GEOL 414/514

CHEMICAL WEATHERING

Chapter 7

LANGMUIR

GENERAL OBSERVATIONS

1. Most chemical weathering occurs in the vadose zone of soils
2. The rate of chemical weathering is usually incr'd if the rate of physical or mechanical weathering is incr'd
3. The rate of chemical weathering is proportional to the soil organic/biological activity, include abundance of vegetation
4. The chemical weathering rate of a given soil is proportional to the infiltration (percolation) rate of water

GENERAL OBSERVATIONS

5. The rate of chemical weathering inc with inc temp
6. Chemical weathering generally involves the attack of H_2O & assoc acidity, & atmos O_2 (oxid'n) on P.M.'s
7. Compared with the parent rock, mineral products of weathering are usually more hydrated (as clays), have lower metal cation conc's relative to Al & Si (clays & qtz), are oxidized (Fe^{+3} oxyhydroxides), or are chem ppts such as carbonates or evaporites
8. Dissolved products of weathering include major cations & anions in natural waters & dissolved silica

GENERAL OBSERVATIONS

- Problem in determining detailed weathering reactions
- Need chemical analysis at different stages of weathering
- Difficult to know if different stages sampled had same original composition
- Also need reference mineral or element; one that weathers little
- Must make several key assumptions

COMMON WEATHERING PRODUCTS

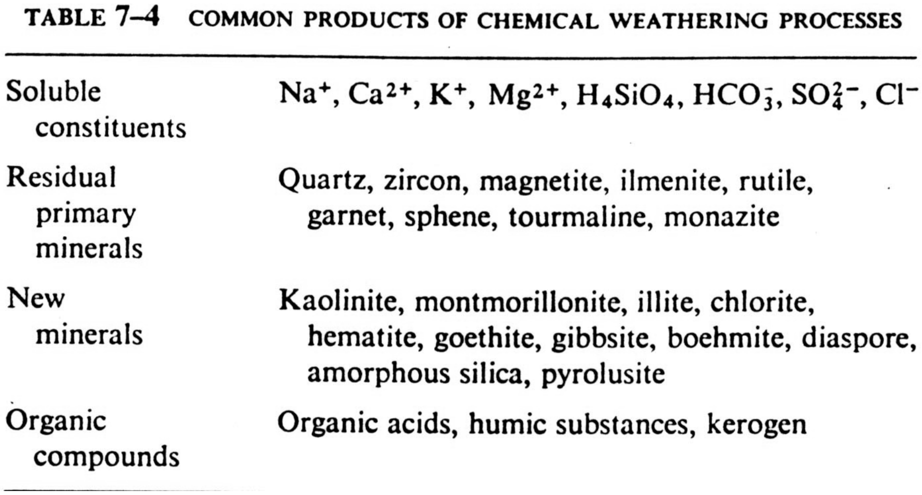


TABLE 7–4 COMMON PRODUCTS OF CHEMICAL WEATHERING PROCESSES

Soluble constituents	Na^+, Ca^{2+}, K^+, Mg^{2+}, H_4SiO_4, HCO_3^-, SO_4^{2-}, Cl^-
Residual primary minerals	Quartz, zircon, magnetite, ilmenite, rutile, garnet, sphene, tourmaline, monazite
New minerals	Kaolinite, montmorillonite, illite, chlorite, hematite, goethite, gibbsite, boehmite, diaspore, amorphous silica, pyrolusite
Organic compounds	Organic acids, humic substances, kerogen

(from Brownlow)

ROCK WEATHERING

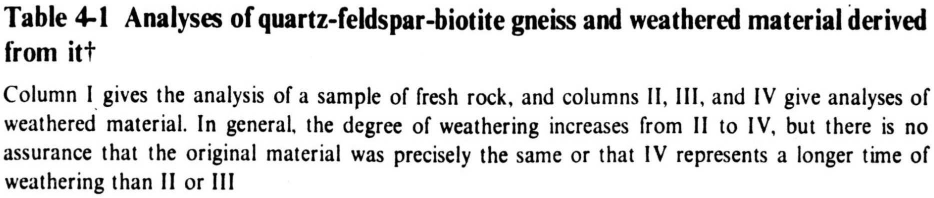
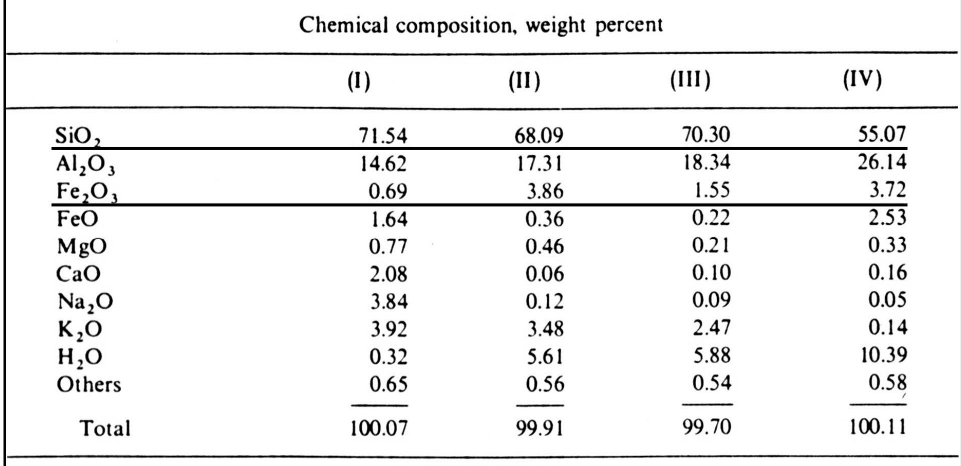


Table 4-1 Analyses of quartz-feldspar-biotite gneiss and weathered material derived from it†

Column I gives the analysis of a sample of fresh rock, and columns II, III, and IV give analyses of weathered material. In general, the degree of weathering increases from II to IV, but there is no assurance that the original material was precisely the same or that IV represents a longer time of weathering than II or III

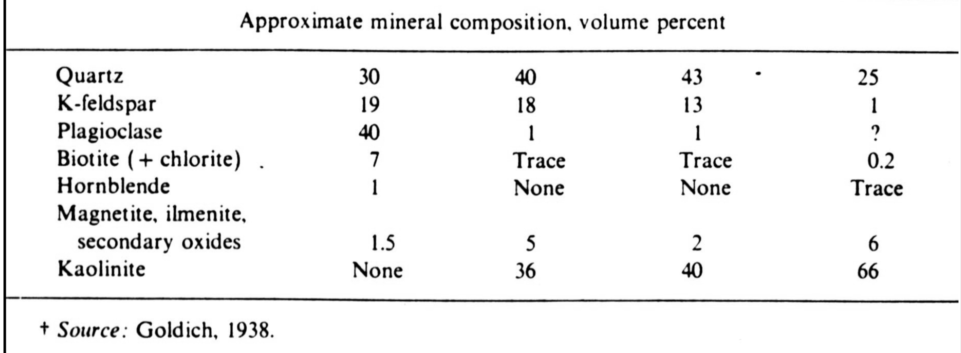
ROCK WEATHERING - 2



Chemical composition, weight percent

	(I)	(II)	(III)	(IV)
SiO_2	71.54	68.09	70.30	55.07
Al_2O_3	14.62	17.31	18.34	26.14
Fe_2O_3	0.69	3.86	1.55	3.72
FeO	1.64	0.36	0.22	2.53
MgO	0.77	0.46	0.21	0.33
CaO	2.08	0.06	0.10	0.16
Na_2O	3.84	0.12	0.09	0.05
K_2O	3.92	3.48	2.47	0.14
H_2O	0.32	5.61	5.88	10.39
Others	0.65	0.56	0.54	0.58
Total	100.07	99.91	99.70	100.11

ROCK WEATHERING - 3



Approximate mineral composition, volume percent

	(I)	(II)	(III)	(IV)
Quartz	30	40	43	25
K-feldspar	19	18	13	1
Plagioclase	40	1	1	?
Biotite (+ chlorite)	7	Trace	Trace	0.2
Hornblende	1	None	None	Trace
Magnetite, ilmenite, secondary oxides	1.5	5	2	6
Kaolinite	None	36	40	66

† *Source:* Goldich, 1938.

CHANGES IN ROCK COMPOSITION

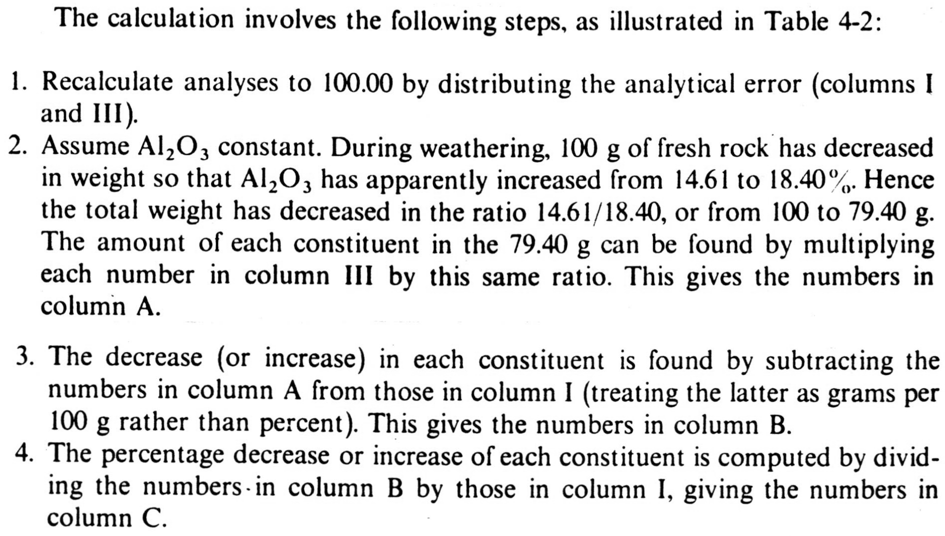
- Expression of conc's as oxides
  - started when it was thought that most forms were oxides
  - still convenient
    - most minerals contain significant amounts of oxygen
    - comp. sums to ≈ 100%

CHANGES IN ROCK COMPOSITION

Use of Al as reference element:

- oxide is very insoluble
- Al_2O_3 shows greatest <u>apparent</u> increase in weathered materials
- of major elements, Al is <u>least</u> abundant in stream & ground waters
- but not absent from these waters

CALCULATION OF LOSSES & GAINS



The calculation involves the following steps, as illustrated in Table 4-2:

1. Recalculate analyses to 100.00 by distributing the analytical error (columns I and III).
2. Assume Al_2O_3 constant. During weathering, 100 g of fresh rock has decreased in weight so that Al_2O_3 has apparently increased from 14.61 to 18.40%. Hence the total weight has decreased in the ratio 14.61/18.40, or from 100 to 79.40 g. The amount of each constituent in the 79.40 g can be found by multiplying each number in column III by this same ratio. This gives the numbers in column A.
3. The decrease (or increase) in each constituent is found by subtracting the numbers in column A from those in column I (treating the latter as grams per 100 g rather than percent). This gives the numbers in column B.
4. The percentage decrease or increase of each constituent is computed by dividing the numbers in column B by those in column I, giving the numbers in column C.

WEATHERING

Al as Al_2O_3 is basis of weathering calculations

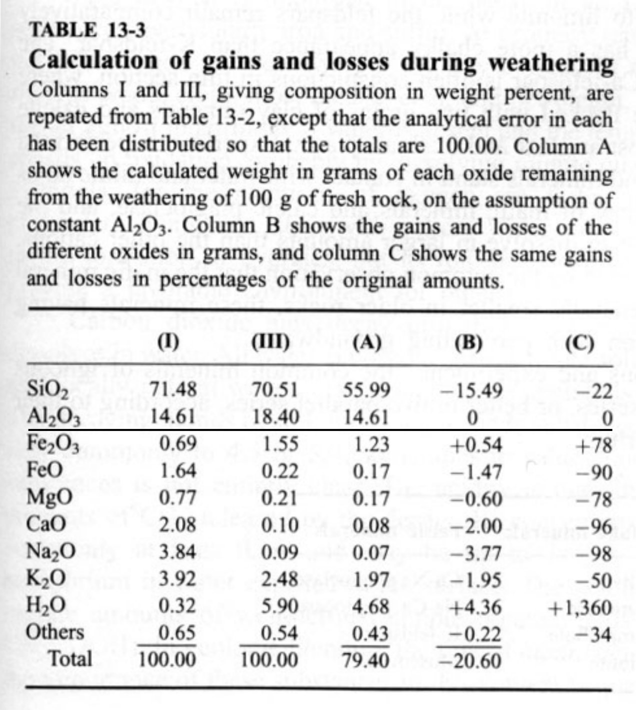


TABLE 13-3

Calculation of gains and losses during weathering

Columns I and III, giving composition in weight percent, are repeated from Table 13-2, except that the analytical error in each has been distributed so that the totals are 100.00. Column A shows the calculated weight in grams of each oxide remaining from the weathering of 100 g of fresh rock, on the assumption of constant Al_2O_3. Column B shows the gains and losses of the different oxides in grams, and column C shows the same gains and losses in percentages of the original amounts.

	(I)	(III)	(A)	(B)	(C)
SiO_2	71.48	70.51	55.99	−15.49	−22
Al_2O_3	14.61	18.40	14.61	0	0
Fe_2O_3	0.69	1.55	1.23	+0.54	+78
FeO	1.64	0.22	0.17	−1.47	−90
MgO	0.77	0.21	0.17	−0.60	−78
CaO	2.08	0.10	0.08	−2.00	−96
Na_2O	3.84	0.09	0.07	−3.77	−98
K_2O	3.92	2.48	1.97	−1.95	−50
H_2O	0.32	5.90	4.68	+4.36	+1,360
Others	0.65	0.54	0.43	−0.22	−34
Total	100.00	100.00	79.40	−20.60	

COMPONENT VARIATION UPON WEATHERING

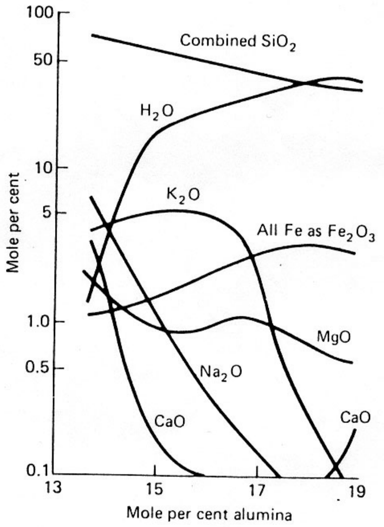


Figure 7–5 Variation diagram for the weathering of the Morton granite gneiss, Minnesota. A logarithmic vertical scale is used to plot mole per cent (weight per cent from chemical analysis divided by molecular weight) for each oxide, and mole per cent of Al_2O_3 is used on the horizontal scale as a measure of the extent of weathering. Combined SiO_2 refers to SiO_2 in silicate minerals other than quartz. Silica from quartz is not plotted. Fresh rock composition is plotted on the left, intermediate soils in the middle, and the final soil at the extreme right.

(from Brownlow)

MINERAL VARIATION UPON WEATHERING

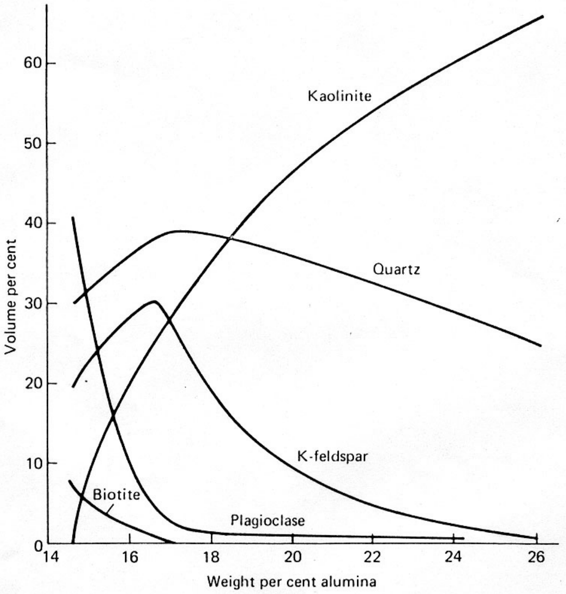
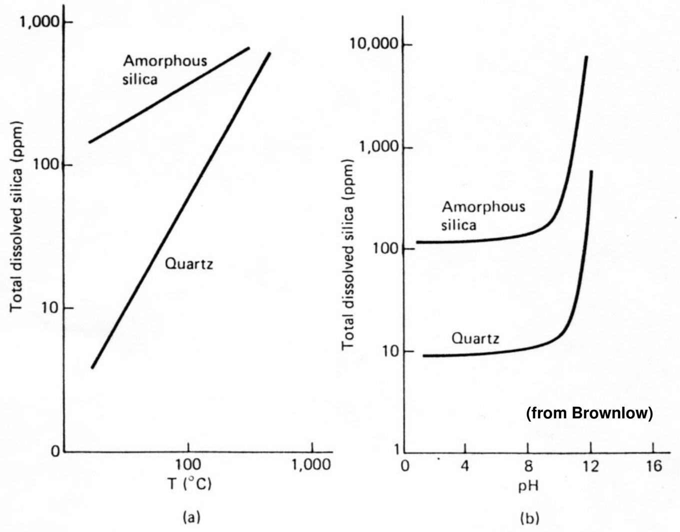


Figure 7–6 Mineral-variation diagram for the weathering of the Morton granite gneiss, Minnesota. Weight per cent Al_2O_3 is used as a measure of the extent of weathering. Mineralogy of the fresh rock is plotted on the left and mineralogy of the final soil at the extreme right.

(from Brownlow)

SOLUBILITY OF SILICA



(from Brownlow)

Figure 7–2 Solubility of silica as a function of temperature and pH: (a) solubility as a function of temperature at pH < 7; (b) solubility as a function of pH at 25°C.

AGENTS OF CHEMICAL WEATHERING

- **Agents:**
  Moisture (H_2O)
  O_2
  CO_2
  Organic acids
- **Types of reactions:**
  - **Solution**
    $NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O$
  - **Hydration**
    $CaSO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O$

CHEMICAL WEATHERING

Types of reactions, cont:

- Carbonate weathering
  key is CO_3^{-2} + H^+ ⇒ HCO_3^{-2} (stable)
- Oxidation
  - Fe and Mn compounds
  - Other sulfides
  - most decomposition reactions occur in steps - many not yet clearly understood

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CHEMICAL WEATHERING -2

Oxidation of pyrite:

<u>Oxidation of S</u>:

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$

<u>Oxidation of Fe</u>:

$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe(SO_4)_3 + 2H_2O$

<u>Hydrolysis of Fe^{+3}</u>:

$Fe(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_{3(s)} + 3H_2SO_4$

CHEMICAL WEATHERING - 3

- Hydrolysis (of silicates)
- Most silicates weather by hydrolysis
- $Mg_2SiO_4 + H_2CO_3 \rightarrow 2Mg^{+2} + 4HCO_3^{-2} + H_4SiO_4$
- Silicic acid is weaker than carbonic acid and is very weakly ionized
- Weathering scheme is very complex due to the presence of several different cations in silicates

CHEMICAL WEATHERING - 4

- Alumino-silicates ⇨ $^{\text{weathering}}$ ⇨ clay minerals
- Hydrolysis of silicates increases basicity of system - OH^- or HCO_3^- ions produced
- Constraint of pH: (keeps pH ≈ 9.0)
- $H_2O + SiO_2\,(qtz) + OH^- \rightarrow H_3SiO_4^- \quad K=10^{0.4}$
- $H_4SiO_4\,(aq) + OH^- \rightarrow H_3SiO_4^- + H_2O \quad K=10^{4.2}$

THE SOIL

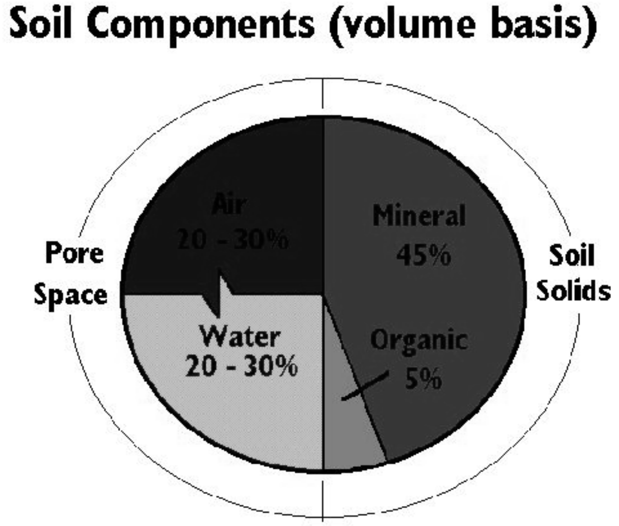
Weathering of the Earth's crust:
    raw materials for soil formation

- Igneous rocks
- Sedimentary rocks
- Metamorphic rocks

Soil has three (four) components:

- Mineral (inorganic)
- Organic matter
- Pore spaces (air & water)

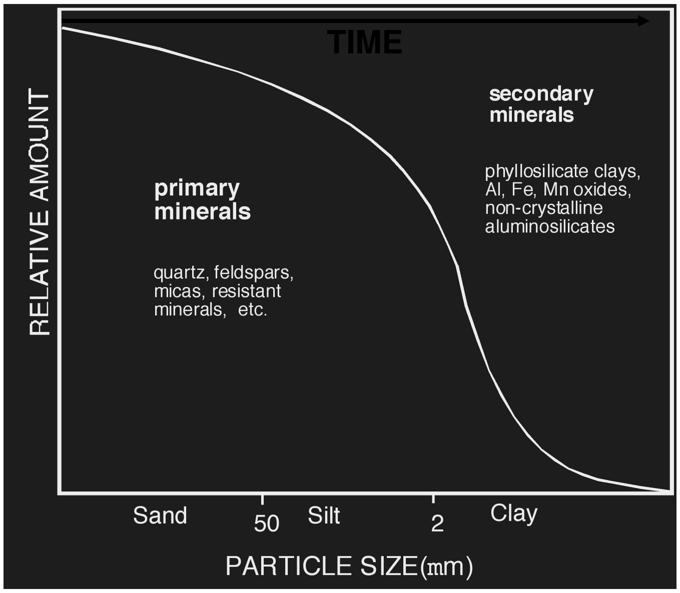
THE SOIL


Soil Components (volume basis)

Soil Composition:
Mineral soil particles

- **Sand - (coarse particles):**
  50 to 2000 micrometers (µm) diameter
- **Silt - (medium sized particles):**
  2 to 50 µm diameter
- **Clay - (fine particles):**
  < 2 µm diameter

RELATIVE ABUNDANCE OF PRIMARY AND SECONDARY MINERALS



SOIL COMPOSITION
Organic Component:

- Living soil organisms
  - Invertebrates
  - Bacteria & Fungi
  - Important function as decomposers
- Plant roots
  - Major portion of soil biomass
- Decomposing organic matter (OM)
  - Food source for soil organisms
- Humus (highly decomposed, colloidal, OM)
  - Most chemically active organic component

SOIL COMPOSITION
Pore Spaces:

- Approximately 50% of soil volume
- Air or water depending upon conditions
- Higher conc of CO_2, H_2O vapor that atmos air
- Importance of O_2 diffusion to roots
- Clay soils:
  - Small pores hold water tightly
  - Air movement is limited
- Sandy Soils:
  - Large pores, rapid water drainage; little remains
  - Free movement of air, gasses

SOIL COMPOSITION:
Soil Water

- Saturation:
  - flooding rain, irrigation

- Field capacity:
  - moisture content when water has drained away due to gravity forces
  - clay soils hold more water than sandy soils

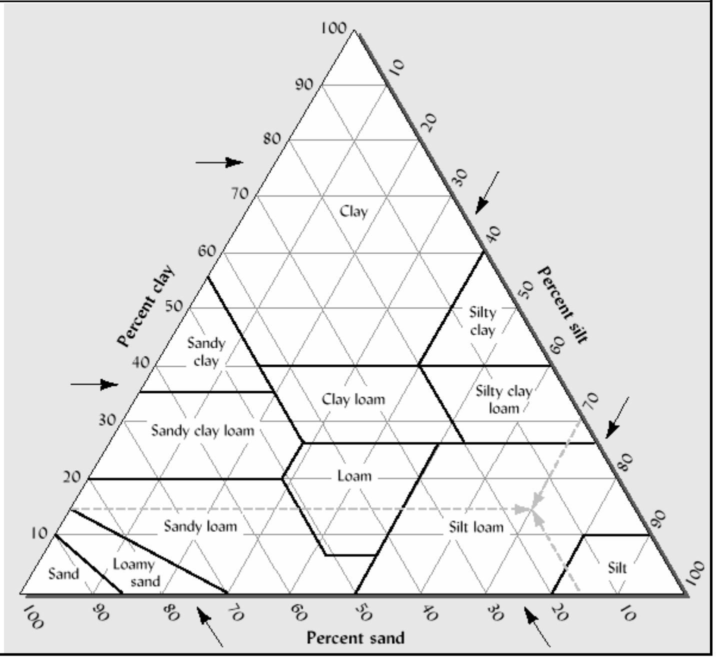
- Permanent wilting point:
  - soil is so dry plants cannot remove remaining water
  - no water movement in soil at this point

IMPORTANT SOIL CHARACTERISTICS

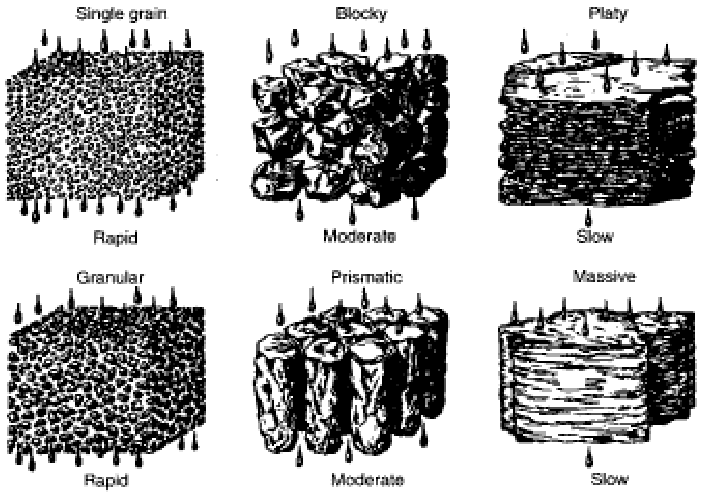
- Soil texture and clay minerals
- Soil structure
- Soil water
- Soil atmosphere
- Soil pH
- Salinity

SOIL TEXTURAL CLASSES

The major soil textural classes are defined by the percentages of sand, silt, and clay according to the heavy boundary lines shown on the textural triangle.



SOIL STRUCTURE AND PERCOLATION OF WATER



IMPORTANT PHYSICO-CHEMICAL PROPERTIES

- Cation sorption and exchange
- Cation replacement order
- Cation adsorption vs desorption
- Ion exchange equation
- Anion adsorption
- Water adsorption
- Soil pH - acid or alkaline - affects ion exchange and soil reactions

FACTORS INFLUENCING SOIL FORMATION

1. Parent materials (geologic or organic precursors to the soil

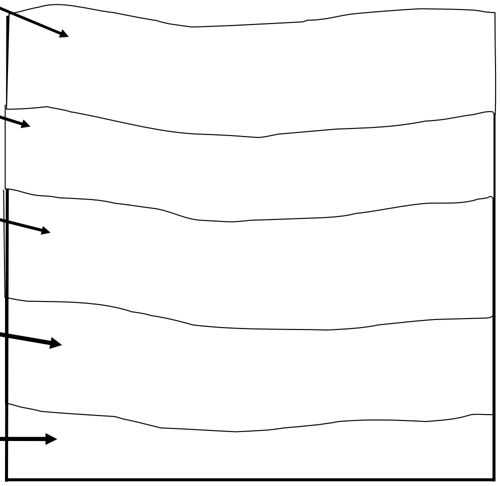
2. Climate (primarily precipitation & temperature)

3. Biota (living organisms, especially native vegetation, microbes, soil animals & humans

4. Topography (slope, aspect & landscape position)

5. Time (the period of time since the parent materials became exposed to soil formation factors)

PRIMARY SOIL HORIZONS



A Horizon
Organic rich
Highest organism
activity

E Horizon
Zone of leaching,
eluviation

B Horizon
Weathered,
Accumulation of
Clays, oxides

C Horizon
Parent Material;
May be multiple
layers

R Horizon
Bedrock
In Hampton Roads:
2000 ft deep

ALLUVIAL SOIL

Note many layers of very different types of parent material

From
Maryland

Note buried A and B Horizons

AGE OF SOIL

- Soil age is based on development of key or "diagnostic" horizons
- Soil age not based on chronologic age
- Immature - few and/or weakly developed horizonation (weathering)
- Mature - maximum (or near) number of horizons with well defined char's and extensive weathering

SOIL CLASSIFICATION

- Pedocal - high amounts of $CaCO_3$ and/or $CaSO_4$ in profile; occur in lowrainfall areas; high soil pH

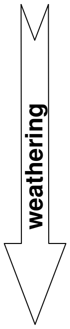
- Pedalfer - high amounts of Fe & Al compounds in profile; extensive profile leaching; low soil pH; > 25 in. annual precip'n

SOIL CLASSIFICATION

USDA Soil Classification - Table 7-4

Soil Orders:

- Entisols
- Inceptisols
- Mollisols
- Alfisols
- Ultisols
- Oxisols



- Vertisols
- Aridisols
- Spodosols
- Histisols
- Andisols

EXTREME SOIL WEATHERING

End products of soil weathering:

- Laterites - contain hematite, goethite, gibbsite, boehmite, rarely diaspore
- ferruginous laterite - mostly hematite & goethite
- aluminous laterite - mostly gibbsite, boehmite & diaspore

CRUSTAL WEATHERING AND CLIMATE

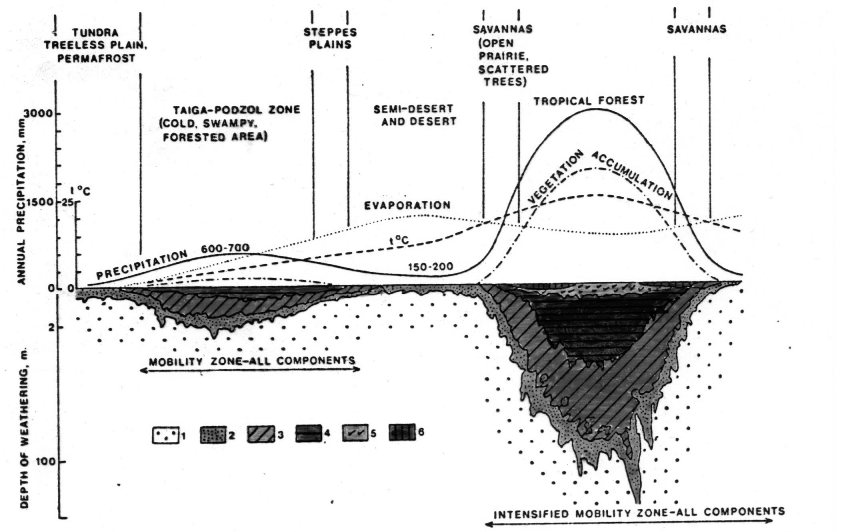


Figure 4-10. Formation of a leached, decomposed weathered crust in tectonically inactive areas: (1) new crust; (2) grus zone, little modified chemically; (3) hydromica-montmorillonite-beidellite zone; (4) kaolinite zone; (5) ochers, Al_2O_3; (6) hard layer $Fe_2O_3-Al_2O_3$; [redacted]

IMPORTANT SOIL PROPERTIES

Many soil properties are important in the field of environmental geochem:

- Mineralogy
- Organic matter content (%OM)
- Cation exchange capacity (CEC)
- Porosity/permeability
- Texture
- pH

QUARTZ SOLUBILITY

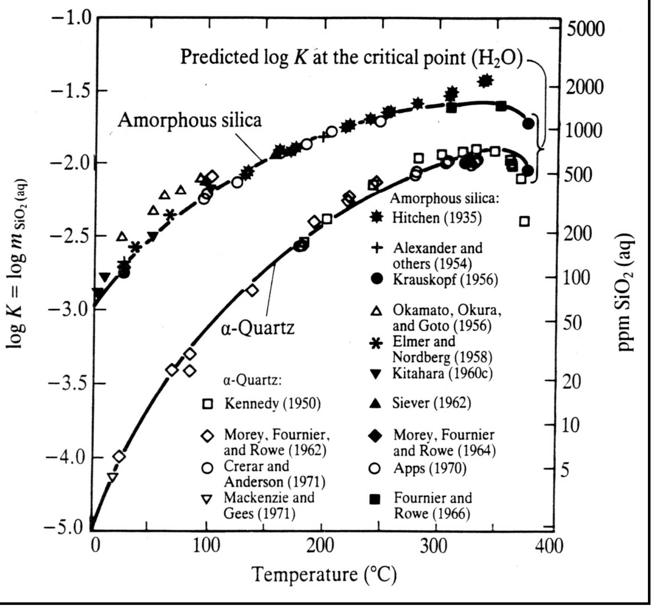
- Silica and the silicates comprise ~90% of earth's crust
- SiO_2 (silica): quartz, amethyst, agate, opal
- Different polymorphs of silica:
  α-quartz, β-quartz, tridymite, cristobalite, stishovite and coesite plus amorphous forms
- Chert is an impure form of microcrystalline α-quartz, often described as chalcedony
- Opal is amorphous silica containing water
- Many studies have been conducted on the aqueous transport of silica
- α-quartz is a very common form and we'll examine prop's

QUARTZ SOLUBILITY - 2

Solubility of α-quartz & amorphous silica

Solubility of two forms are orders of magnitude apart

Note variability of experimental results (symbols)



QUARTZ SOLUBILITY - 3

- The solubility of other forms of other forms of silica falls between these two curves
- At equilibrium, at pH <9:

SiO_2 (quartz) + $2H_2O \leftrightarrows H_4SiO4$

- For nearly pure quartz and H2O,

$K_{4\text{-}1} = a_{H4SiO4} \approx m_{H4SIO4}$ assuming $\gamma_{H4SiO4} = 1$

$K_{4\text{-}1} = \sim 10^{-4}\ m$

H_4SiO_4 is a weak acid

$H_4SiO_4 \leftrightarrows H_3SiO_4^- + H^+$ $K = 10^{-9.9}$

$H_3SiO_4^- \leftrightarrows H_2SiO_4^{-2} + H^+$ $K = 10^{-11.7}$

QUARTZ SOLUBILITY - 4

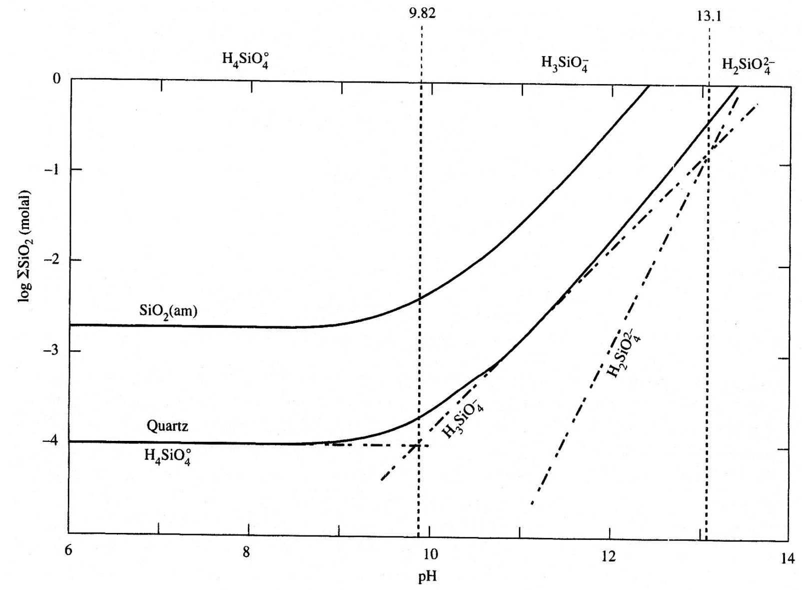
- For total conc of aqueous silica in solution:

$$m_{SiO2(aq)total} = m_{H4SiO4} + m_{H3SiO4-} + m_{H2SiO4-2}$$

$$m_{SiO2(aq)total} = K_{(4\text{-}1)} + K_{(4\text{-}1)}K_{(4\text{-}3)} / m_{H+} + K_{(4\text{-}1)}K_{(4\text{-}3)}K_{(4\text{-}4)} / m^2_{H+}$$

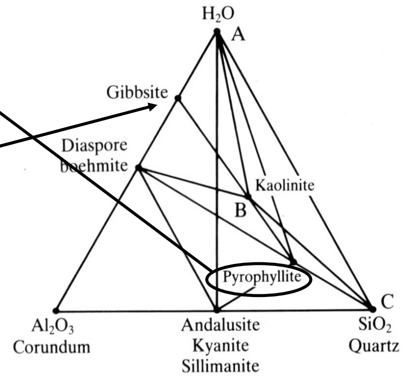
- At $m_{H+} = < 10$ (pH > 9), the two right-hand terms of Eq 4-6 (above) become important
- Note the change in solubility as a function of pH (Fig 7-7)

QUARTZ SOLUBILITY - 5



KAOLINITE SOLUBILITY

- **A clay mineral formed by weathering & hydrothermal alteration of other aluminosilicates, esp feldspars**
- **[$Al_2Si_2O_5(OH)_4$] - generally considered the end member of the phyllosilicates**



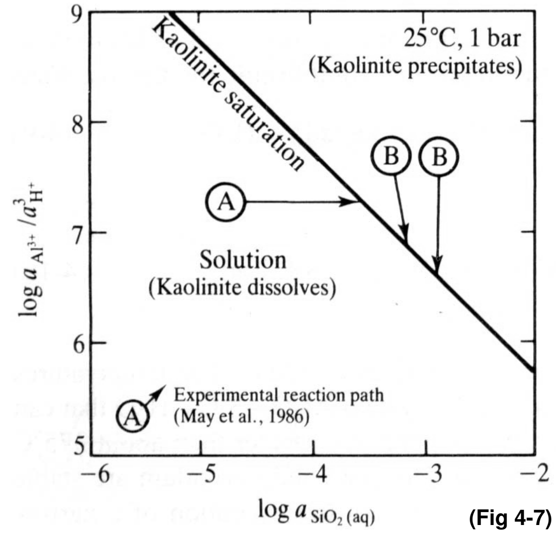
Pyrophyllite – [$Al_2Si_4O_{10}(OH)_2$], "ideal" 1:1 clay with no charge

Gibbsite – [$Al(OH)_3$]

KAOLINITE SOLUBILITY - 2

Points A & B represent changes in solution comp’n over a 1237 day time period.

Note axes units; this is known as an activity-activity diagram.

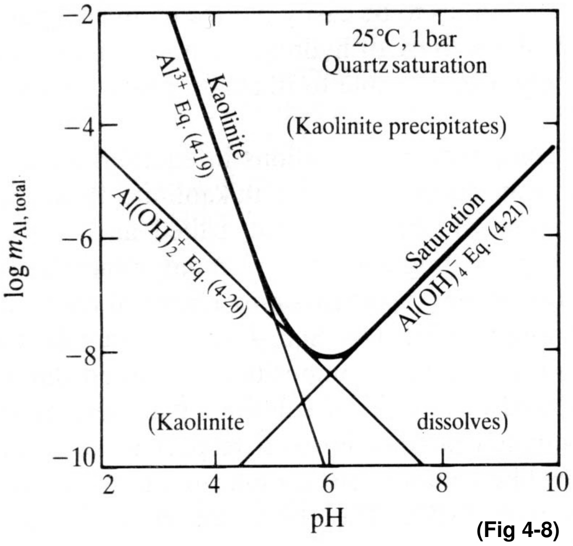


(Fig 4-7)

KAOLINITE SOLUBILITY - 3

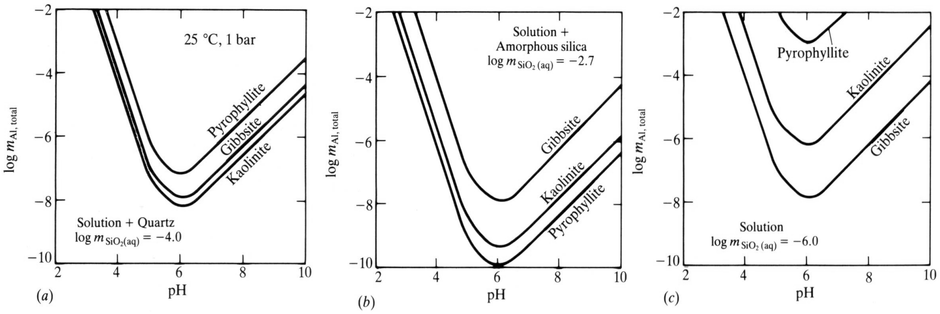
Kaolinite stability relative to Al species & H$^+$

Note shape of curve, pH & $m_{\mathrm{Al+3}}$



(Fig 4-8)

KAOLINITE SOLUBILITY - 4



It is not surprising that the solubility curves for other aluminosilicate & alumino-hydroxy minerals are similar to that of kaolinite

SOLUBILITY OF TWO COMPOUNDS OF Fe

Solubility of Fe compounds is highly variable

Note stability zones for soluble species

Note similarity of curves to those of Al hydroxides