rightarrow 2H_4SiO_4 + Al_2O_3 \bullet 3H_2O$$

Congruent Mineral Dissolution

- Complete dissolution: solubilization of all mineral constituents.
  - Example: calcium carbonate -> constituent ions:

    $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$

  - 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:

    $FeS_2 + 8H_2O + 15O_2 \rightarrow 2Fe_2O_3 + 16H^+ + 8SO_4^{2-}$

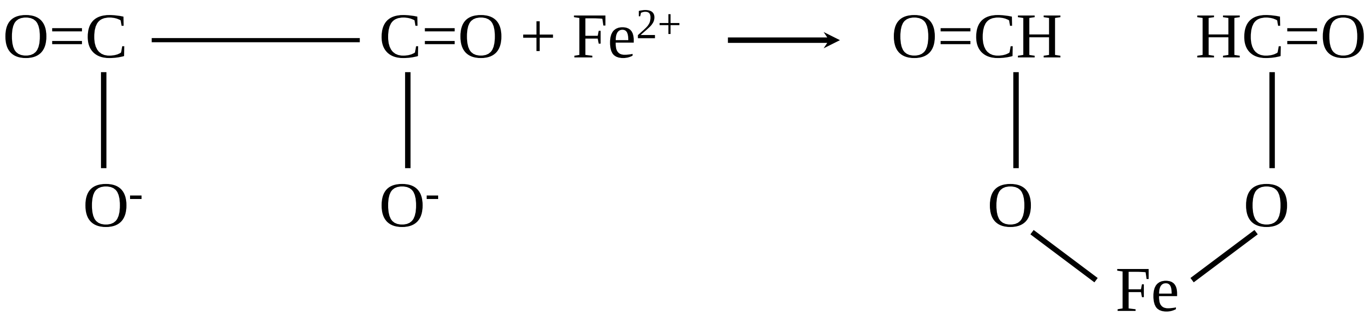
Organic Acids

- 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 (cont' d.)

- Oxalic Acid: HOOC-COOH, or $H_2C_2O_4$



- 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 10-100x

- 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 µm in size

- Two types of layers
  - Si layers
  - Al layers (with other cations, e.g., Fe, Mg)
  - Layers are held together by shared O atoms
  - Different clays are classified on the basis of the #, order, ratio of these layers

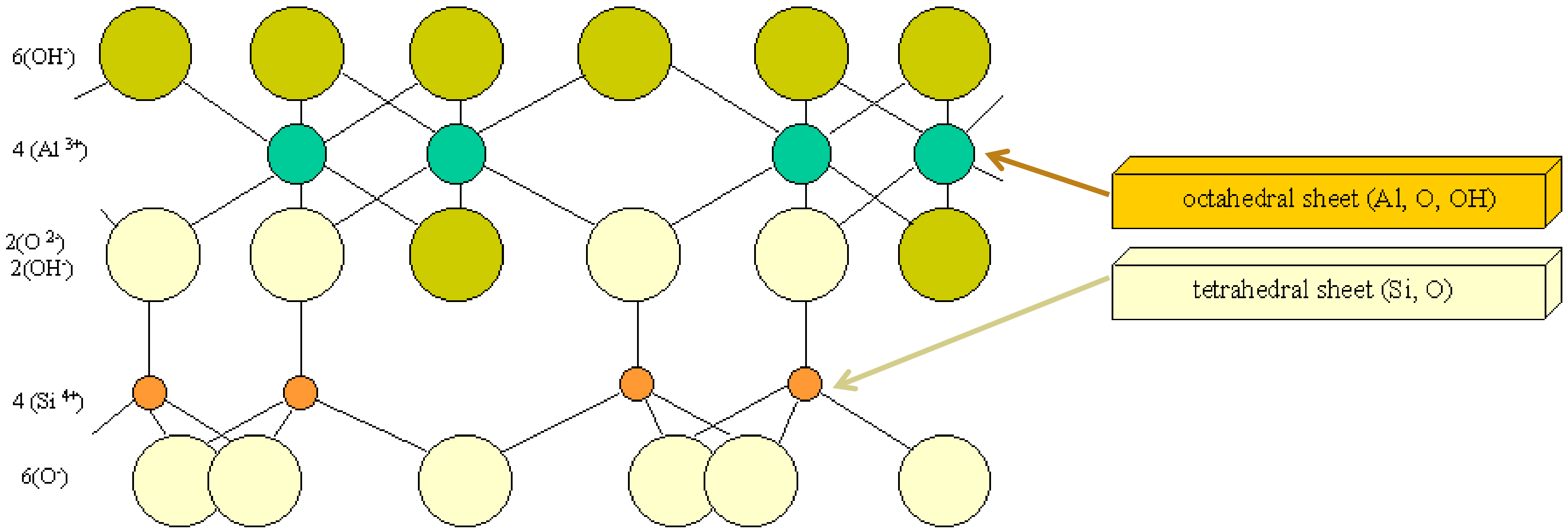
    - Moderately weathered clays (montmorillonite, illite)
      - 2:1 ratio of Si:Al

    - More weathered clays (kaolinite)
      - 1:1 ratio of Si:Al, reflecting a greater Si-loss.

1:1 Clay Mineral Structure: Kaolinite

$Al_2Si_2O_5(OH)_4$

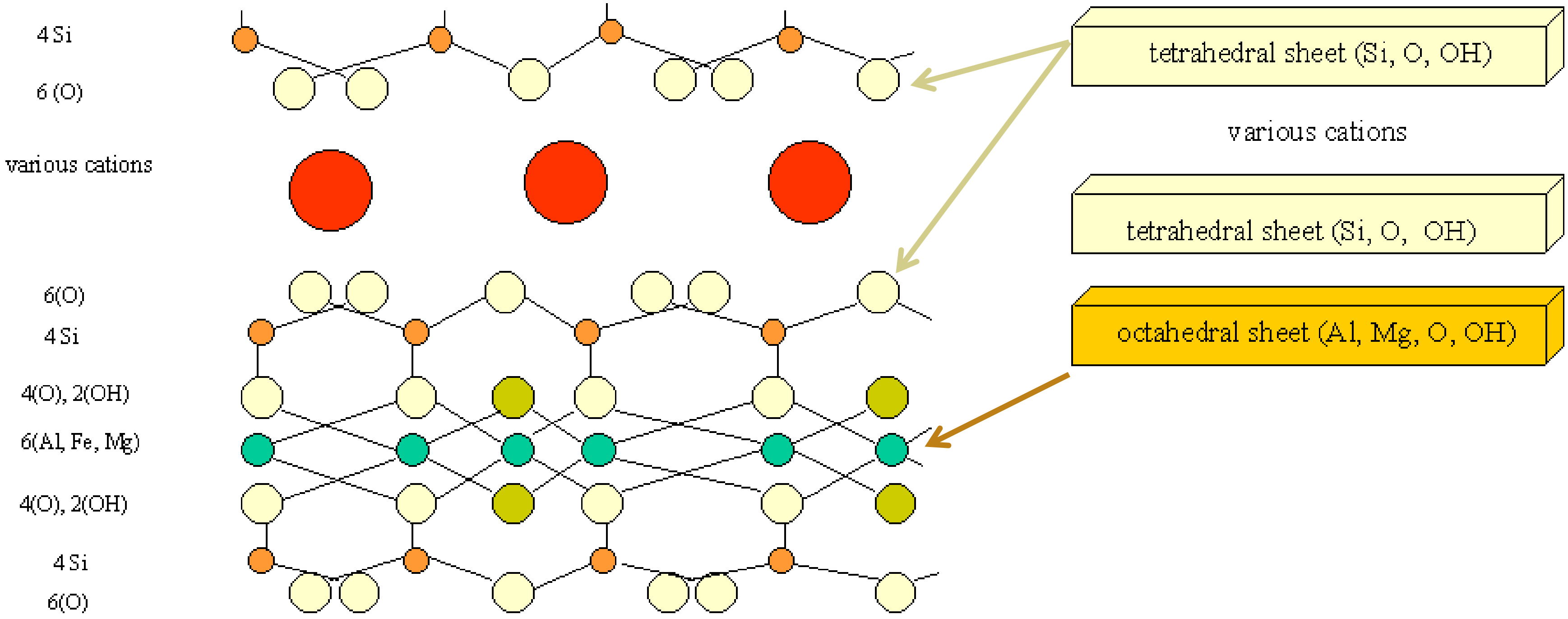
Diagrammatic Representation of Kaolinite



2:1 Clay Mineral Structure: Montmorillonite

$Na_{0.2}Ca_{0.1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$

Diagrammatic Representation of Montmorillonite



2° Mineral Formation Impacts Bioavailability

- Ions released from 1° minerals may not stay in solution if they are taken up into *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 [$Al(OH)_3$], 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 loose all Si^{4+}, Ca^{2+}, K^+ to runoff
  - Leave behind Fe and Al oxides and hydrous oxides (laterites, bauxites)

Phosphorus (P) Minerals

- P is often a limiting nutrient
- Apatite is the dominant 1° mineral, weathers congruently:

  $Ca_5(PO_4)_3(F,OH) + 4H_2CO_3 \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + 4HCO_3^- + H_2O$

- Solubilized P is either taken up by biota or re-precipitated into 2° minerals
  - Occluded in Fe and Al oxides / oxyhydroxides
  - Biologically unavailable when occluded
  - Bioavailability of P can be tied to abundance of organic acid chelators (fungi → oxalate)

pH Controls which 2° P Minerals Form

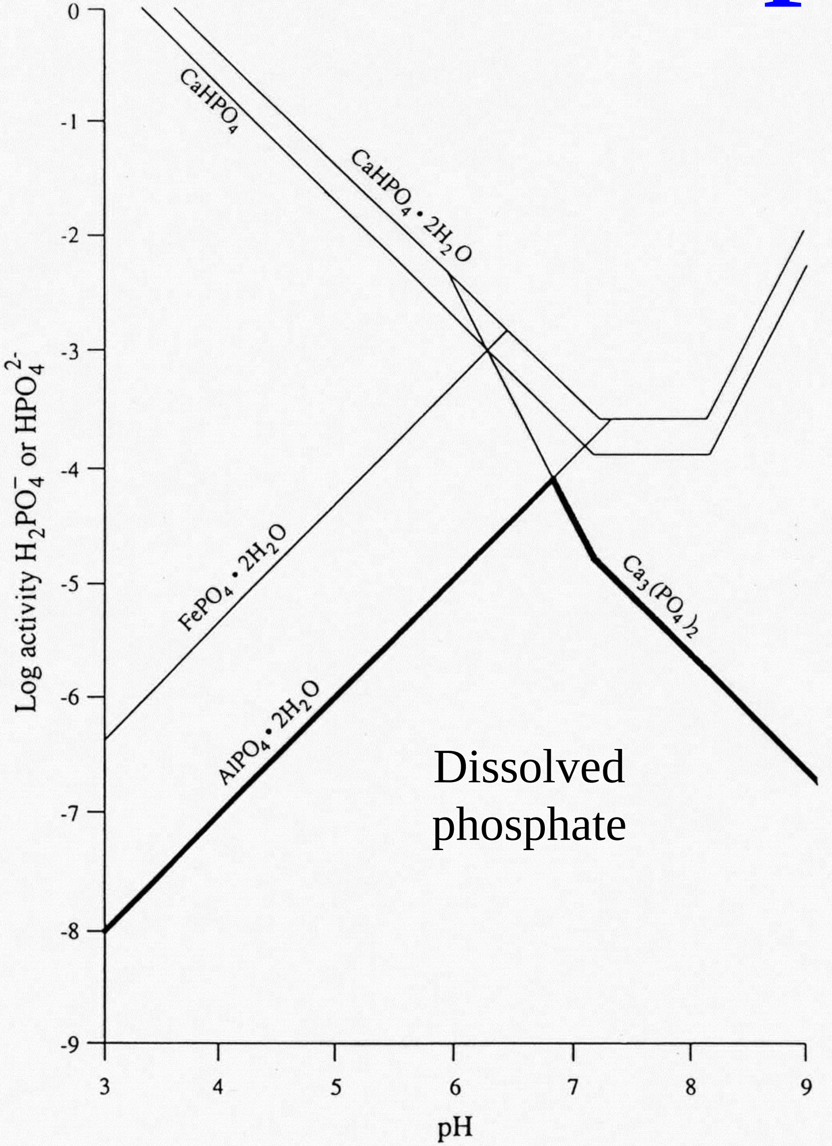


Figure 4.10 The solubility of P in soil solution as a function of pH. Precipitation with Al sets the upper limit on dissolved phosphate at low pH (bold line); precipitation with Ca sets a limit at high pH. Phosphorus is most available at a pH of approximately 7.0. Modified from Lindsay and Vlek (1977).

Evolution of Soil P Impacts Bioavailability

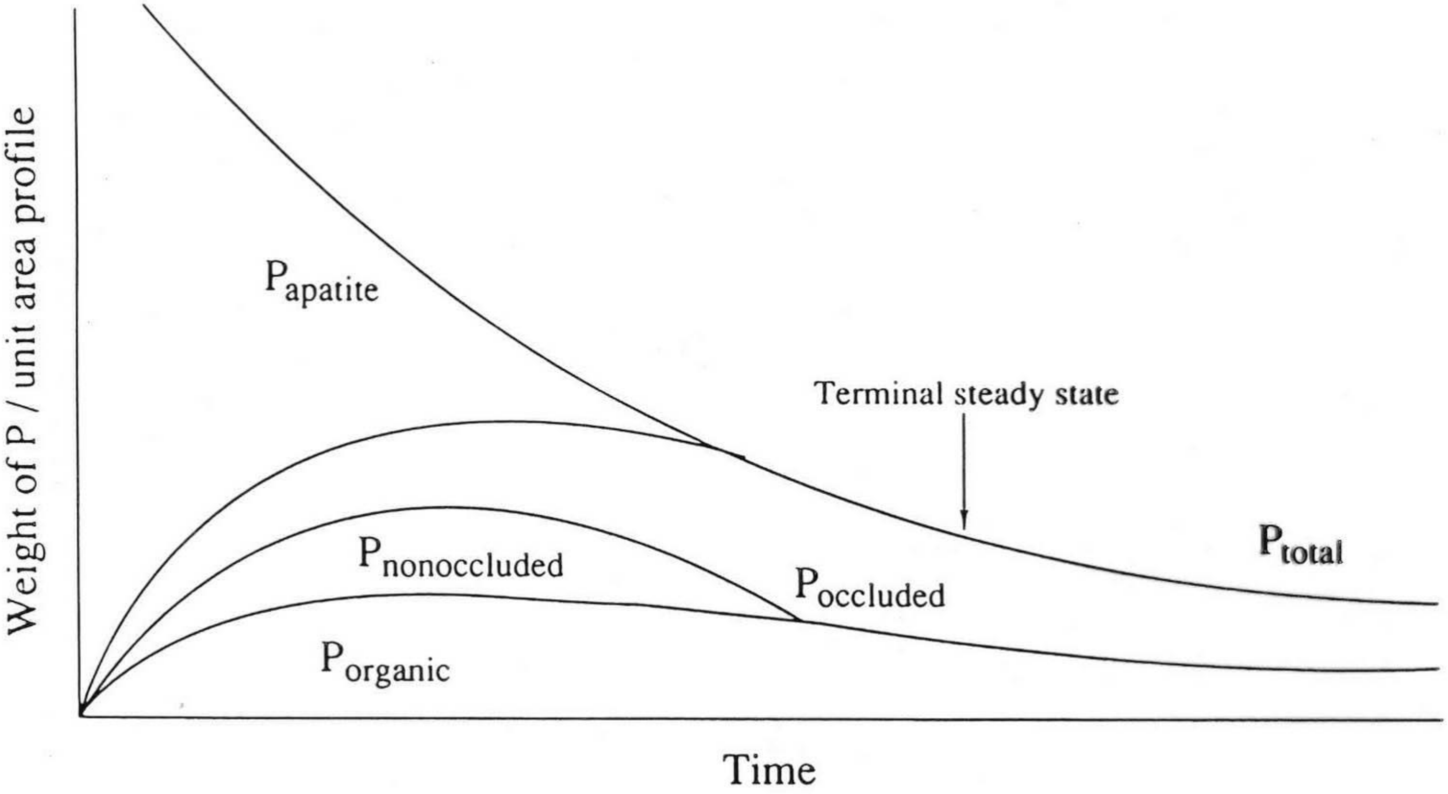


Figure 4.11 Changes in the forms of phosphorus found during soil development on sand dunes in New Zealand. Modified from Walker and Syers (1976).

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
  - Soil organic matter (-OH, -OOH) has net negative charge, attracts cations (Ca^{2+}, K^+, NH_4^+) (pH-dependent)
- 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:

$$Al^{3+} > H^+ > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > Na^+$$

Progression of Cation Exchange Capacity 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:

$$pH - \tfrac{1}{2}(pCa) = k \qquad (4.8)$$

  - Explains why pH of many temperate soils is unaltered by acid rain

- Strongly acid tropical soils have little CEC reactions involving Al buffer acidity:

- Reactions involving Al buffer acidity

- Release of Al^{3+} to soil solution increases soil acidity:

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)

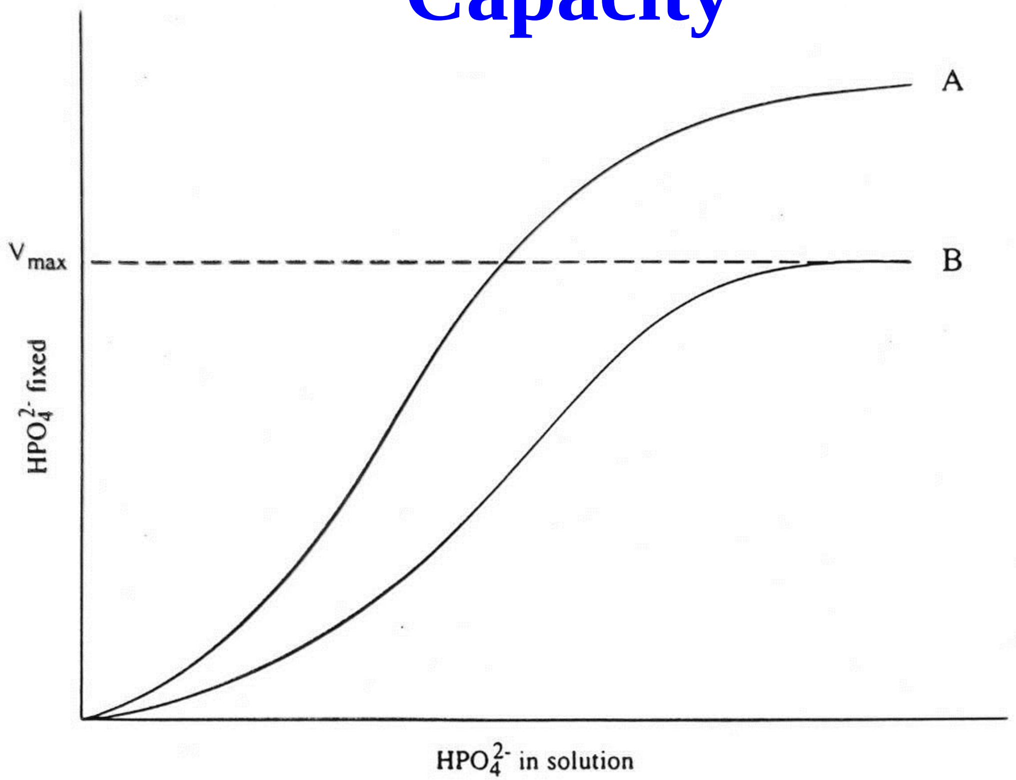
- Anion adsorption follows the sequence:

  $PO_4^{3-} > SO_4^{2-} > Cl^- > NO_3^-$

- Strong PO_4^{3-} adsorption explains why P frequently is limiting in tropical soils

- AAC is often modeled using Langmuir isotherms

Experimental Determination of Sorption Capacity



The Langmuir adsorption isotherm is used to compare the affinity of soils for anions as a function of the concentration of the anion in solution. If soil B has a lower affinity for phosphate than soil A, at equal concentrations of phosphate in solution more P will be available in soil B. Conversely, if these soils are exposed to long-term additions of solutions with a given phosphate concentration, it will take longer for soil A to equilibrate with that solution (see Johnson and Cole 1980, Reuss and Johnson 1986). (From Fig 4.8 of Schlesinger, 2nd ed.)

Weathering Rates

- Estimates of weathering rates allow us to relate the biogeochemistry of watersheds to global element cycling (*primary source of many nutrients*)

- These rates are difficult to evaluate because processes occur slowly and are difficult to isolate

- Classical Approach: Infer rates from residuum in soil profile and/or losses in stream water

- Global weathering rates inferred from dissolved and suspended load of rivers

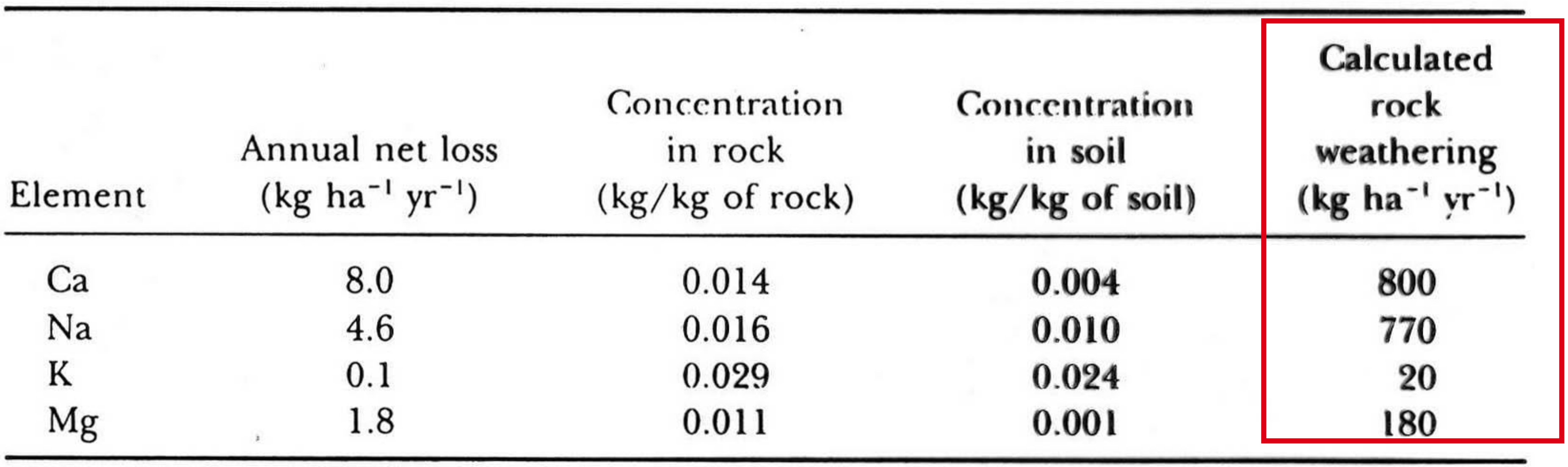
The Hubbard Brook Forest

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

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

- Solution to this equation differs for different ions as a result of different propensities for:
  - Biological uptake
  - Formation of 2° minerals

Table 4.4 Calculation of the Rate of Primary Mineral Weathering, Using the Streamwater Losses and Mineral Concentrations of Cationic Elements[a]

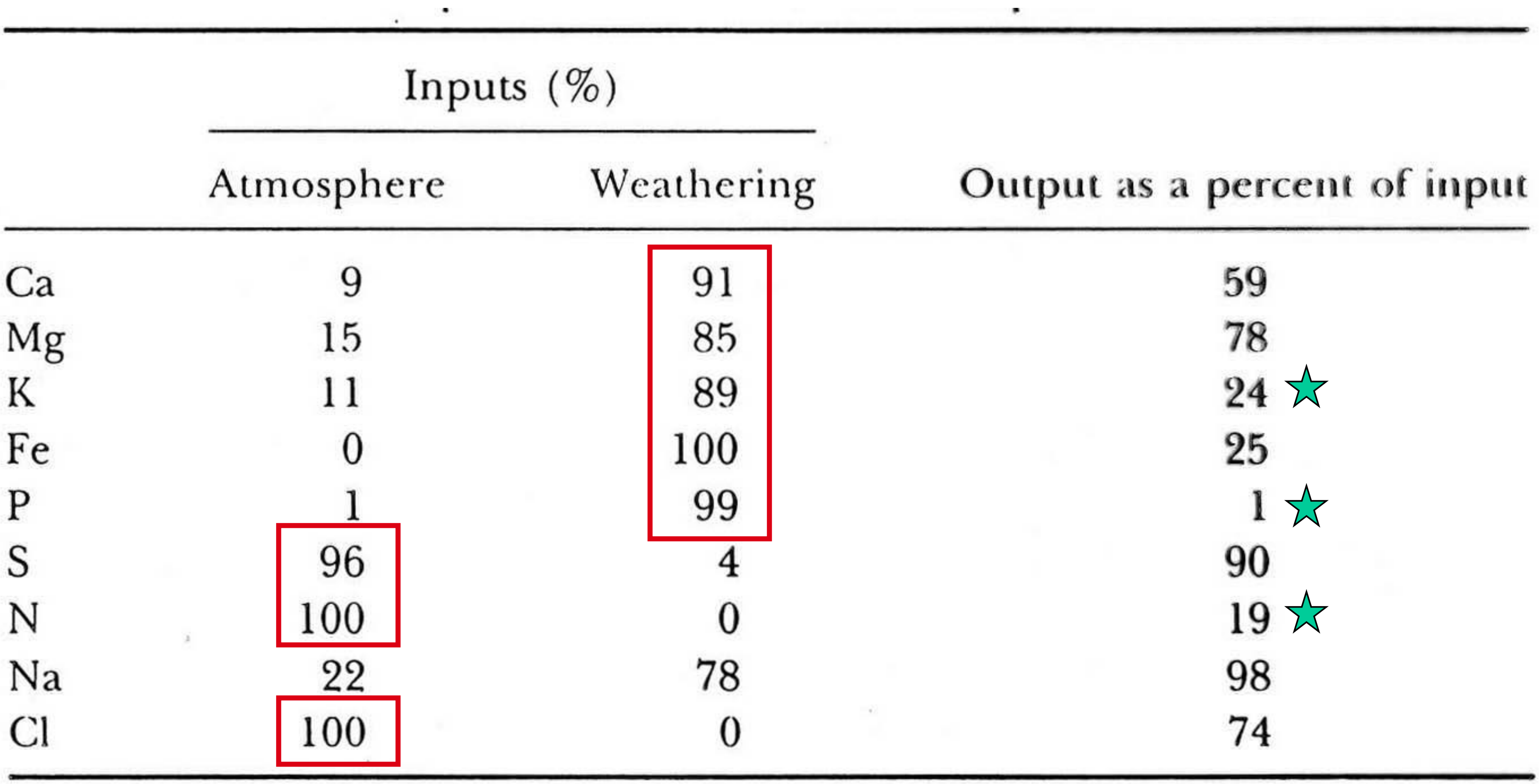


Element	Annual net loss (kg ha^{-1} yr^{-1})	Concentration in rock (kg/kg of rock)	Concentration in soil (kg/kg of soil)	Calculated rock weathering (kg ha^{-1} yr^{-1})
Ca	8.0	0.014	0.004	800
Na	4.6	0.016	0.010	770
K	0.1	0.029	0.024	20
Mg	1.8	0.011	0.001	180

[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 (%)		
	Atmosphere	Weathering	Output as a percent of input
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

- Useful to look at Cl and Si
  - 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

- Losses 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:

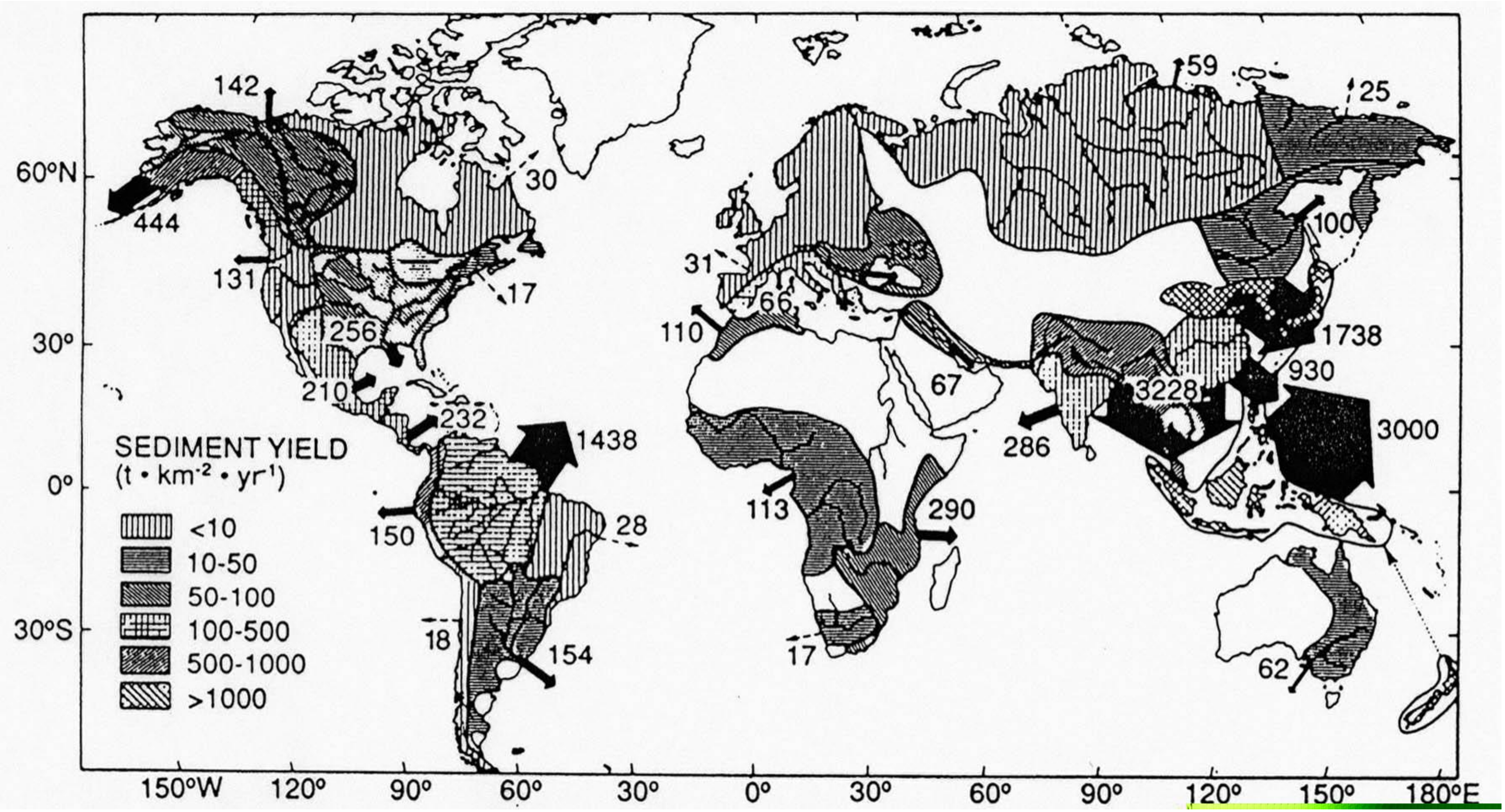
$$Ca > Na > Mg > K > Si > Fe > Al$$

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
  - Mean rate ≈ 1000 kg/ha/yr
  - ≈ 75% carried as suspended sediments in rivers
  - Today's rates higher due to land use (Figs. 4A & 4B)
  - 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

Annual sediment flux from major drainage basins to the world’s oceans



Data are millions of tons (10^{12} g) per year, and arrows are drawn proportional to the flux. From Milliman and Meade (1983).

Brief Lecture Summary

- Rates of weathering and soil development are strongly affected by biota
  - Carbonic acid weathering
  - Production of organic acids

- Rates of mechanical weathering impact rates of chemical weathering via production of surface area for reaction

- Chemical weathering produces essential nutrients
  - Congruent vs. incongruent weathering
  - Impact of 2° mineral formation on bioavailability
  - Impact of soil mineralogy on bioavailability

- The weathering – climate connection is modulated by production and consumption of CO_2
  - Impacts global element cycles