EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Geochemistry on the Earth's surface for analytical geochemists

3c. Weathering processes and soils

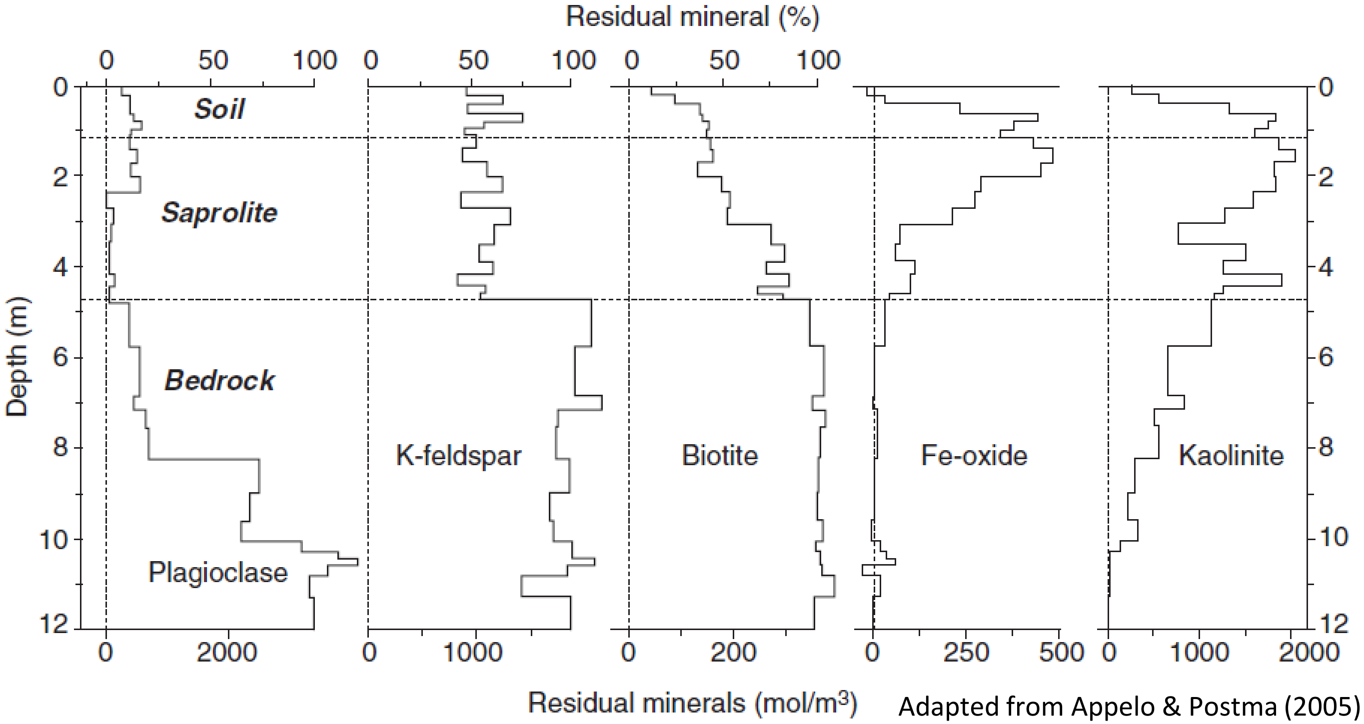
Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Outline

- What is weathering?
- Goldich scheme
- Physical weathering
- Chemical weathering
  - Oxidation
  - Hydrolysis
  - Hydration
  - Dissolution
- Biological weathering
- Congruent and incongruent weathering
- Weathering products (stability diagrams)
- Soils

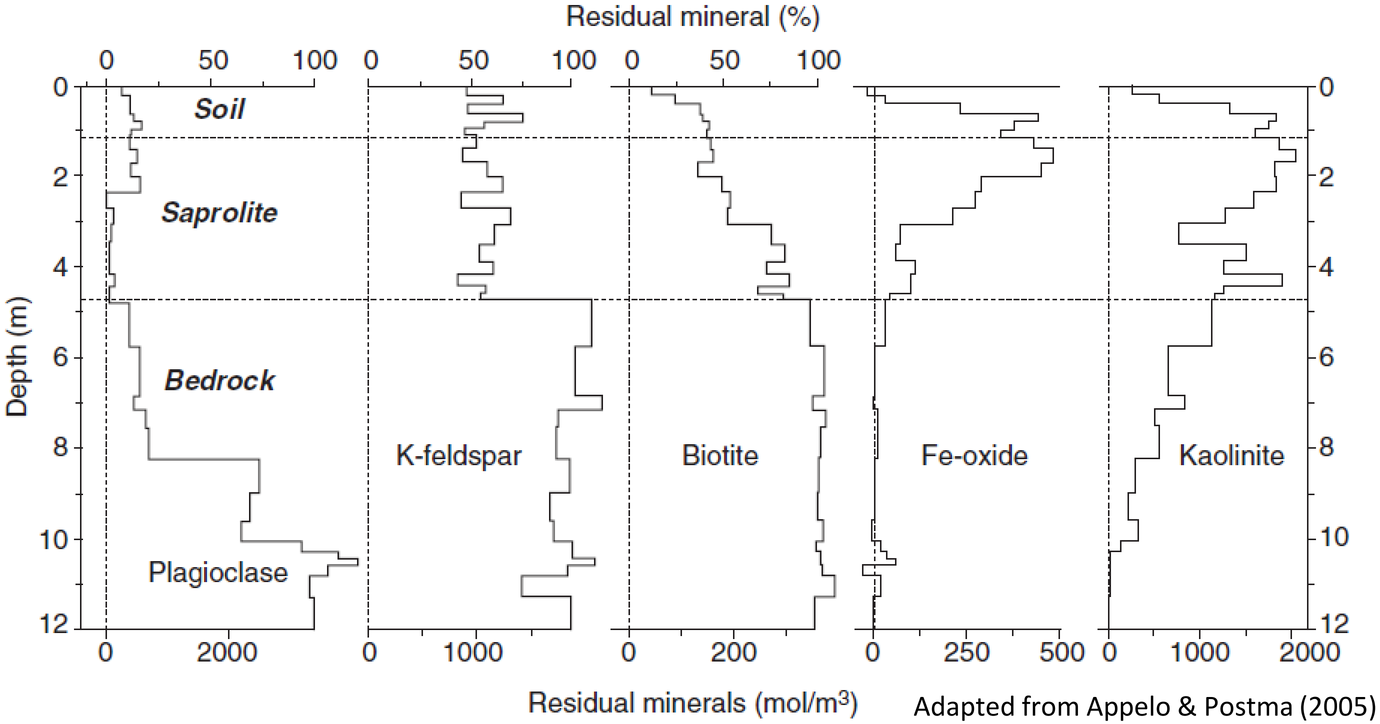
WEATHERING

Soil profile over granodiorite



Adapted from Appelo & Postma (2005)

Soil profile over granodiorite



Adapted from Appelo & Postma (2005)

Which minerals they are least stable?

What happened during weathering with the elements present in the primary minerals ?

Weathering

- The breakdown of rocks and minerals by the action of the atmosphere, water and biota.
- Types of weathering
  - Physical
  - Chemical
  - Biological

Weathering of a sandstone wall in Kokořínsk.

Importance of weathering

Importance of weathering

- Source of substances in water
- Source of nutrients for biota
- Source of mineral raw materials (bauxite)
- Modeling of the Earth's surface
- CO_2 absorption
- Absorption of H^+
- Formation and development of soils
- …

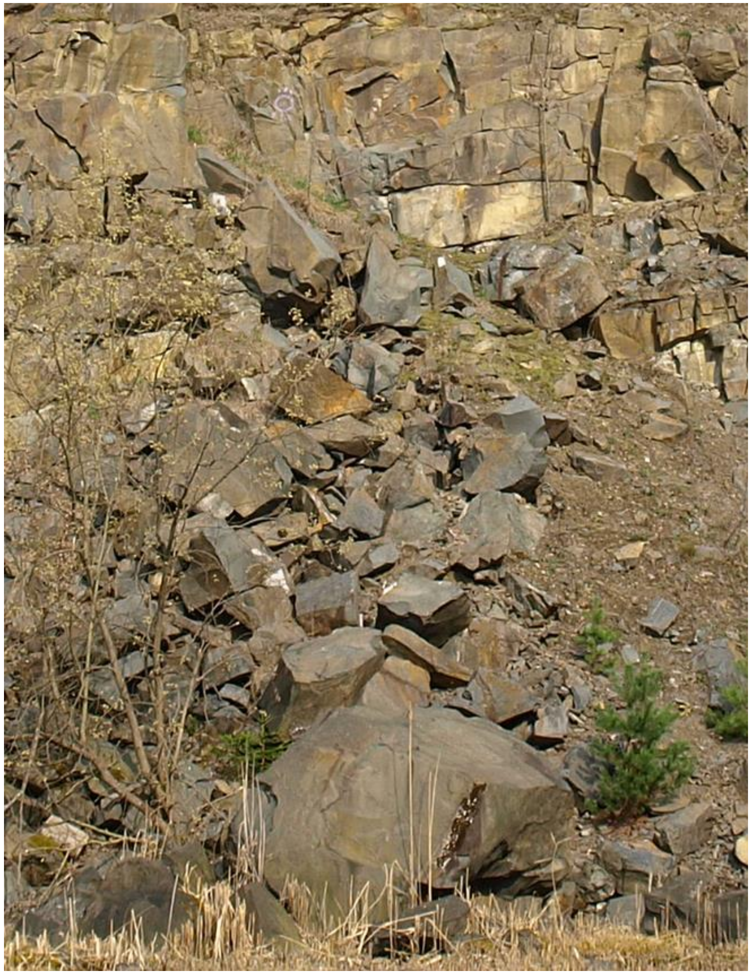
Physical weathering

- Mechanical breaking of rocks into smaller pieces
- Change in shape and size, composition does not change
- Frost weathering
- Plant roots
- Animal digging
- Abrasion, particle impacts, grinding
- Thermal stress
- etc.

Weathering of sandstones in the Broumovsk region

Chemical weathering

- Minerals unstable on the Earth's surface change into secondary minerals
  - Especially clay minerals, hydroxides, oxides, carbonates and sulfates
  - The composition of the resulting minerals is given by
    - Climate
    - Mother rock
    - Soil evolution
    - Biotic factors
    - Topography…
- Three essential phenomena of weathering:
  1. Change of oxidation states of metals
  2. Entry of H^+, OH^- or H_2O into the mineral structure
  3. Dissolution and transport of part of the mineral in solution



Weathering of rock-face in the Drahan Highlands – fresh rocks (dark gray-blue color) are colored brown by a coating of iron oxides.

Thermodynamics

- Olivine under high pressure and temperature:

$$\underset{\substack{\text{forsterite}\\ \text{(olivine)}}}{Mg_2SiO_{4(s)}} + \underset{\text{quartz}}{SiO_2} \rightarrow \underset{\substack{\text{enstatite}\\ \text{(pyroxene)}}}{2\,MgSiO_{3(s)}}$$

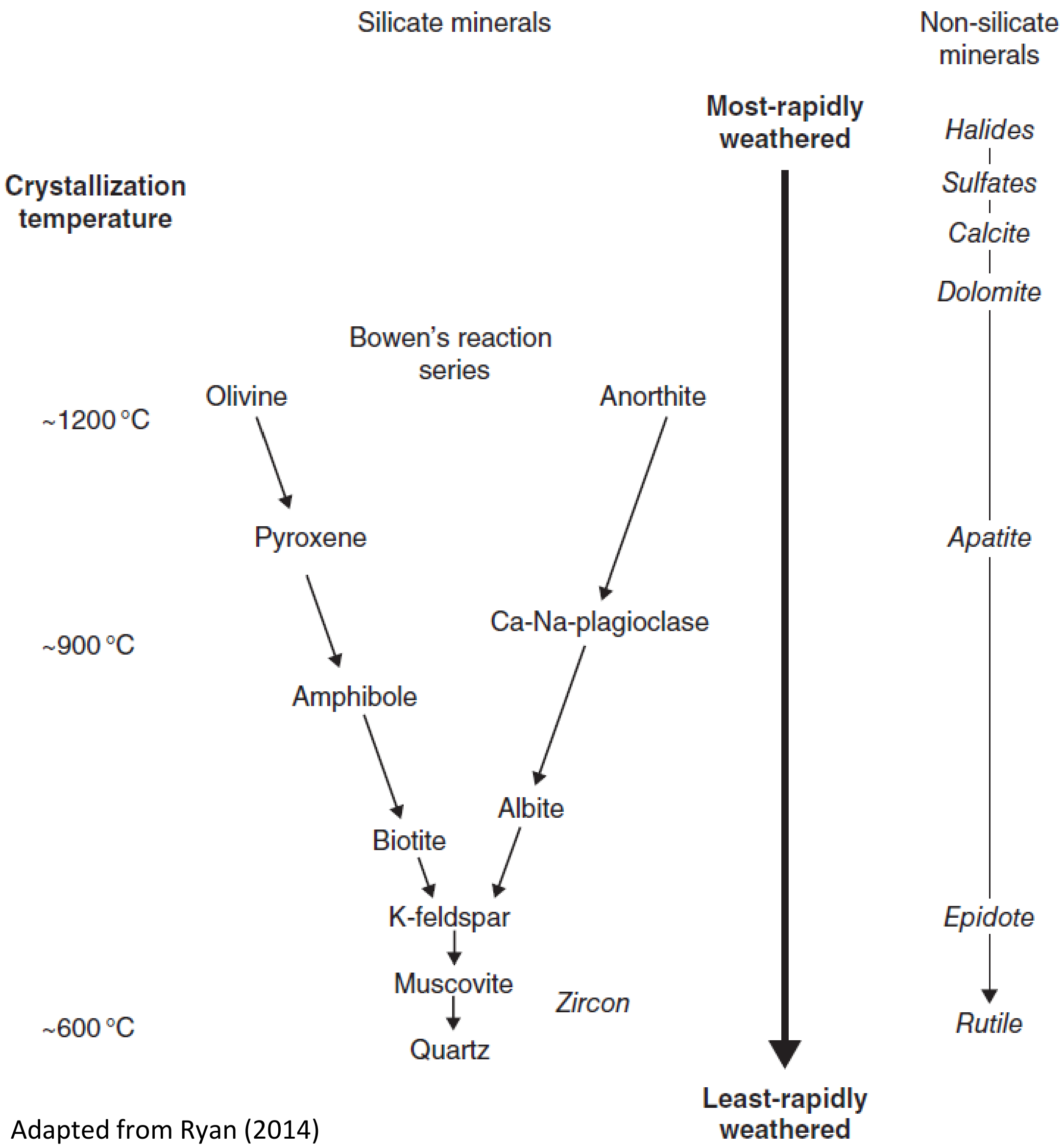
- Olivine under low pressure and temperature

$$Mg_2SiO_{4(s)} + 4H_2CO_{3(aq)} \rightarrow \boxed{2Mg^{+2}{}_{(aq)} + H_4SiO_{4(aq)} + 4HCO_3^-{}_{(aq)}}$$

Soil solutions

- In both cases, a decrease in the overall **Gibbs function**

Goldich scheme



Adapted from Ryan (2014)

- Sequence of rates of progressive mineral weathering
- The opposite of Bowen's diagram of mineral crystallization
- Polymerization of SiO_2 tetrahedra
  - The proportion of ionic bonds
- Resistance to H^+ and H_2O

Chemical weathering

- The presence of water – environment for reactions
- The fundamental influence of the atmosphere
  - Dissolving gases in water (open/closed system)
- Binding on the ground
- The great importance of an acidic environment
  - Especially atmospheric CO_2
  - H^+ is small and easily diffuses into the structure

Congruent dissolution

- Congruent weathering
  - Complete dissolution of the mineral into solution
  - The composition of the solution fully reflects the composition of the mineral

$$Mg_2SiO_{4(s)} + 4H_2CO_{3(aq)} \rightarrow 2Mg^{+2}{}_{(aq)} + H_4SiO_{4(aq)} + 4HCO_3^-{}_{(aq)}$$

- Incongruent weathering
  - Secondary minerals are formed during weathering
  - Therefore, the composition of the solution does not reflect the complete composition of the original rock

$$Fe_2SiO_4 + \frac{1}{2}O_2 + 2H_2O \rightarrow Fe_2O_3 + H_4SiO_4$$

Types of chemical weathering

- Oxidation
- Hydrolysis
- Hydration
- Dissolution

Oxidation

- Increase in oxidation number of cations (loss of e^{-})
- In minerals, usually the reaction of Fe^{2+} or S^{2-} with oxygen

$$\mathrm{Fe_2SiO_4} + \frac{1}{2}\mathrm{O_2} + 2\mathrm{H_2O} \rightarrow \mathrm{Fe_2O_3} + \mathrm{H_4SiO_4}$$

- In some environments, **reduction**
- $2Fe_2O_3$ (Hematite) - O_2 -> 4FeO (iron oxide)

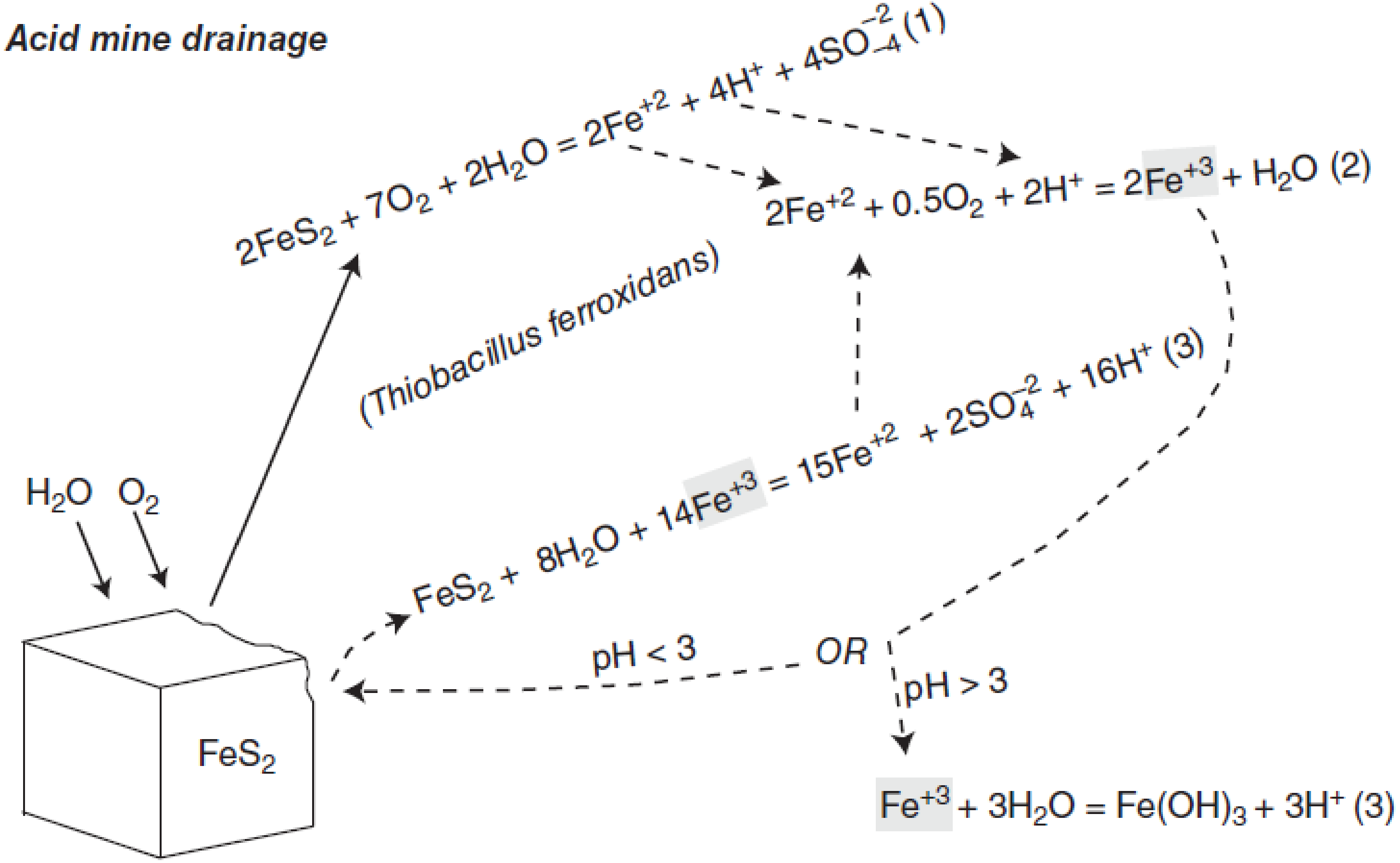
Acid mine waters

$$\mathrm{2FeS_{2(l)} + 2H_2O_{(l)} + 7O_{2(g)} \rightarrow 2Fe^{+2}{}_{(aq)} + 4H^{+}{}_{(aq)} + 4SO_4^{-2}{}_{(aq)}}$$

$$\mathrm{Fe^{+2}{}_{(aq)} + 2H_2O_{(l)} \rightarrow FeOOH_{(s)} + 3H^{+}{}_{(aq)}} + e^{-}$$

- The oxidation of pyrite is partly anomalous in terms of weathering processes – it releases H^+ and the pH decreases
  - Acid mine waters - min. 5% pyrite in the rock
  - Carbonates and silicates no longer buffer
  - $^{-}$ energy
  - Environmental problem

Acid mine waters



Acid mine drainage

$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{+2} + 4H^+ + 4SO_4^{-2}$ (1)

$2Fe^{+2} + 0.5O_2 + 2H^+ = 2Fe^{+3} + H_2O$ (2)

(*Thiobacillus ferroxidans*)

$FeS_2 + 8H_2O + 14Fe^{+3} = 15Fe^{+2} + 2SO_4^{-2} + 16H^+$ (3)

$Fe^{+3} + 3H_2O = Fe(OH)_3 + 3H^+$ (3)

Adapted from Ryan (2014)

Hydrolysis

$$\underset{\text{K-feldspar}}{2KAlSi_3O_{8(s)}} + \underset{\text{carbonic acid}}{2H_2CO_{3(aq)}} + 9H_2O_{(l)}$$

$$\rightarrow \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_{4(s)}} + 2K^{+}{}_{(aq)}$$

$$+ \underset{\text{dissolved silica}}{4H_4SiO_{4(aq)}} + \underset{\text{bicarbonate}}{2HCO_3^{-}{}_{(aq)}}$$

- Cations in the mineral are replaced by H $^+$
  - Dissolution or formation of secondary
- Monovalent ions are not replaced
- Smaller ions before larger ones

Hydration

$$Fe_2O_{3(s)} + H_2O_{(l)} \rightarrow 2FeOOH_{(s)}$$

- Involvement of H_2O molecules in the structure
  - a new structure is created
  - and OH^- or H^+
- Unlike hydrolysis, all water is involved
- Volume increase - rock deformation
- Especially the surface of minerals
- Hydrated minerals dissolve better in water

Dissolution

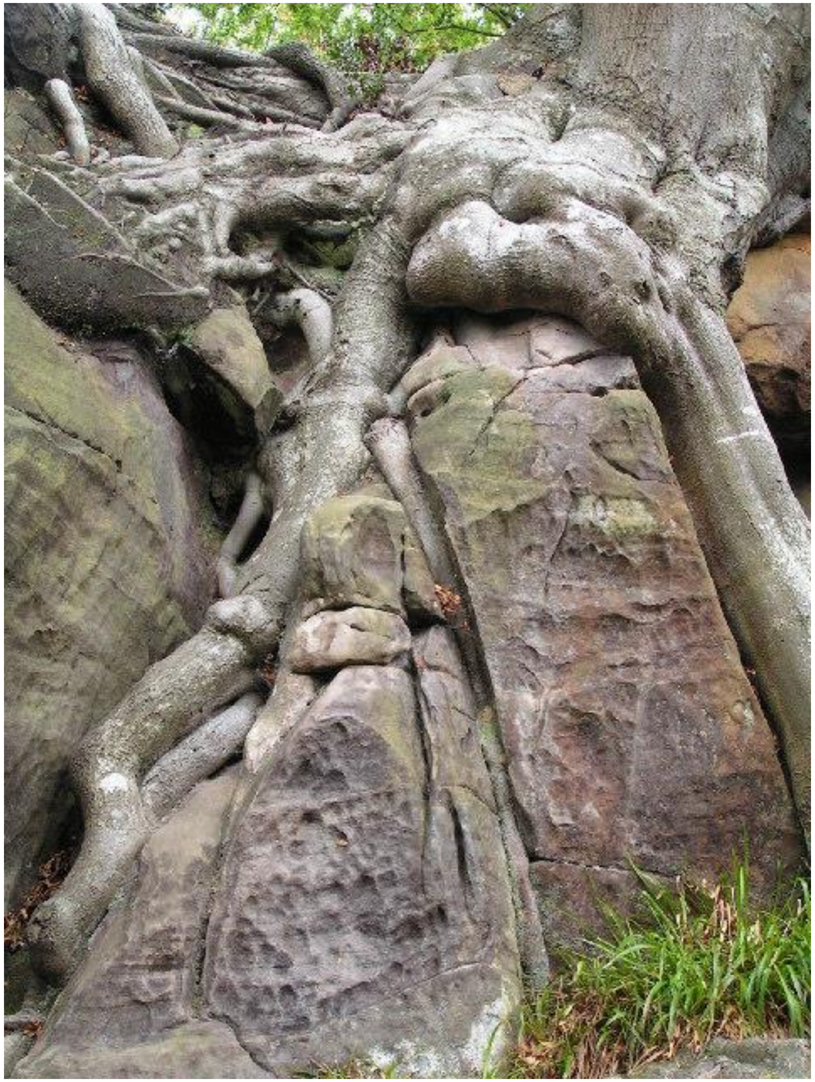
- Especially minerals with ionic bonding
- Decomposition into ions in the presence of water
  - Covalent bonds in water and in anion and cation of a mineral are stronger than between anion and cation

$$\mathrm{CaCO_3(s)} = \mathrm{CO_3^{2-}} + \mathrm{Ca^{2+}}$$

- The CO covalent bond is preserved in solution

Biological weathering

- Physical
  - Rock erosion
  - Mixing
- Chemical
  - Release of organic acids
  - Cation exchange
  - Catalysis of decomposition processes
  - Soil moisture

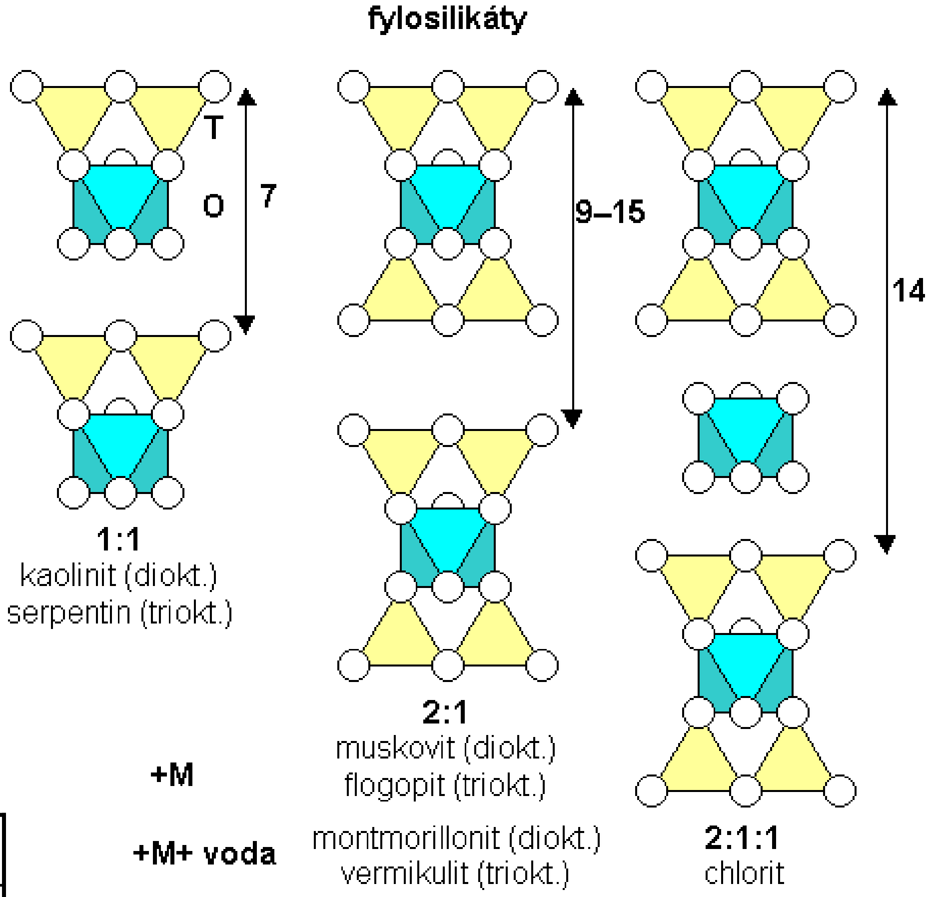


From Nigel Chadwick , CC BY-SA 2.0,
https://commons.wikimedia.org/w/index.php?curid=9149572

Weathering products

- The weathering of rock-forming minerals mainly produces **clay minerals**

  .
  - Phyllosilicates
  - Alternation of octahedral and tetrahedral layers
  - substitution of Al^{3+} for Si^{4+} creates a charge imbalance balanced by the entry of cations



Group	**General formula**
Smectite	$_{\mathrm{Al2\ (}}\mathrm{OH\ )\ 2Si40}_{10\ \_}$ –
Illit	$K_{0-2}Al_4(Si_{8-6}Al_{0-2})O_{20}(OH)_4$
Ka o linit	Al2Si205

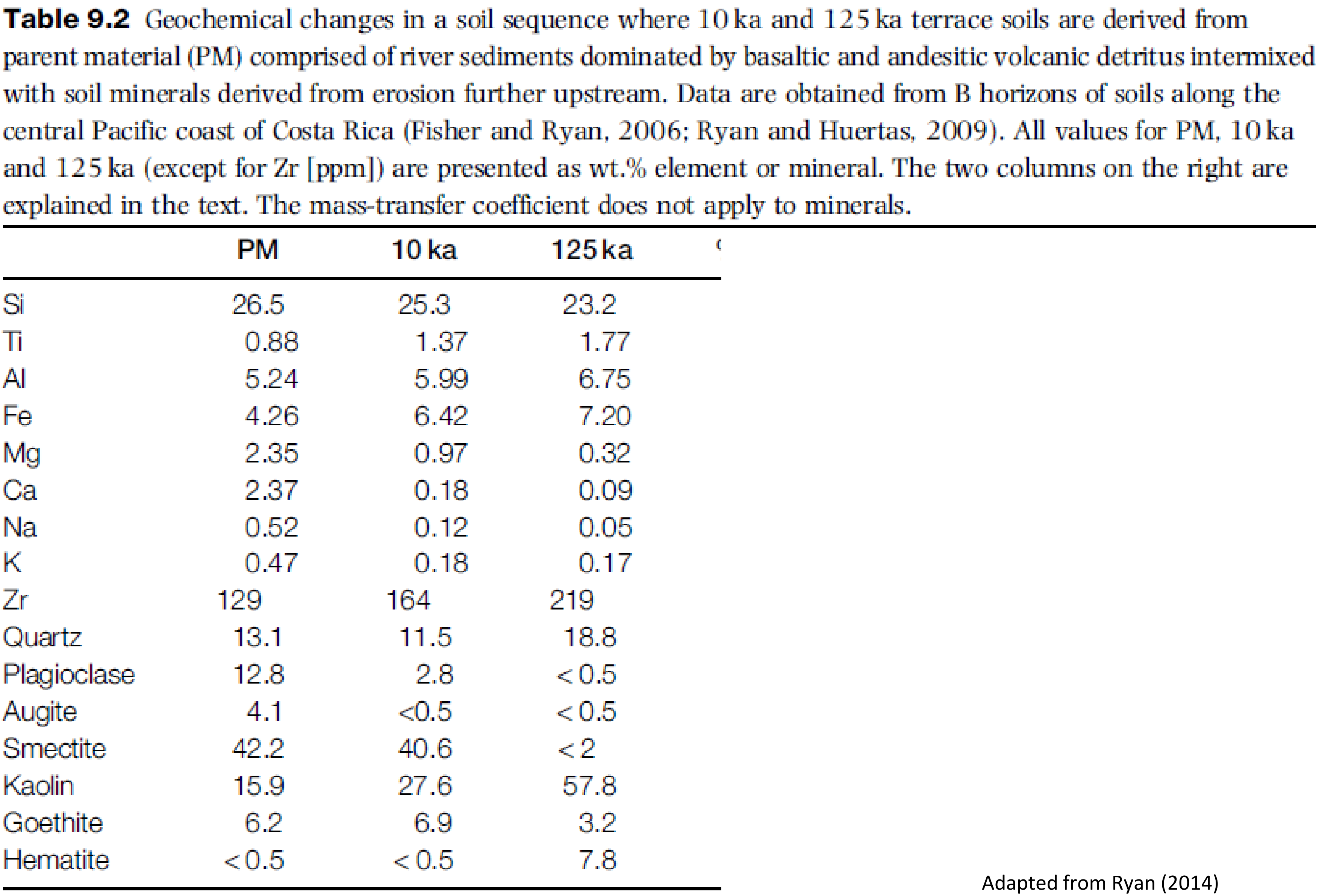


Table 9.2 Geochemical changes in a soil sequence where 10 ka and 125 ka terrace soils are derived from parent material (PM) comprised of river sediments dominated by basaltic and andesitic volcanic detritus intermixed with soil minerals derived from erosion further upstream. Data are obtained from B horizons of soils along the central Pacific coast of Costa Rica (Fisher and Ryan, 2006; Ryan and Huertas, 2009). All values for PM, 10 ka and 125 ka (except for Zr [ppm]) are presented as wt.% element or mineral. The two columns on the right are explained in the text. The mass-transfer coefficient does not apply to minerals.

	PM	10 ka	125 ka
Si	26.5	25.3	23.2
Ti	0.88	1.37	1.77
Al	5.24	5.99	6.75
Fe	4.26	6.42	7.20
Mg	2.35	0.97	0.32
Ca	2.37	0.18	0.09
Na	0.52	0.12	0.05
K	0.47	0.18	0.17
Zr	129	164	219
Quartz	13.1	11.5	18.8
Plagioclase	12.8	2.8	< 0.5
Augite	4.1	<0.5	< 0.5
Smectite	42.2	40.6	< 2
Kaolin	15.9	27.6	57.8
Goethite	6.2	6.9	3.2
Hematite	< 0.5	< 0.5	7.8

Adapted from Ryan (2014)

Soils on the river terrace are formed by the weathering of volcanic detritus.

1. Express the change in element and mineral content in %.
2. Based on the change in element content, sort them by mobility.

What determines weathering processes?

$$3\mathrm{Na(AlSi_3)O_8} + \mathrm{Mg^{2+}} + 4\mathrm{H_2O} \rightarrow 2\mathrm{Na_{0.5}(Al_{1.5}Mg_{0.5})Si_4O_{10}(OH)_2} + 2\mathrm{Na^+} + \mathrm{H_4SiO_4}$$

albite *montmorillonite*

$$2\mathrm{Na(AlSi_3)O_8} + 2\mathrm{H^+} + 9\mathrm{H_2O} \rightarrow \mathrm{Al_2Si_2O_5(OH)_4} + 2\mathrm{Na^+} + 4\mathrm{H_4SiO_4}$$

albite *kaolinite*

$$\mathrm{Na(AlSi_3)O_8} + \mathrm{H^+} + 7\mathrm{H_2O} \rightarrow \mathrm{Al(OH)_3} + \mathrm{Na^+} + 3\mathrm{H_4SiO_4}$$

albite *gibbsite*

Adapted from Appelo & Postma (2005)

What determines whether it weathers to montmorillonite, kaolinite, or gibbsite ?

What determines weathering processes?

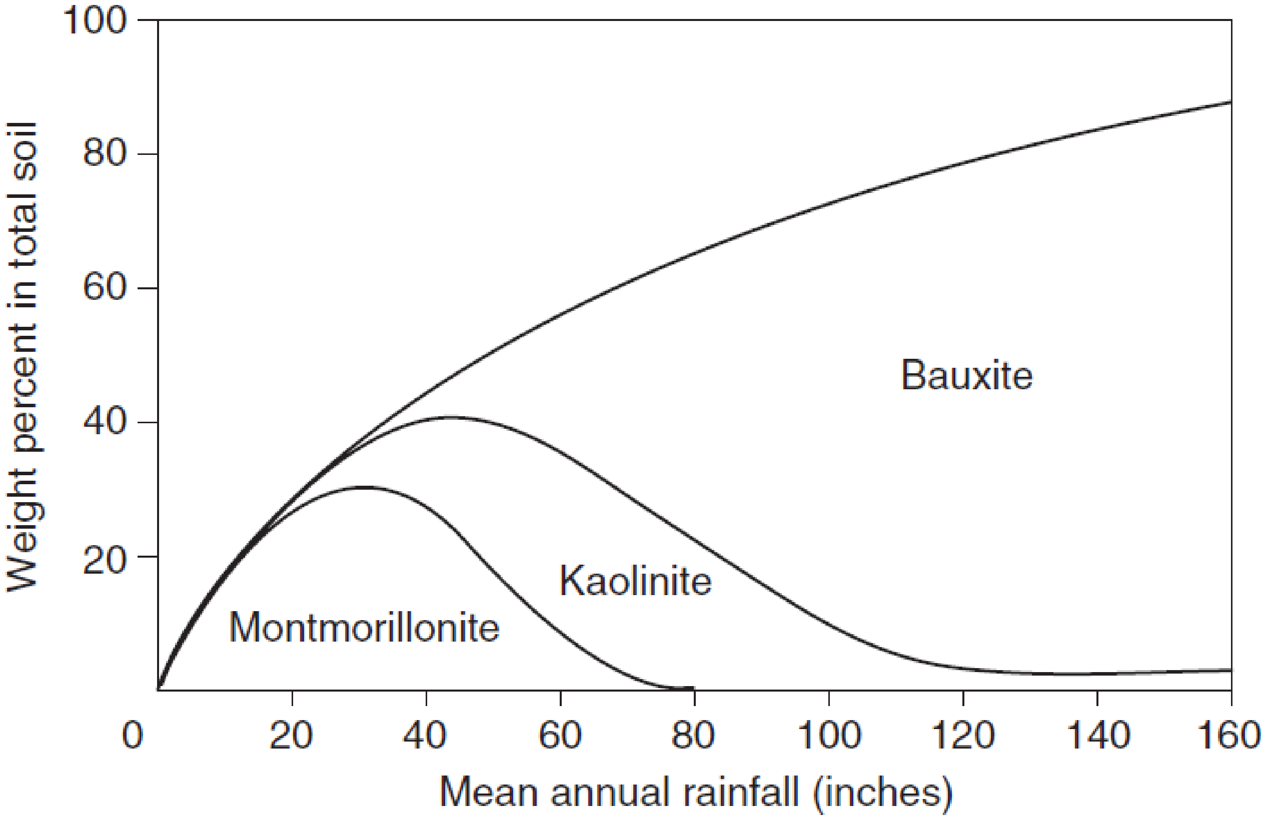


Figure 8.4. Weathering products on volcanic rocks on the island of Hawaii as a function of mean annual rainfall. Bauxite corresponds to Al-hydroxides and the contents of different minerals are plotted cumulatively as weight percent of the total soil (Berner, 1971).

Adapted from Appelo & Postma (2005)

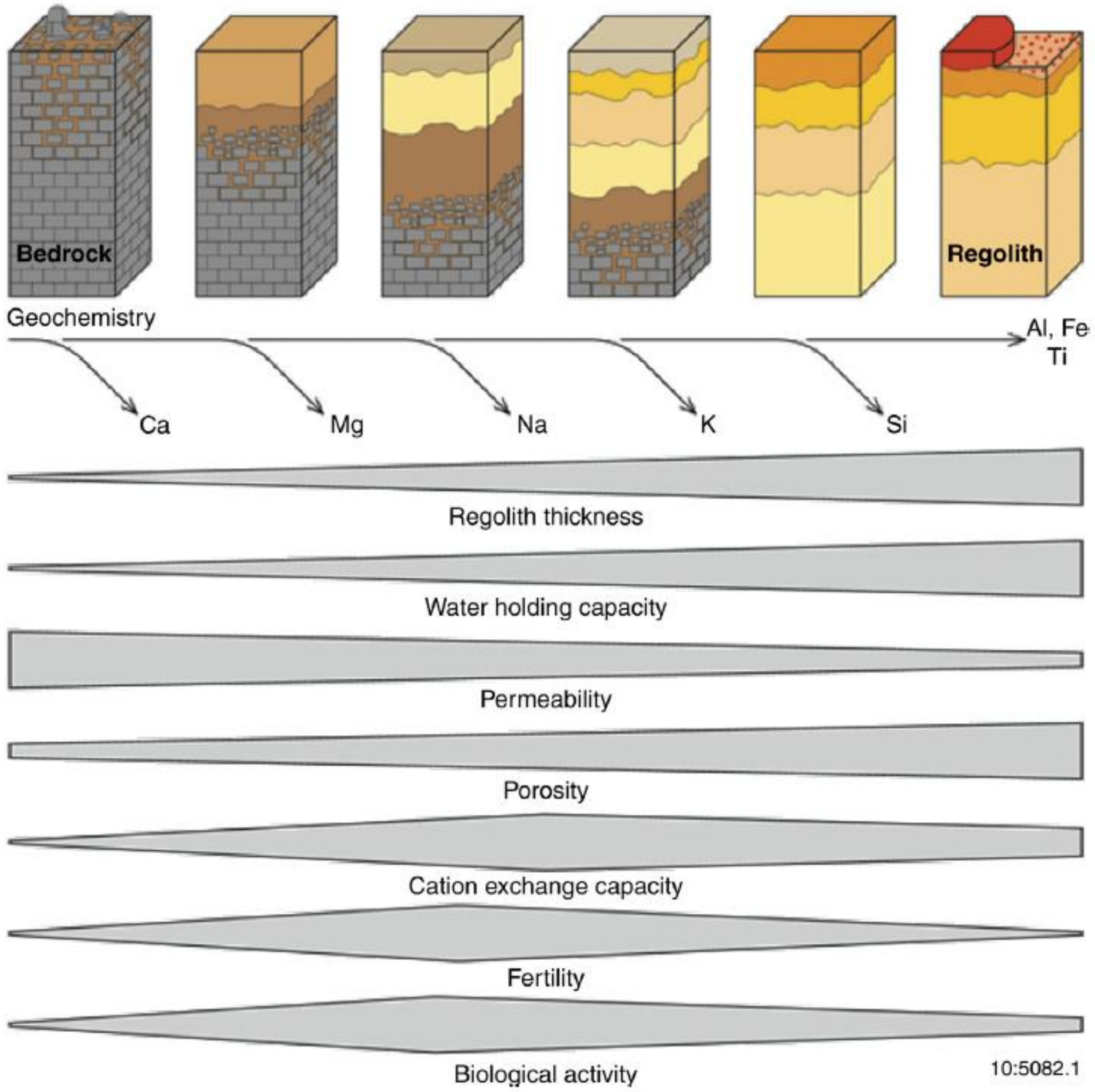


FIGURE 4.6 **Evolution of an idealized regolith profile.** *(From Wilford (2011b), weathering intensity map of the Australian continent. AusGeo News 101, March 2011.)*

Adapted from Giardino & Hauser (20 1 5)

Chemical change index

- CIA – chemical index change
- An effort to quantify weathering
- A number of other indexes

$$\mathrm{CAI} = 100 * \mathrm{Al_2O_3} \div (\mathrm{Al_2O_3} + \mathrm{CaO} + \mathrm{Na_2O} + \mathrm{K_2O})$$

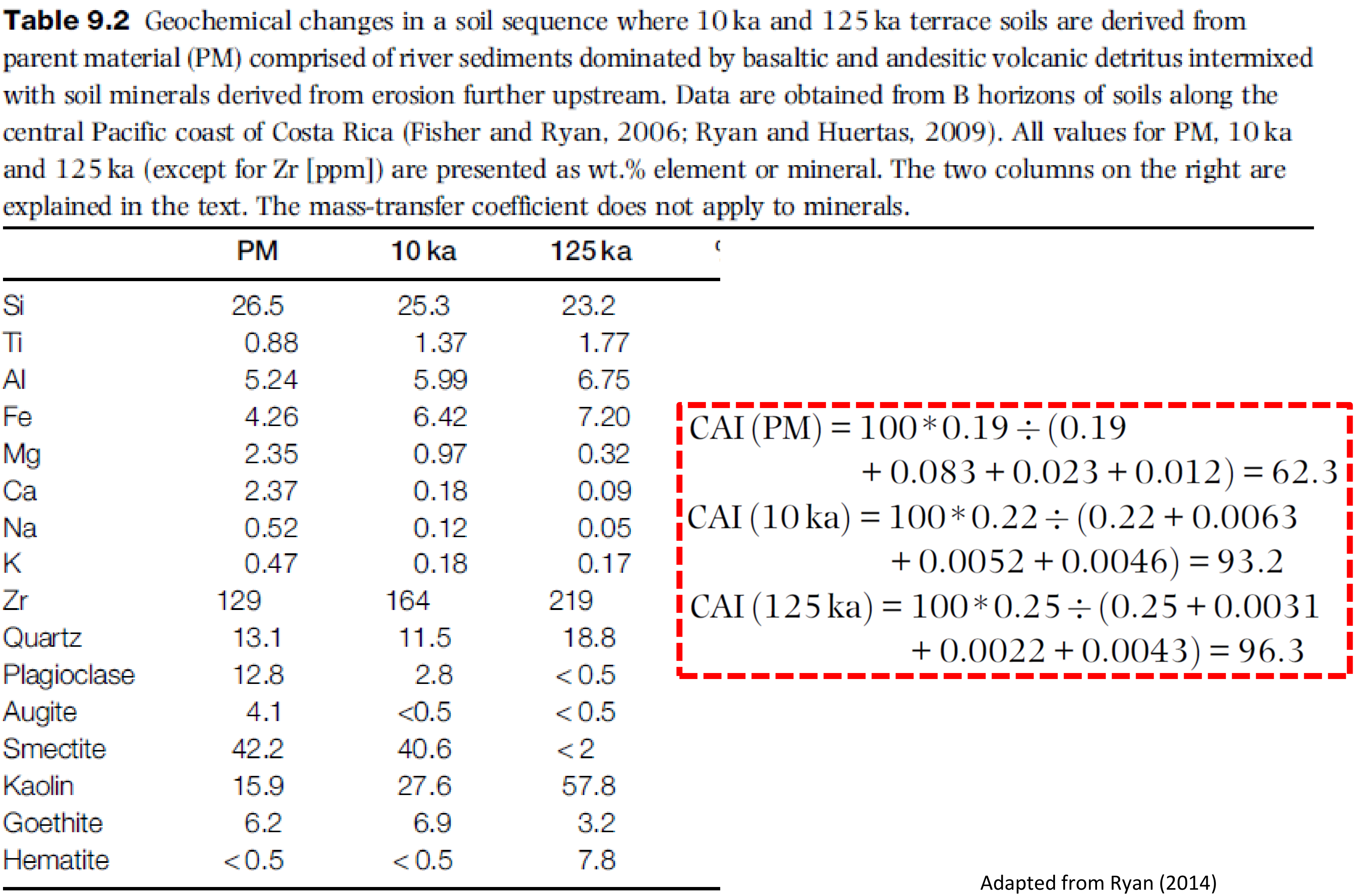


Table 9.2 Geochemical changes in a soil sequence where 10 ka and 125 ka terrace soils are derived from parent material (PM) comprised of river sediments dominated by basaltic and andesitic volcanic detritus intermixed with soil minerals derived from erosion further upstream. Data are obtained from B horizons of soils along the central Pacific coast of Costa Rica (Fisher and Ryan, 2006; Ryan and Huertas, 2009). All values for PM, 10 ka and 125 ka (except for Zr [ppm]) are presented as wt.% element or mineral. The two columns on the right are explained in the text. The mass-transfer coefficient does not apply to minerals.

	PM	10 ka	125 ka
Si	26.5	25.3	23.2
Ti	0.88	1.37	1.77
Al	5.24	5.99	6.75
Fe	4.26	6.42	7.20
Mg	2.35	0.97	0.32
Ca	2.37	0.18	0.09
Na	0.52	0.12	0.05
K	0.47	0.18	0.17
Zr	129	164	219
Quartz	13.1	11.5	18.8
Plagioclase	12.8	2.8	< 0.5
Augite	4.1	<0.5	< 0.5
Smectite	42.2	40.6	< 2
Kaolin	15.9	27.6	57.8
Goethite	6.2	6.9	3.2
Hematite	< 0.5	< 0.5	7.8

$$\text{CAI (PM)} = 100 * 0.19 \div (0.19 + 0.083 + 0.023 + 0.012) = 62.3$$

$$\text{CAI (10 ka)} = 100 * 0.22 \div (0.22 + 0.0063 + 0.0052 + 0.0046) = 93.2$$

$$\text{CAI (125 ka)} = 100 * 0.25 \div (0.25 + 0.0031 + 0.0022 + 0.0043) = 96.3$$

Adapted from Ryan (2014)

Soils on the river terrace are formed by the weathering of volcanic detritus.

1. Express the change in element and mineral content in %.
2. Based on the change in element content, sort them by mobility.

Weathering rate

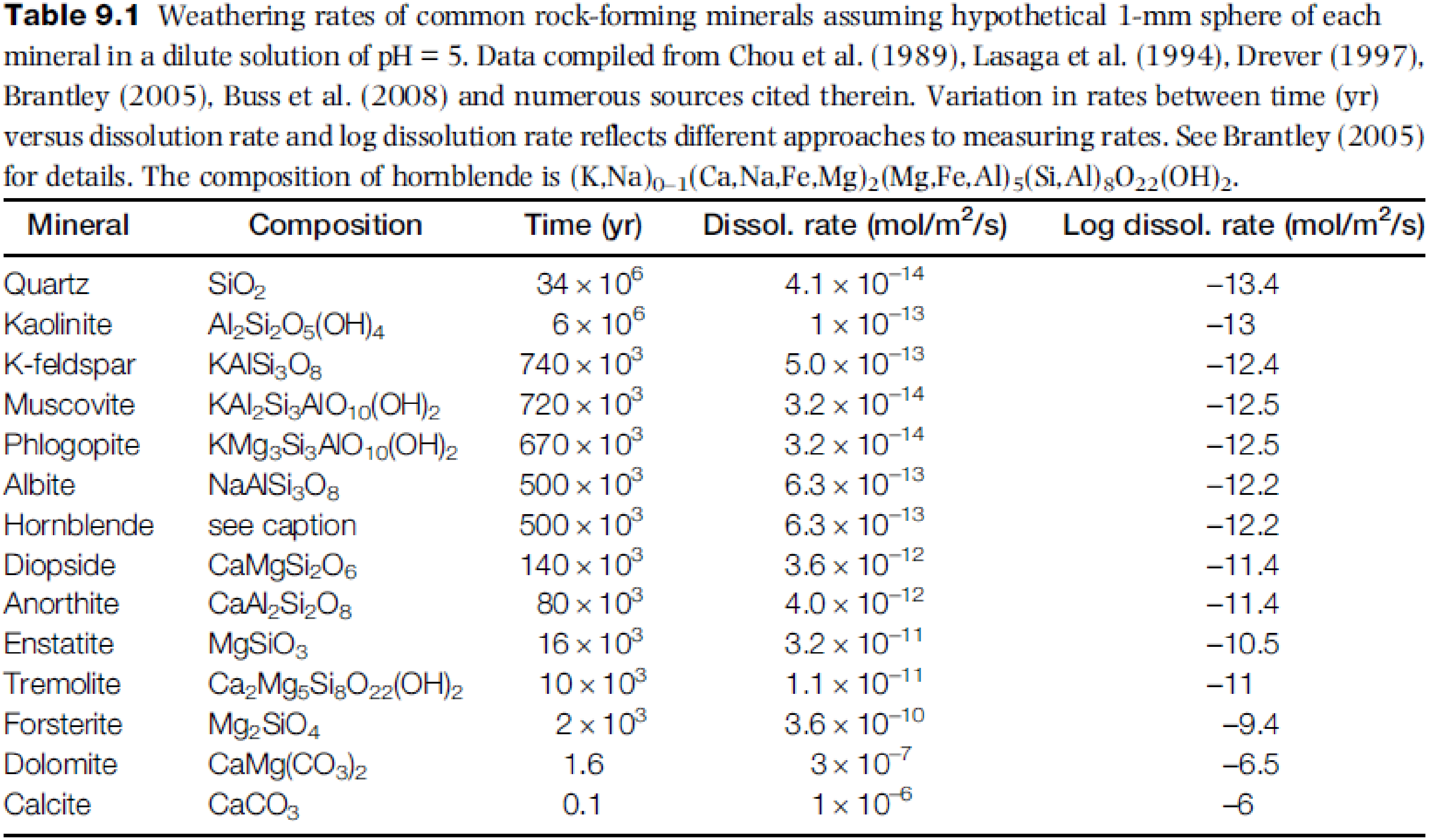


Table 9.1 Weathering rates of common rock-forming minerals assuming hypothetical 1-mm sphere of each mineral in a dilute solution of pH = 5. Data compiled from Chou et al. (1989), Lasaga et al. (1994), Drever (1997), Brantley (2005), Buss et al. (2008) and numerous sources cited therein. Variation in rates between time (yr) versus dissolution rate and log dissolution rate reflects different approaches to measuring rates. See Brantley (2005) for details. The composition of hornblende is $(K,Na)_{0-1}(Ca,Na,Fe,Mg)_2(Mg,Fe,Al)_5(Si,Al)_8O_{22}(OH)_2$.

Mineral	Composition	Time (yr)	Dissol. rate (mol/m^2/s)	Log dissol. rate (mol/m^2/s)
Quartz	SiO_2	34×10^6	4.1×10^{-14}	–13.4
Kaolinite	$Al_2Si_2O_5(OH)_4$	6×10^6	1×10^{-13}	–13
K-feldspar	$KAlSi_3O_8$	740×10^3	5.0×10^{-13}	–12.4
Muscovite	$KAl_2Si_3AlO_{10}(OH)_2$	720×10^3	3.2×10^{-14}	–12.5
Phlogopite	$KMg_3Si_3AlO_{10}(OH)_2$	670×10^3	3.2×10^{-14}	–12.5
Albite	$NaAlSi_3O_8$	500×10^3	6.3×10^{-13}	–12.2
Hornblende	see caption	500×10^3	6.3×10^{-13}	–12.2
Diopside	$CaMgSi_2O_6$	140×10^3	3.6×10^{-12}	–11.4
Anorthite	$CaAl_2Si_2O_8$	80×10^3	4.0×10^{-12}	–11.4
Enstatite	$MgSiO_3$	16×10^3	3.2×10^{-11}	–10.5
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	10×10^3	1.1×10^{-11}	–11
Forsterite	Mg_2SiO_4	2×10^3	3.6×10^{-10}	–9.4
Dolomite	$CaMg(CO_3)_2$	1.6	3×10^{-7}	–6.5
Calcite	$CaCO_3$	0.1	1×10^{-6}	–6

Adapted from Ryan (2014)

Stability diagram

- For certain conditions, specific minerals will be stable
- Thermodynamics matters
- Diagrams help assess the developmer

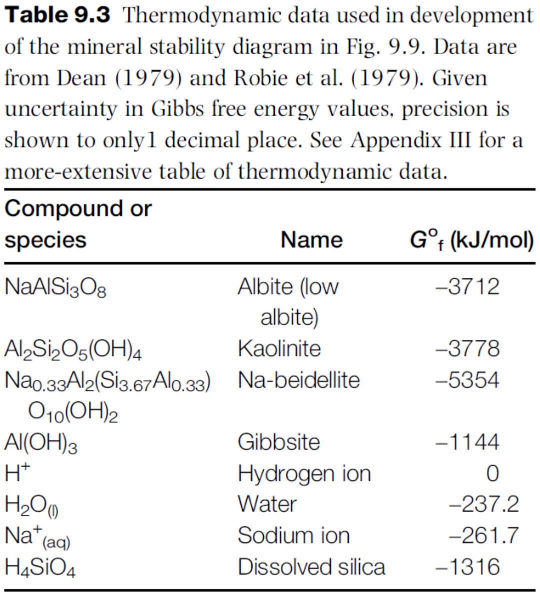
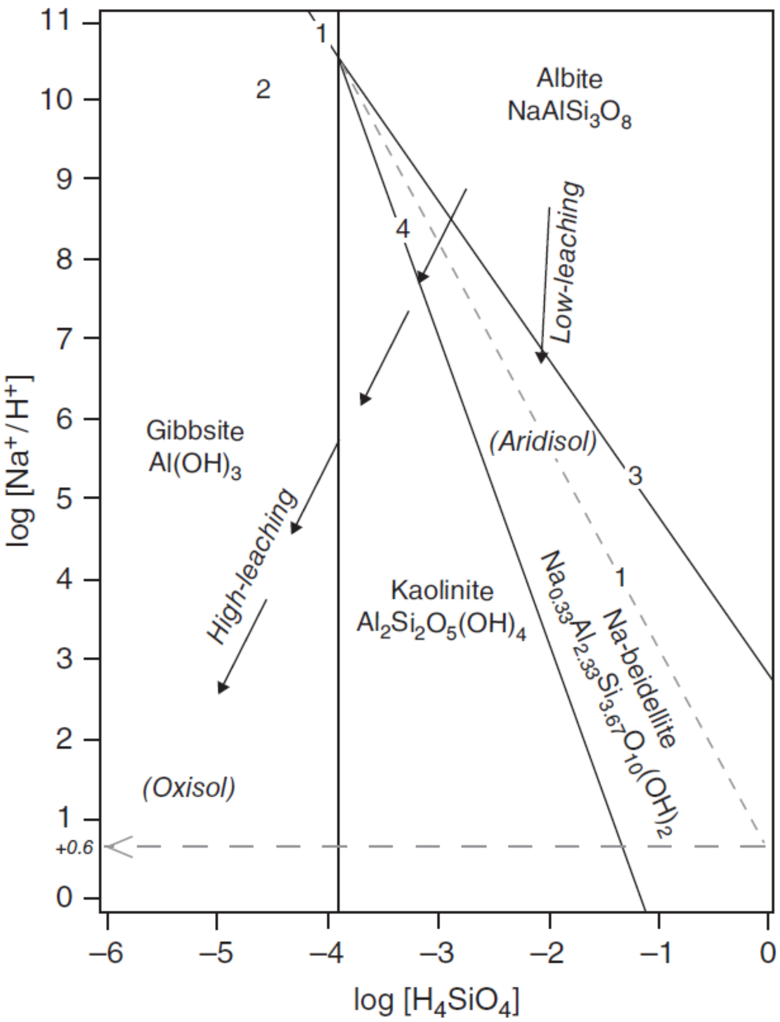


Table 9.3 Thermodynamic data used in development of the mineral stability diagram in Fig. 9.9. Data are from Dean (1979) and Robie et al. (1979). Given uncertainty in Gibbs free energy values, precision is shown to only 1 decimal place. See Appendix III for a more-extensive table of thermodynamic data.

Compound or species	Name	G^{o}_{f} (kJ/mol)
$NaAlSi_3O_8$	Albite (low albite)	–3712
$Al_2Si_2O_5(OH)_4$	Kaolinite	–3778
$Na_{0.33}Al_2(Si_{3.67}Al_{0.33})O_{10}(OH)_2$	Na-beidellite	–5354
$Al(OH)_3$	Gibbsite	–1144
H^+	Hydrogen ion	0
$H_2O_{(l)}$	Water	–237.2
$Na^+_{(aq)}$	Sodium ion	–261.7
H_4SiO_4	Dissolved silica	–1316



Adapted from Ryan (201

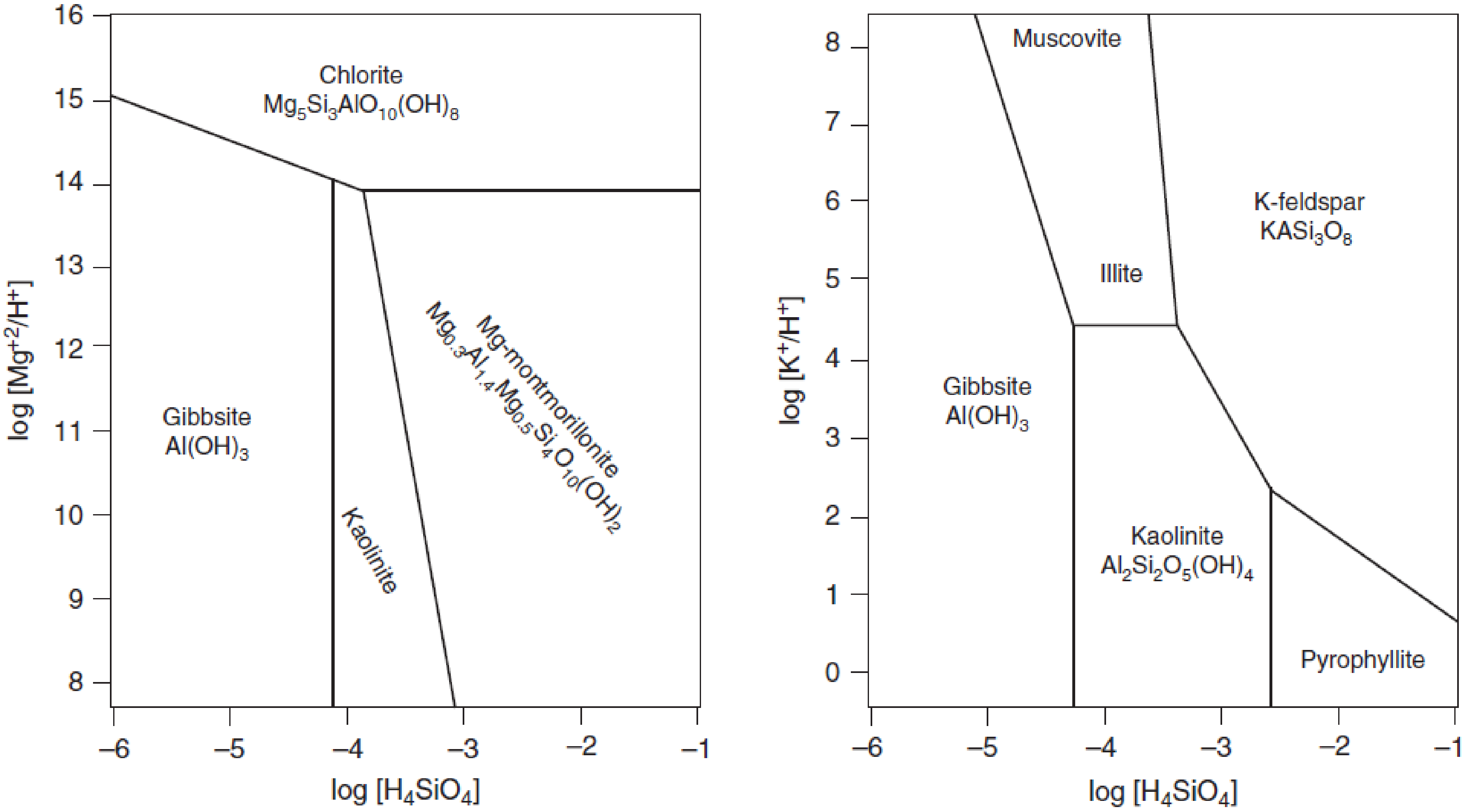


Fig. 9.9 Mineral stability diagram for systems Al–Mg–Si–O–H (left, modified from Lee et al., 2003) and K–Al–Si–O–H, 25 °C, 1 atm.

Adapted from Ryan (2014)

One of the products of weathering

SOIL

Soil

From The original uploader was Mikhail's grandson at Ukrainian Wikipedia - own thesis , CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=24550054

Black soil on loess.

- A mixture of minerals, organic matter, gases, liquids and organisms
- Substrate for plant growth
- Water retention and purification
- Interaction with the atmosphere
- Habitat for an organism

Soil-forming influences

- Climate
  - Precipitation and temperature – breakdown, transport to **leaching**
- Living organisms
  - Bacteria obtaining energy by the decomposition of minerals, plant roots, decomposition of org . mass…
- Relief
  - Drainage, sedimentation
- Mother rock
- Time
- Anthropogenic influences

Climate

- Large role, directed by:
  - Intensity of weathering
  - Retention of weathering products in soil
- Temperature
  - Higher temperatures – higher biological activity
- Precipitation
  - Environment, material relationship, H^{+} source
  - Effective precipitation - soil leaching vs. salting (crust formation)
- Humid Tropics × Arid Polar Regions

Organism

- Acceleration of reactions by microbial activity
- Nutrient uptake by plant roots – loss of ions in soil water
- Rhizosphere – surrounds roots, organic acids, concentration gradient given by nutrient intake
- Humic and fulvic acids (from the decomposition of organic matter)
- Mechanical mixing of sediment - aeration

Relief

- Hilltops and hillsides higher erosion – the water table is deeper and the water flows faster
- In lower areas, the benefit of ions in the solution slows down weathering
- Peaks – oxidizing × base of slopes – reducing (gley)

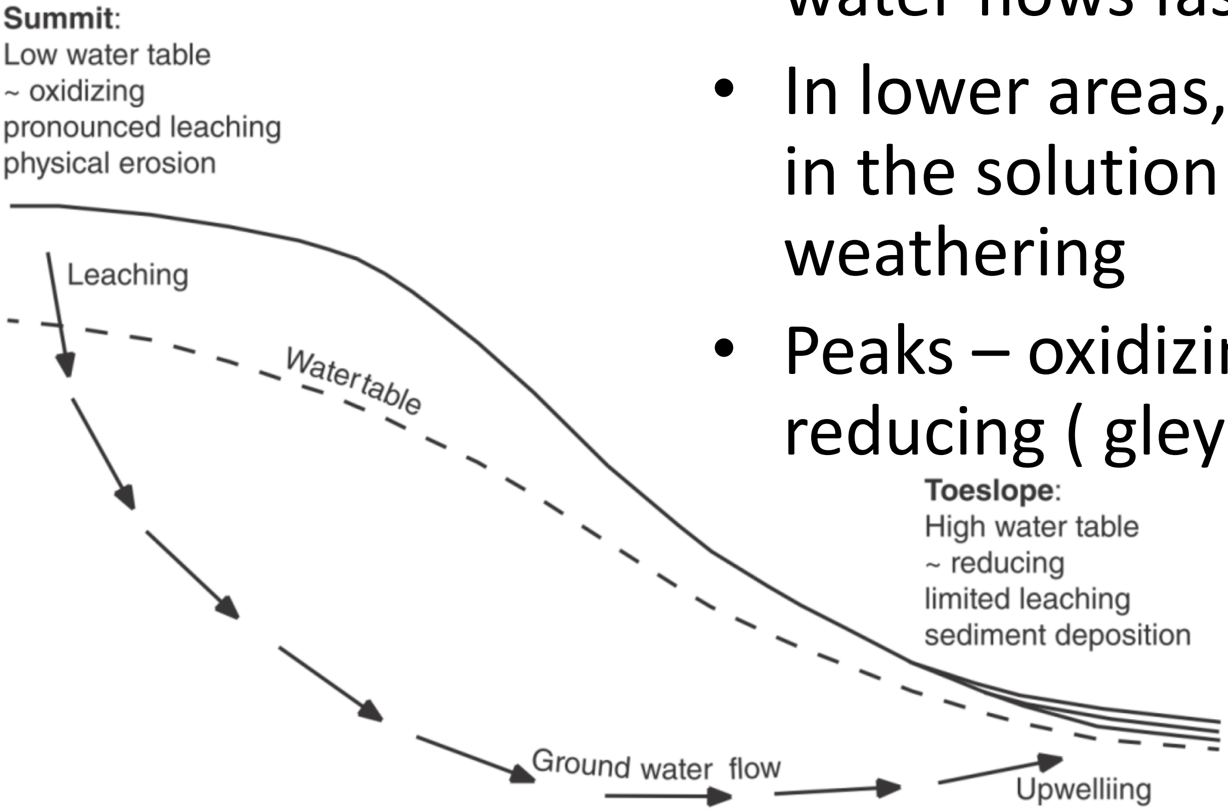


Fig. 9.4 Sketch of a topographic transect indicating factors that tend to enhance chemical weathering rates in summit positions, and those that tend to inhibit chemical weathering in toeslope positions.

Adapted from Ryan (2014)

Mother rock

- The mineral composition determines the rate of weathering and the chemical composition of the soil water
- Basalts – rapid weathering, waters rich in Ca-Mg cations
- Granites – slower weathering, water enriched with K-Na
- Tectonic faulting, exposed surfaces, permeability/impermeability

Time

- Decomposition of unstable minerals limited by kinetics!
- Processes outside the rest
- Irreversible
- Steady state not always achievable
- Fast start, then they slow down

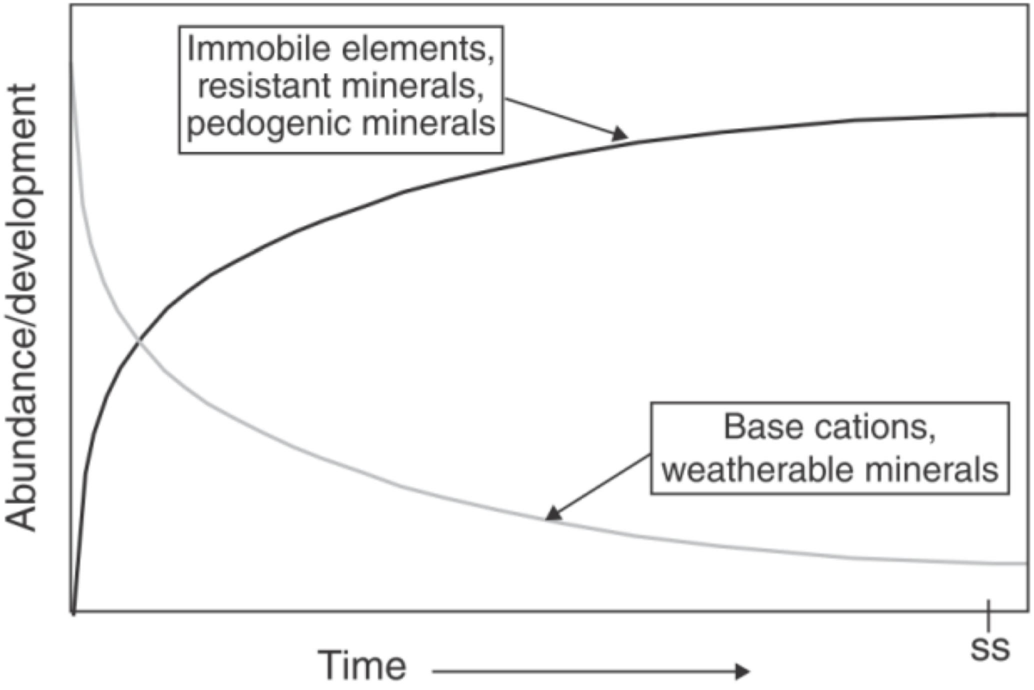


Fig. 9.5 Curves depicting typical evolution of soil characteristics with time. The black curve represents constituents that increase in concentration or degree of development with time (e.g. [Al^{+3}], carbonate horizon thickness), whereas the gray curve depicts the trajectory of constituents that tend to decrease over time (e.g. [Na^{+}], [parent materials]). See text for full explanation. The location on the *x*-axis labeled as "ss" indicates the point in time at which steady-state conditions have developed.

Adapted from Ryan (2014)

Anthropogenic factors

- Acid rain (acceleration of decomposition processes)
  - Solubility of Al
- Dry fallout (heavy metals)
- Fertilization
- Water pollution
- Replacement of sorbed nutrient cations

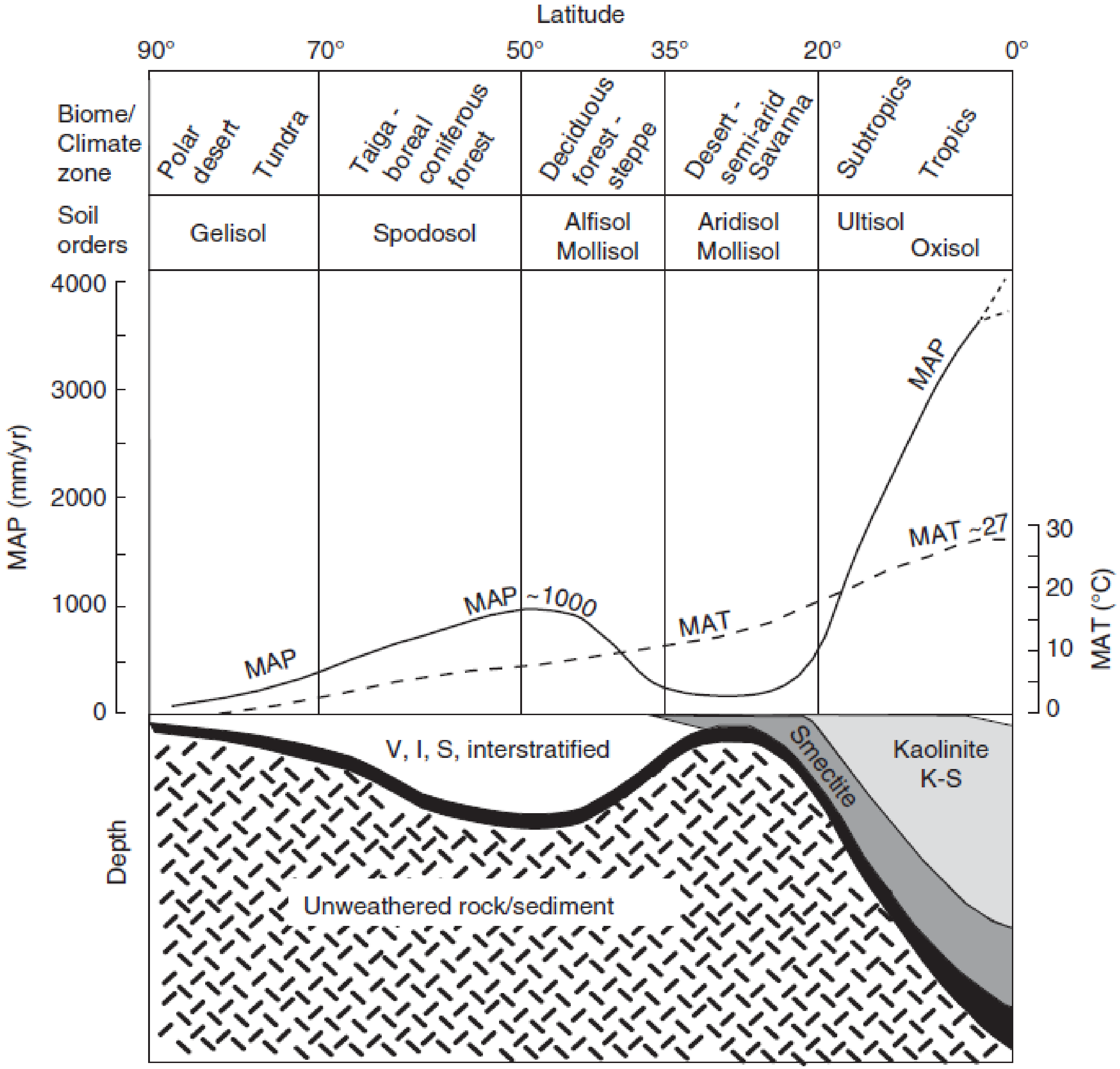


Fig. 9.7 Schematic sketch of soil minerals and relative depths of typical soils across a latitudinal transect, from pole to equator. Soil depth in the tropics may be tens of meters, whereas in other regions is typically < 2 m. Common soil orders for each latitudinal zone are provided. MAP = mean annual precipitation, MAT = mean annual temperature, V = vermiculite, I = illite, S = smectite, K-S = interstratified kaolin-smectite. (Modified from Strakhov 1967 and Birkeland 1999.)

Adapted from Ryan (2014)

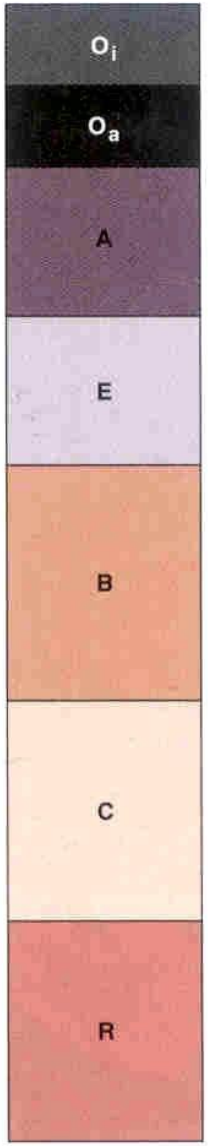
Soil structure

- With the month products weathering , org. substances and residues original ones rocks and water
- T typical soil : 5% organic substances , 95% inorganic
- P sequence layer (soil profile) depends on _ climate (T, precipitation etc.), vegetation , time and substrate horny

Soil - profiles

Soils
Soil profile
Soil horizons

Humus – insoluble, refractory organic substances



Oi – leaves and organic waste, mostly undecomposed
Oa – organic waste, partially decomposed
A – dark colored horizon of a mixture of minerals and organic substances, high biological activity, organic (fulvic) acids dissolve/ complex Fe and Al and I bring below
E – light-colored horizon, loss of clay minerals, organic substances, oxides (areas of intense leaching)
B – maximum accumulation of clay minerals and oxides, less organic substances, retention of substances carried away from A
(K – in arid regions precipitation of calcite, gypsum or halite – caliche , hardpan)
C – weathered source material, sometimes absent, weathering dominated by CO_2 produced in the soil
R – source rock

Sometimes horizons are completely missing
Sometimes special – laterites (latere – brick) – soils washed out of basic cations, dominated by gibbsite , kaolinite, FeOOH .

Soil Geochemistry

- Acid-base and exchange reactions in soils
- Macronutrients
- Micronutrients
- Pesticides and chemical wastes in soils
- Land loss – desertification

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie

č. CZ.02.2.69/0.0/0.0/16_018/0002593

Resources

- Images are from the following books:
  - , P. (2014). Environmental and Low Temperature Geochemistry. John Wiley and Sons . 402 p. ISBN 978-1-4051-8612-4 (pbk .)
  - Appelo , C. A. J., & Postma , D. (2005). Geochemistry, groundwater and pollution : (2nd ed.). Leiden:
  - Giardino , John; Houser, Christ (2015). Principles and dynamics of the critical zone. Elsevier. pp. 1–4. ISBN 9780444633699.