

Lecture 12

Weathering, Secondary Minerals and Surface Reactions

(in the context of soils)

Please read White Ch6 (249-end) and digital Ch13 (563 570)

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Rock weathering transfers chemicals between the geosphere, hydrosphere and biosphere.

This general process is a major factor in:

1. the rock cycle
2. the sustenance of terrestrial ecosystems
3. the compositions of the oceans
4. the composition of the atmosphere.

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Weathering is controlled by

- ✓ physical
- ✓ chemical
- ✓ biological processes

Chemical and biological weathering are almost always mediated by H₂O.

During weathering new solid materials are formed and the composition of the mediating H₂O is modified.

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The **rates of weathering and alteration**, and thus rates of soil (or sediment) accumulation and maturation, are governed by climate:

- ✓ temperature,
- ✓ the availability of H₂O
- ✓ biome factors (flora/fauna and the DOC they produce)

The **formation of a soil** is also dependent upon

- ✓ the bedrock type in the area
- ✓ physical factors (such as rock porosity and texture)
- ✓ mineralogic factors (solubility)
- ✓ Soils are also susceptible to many anthropogenic (human-induced) effects.

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How do we know which minerals will form during rock alteration to form secondary geological deposits?

The minerals found in an environment of active rock weathering reflect **coupled relationships** between mineral stability and mediating water chemistry.

To determine which **alteration minerals** are stable at a given T, P and H₂O composition, we must consider:

- ✓ the various mineral transformation equilibria
- ✓ the aqueous solubilities of the chemical species involved.

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Multiple additional factors are involved, such as

- ✓ original rock type
- ✓ temperature
- ✓ pressure
- ✓ water composition
- ✓ Organic matter content
- ✓ pH

e.g., basalt alteration on the undersea flanks of a Hawaiian volcano is much different than alteration on the upper flanks of the same volcano above sea level - the rock type is the same but the water composition, P, and T are all different.

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Weathering

Let's look at some of the common solids involved in weathering. Primary minerals can be weathered from the source rock intact (mineralogically) or dissolved.

Remember **congruent** and **incongruent** dissolution

The susceptibility of a given mineral to dissolution is related to that mineral's stability at the P, T and pE conditions of the earth's surface.

The higher their T and P of formation (and the lower the pE), the more susceptible to weathering their minerals are.

Many crustal rocks were formed at elevated P and/or T, and lower pE, in the lower crust or upper mantle.

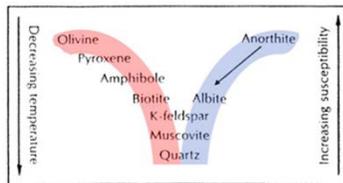


Figure 20.2 Schematic representation of Bowen's reaction series, which is used here to show that minerals that crystallize early and at high temperature from magma (olivine, Ca-plagioclase) are more susceptible to weathering than those that form later at somewhat lower temperatures (muscovite, quartz).

Faure, *Principles and Applications of Inorganic Geochemistry*

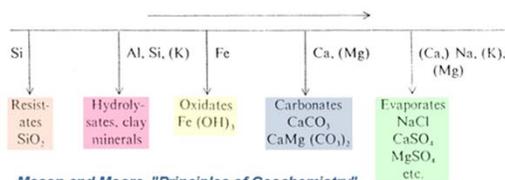
The Bowen's reaction series (a gross generalization of mineral stability as a function of magma temperature) can also be used to understand weathering of many silicate minerals, because high temperature minerals are the first to form from a crystallizing magma and are more susceptible to weathering.

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Generalized Steps in the Chemical Breakdown of a Rock

1. Minerals that are especially resistant to chemical and mechanical breakdown collect as granular material. Of these, the commonest is quartz, and the product is a quartz sand or a sandstone showing a marked enrichment in silicon with respect to the parent material. This may be compared to the separation of silica in the first stage of a rock analysis.
2. Accumulation of the products of chemical breakdown of aluminosilicates, giving a mud consisting essentially of the clay minerals. This results in concentration of aluminum and also of potassium by adsorption. The process corresponds to the second step in a rock analysis, the separation of alumina and other easily hydrolyzed bases.
3. Along with the formation of argillaceous sediments, but often separated in space and time, iron is precipitated as ferric hydroxide. In this process oxidation from the ferrous to the ferric state precedes precipitation by hydrolysis. Concentration of iron is the result, sometimes to the extent of the formation of iron ores.
4. Calcium is precipitated as calcium carbonate either by purely inorganic processes or by the action of organisms. Limestones are formed and calcium thereby concentrated. This may result in almost quantitative separation of calcium, as in a chemical analysis. Limestone can be partly or wholly converted to dolomite by the metasomatic action of magnesium-rich solutions and magnesium thereby precipitated and concentrated together with calcium.
5. The bases that remain in solution collect in the ocean, from which they are removed in quantity only by evaporation, giving rise to salt deposits. The most important of these bases is of course sodium, but lesser amounts of potassium and magnesium also accumulate in sea water.

The chemical breakdown of a rock by weathering can be represented by the following scheme:



Mason and Moore, "Principles of Geochemistry"

When the common rock-forming minerals are weathered, a similar sequence of events ensues regardless of the starting rock composition.

The most soluble elements are transported in aqueous solutions to a new location (eventually the sea).

The least soluble elements are largely left behind at the site of weathering.

However, given the right weathering solutions, elements of any solubility may be dissolved during weathering, re-deposited by the aqueous solution somewhere down its flow path, and then re-dissolved in a later episode of weathering.

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Soil Composition Basics

- ✓ **Inorganic** constituents:
 - A. Very resistant Primary minerals
 - B. Alteration minerals (Minerals stable at high temperatures and pressures are broken down into hydrous sheet silicates (clays) and oxide minerals (Fe, Al and Mn oxides))
 - C. Precipitation minerals (mostly carbonates/hydroxides)
- ✓ **Organic** constituents derived from flora, and soil microorganisms.
- ✓ **Typical proportion** is 95% inorganic material and 5% organic matter - highly variable though.

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Figure 6.4 Weathering of primary rock-forming minerals. (After Fieldes and Swindale, *New Zealand J. Sci. Tech.* 36B, 140, 1954)

Clay mineral groups

Group	Layer type	Layer charge	Typical chemical formula or range in composition
Kaolinite	1:1	<0.01	$Al_2Si_2O_5(OH)_4$
Illite	2:1	1.4–2.0	$K_{0.5-0.75}Al_2(Al_{0.5-0.75}Si_{1.25-1.5}O_{10})(OH)_2$
Smectite	2:1	0.5–1.2	$Na_{0.35}(Al_{1.65}Mg_{0.35})Si_4O_{10}(OH)_2 \cdot nH_2O$
Vermiculite	2:1	1.2–1.8	$(Mg,Ca)_{0.35}(Mg,Fe^{2+}, Al)_3((Al,Si)_4O_{10})(OH)_2 \cdot 4H_2O$
Chlorite	2:1 with hydroxide interlayer	variable	$(Mg,Al,Fe)_6((Al,Si)_4O_{10})(OH)_8$

The layer charge represents the typical range in mols of excess electron charge per chemical formula unit of the clay mineral produced by isomorphous substitutions. Modified from Sposito (1989) and Deer (1971). Formula for smectite corresponds to an average montmorillonite. Compositions for illite, vermiculite, and chlorite illustrate typical ranges in compositions. Not all possible compositions are shown.

Alteration minerals:

The structure and composition of these solids is important because they modify soil water and affect the availability of nutrients to plants.

The types of secondary minerals formed from the weathering and hydrolysis of common primary minerals are given below.

The mineral names are not important here, except to note that

- ❖ both clays and oxides can be formed
- ❖ ion exchange with water is involved, as we will see in the next lecture.

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Increased water flow during weathering leads to increased leaching of cations, which...

- ✓ Transforms weathering minerals
- ✓ lowers charge and cation exchange capacity (CEC) on clays.

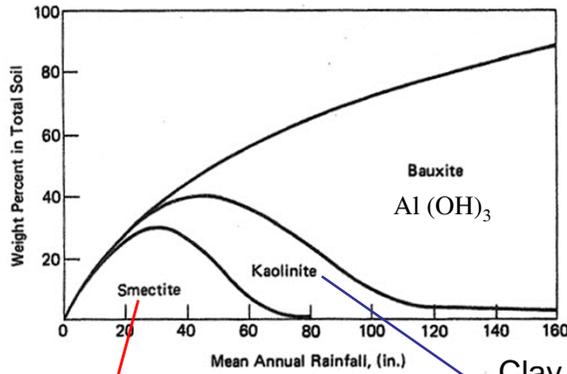


Figure 4.5 Weathering products of basalt in Hawaii. Note the excellent correlation of clay mineral type with rainfall in agreement with predictions based on the degree of flushing of the soil with water. (After G. D. Sherman. "The Genesis and Morphology of the Alumina-rich Laterite Clays," In *Problems in Clay and Laterite Genesis*, p. 159. © 1952 by the Amer. Inst. Min. Metal. Eng., reprinted by permission of the publisher.)

Na, Ca containing clay

Clay mineral depleted in Alkalis & Alkali Earths: $Al_2Si_2O_5(OH)_4$

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Simple oxide/ hydroxide examples are goethite and gibbsite.

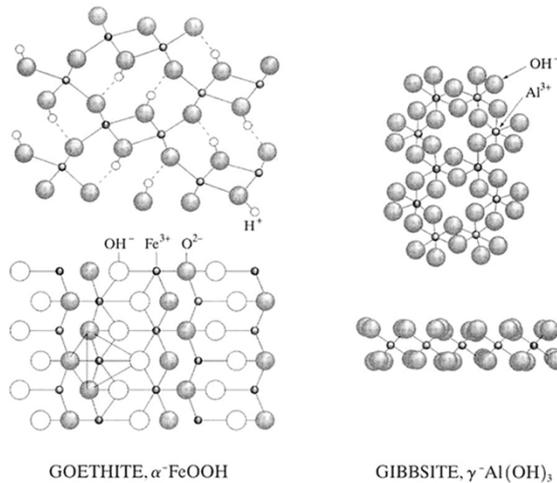
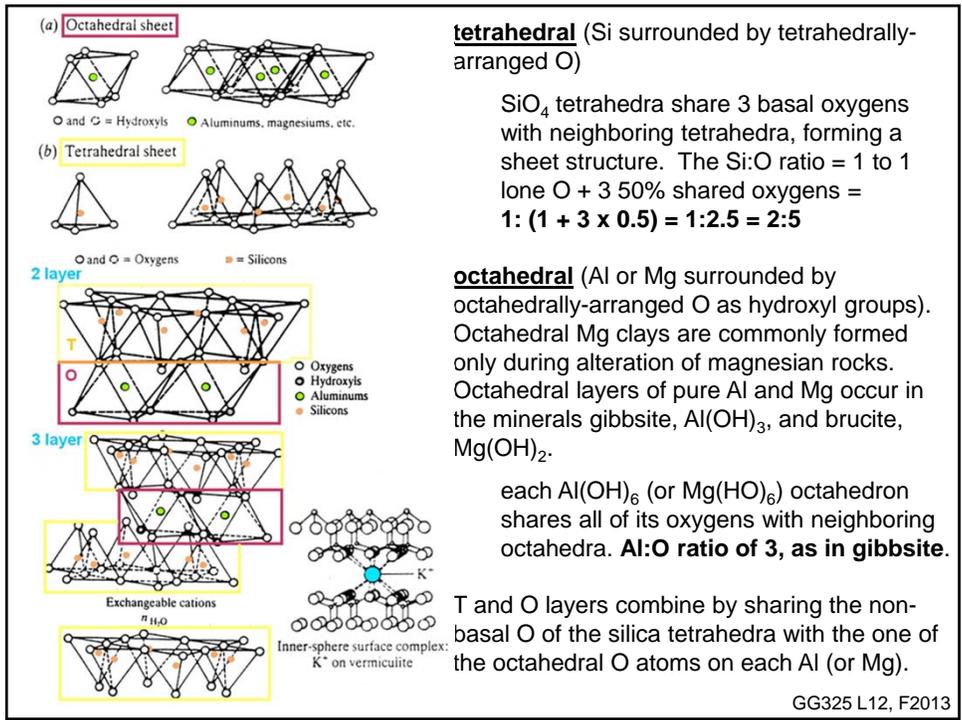
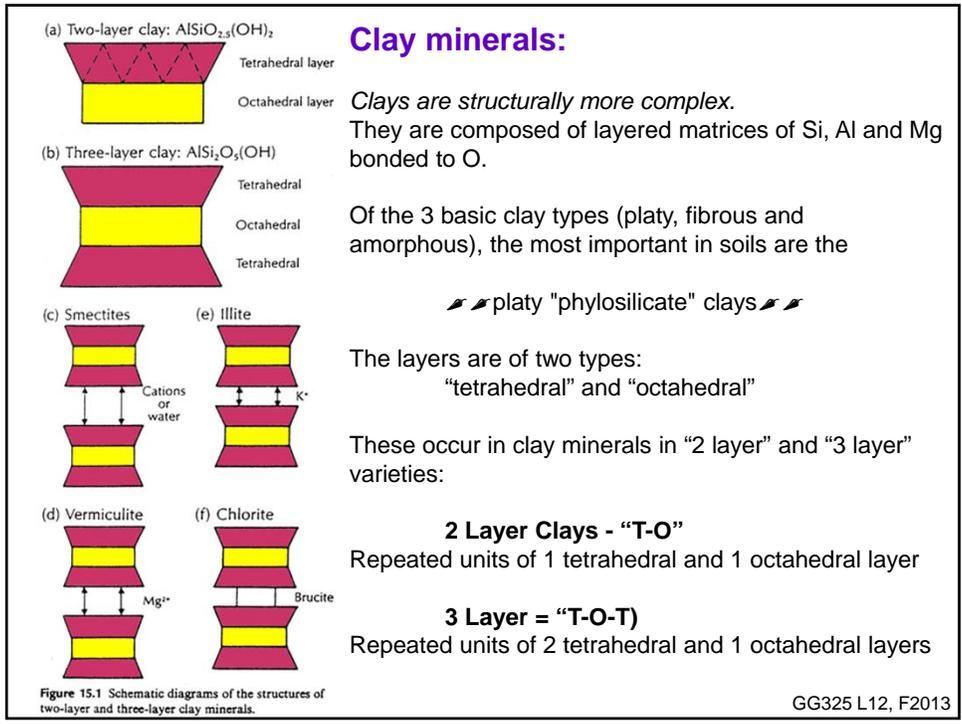


FIGURE 4-7 Structures of goethite and gibbsite, showing $FeO_4(OH)_3$ and $Al(OH)_6$ octahedra in sheets. Dashed lines in goethite structure represent hydrogen bonds between OH and O ions (from *The Surface Chemistry of Soils* by Garrison Sposito. Copyright © 1984 by Garrison Sposito. Used by permission of Oxford University Press, Inc.).

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T-O clays:

we can think of each Al as having effectively lost one O atom to a Si, and Al:O goes from 1:3 to 1:2 (octahedral O atoms are actually in hydroxide form).

Kaolinite, the simplest T-O clay, has Si:O of 2:5, Al:Si of 1:1 (or 2:2) and Al:OH of 1:2 (or 2:4).

This gives the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$.



T-O-T clays:

Similar arguments can be made to show that T-O-T clays have Si:Al of 2:1

The simplest chemical formula is $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ (pyrophyllite).

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Ion Substitution in clays:

Structural octahedral and tetrahedral cations in clays can be substituted for by other ions.

Octahedral site replacement is by ions such as Fe^{+3} , Fe^{+2} , Cr^{+3} , Zn^{+2} , Li^{+} .

Tetrahedral Si replacement is less common and mostly limited to Al-for-Si substitution.

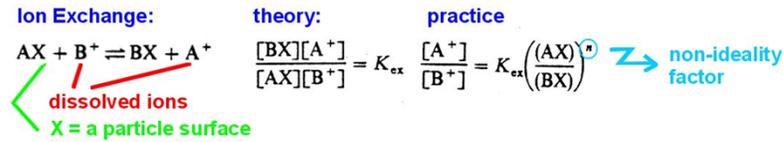
Structural substitutions result in a charge imbalance on the clay backbone that is balanced by addition of *non-structural ions* to the *interlayer* region and **accounts for the cation exchange capacity ("CEC") of clays** (the ability to hold and exchange charged ions with solution).

Ion substitution gives clays exchangeable ion sites that can exert a compositional control on aqueous solutions contacting them. The degree of substitution depends on the environment of their formation.

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ion exchange reactions on clays (and other natural surfaces)

Some solid compounds can physically trade ions with aqueous solutions, affecting the ionic composition of both.



POC and Clay minerals (phyllosilicates) are both in this category.

Ion exchange:

Moving a particle from one aqueous ionic solution to another can cause the population of attached ions and dissolved ions to change.

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An example *Ion Exchange* for a montmorillonite clay in river (fresh) water and sea (salty) water is given below. This clay has:

[0.16 mole Ca^{2+} , 0.07 mole Na^+ and 0.04 mole Mg^{2+} of exchangeable ions]
[mole clay mineral]

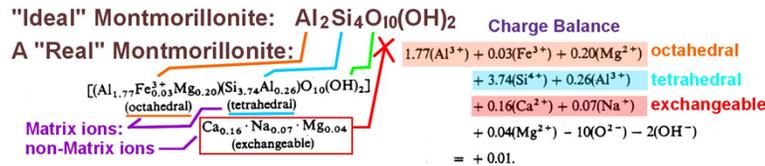


TABLE 10.8 INTERACTION OF FLUVIAL CLAYS WITH SEAWATER^a

	Σ cations (meq 100 g ⁻¹)	Original Exchange Composition (equivalent fractions)				Equilibrium Composition in Seawater (equivalent fractions) ^b			
		X_{Na}	X_{Mg}	X_{Ca}	X_K	X_{Na}	X_{Mg}	X_{Ca}	X_K
Clays originally equilibrated with river water ^c									
Dakota montmorillonite	54.3	0.03	0.28	0.66	0.002	0.50	0.22	0.26	0.02
Texas montmorillonite	80.9	0.03	0.23	0.71	0.007	0.55	0.22	0.19	0.03
Bath kaolinite	6.2	0.06	0.18	0.51	0.008	0.38	0.32	0.24	0.06
Dry clay minerals									
Wyoming montmorillonite	70.2	0.46	0.18	0.27	0.02	0.53	0.39	0.04	0.04
Mixed layer	38.5	0.01	0.23	0.39	0.08	0.56	0.32	—	0.07
Illite	16.8	0.01	0.01	0.74	0.15	0.47	0.24	0.11	0.17

^a Based on data presented by F. L. Sayles and P. C. Mangelsdorf, *Geochim. Cosmochim. Acta*, 41, 951 (1977).

^b After equilibration for 7 to 12 days.

^c Artificial "mean world river water."

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Ion exchange capacities:

Each material has its own specific capability to exchange ions with solution, which is defined by a **cation exchange capacity ("CEC")**.

Table 15.9 Cation Exchange Capacity (CEC) of Various Clay Minerals

Mineral	CEC, meq/100 g at pH = 7.0
Kaolinite	3-15
Chlorite	10-40?
Illite	10-40
Glaucanite	11-20+
Palygorskite	20-30
Allophane	~ 70
Smectite (montmorillonite)	70-100
Vermiculite	100-150

SOURCE: Garrels and Christ (1965).

CECs are usually reported in units of meq/[100g of solid])

CEC is measured by repeatedly equilibrating the material with solutions of pure NaCl in water until no other ions come off the mineral and then analyzing for the amount of exchangeable Na⁺ or Cl⁻ it has acquired.

Remember, an **equivalent (eq)** is a mole of charge, so 1 mole of NaCl in water produces 1 equivalent of Na⁺ ions where as 1 mole of MgSO₄ produces 2 equivalents of Mg²⁺. a milliequivalent (meq) is 10⁻³eq.

Another useful ion exchange term is **Exchangeable Cation Status (ECS)**. This is the CEC of a particular ion on a solid or colloid in a mixed-ion solution.

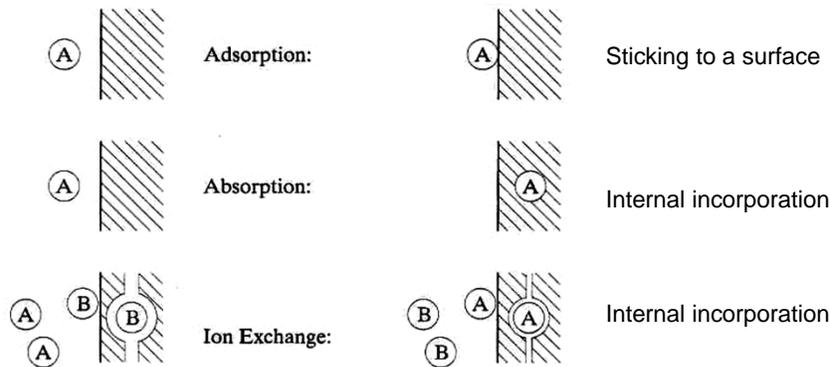
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non-stoichiometric surface interactions with aqueous solutes:

Solids in soils and sediments interact with pore water to exchange compositional attributes.

3 mechanisms of compositional “exchange” operate:

FIGURE 4-25 Processes of adsorption, absorption, and ion exchange.



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non-stoichiometric surface interactions...

are **ALSO** important throughout the hydrosphere for affecting waters and particle compositions, so let's look at them in more detail.

Most surface interactions involve charge transfer reactions

Particle Surfaces can Acquire Charge by 3 Mechanisms:

- ion exchange reactions (as just discussed)
- acid-base (primary mechanism)
- charge transfer (e.g., ligand/donor, sorption)

Each compound has specific properties that dictate how and when it will take a charge and how much charge it will take.

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acid-base reactions giving rise to charge on solid surfaces in H₂O.

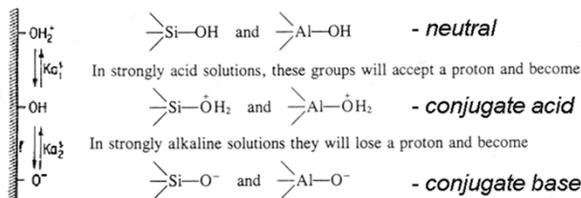
Gain or loss of a **proton** by an acidic or basic functional group of the solid's surface (*this is chemically equivalent to protonation-deprotonation reaction of solutes*)

Each functional group has an equilibrium constant for loss of a proton (K_a) and gain of a proton (K_b) in water.

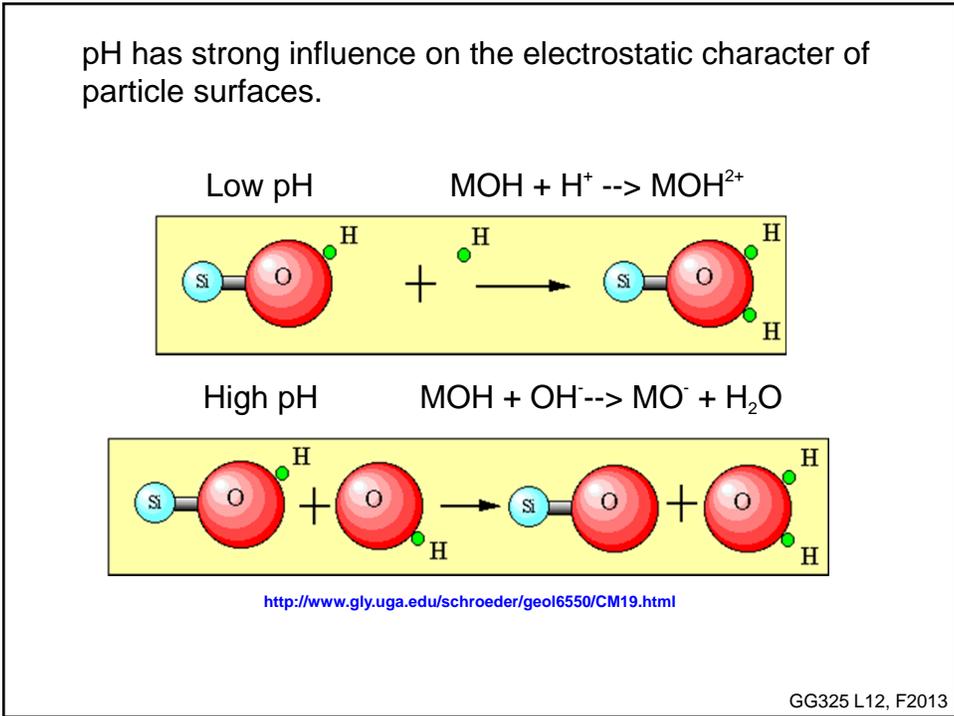
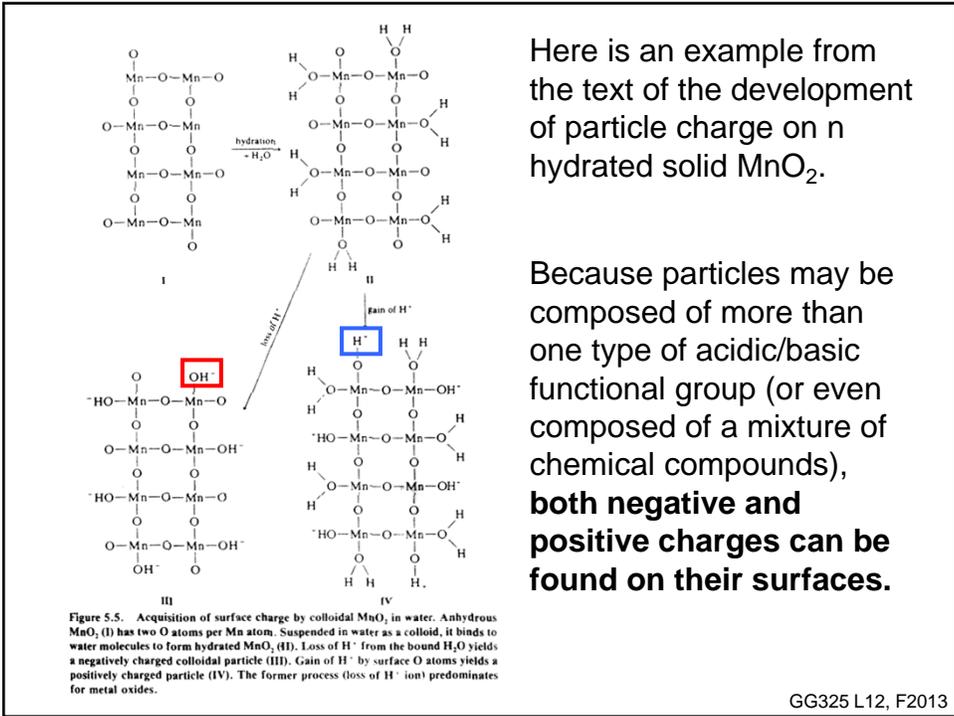
Like any acid or base, these K values are pH dependent.

For instance, the R-OH (hydroxyl group) of an organic or inorganic compound can lose a proton to become R-O⁻ or gain one to become R-OH₂⁺.

Whether or not it is attached to a solid is immaterial.



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“Isoelectric point” or the “Zero Point of Charge (ZPC)”

the pH at which the sum of all acid-base surface charges are balanced (neutral)

At the ZPC the particle is neither protonated (excess + charge) or deprotonated (excess - charge) in a net sense.

When pH > ZPC, the particle surface carries a – charge.

When pH < ZPC, the particle surface carries a + charge.

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ZPC for various minerals in pure water (no other ions present) and their charge polarity are given in these tables.

Table 15.8 Isoelectric Points of Various Natural Materials when Suspended in Water of Varying Acidity but Lacking Dissolved Electrolytes

Material	pH	Polarity in acid medium	Polarity in basic medium
SiO ₂ (amorph.)	1.0-2.5	-*	-
Quartz	2.0	-	-
MnO ₂ (different forms)	2.0-4.5	-	-
Albite	2.0	-	-
Montmorillonite	2.5	-	-
Kaolinite	4.6	-	-
Hematite	5-9	±	±
Magnetite	6.5	+	-
Goethite	6-7	±	±
Limonite (Fe ₂ O ₃ · nH ₂ O)	6-9	±	±
Anatase (TiO ₂)	7.2	+	-
Gibbsite	~9	+	+
Corundum	9.1	+	+
Periclase (MgO)	12.4	+	+

* The polarity changes from negative to positive at pH values less than the isoelectric point. Thus the charge is negative if the pH is greater than the isoelectric point. Acid and basic are defined relative to pH = 7.0 at 25°C.

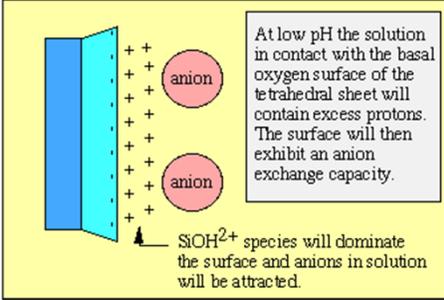
After Drever (1982), Table 4.2; Stumm and Morgan (1970).

TABLE 10.6 ZERO POINT OF CHARGE*

Material	pH _{ZPC}
α-Al ₂ O ₃	9.1
α-Al(OH) ₃	5.0
γ-AlOOH	8.2
CuO	9.5
Fe ₃ O ₄	6.5
α-FeOOH	7.8
γ-Fe ₂ O ₃	6.7
“Fe(OH) ₃ ”(amorph)	8.5
MgO	12.4
δ-MnO ₂	2.8
β-MnO ₂	7.2
SiO ₂	2.0
ZrSiO ₄	5
Feldspars	2-2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0
Chrysotile	>12

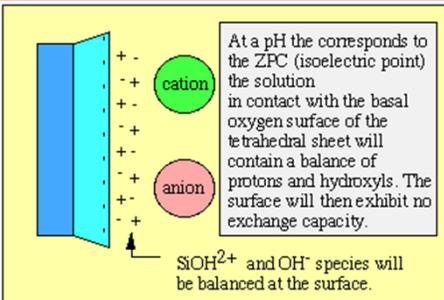
* The values are from different investigators who have used different methods and are not necessarily comparable. They are given here for illustration.

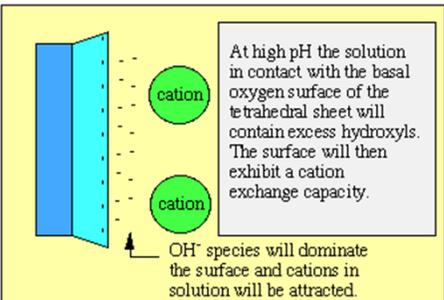
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The pH that corresponds to the **ZPC** is referred to as the isoelectric point.

Electrostatic charge repulsion between particles and solutes is minimized at this point.





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