

Sorción

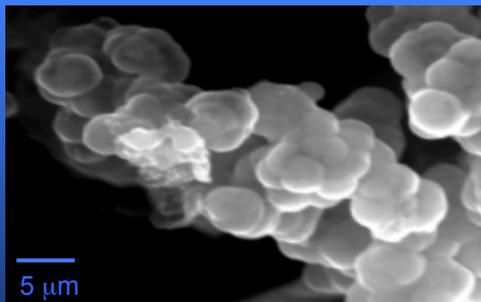
Adsorción-Absorción

Superficie específica

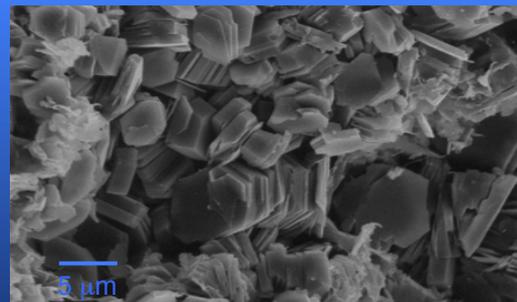
$$\zeta = \frac{A}{V} = \frac{N4\pi r^2}{N4/3\pi r^3} = \frac{3}{r}$$

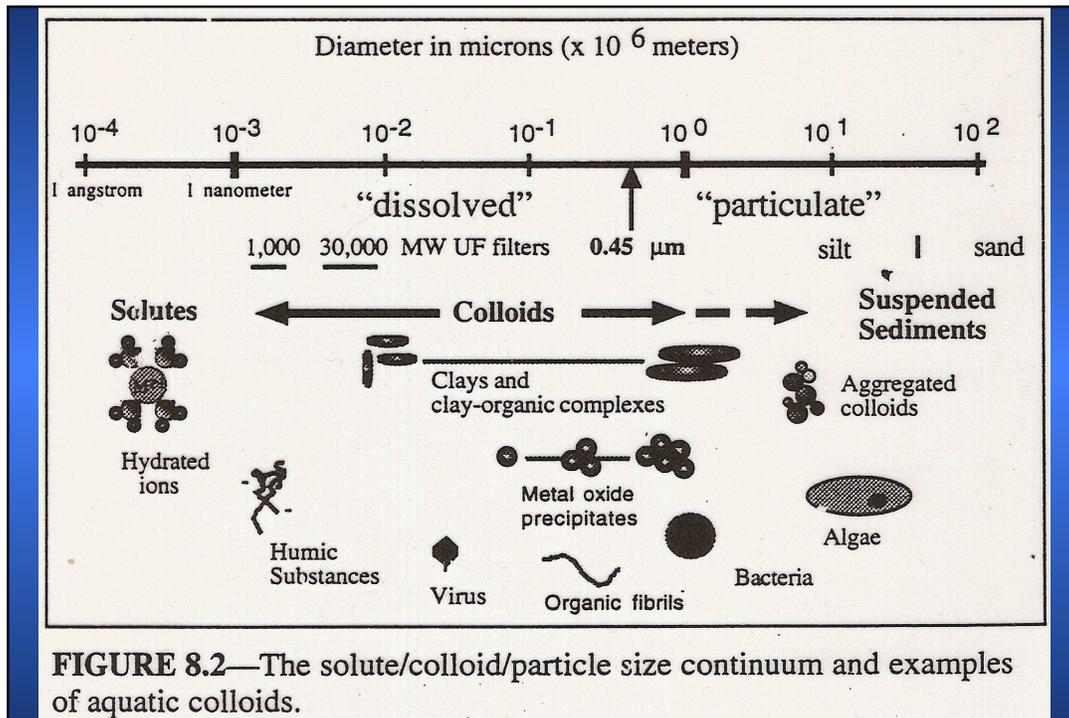
Ej.:
 $R = 1\mu\text{m} \rightarrow \zeta = 3 \cdot 10^6 \text{ m}^2\text{m}^{-3} \cong 10^3 \text{ m}^2\text{g}^{-1}$
 $= 1 \text{ ha}/10\text{kg}$

oxihidróxidos de Fe y Al:



arcillas:





Carga superficial: lugares de adsorción

La concentración de lugares de adsorción por unidad de superficie de un sólido:
 -es un parámetro a estimar en experimentos de adsorción (ver después)
 -se puede calcular a partir de la estructura.

Ej.: montmorillonita: $\text{Na}_{0.3}(\text{Si}_{3.8}\text{Al}_{0.2})(\text{Al}_{1.9}\text{Mg}_{0.1})\text{O}_{10}(\text{OH})_2$

si se substituye el Na^+ que compensa el déficit de carga:

$$n_s = \frac{0.3q_e}{2(9 \times 5.2)\text{\AA}^2} \approx 3 \cdot 10^{-3} q_e \text{\AA}^{-2} = 0.3 q_e \text{nm}^{-2}$$

Los minerales tienen en general:
 filosilicatos: 0.5 a 5 sitios/ nm^2
 óxidos amorfos: 10 a 20 sitios/ nm^2

TABLE 10.2 Some measured or estimated surface areas (S_A) and maximum surface-site densities (N_S) (chiefly negative) for geological materials

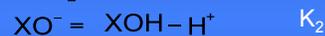
Mineral/phase	S_A (m ² /g)	Source	N_S (sites/area or wt)	Source
α -FeOOH (goethite)	45 to 169	†	2.6 to 16.8/nm ² 18/nm ² ; 1.35×10^{-3} mol/g	‡ §
α -Fe ₂ O ₃ (hematite)	1.8 (natural) 3.1 (synthetic)	§	5 to 22/nm ²	‡
Fe(OH) ₃ · nH ₂ O (ferrihydrite)	250, 306 600	§ 	20/nm ² 0.1 to 0.9 mol per mol of Fe	‡ §
MnO ₂ (synthetic and natural birnessite)	290 (fresh) 143 (aged) 180 (natural)	†	18/nm ² 2/nm ²	† ‡
SiO ₂ (quartz)	0.14		4.2 to 11.4/nm ²	#
SiO ₂ gel [SiO ₂ (am)]	53, 292 170, 180	‡ ††	4.5 to 12/nm ² 5/nm ²	‡ #
α -Al(OH) ₃ (gibbsite)	120		2 to 12/nm ²	‡
γ -Al(OH) ₃ (bayerite)	156	#	6 to 9/nm ²	‡
TiO ₂ (rutile)	5 to 19.8	††	5.8/nm ² 12.2/nm ²	†† #
kaolinite	10 to 38 12	‡ 	1.3 to 3.4/nm ² 1.2 to 6.0/nm ²	‡ ‡‡, §§
illite	65 to 100		0.4 to 5.6/nm ²	‡‡, §§
montmorillonite (Na form)	600 to 800 (esp. interlayer)	‡,	0.4 to 1.6/nm ²	‡‡, §§
organic substances in soils; humic materials	260 to 1300	§§	2.31/nm ² assumed 1 to 5×10^{-3} mol/g	§§
bulk composite geological materials (except smectites); assumes Fe ₂ O ₃ · H ₂ O with an area of 600 m ² /g and 0.205 mol sites/mol Fe	600	‡	range 1 to 7/nm ² mean value of 2.31/nm ² ; 3.84 μ mol sites/m ²	‡

Source: †Catts 1982. ‡Davis and Kent 1990. §Hsi 1981. *Schwarzenbach et al. 1993. †James and Parks 1982. ††Kent et al. 1986. †††Computed from information given by Schwarzenbach et al. 1993. †††Estimated from CEC values in Table 10.4. Sposito (1989) suggests -9×10^{-3} to $+1 \times 10^{-3}$ mol/g.

Punto de carga neta cero (PZNPC)

Es un valor experimental que se obtiene mediante variación de pH hasta conseguir la floculación de partículas coloidales → carga superficial cero → no hay repulsión eléctrica.

Sea agua pura y una superficie adsorbente:

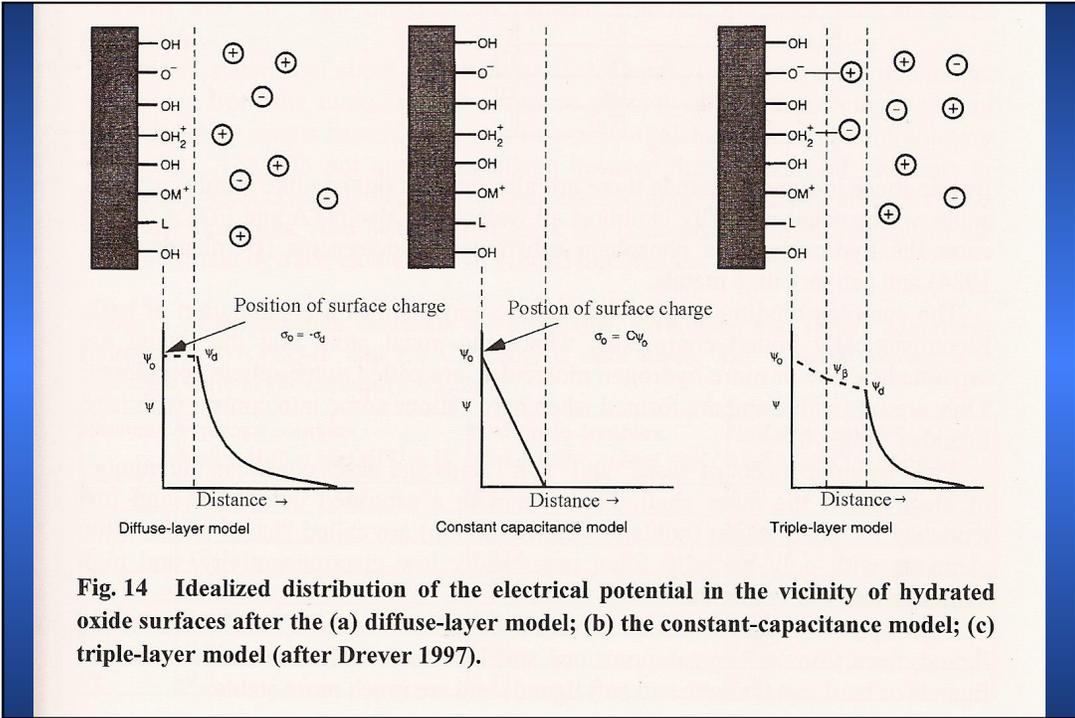
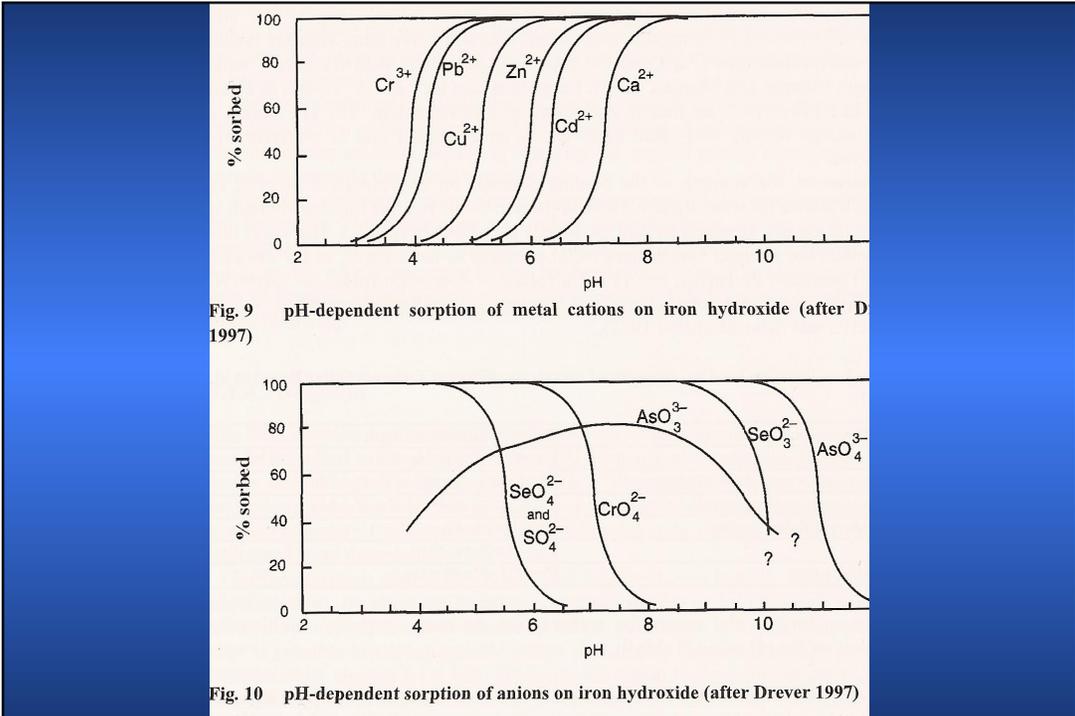


En el punto de carga neta cero:

$$\frac{[\text{XOH}][\text{H}^+]}{K_1} = \frac{[\text{XOH}]}{K_2[\text{H}^+]}$$

No hay campo electrostático porque en PZNPC no hay carga superficial:

$$[\text{H}^+]^2 = \frac{K_1}{K_2} \longrightarrow \text{PZNPC} = \frac{1}{2} (\log K_1 - \log K_2)$$



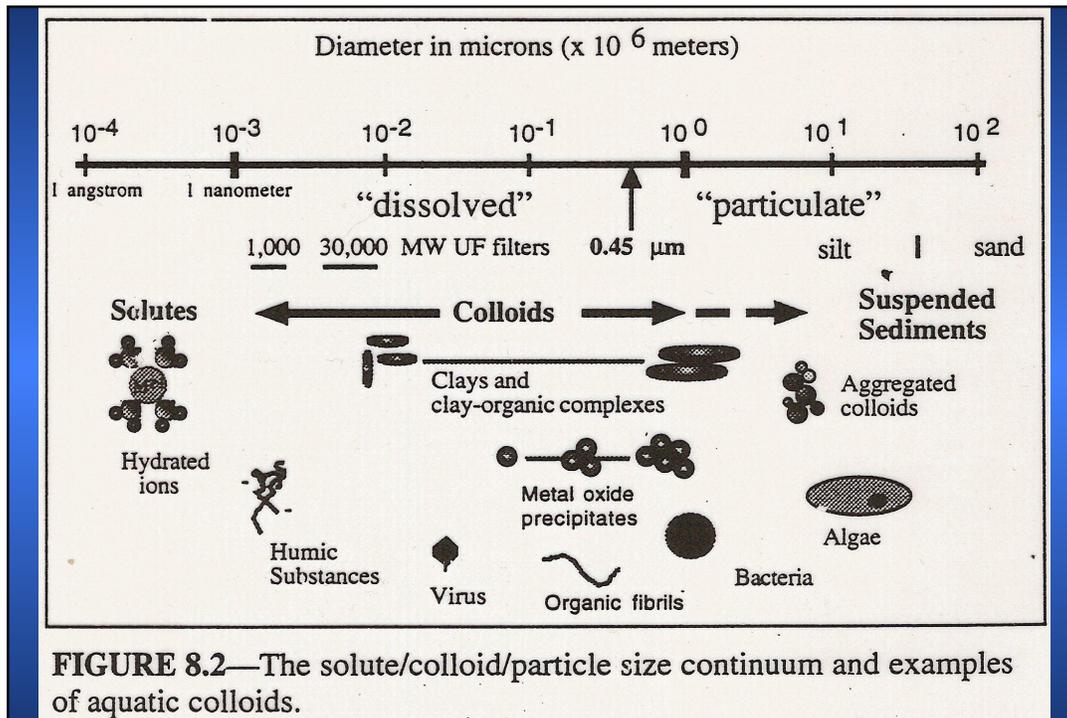


Table 7.1 Type of Colloids present in Natural Systems

① **River-borne Particles**

- Products of weathering and soil colloids, e.g., aluminum silicates, kaolinite, gibbsite, SiO_2
- Iron(III) and manganese(III,IV) oxides
- Phytoplankton, biological debris, humus colloids (colloidal humic acid), fibrils¹⁾
- So-called “dissolved” iron(III) consists mainly of colloidal Fe(III) oxides stabilized by humic or fulvic acids

② **Soil Colloids**

- Kaolinite particles. Typically about 50 unit layers of hexagonal plates are stacked irregularly and interconnected through H-bonding between the OH-groups of the octahedral sheet and the oxygens of the tetrahedral sheet (Fig. 3.9) (Sposito, 1989)
- Illite and other 2:1 layer type clay minerals. Platelike particles stacked irregularly
- Smectites and vermiculites have a lesser tendency to agglomerate because their layer charge is smaller than that of illite
- Humus, colloidal humic acids, fibrils
- Iron hydrous oxides
- Polymeric coatings of soil particles by humus, by hydrous iron(III) oxides and hydroxo-Al(III) compounds

③ **Sediment Colloids**

- in addition to the colloids listed above:
- Sulfide and polysulfide colloids in anoxic sediments

④ **Biological Colloids**

- Microorganisms, virus, biocolloids, fibrils

¹⁾ fibrils = elongate organic colloids with a diameter of 2 – 10 nm and composed in part of polysaccharide

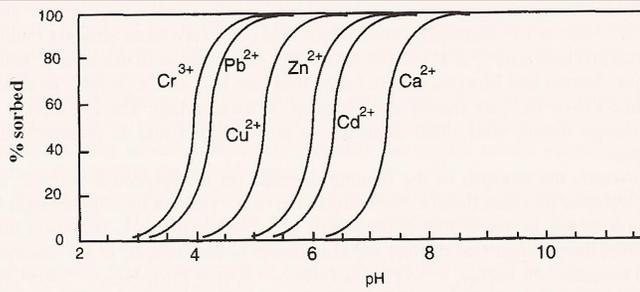


Fig. 9 pH-dependent sorption of metal cations on iron hydroxide (after D 1997)

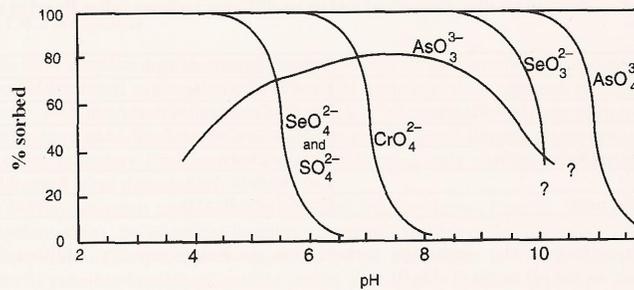


Fig. 10 pH-dependent sorption of anions on iron hydroxide (after Drever 1997)

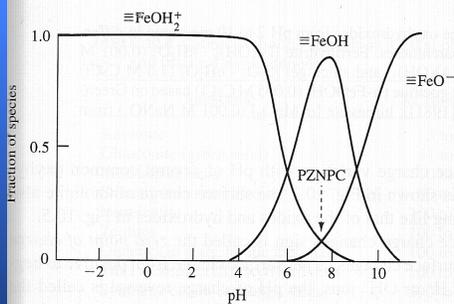
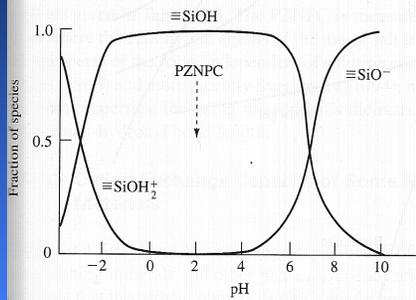
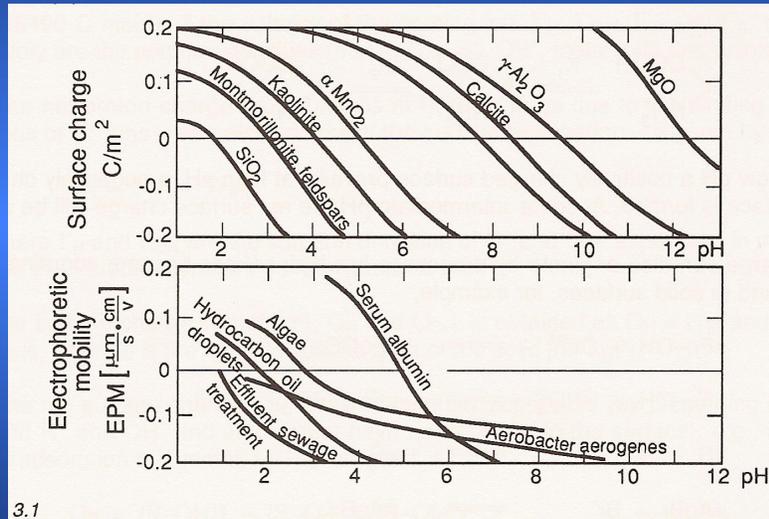


Figure 10.4 Schematic distribution of charged surface species (denoted by the triple dashes) on (a) silica gel and (b) ferrihydrite as a function of pH, showing for both the predominance of positive, neutral, and negatively charged surface species with increasing pH. The pH of the PZNPC is found where the net surface charge is zero (i.e., $[\equiv\text{SiOH}_2^+] = [\equiv\text{SiO}^-]$ and $[\equiv\text{FeOH}_2^+] = [\equiv\text{FeO}^-]$). Based on Healy (1974).

Surface Charge of some minerals



3.1

From Stumm, 1992

Point of Zero Net Proton Charge (PZNPC) of some minerals

Solid	pH _{PZNPC}	Solid	pH _{PZNPC}
SiO ₂ (quartz)	1 to 3 (2.91)	MnO _x (general)	1.5 to 7.3
SiO ₂ (amorphous)	3.5 (3.9)	α-MnO ₂ (cryptomelane)	4.5
Na-feldspar	6.8 (5.2)	β-MnO ₂ (pyrolusite)	4.6 to 7.3 (4.8)
K-feldspar	(6.1)	CuO (tenorite)	9.5 (8.6)
Montmorillonite	≤ 2 to 3	MgO (periclase)	12.4 (12.24)
Kaolinite	≤ 2 to 4.6 (4.66)	α-Al(OH) ₃ (gibbsite)	10.0 (9.84)
Muscovite	(6.6)	CaCO ₃ (calcite)	8.5, 10.8
Mg-silicates	9 to 12	Ca ₅ (PO ₄) ₃ F (fluorapatite)	4 to 6
α-Fe ₂ O ₃ (natural hematite)	4.2 to 6.9	Ca ₅ (PO ₄) ₃ (OH) (hydroxyapatite)	≤ 8.5
Fe(OH) ₃ (amorphous)	8.5 to 8.8	FePO ₄ · 2H ₂ O (strengite)	2.8
α-FeOOH (goethite)	5.9 to 6.7	AlPO ₄ · 2H ₂ O (variscite)	4
Mn(II) manganite	1.8	Algae	2
σ-MnO ₂ (birnessite)	1.5 to 2.8	Sewage effluent (bacteria, etc.)	2

Source: Values are from Parks (1965), Sverjensky (1994), and Stumm and Morgan (1996). Values estimated by Sverjensky (1994) are given in parentheses.

From Langmuir, 1997

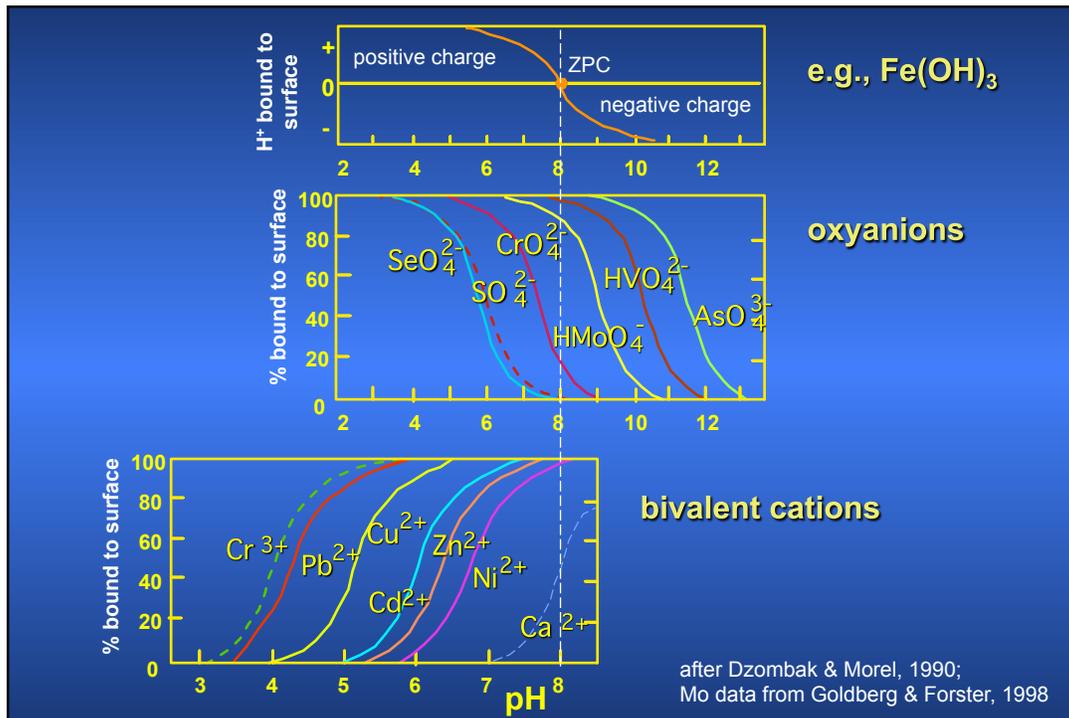


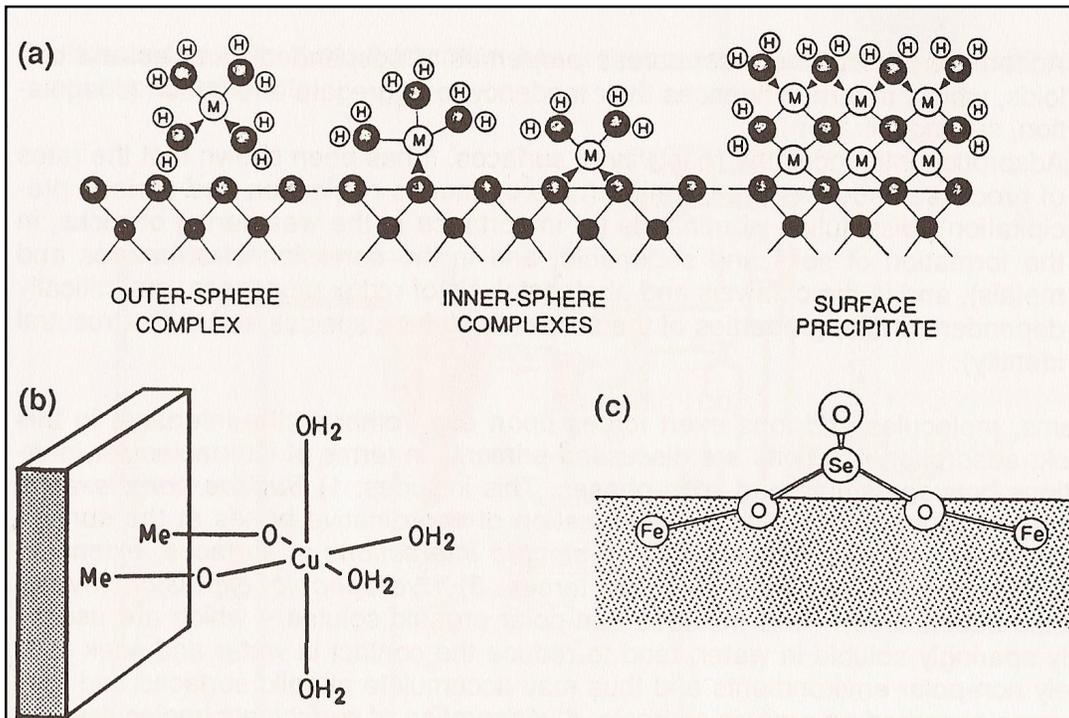
Table 8 Relative binding strength of metals on different sorbents (after Bunzl et al. 1976)

Substance	Relative binding strength
Clay minerals, zeolites	Cu>Pb>Ni>Zn>Hg>Cd
Fe, Mn-oxides and -hydroxides	Pb>Cr=Cu>Zn>Ni>Cd>Co>Mn
Organic matters (in general)	Pb>Cu>Ni>Co>Cd>Zn=Fe>Mn
Humic- and Fulvic acids	Pb>Cu=Zn=Fe
Peat	Cu>Pb>Zn>Cd
degraded peat	Cu>Cd>Zn>Pb>Mn

Corresponding to the respective sorbent, ion exchange capacity additionally depends on the pH value (Table 9).

Table 9 Cation exchange capacity at pH 7 and their dependency (after Langmuir 1997)

Substance	CEC (meq/100g)	pH dependency
Clay minerals		
Kaolinite	3-15	high
Illite and Chlorite	10-40	low
Smectite Montmorillonite	80-150	rare or non existent
Vermiculite	100-150	negligible
Zeolites	100-400	negligible
Mn (IV) and Fe (III) Oxyhydroxides	100-740	high
Humic matter	100-500	high
synthetic cation exchangers	290-1020	low



Sorption

Adsorption

Outer-Sphere Complex Inner-Sphere Complexes Surface Precipitate

Precipitation

Solid Solution

Diffusion

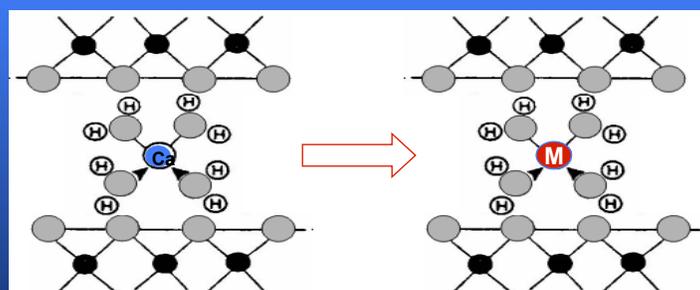
Co-precipitation

Intercambio iónico

Algunos minerales (por ej. zeolitas, arcillas) presentan déficit de carga electrostática estructurales, debido a la existencia de sustituciones isomórficas (por ej. Al^{3+} por Si^{4+}).

El defecto de carga es compensado por iones en ciertas posiciones intracristalinas y superficies (Na^+ , K^+ , Ca^{2+} , Mg^{2+}).

Intercambio entre iones en posiciones intracristalinas/superficies e iones en solución.



Brown (1990)

Intercambio iónico

TABLE 10.4 Cation exchange capacities (CEC's) of some substances measured at pH 7 and their pH dependences

Substance	CEC(meq/100 g)	pH dependence
Kaolinite	3 to 15	strong
Glaucanite (green sand)	11 to 20	slight
Illite and chlorite	10 to 40	slight
Smectite-montmorillonite	80 to 150	absent or negligible
Vermiculite	100 to 150	negligible
Zeolites	100 to 400	negligible
Organics in soils, humic materials	100 to 500	strong
Mn(IV) and Fe(III) oxyhydroxides	100 to 740	strong
Synthetic cation exchange resins	290 to 1020	slight

Source: Grim (1968); Brady (1974); Mumpton (1977); Bodek et al. (1988); Lide (1995).

Langmuir (1997)

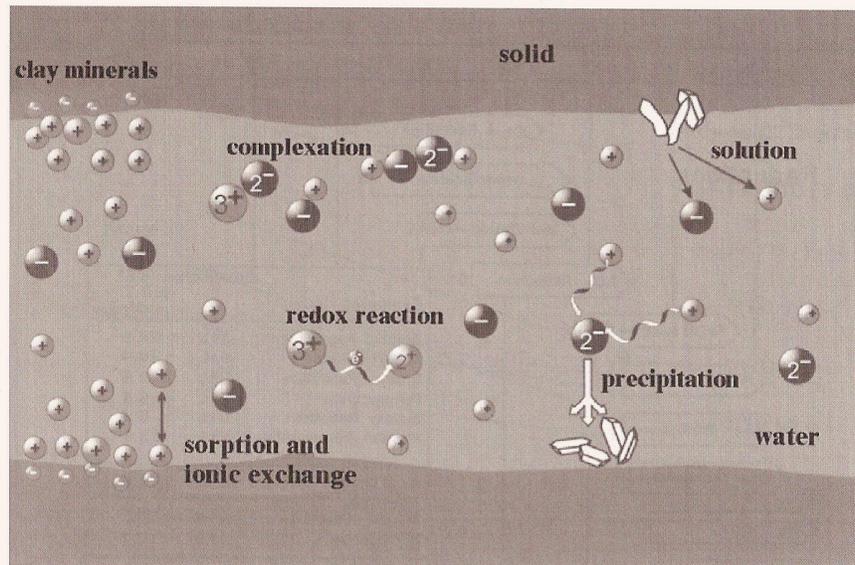


Fig. 21 Synopsis of the interaction processes in aqueous systems

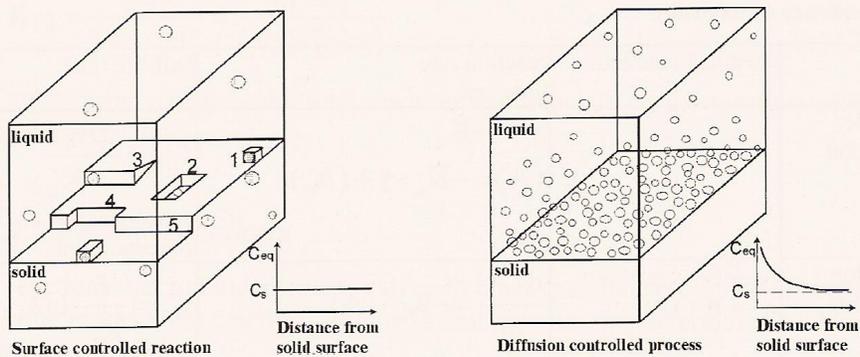
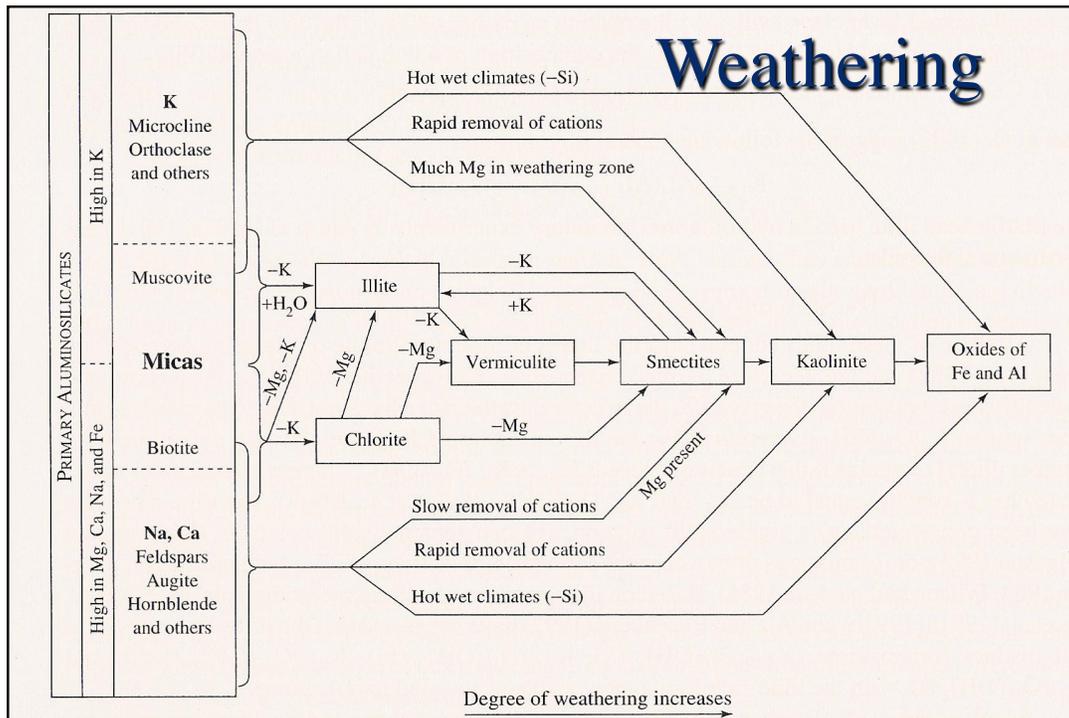


Fig. 23 Comparison between surface-controlled reactions (left; 1= interstitial sites, 2= vacant sites, 3= screw dislocation, 4= jump dislocation, 5=step dislocation) and diffusion-controlled processes (right)



Silicates

A

B

Oxygen atoms on points of tetrahedron

Silicon atom in center of tetrahedron

Class	Arrangement of SiO ₄ tetrahedron	Unit composition	Mineral examples
(A) Independent tetrahedra		(SiO ₄) ⁴⁻	Olivine: The composition varies between Mg ₂ SiO ₄ and Fe ₂ SiO ₄
(B) Single chains		(SiO ₃) ²⁻	Pyroxene: The most common pyroxene is augite. Ca(Mg, Fe, Al)(Al, Si) ₂ O ₆
(C) Double chains		(Si ₄ O ₁₁) ⁶⁻	Amphibole: The most common amphibole is hornblende. NaCa ₂ (Mg, Fe, Al) ₅ (Si, Al) ₇ O ₂₂
(D) Sheet silicates		(Si ₂ O ₅) ²⁻	Mica, clay minerals, chlorite. e.g.: muscovite, KAl ₂ (Si ₃)AlO ₁₀
(E) Framework silicates		SiO ₂	Quartz: SiO ₂ Feldspar: As an example, potassium feldspar is KAlSi ₃ O ₈

Weathering

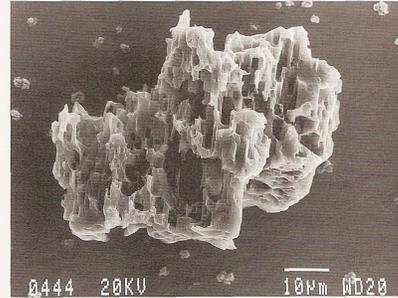
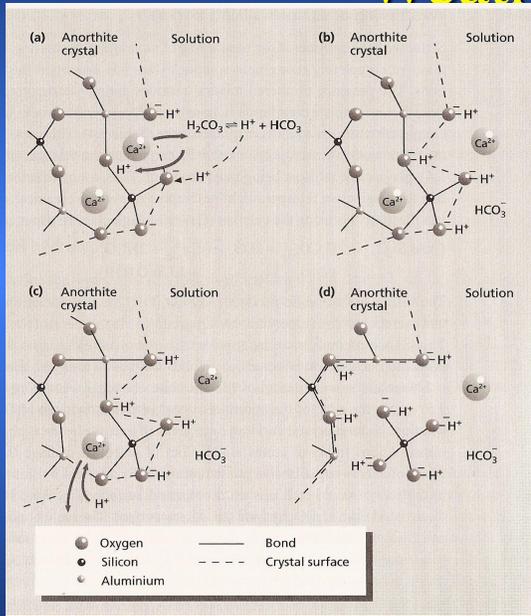
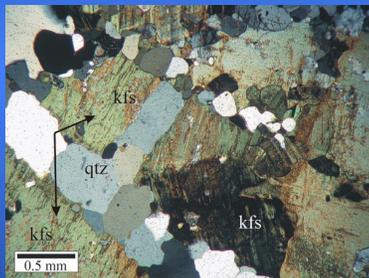


Fig. 3.6 Scanning electron micrograph showing square-shaped etch pits developed on dislocations in a feldspar from a southwestern England granite. Note that in places the pits are coalescing, causing complete dissolution of the feldspar. Scale bar = 10 µm. Photograph courtesy of [unclear]

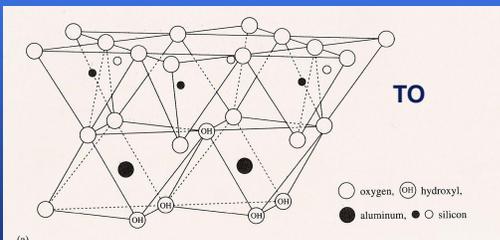
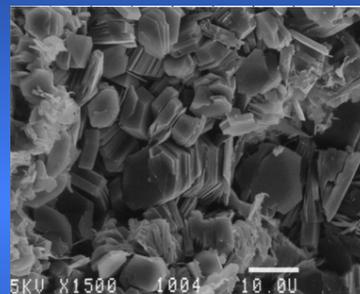
K-feldspar → kaolinite → gibbsite



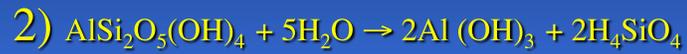
K-feldspar



kaolinite

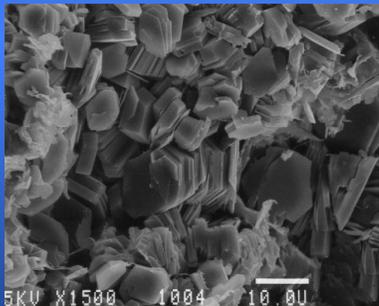


K-feldspar -> kaolinite -> gibbsite



kaolinite

gibbsite

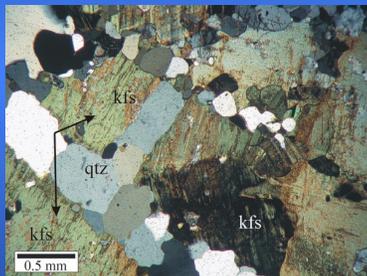


K-feldspar -> kaolinite -> gibbsite



K-feldspar

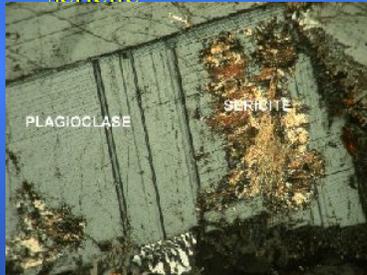
sericite (illite)



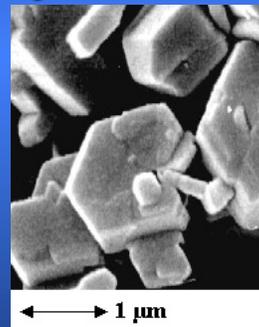
K-feldspar -> kaolinite -> gibbsite



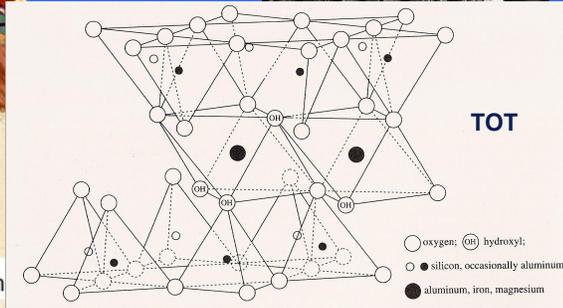
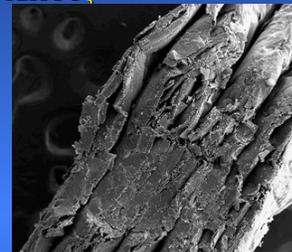
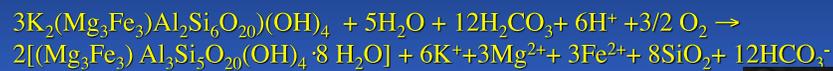
sericite

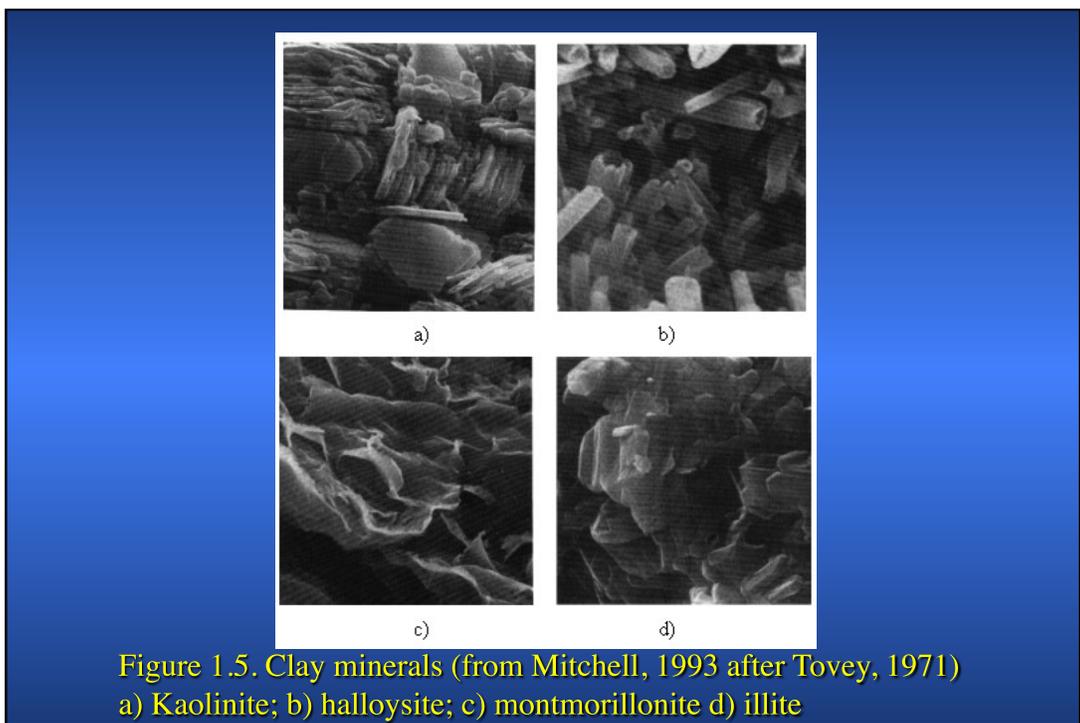
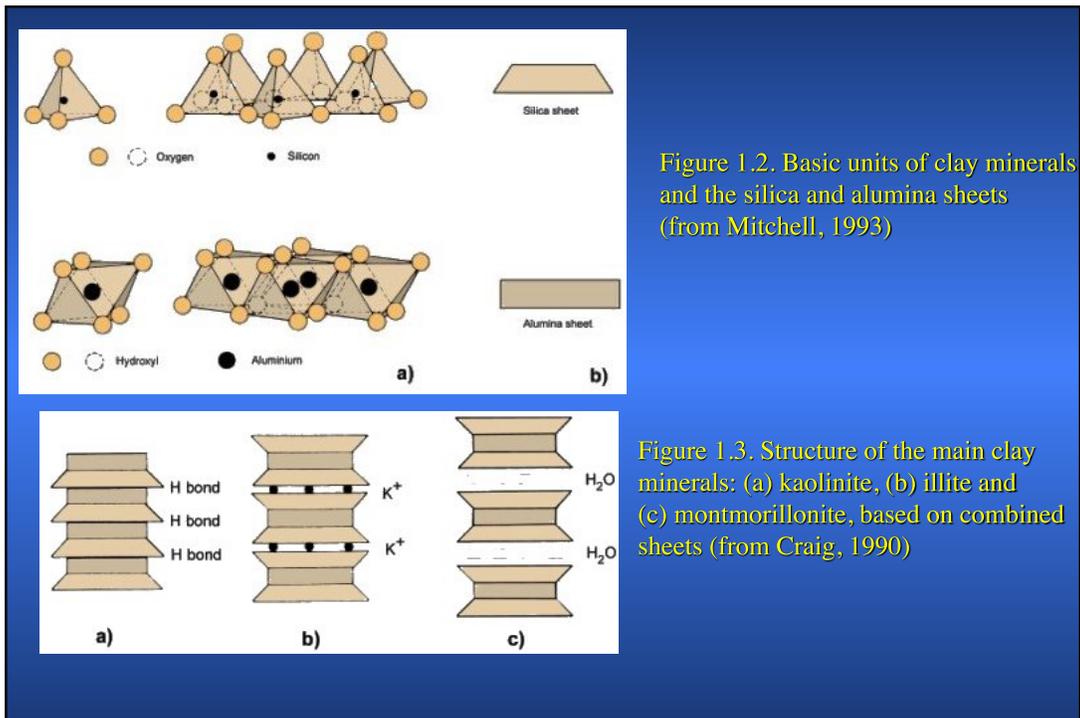


gibbsite

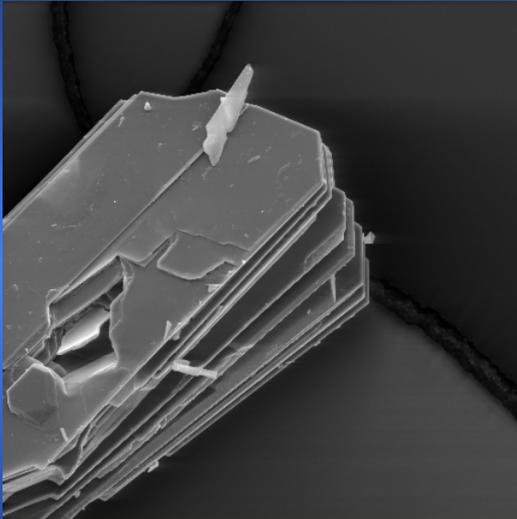


Biotite -> vermiculite

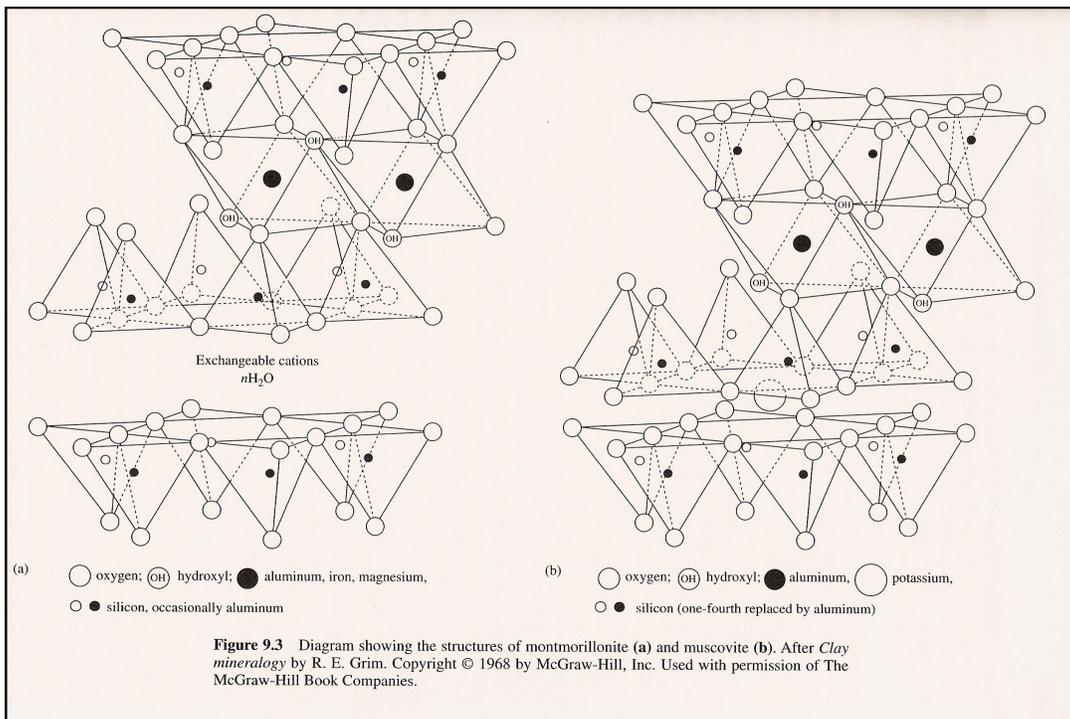




Nanomineralogy



<http://www.nanomineral.info/>



Weathering

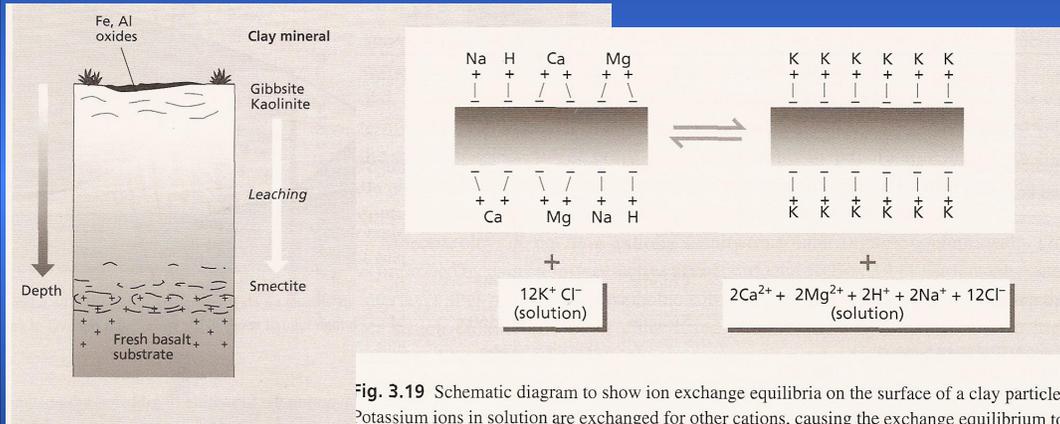
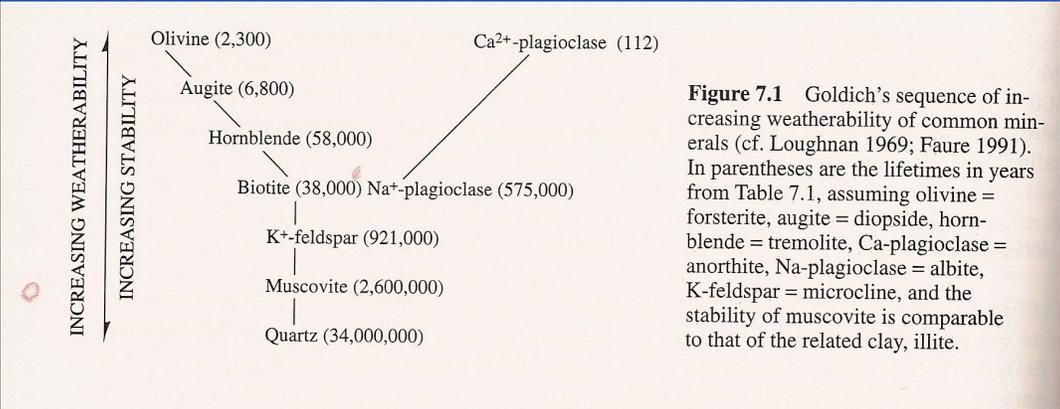
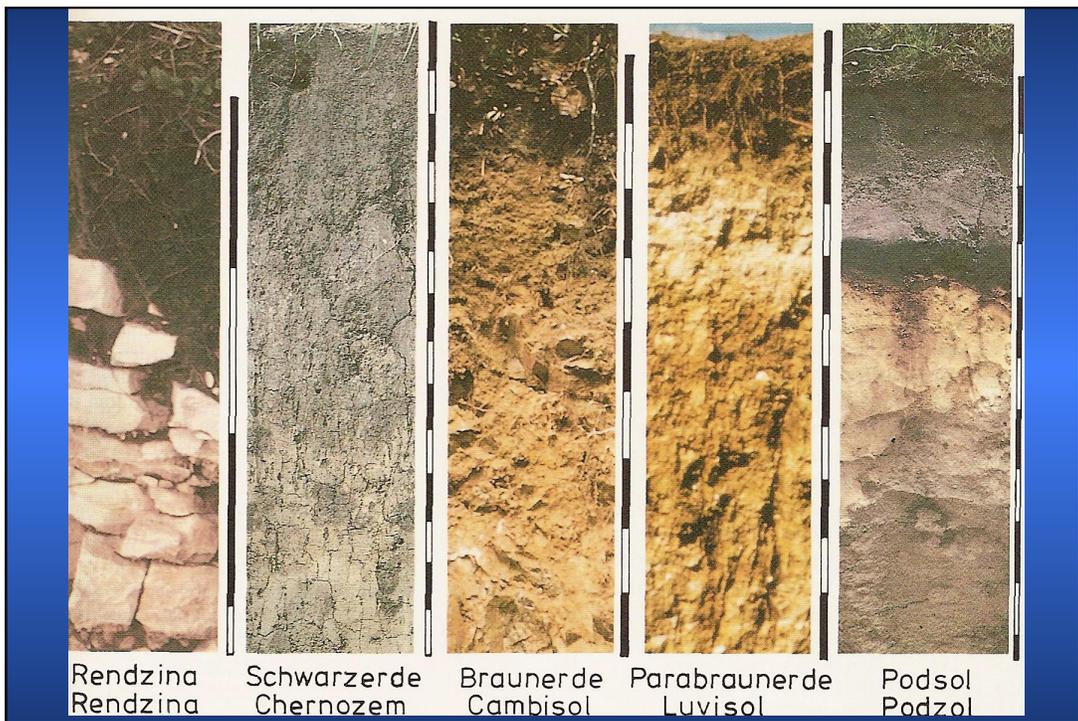
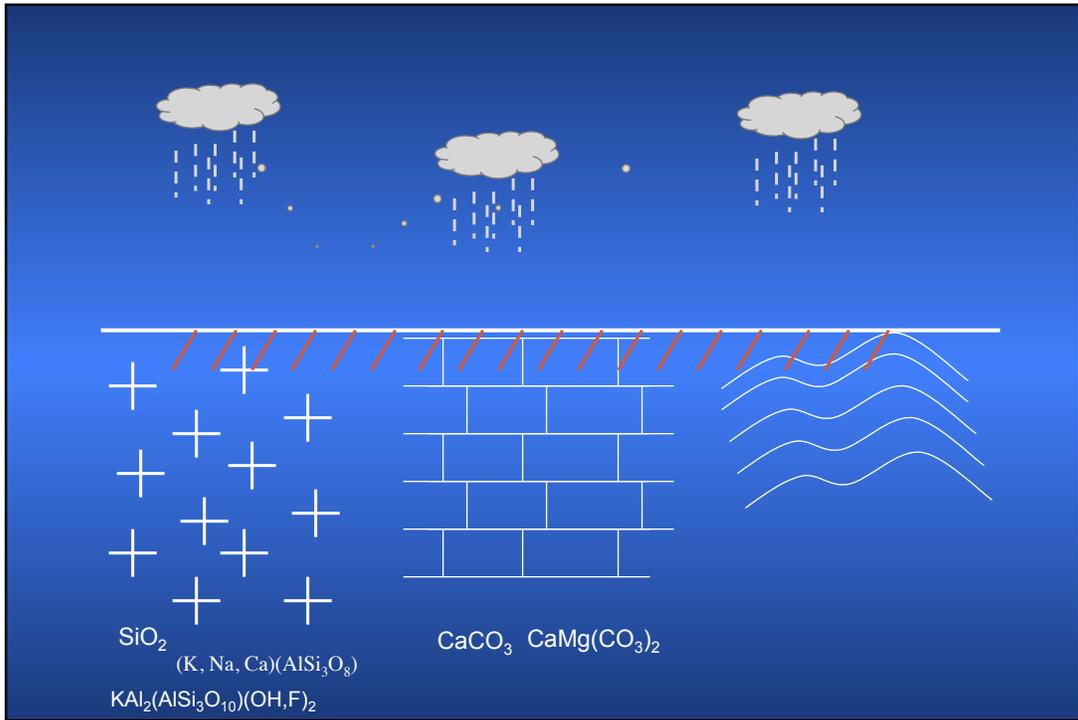
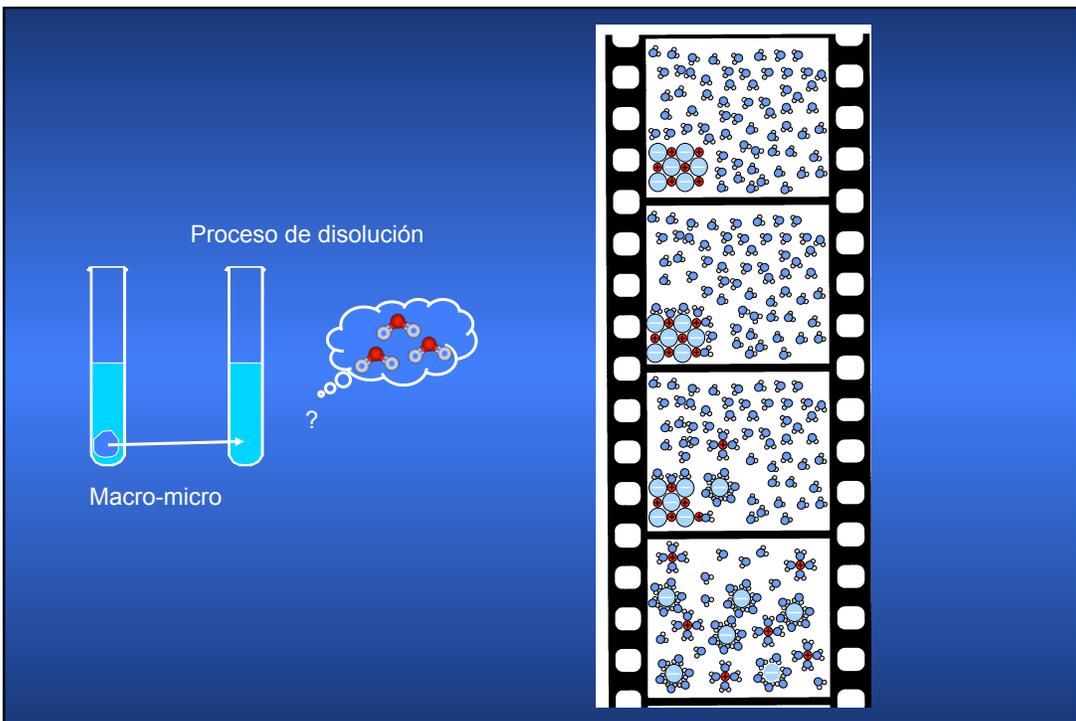


Fig. 3.18 Idealised vertical distribution of clay minerals formed under leaching conditions in soils developed on basalt. CIA values increase from 30–40 in fresh rock to near 100 in heavy

Weathering







Equilibrium constant K

Termodinámica de soluciones acuosas

La Ley de la acción de masas:

En principio cada reacción química de equilibrio se puede describir con la ley de la acción de masas.

a, b, c, d numero de moles



A & B reactantes

C & D productos

Constante de equilibrio $K = \frac{\{C\}^c \cdot \{D\}^d}{\{A\}^a \cdot \{B\}^b}$

Producto de las actividades (concentraciones)

Producto de las actividades (concentraciones)

Termodinámica de soluciones acuosas

K = constante de equilibrio termodinámica o de constante de disociación

-Disolución/precipitación:

K_s = constante de solubilidad

-Complejos (formación/destrucción):

K = constante de complejación, constante de estabilidad

-Reacciones superficiales (sorpción)

K_d = coeficiente de distribución

K_x = coeficiente de selectividad

-Reacciones redox

K = constante de estabilidad

Termodinámica de soluciones acuosas

Importante:

Las constantes de equilibrio son válidas solo para el estado estándar:

Significa en nuestro caso:

$T = 25^\circ\text{C}$

Fuerza Iónica $I = 0$

Equilibrium Constant

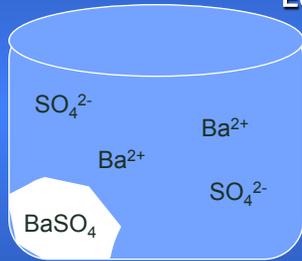


productos

reactantes

Equilibrium constant for the dissolution reaction

$$K = \frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{[\text{BaSO}_4]} = 10^{-9.98} \text{ (25}^\circ\text{C)}$$



For aquatic species (e.g H₂CO₃, HCO₃⁻)

Mineral equilibrium

Complex and Surface complexation

K great (100) = log K = 2 => Ba²⁺ + SO₄²⁻ >> BaSO₄

K small (0.01) = log K = -2 => Ba²⁺ + SO₄²⁻ << BaSO₄

log K

Equilibrium constant K

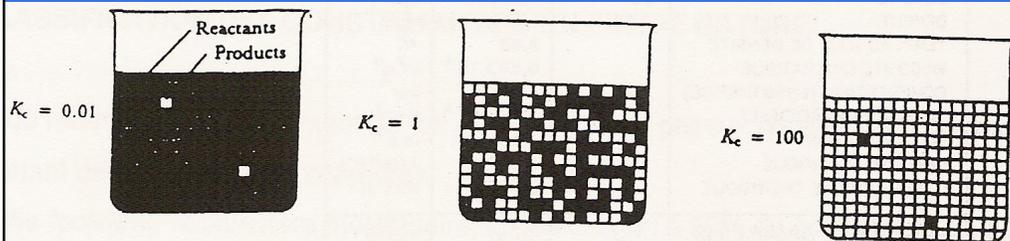


TABLE A1.2 (continued)

II Oxide and Hydroxide Species					
Reaction	ΔH_f° (kcal/mol)	log K	Reaction	ΔH_f° (kcal/mol)	log K
$\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$	13.362	-14.000	$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$	10.4	-2.19
$\text{Li}^+ + \text{H}_2\text{O} = \text{LiOH}^\circ + \text{H}^+$	0.0	-13.64	$\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^\circ + 2\text{H}^+$	17.1	-5.67
$\text{Na}^+ + \text{H}_2\text{O} = \text{NaOH}^\circ + \text{H}^+$	0.0	-14.18	$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^\circ + 3\text{H}^+$	24.8	-12.56
$\text{K}^+ + \text{H}_2\text{O} = \text{KOH}^\circ + \text{H}^+$	—	-14.46	$\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}(\text{OH})_4^\circ + 4\text{H}^+$	31.9	-21.6
$\text{Ca}^{2+} + \text{H}_2\text{O} = \text{CaOH}^+ + \text{H}^+$	—	-12.78	$2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	13.5	-2.95
$\text{Mg}^{2+} + \text{H}_2\text{O} = \text{MgOH}^+ + \text{H}^+$	—	-11.44	$3\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	14.3	-6.3
$\text{Sr}^{2+} + \text{H}_2\text{O} = \text{SrOH}^+ + \text{H}^+$	—	-13.29	$\text{Al}^{3+} + \text{H}_2\text{O} = \text{AlOH}^{2+} + \text{H}^+$	11.49	-5.00
$\text{Ba}^{2+} + \text{H}_2\text{O} = \text{BaOH}^+ + \text{H}^+$	—	-13.47	$\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	26.90	-10.1
$\text{Ra}^{2+} + \text{H}_2\text{O} = \text{RaOH}^+ + \text{H}^+$	—	-13.49	$\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3^\circ + 3\text{H}^+$	39.89	-16.9
$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$	13.2	-9.5	$\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	42.30	-22.7
$\text{Mn}^{2+} + \text{H}_2\text{O} = \text{MnOH}^+ + \text{H}^+$	14.4	-10.59			

Mineral	Reaction	ΔH_r° (kcal/mol)	log K
Portlandite	$\text{Ca}(\text{OH})_2 + 2\text{H}^+ = \text{Ca}^{2+} + 2\text{H}_2\text{O}$	-31.0	22.8
Brucite	$\text{Mg}(\text{OH})_2 + 2\text{H}^+ = \text{Mg}^{2+} + 2\text{H}_2\text{O}$	-27.1	16.84
Pyrolusite	$\text{MnO}_2 + 4\text{H}^+ + 2e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	-65.11	41.38
Hausmanite	$\text{Mn}_3\text{O}_4 + 8\text{H}^+ + 2e^- = 3\text{Mn}^{2+} + 4\text{H}_2\text{O}$	-100.64	61.03
Manganite	$\text{MnOOH} + 3\text{H}^+ + e^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	—	25.34
Pyrochroite	$\text{Mn}(\text{OH})_2 + 2\text{H}^+ = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	—	15.2
Gibbsite (crystalline)	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	-22.8	8.11
Gibbsite (microcrystalline)	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	(-24.5)	9.35
Al(OH) ₃ (amorphous)	$\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{3+} + 3\text{H}_2\text{O}$	(-26.5)	10.8
Goethite	$\text{FeOOH} + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$	—	-1.0
Ferrihydrite (amorphous to microcrystalline)	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{3+} + 3\text{H}_2\text{O}$	—	3.0 to 5.0

Mineral Equilibrium



Como BaSO_4 es un sólido, c es constante =>

Equilibrium constant for the dissolution reaction

$$K = [\text{Ba}^{2+}] + [\text{SO}_4^{2-}] = 10^{-9.98} \text{ (25}^\circ\text{C)}$$

$$[m_{\text{Ba}^{2+}}] [m_{\text{SO}_4^{2-}}] \approx 10^{-9.98}$$

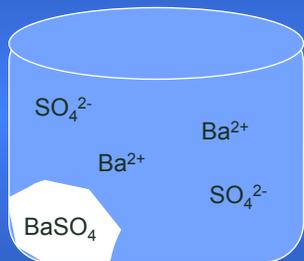
= producto de solubilidad

$$m_{\text{Ba}^{2+}} = m_{\text{SO}_4^{2-}}$$

$$[m_{\text{Ba}^{2+}}] [m_{\text{Ba}^{2+}}] \approx 10^{-9.98}$$

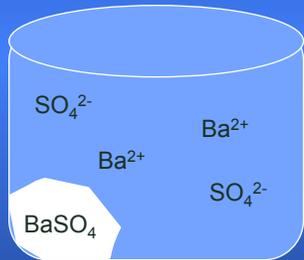
$$m_{\text{Ba}^{2+}} = 10^{-4.99} \text{ moles/L} \times 137\text{g/mole} \times 1000\text{mg/g} = 1.4 \text{ mg/L}$$

$$m_{\text{SO}_4^{2-}} = 10^{-4.99} \text{ moles/L} \times 96\text{g/mole} \times 1000\text{mg/g} = 1.0 \text{ mg/L}$$



Ion Activity Product & Saturation Index

$$IAP_{\text{barite}} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = [10^{-4.99}] [10^{-4.99}] = 10^{-9.98} = K$$



$$\text{Saturation index (SI)} = \log \frac{IAP}{K_{\text{mineral}}}$$

SI = 0; mineral is in equilibrium
SI < 0; mineral is undersaturated
SI > 0; mineral is oversaturated

Fuérza Ionica & Actividad

Termodinámica de soluciones acuosas

Fuerza iónica:

Es una medida macroscópica de las interacciones (coulombianas) : concentración de especies disueltas y su carga eléctrica.

$$I = \frac{1}{2} \sum m_i z_i^2$$

Ej. electrolito monovalente-monovalente: NaCl

$$I = \frac{1}{2} (m_{Cl^-} (-1)^2 + m_{Na^+} (+1)^2) = \frac{1}{2} 2m_{Cl^-} = m_{Cl^-} = m_{Na^+} = m_{NaCl}$$

Ej. electrolito monovalente-divalente: CaCl₂

$$I = \frac{1}{2} (2m_{Cl^-} (-1)^2 + m_{Ca^{2+}} (+2)^2) = \frac{1}{2} (2m_{Cl^-} + 4m_{Ca^{2+}}) = \frac{1}{2} (m_{CaCl_2} + 4m_{CaCl_2}) = \frac{5}{2} m_{CaCl_2}$$

Equivalencia con la conductividad Ω (μ S/cm):

$$I = 0.8 \times 10^{-5} \cdot \Omega \quad \text{aguas Na-Cl}$$

$$I = 1.7 \times 10^{-5} \cdot \Omega \quad \text{aguas Ca-SO}_4, \text{ Mg-SO}_4$$

$$I = 1.9 \times 10^{-5} \cdot \Omega \quad \text{aguas Ca-(HCO}_3)_2$$

Termodinámica de soluciones acuosas

Actividad:

$$a_i = f_i \cdot c_i$$

a_i actividad

c_i concentraciones

i respecto de una especie

f_i coeficiente de actividad

Actividad del soluto

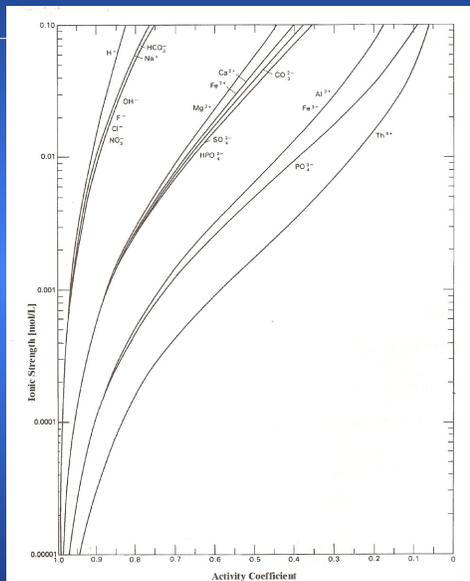


Fig. 2 Relation between ionic strength and activity coefficient in a range up to 0.1 mol/L (after Hem 1985)

Actividad del soluto: medida experimental

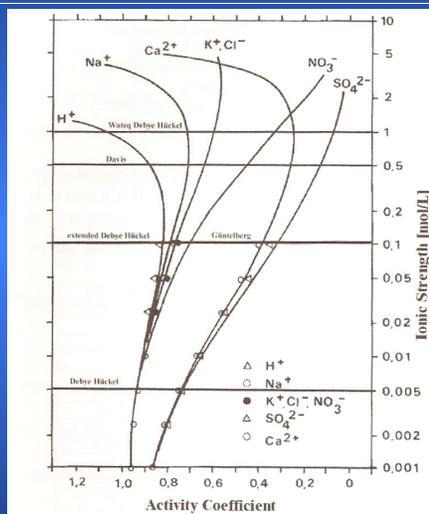


Fig. 3 Relation of ionic strength and activity coefficient in higher concentrated solutions, (up to 1 = 10mol/kg), valid range for the different theories of dissociation are indicated as lines (modified after Garrels and Christ 1965)

Actividad del agua: valor calculado

Ley de Raoult:

la actividad de la fase mayoritaria se aproxima a la fracción molar.

$$\chi_{\text{H}_2\text{O}} = \frac{N_{\text{H}_2\text{O}}}{N_{\text{H}_2\text{O}} + N_{\text{soluto}}} = \frac{1000/18}{1000/18 + \sum m_i} = \frac{55.51}{55.51 + \sum m_i}$$

Ej.:

	$\sum m_i$	$\chi_{\text{H}_2\text{O}}$ calculada	$a_{\text{H}_2\text{O}}$ experimental
agua marina	1.14	0.98	0.98
salmuera eq. con halita	13.0	0.81	0.75

→ Para la mayoría de soluciones acuosas: $a_{\text{H}_2\text{O}} \approx 1$

→ Para soluciones concentradas: $\chi_{\text{H}_2\text{O}} > a_{\text{H}_2\text{O}}$

porque no se han tenido en cuenta las interacciones ión-disolvente:
una parte de las moléculas de agua quedan atrapadas en la esfera de solvatación y no son activas termodinámicamente.

Actividad del soluto: medida experimental

Actividad media del soluto:

Los iones no están nunca solos en solución, siempre hay sales con iones de signos contrarios
→ solo podemos medir actividades del conjunto de soluto y luego buscaremos la forma que estimar actividades de iones individuales.



Sea una sal que se disuelve:

$$\mu_{AB} = \nu^+ \mu_{A^{z+}} + \nu^- \mu_{B^{z-}} \rightarrow \mu_{\pm} = \nu^+ \mu_+ + \nu^- \mu_-$$

Condición de equilibrio:

Potencial químico medio: es la media aritmética de los potenciales de los iones:

$$\mu_{\pm} = \frac{\nu^+ \mu_+ + \nu^- \mu_-}{\nu^+ + \nu^-} = \frac{\nu^+ \mu_+ + \nu^- \mu_-}{\nu}$$

$$\nu \mu_{\pm} = \nu^+ \mu_+ + \nu^- \mu_-$$

Y teniendo en cuenta que $\mu = \mu^0 + RT \ln a$
la actividad media es la media geométrica de las actividades de los iones

$$\begin{aligned} a_{\pm}^{\nu} &= a_+^{\nu^+} a_-^{\nu^-} \\ \gamma_{\pm}^{\nu} &= \gamma_+^{\nu^+} \gamma_-^{\nu^-} \\ m_{\pm}^{\nu} &= m_+^{\nu^+} m_-^{\nu^-} \end{aligned}$$

Actividad del soluto: medida experimental

El coeficiente de actividad medio γ_{\pm} puede medirse experimentalmente a partir de los cambios en las propiedades de la solución: presión de vapor, punto de ebullición y de congelación, presión osmótica, etc.

Ej.: un experimento corriente consiste en medir $a_{\text{H}_2\text{O}}$ ($=a_1$) para diferentes soluciones con concentraciones de soluto m_2 diferentes. Se establece una relación experimental:

$$a_{\text{H}_2\text{O}} = a_{\text{exp.}}(m_2)$$

A continuación se deduce una expresión teórica de $\gamma_{\pm} = \gamma_{\text{teórica}}(a_1)$ y se substituye a_1 por su relación experimental.

(solo como ejemplo): $a_{\text{exp.}}(m_2)$

$$\ln \gamma_{\pm}^{\text{v}} = -\ln m_2 - \int \frac{55.51}{m_2} d \ln a_{\text{H}_2\text{O}}$$

Actividad de un ión individual: medida experimental

Es práctico para los cálculos disponer de la actividad individual de los iones.

Convenio de MacInnes (1919):

$$\gamma_{\text{K}^+} = \gamma_{\text{Cl}^-}$$

Se basa en que K^+ i Cl^- tienen la misma carga, estructura electrónica semejante y coeficiente de difusión muy parecido.

$$\gamma_{\pm}^{\text{v}} = \gamma_{+}^{\text{v}} \gamma_{-}^{\text{v}} \longrightarrow \gamma_{\text{K}^+} = \gamma_{\text{Cl}^-} = \gamma_{\pm \text{KCl}} \longleftarrow \text{experimental}$$

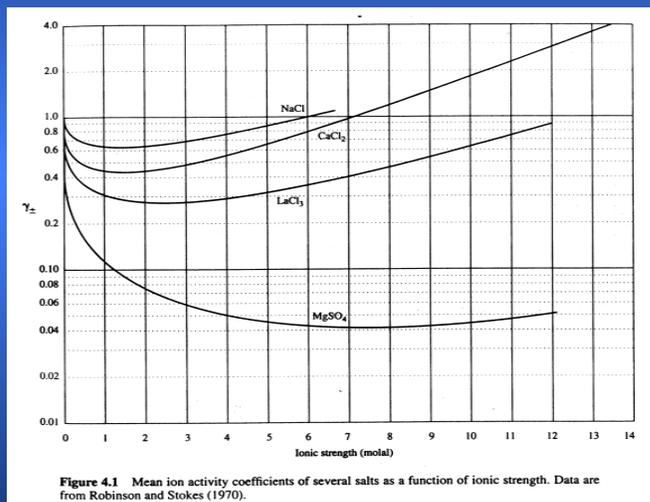
Una vez conocidos γ_{K^+} y γ_{Cl^-} cualquier otro ión puede ser calculado a partir de los datos experimentales de una sal del ión.

$$\gamma_{\pm \text{FeCl}_3}^4 = \gamma_{\text{Fe}^{3+}} \gamma_{\text{Cl}^-}^3 \quad \text{Ej.:}$$

$$\gamma_{\text{Fe}^{3+}} = \frac{\gamma_{\pm \text{FeCl}_3}^4}{\gamma_{\pm \text{KCl}}^3} \longleftarrow \text{experimental}$$

Actividad del soluto: medida experimental

La variación experimental de γ_{\pm} con m_2 o con I (Langmuir, 1997):



Actividad de un ión individual: cálculo

1) Ley restringida de Debye-Hückel

Se basa en la teoría electrostática (Bockris y Reddy, 1973) son una serie de simplificaciones que solo son válidas para soluciones muy diluidas ($I < 0.01$)

- Un ión se considera una carga puntual
- El resto de iones se consideran una nube esférica de carga opuesta
- El agua es un medio dieléctrico continuo no influido por el ión
- Las interacciones son solo electrostáticas

$$\log \gamma_i = -A z_i^2 \sqrt{I}$$

$$\text{donde } A = \frac{(8\pi)^{1/2} N_A^2 e_0^3}{2 \cdot 2.303 (RT \epsilon)^{3/2}} = 0.5092 \text{ a } 25^\circ\text{C}$$

Discusión:

- ✓ $z_i > z_j \rightarrow \gamma_i < \gamma_j$ (ver $\gamma_{\text{Na}^+} > \gamma_{\text{Ca}^{2+}}$)
- ✓ si $I \rightarrow 0$, $\gamma_i \rightarrow 1$ y $\gamma_i \rightarrow \gamma_j$ si $z_i = z_j$ (ver γ_{Na^+} y γ_{K^+})
- ✓ si I aumenta, γ_i disminuye

Actividad de un ión individual: cálculo

2) Ley ampliada de Debye-Hückel

De la ley límite se deduce que $\log \gamma_i - \sqrt{I}$ es una recta.
En cambio, se ve experimentalmente que es una curva y que depende de cada sal (de cada ión).

Esto se debe a que para $I > 0.01$:

→ Un ión no puede considerarse una carga puntual, sino que tiene un radio a_i (valor de ajuste de datos experimentales).

La incorporación de una carga no puntual a la deducción de la ley de DH lleva a:

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}}$$

$$\text{donde } B = \left(\frac{8\pi N_A^2 e^2}{RT \epsilon} \right)^{1/2} = 0.3283 \text{ a } 25^\circ\text{C}$$

Actividad de un ión individual: medida experimental

variación experimental (Langmuir, 1997):

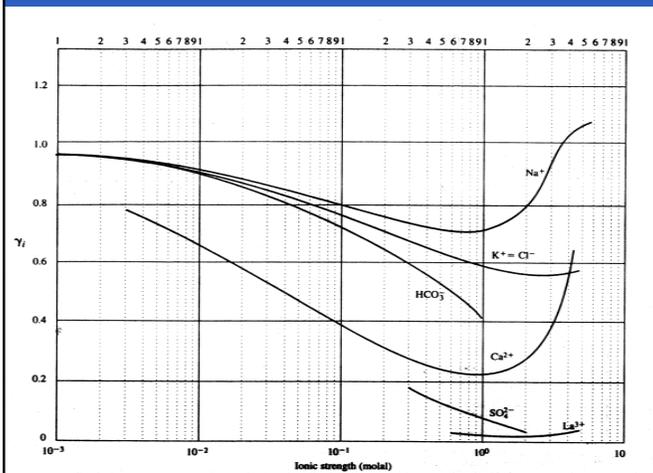


Figure 4.2 Some individual ion activity coefficients computed from mean salt data assuming the MacInnes convention.

cálculo según Debye Huckel:

$$\log \gamma_i = - \frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}}$$

$$z_i > z_j \rightarrow \gamma_i < \gamma_j$$

(ver $\gamma_{\text{Na}^+} > \gamma_{\text{Ca}^{2+}}$)

$$\text{si } I \rightarrow 0, \gamma_i \rightarrow 1 \text{ y } \gamma_i \rightarrow \gamma_j \text{ si } z_i = z_j$$

(ver $\gamma_{\text{Na}^+} \text{ y } \gamma_{\text{K}^+}$)

si I aumenta, γ_i disminuye

