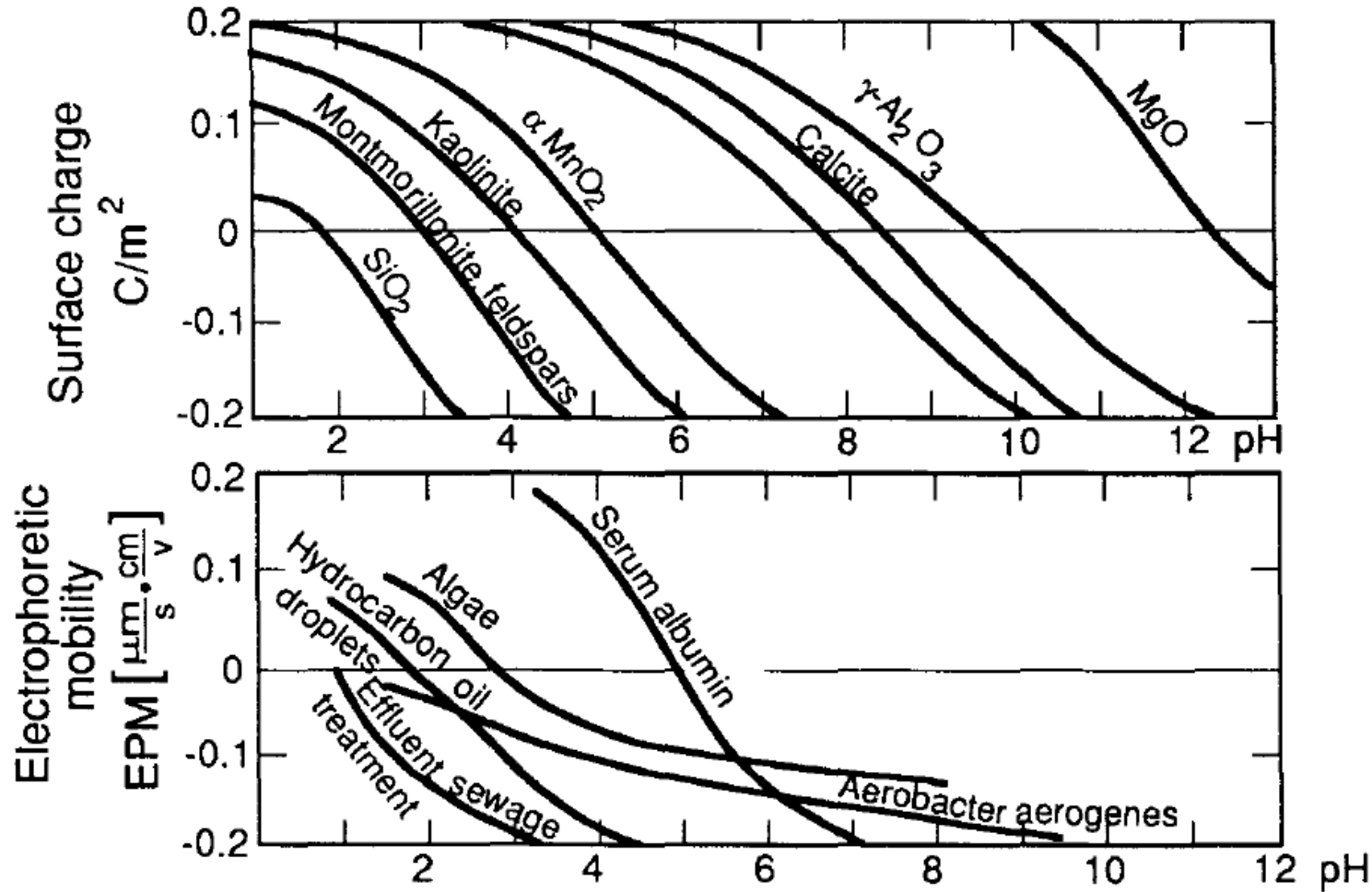# GB481
Geochemie minerálních povrchů

3
Povrchový náboj
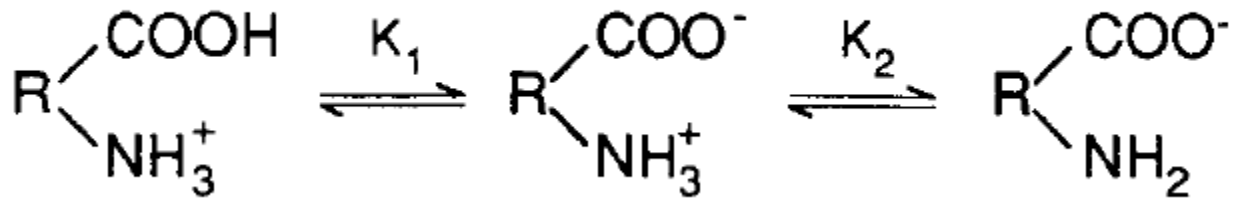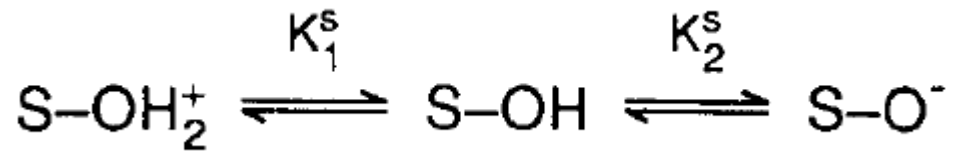# a elektrická dvojvrstva

Josef Zeman
2020

Povrchový náboj

Effect of pH on charge and electrophoretic mobility. In the neutral pH range most suspended solids typically encountered in natural waters are negatively charged. These simplified curves are based on results by different investigators whose experimental procedures are not comparable and may depend upon solution variables other than pH. The curves are meant to exemplify trends and are meaningful in a semiquantative way only. The curve for calcite is for an equilibrium suspension of $CaCO_3$ with air ($p_{CO_2} = 10^{-3.5}$ atm).

Povrchový náboj

Obdoba reakcí ve vodě

$$S-OH_2^+ \xrightleftharpoons{K_1^s} S-OH \xrightleftharpoons{K_2^s} S-O^-$$

$$R{\overset{COOH}{\underset{NH_3^+}{\diagdown}}} \xrightleftharpoons{K_1} R{\overset{COO^-}{\underset{NH_3^+}{\diagdown}}} \xrightleftharpoons{K_2} R{\overset{COO^-}{\underset{NH_2}{\diagdown}}}$$

Povrchový náboj

Koordinační vazby

$$\equiv Fe-OH + Cu^{2+} \rightleftharpoons \equiv FeOCu^+ + H^+$$

$$\equiv Fe-OH + HPO_4^{2-} \rightleftharpoons \equiv Fe-OPO_3^{2-} + H_2O$$

$$\equiv S + HS^- \rightleftharpoons \equiv S-SH^-$$

$$\equiv AgBr + Br^- \rightleftharpoons \equiv AgBr_2^-$$

$$\equiv RCOOH + Ca^{2+} \rightleftharpoons \equiv RCOOCa^+ + H^+$$
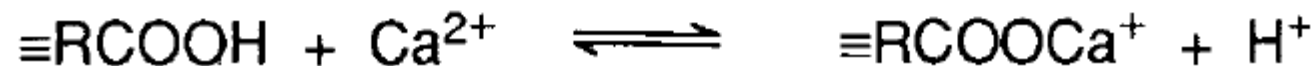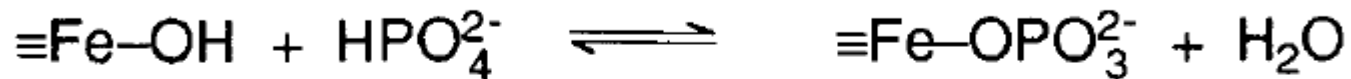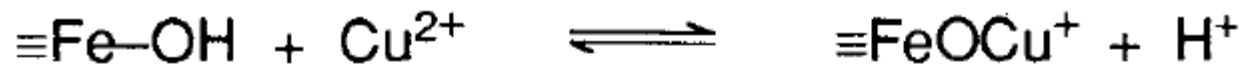
Povrchový náboj

Izomorfní náhrada
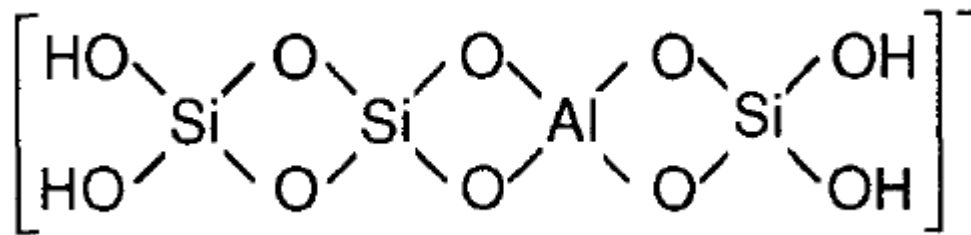
$$Q_P = \{S{-}OH_2^+\} - \{S{-}O^-\} + \{S{-}OM^+\}$$

$$Q_P = \{S{-}OH_2^+\} - \{S{-}O^-\} - \{SA^-\}$$

Povrchový potenciál

Elektrická dvojvrstva

The diffuse double layer
a) Diffuseness results from thermal motion in solution.
b) Schematic representation of ion binding on an oxide surface on the basis of the surface complexation model. s = specific surface area $m^2 kg^{-1}$. Braces refer to concentrations in mol kg^{-1}.
c) The electric surface potential, ψ, falls off (simplified model) with distance from the surface. The decrease with distance is exponential when $\psi < 25$ mV. At a distance κ^{-1} the potential has dropped by a factor of (1/e). This distance can be used as a measure of the extension (thickness) of the double layer (see Eq. 3.8c). At the plane of shear (moving particle) a zeta potential can be established with the help of electrophoretic mobility measurements.
d) Variation of charge distribution (concentration of positive and negative ions) with distance from the surface (Z = charge of the ion).
e) The net excess charge.
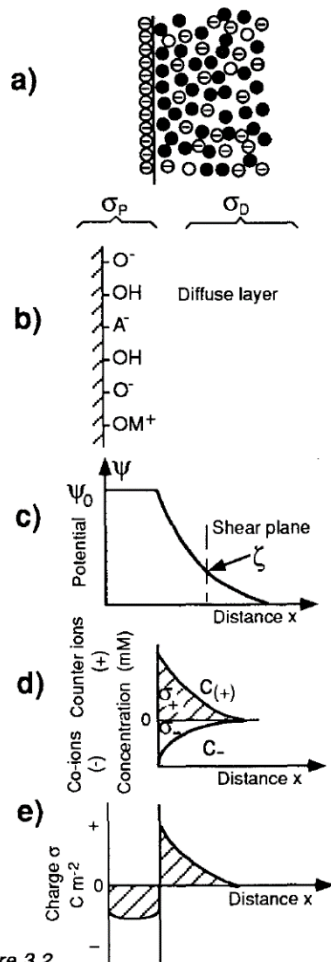
$$\sigma_P = \frac{F}{As} \left[\{S\text{-}OH_2^+\} + \{S\text{-}OM^+\} - \{S\text{-}O^-\} - \{S\text{-}A^-\} \right] \quad \text{(i)}$$

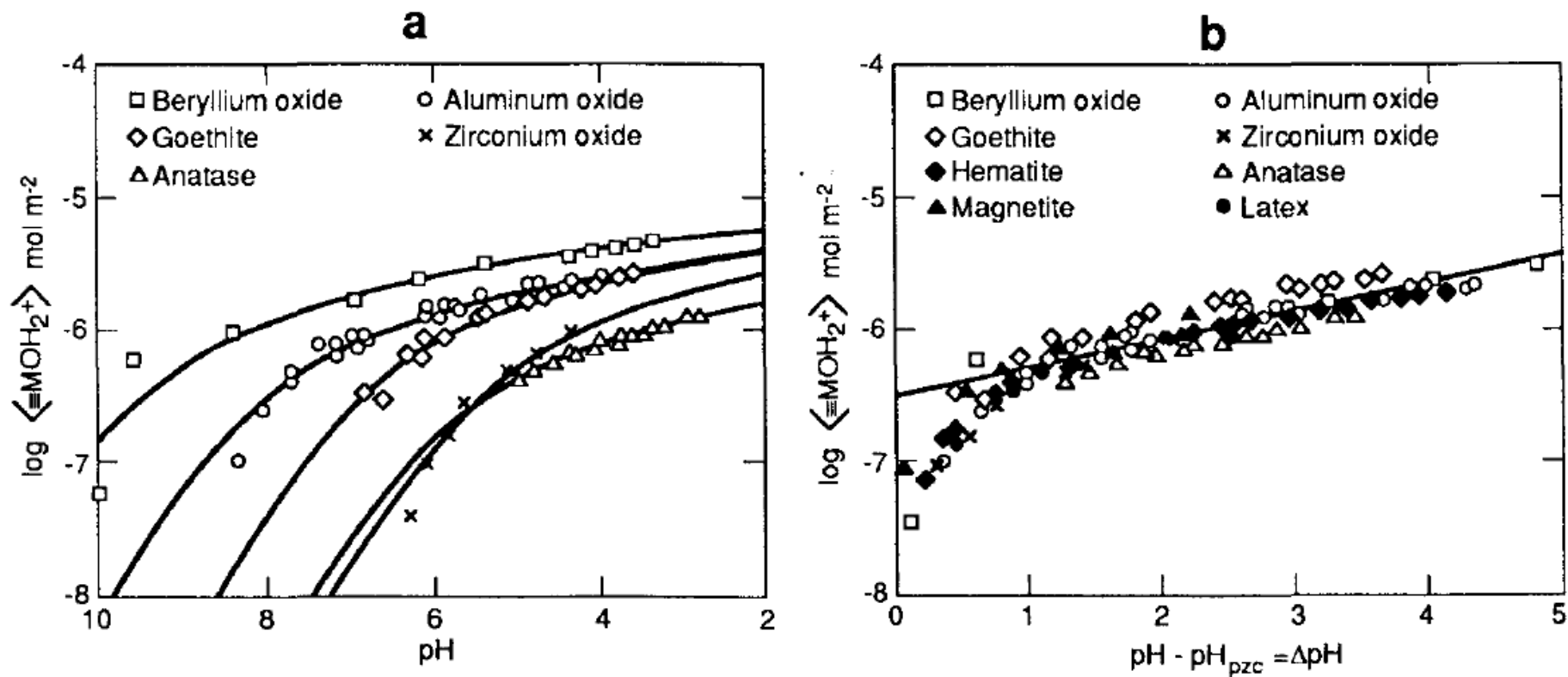$$\sigma_P + \sigma_D = 0 \quad \text{(ii)}$$

approximately

$$\psi = \psi_0 \exp(-\kappa d) \quad \text{(iii)}$$

$$C_+ = C_{x=\infty} \exp\left(\frac{-zF\psi}{RT}\right) \quad \text{(iv)}$$

$$C_- = C_{x=\infty} \exp\left(\frac{zF\psi}{RT}\right) \quad \text{(v)}$$

$$\sigma_P = \left(8RT\varepsilon\varepsilon_0 \, C_x 10^3\right)^{1/2} \cdot \sinh\left(\frac{zF\psi}{2RT}\right) \quad \text{(vi)}$$

ure 3.2

Povrchový náboj

Surface protonation isotherms. Dots represent experimental data from titration curves at ionic strength $I = 0.1$ (Hematite, $I = 0.2$). References are indicated in Table 3.1. The concentration of protonated sites {$=MOH_2^+$} is given in moles m^{-2}. BET surface data were used to calculate the surface concentration.

a) surface protonation vs pH;
b) surface concentration as a function of $pH_{pzc} - pH = \Delta pH$ (Eq. 3.5)

(From Wieland, Wehrli and Stumm, 1988)

$$\Delta G_{tot}^o = \Delta G_{intr}^o + \Delta G_{coul}^o$$

Povrchový náboj

Table 3.1 Protonation isotherm parameters of different oxides (see Fig. 3.4)

Surface		a) pH_{pzc}	b) $pK^s_{a_1}$ (int)	c) C $\mu F/cm^2$	d) a kJ/mol	e) n
TiO_2	f)	6.25	4.92	79	99	0.19
ZrO_2	g)	6.4	4.72	148	51	
δ-Al_2O_3	h)	8.7	7.32	115	68	0.13
α-FeOOH	i)	7.28	6.03	167	47	0.16
α-Fe_2O_3	k)	8.67	7.47	94	83	0.16
Fe_3O_4	g)	6.8	5.63	151	52	
BeO	l)	10.2	8.71	134	58	0.085
Latex	m)	8.0	6.45	113	69	0.14

a) pH of the point of zero charge
b) Intrinsic protonation equilibrium constant (Eq. 2.5)
c) Integral double layer capacitance
d) Interaction energy parameter of the Frumkin Fowler Guggenheim FFG isotherm (see Chapter 4)
   The high site's density used in these calculations yields high values of a
e) Freundlich slope for $\Delta pH > 2$ (slope of Freundlich isotherm; see Chapter 4)
f) Wieland, Wehrli and Stumm (1988)
g) Regazzoni, Blesa and Maroto (1983)
h) Kummert and Stumm (1980)
i) Sigg and Stumm (1981)
k) Fokkink (1987)
l) Furrer and Stumm (1986); n was calculated for $\Delta pH > 4$
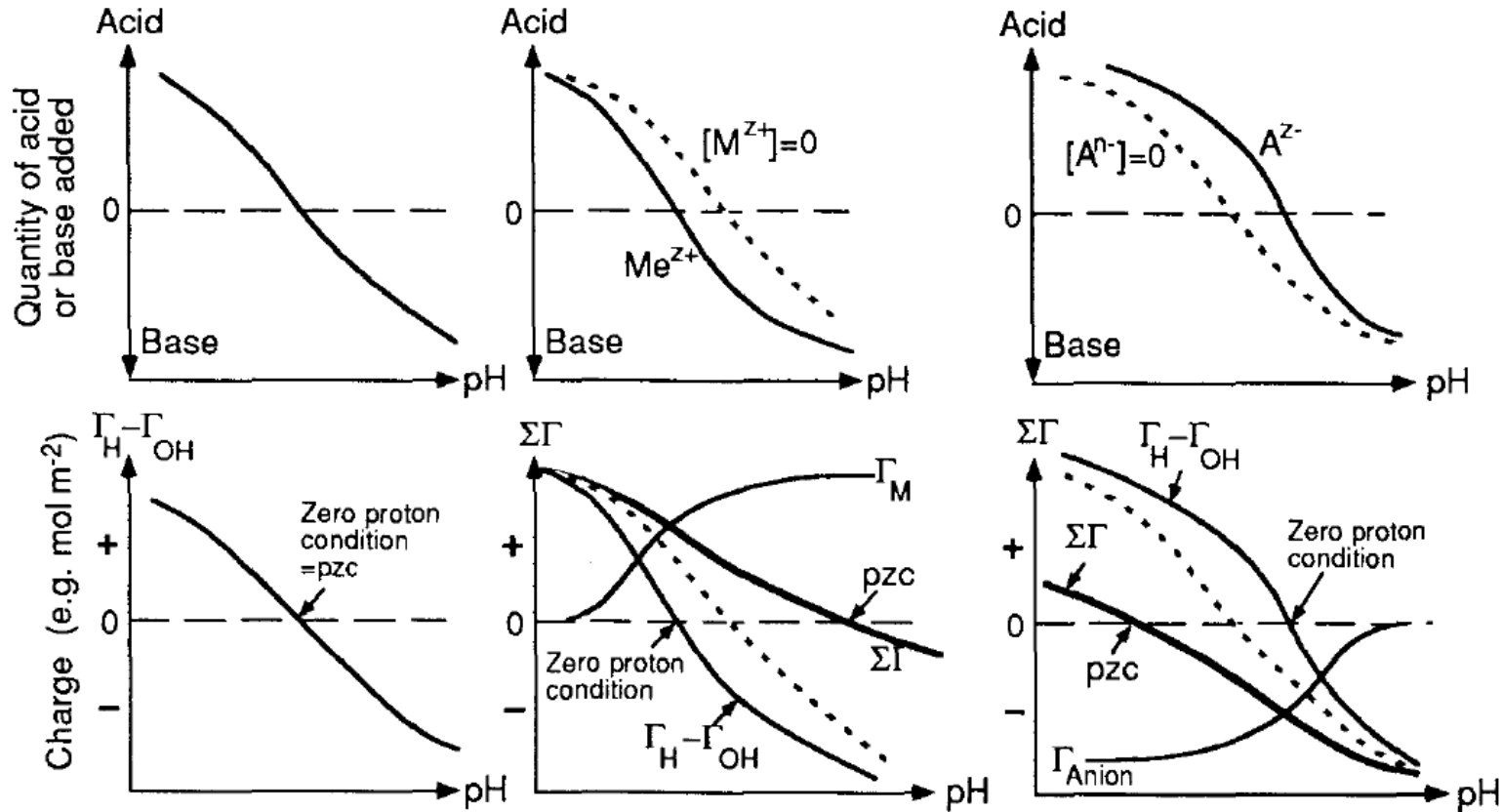m) Harding and Healy (1985)

Povrchový náboj

Absence of specifically adsorbable species

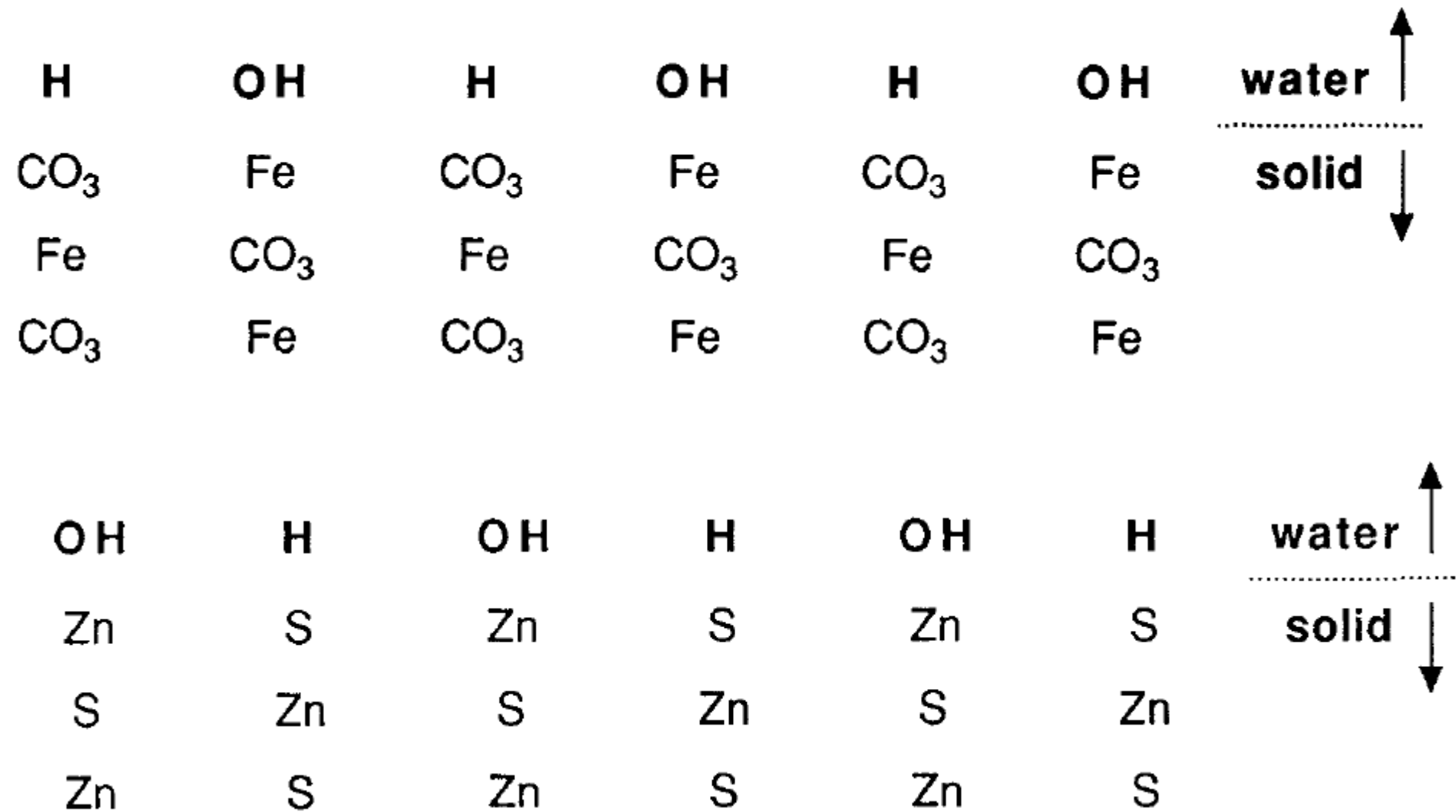Specifically adsorbable M^{z+}

Specifically adsorbable Anion A^{z-}

The net charge at the hydrous oxide surface is established by the proton balance (adsorption of H or OH⁻ and their complexes at the interface *and* specifically bound cations or anions. This charge can be determined from an alkalimetric-acidimetric titration curve and from a measurement of the extent of adsorption of specifically adsorbed ions. Specifically adsorbed cations (anions) increase (decrease) the pH of the point of zero charge (pzc) or the isoelectric point but lower (raise) the pH of the zero net proton condition (pznpc).
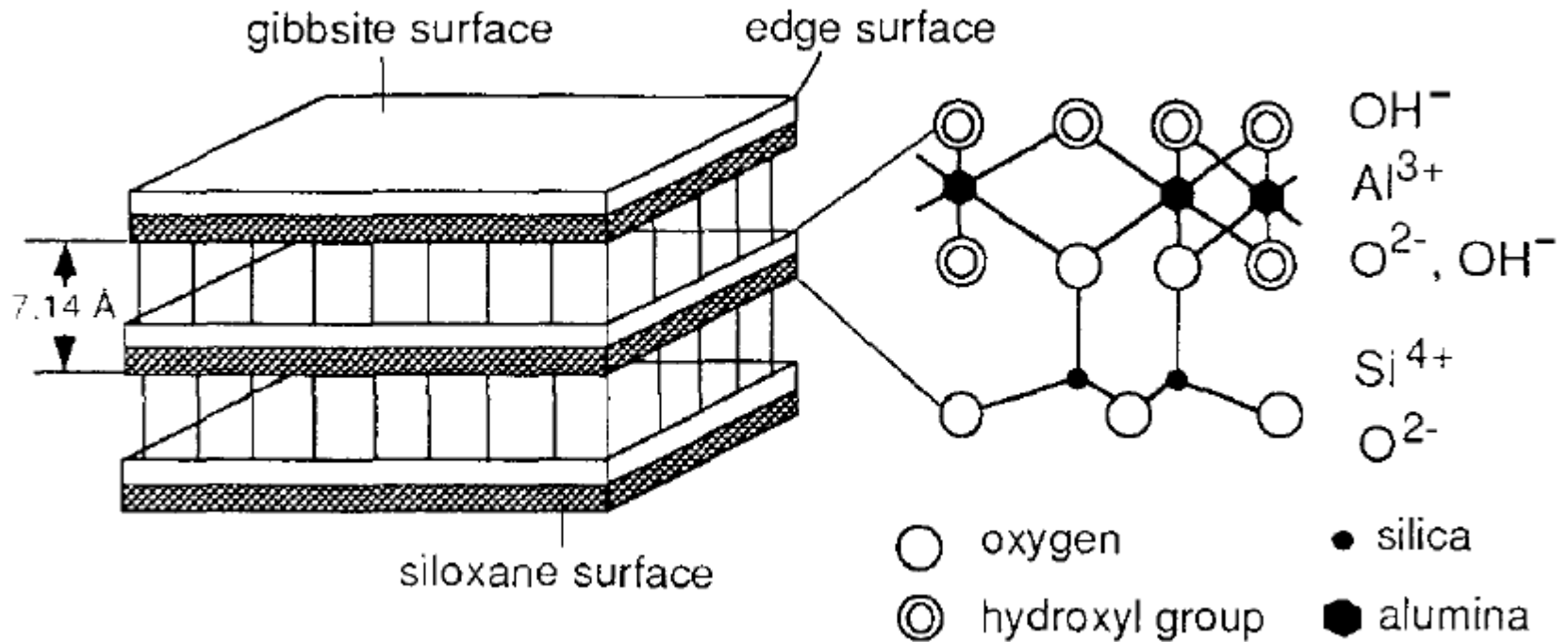
Addition of a ligand, at constant pH, increases surface protonation while the addition of a metal ion (that is specifically adsorbed) lowers surface protonation.

(Modified from Hohl, Sigg and Stumm, 1980, and from Stumm and Morgan, 1981)

Povrchový náboj

H	O H	H	O H	H	O H	water
CO_3	Fe	CO_3	Fe	CO_3	Fe	**solid**
Fe	CO_3	Fe	CO_3	Fe	CO_3	
CO_3	Fe	CO_3	Fe	CO_3	Fe	

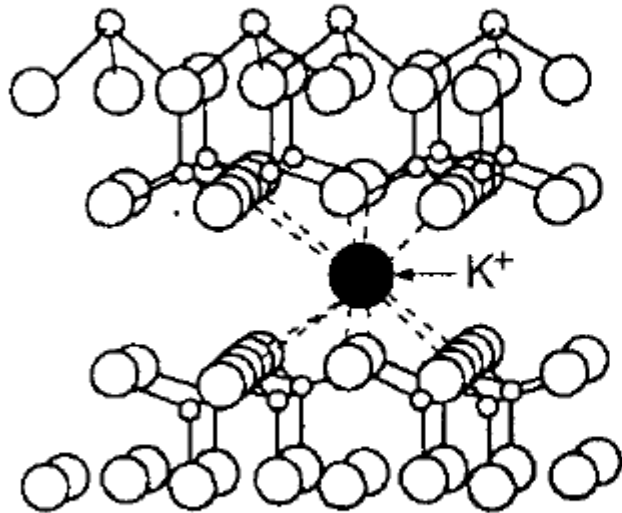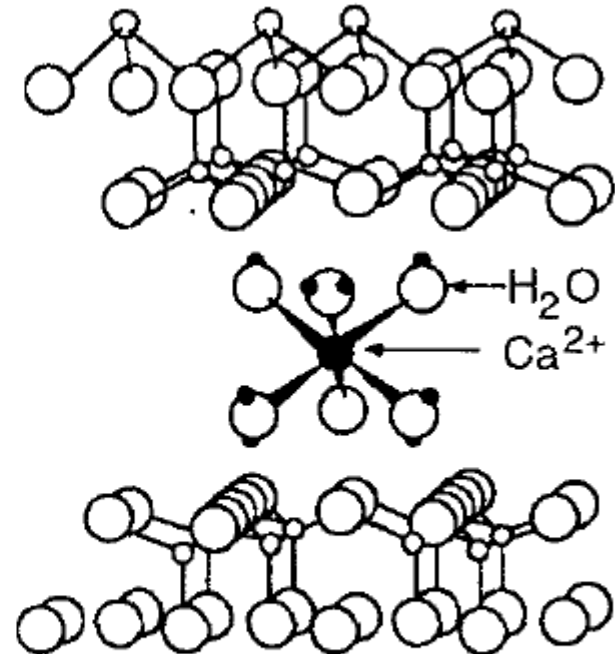| O H	H	O H	H	O H	H	water
Zn	S	Zn	S	Zn	S	**solid**
S	Zn	S	Zn	S	Zn	
Zn	S	Zn	S	Zn	S	

Povrchový náboj

Schematic representation of the kaolinite structure. It reveals the 1:1 structure due to the alternation of silica-type (black) and gibbsite-type layers (white). Furthermore, the edge surface exposes aluminol and silanol groups.

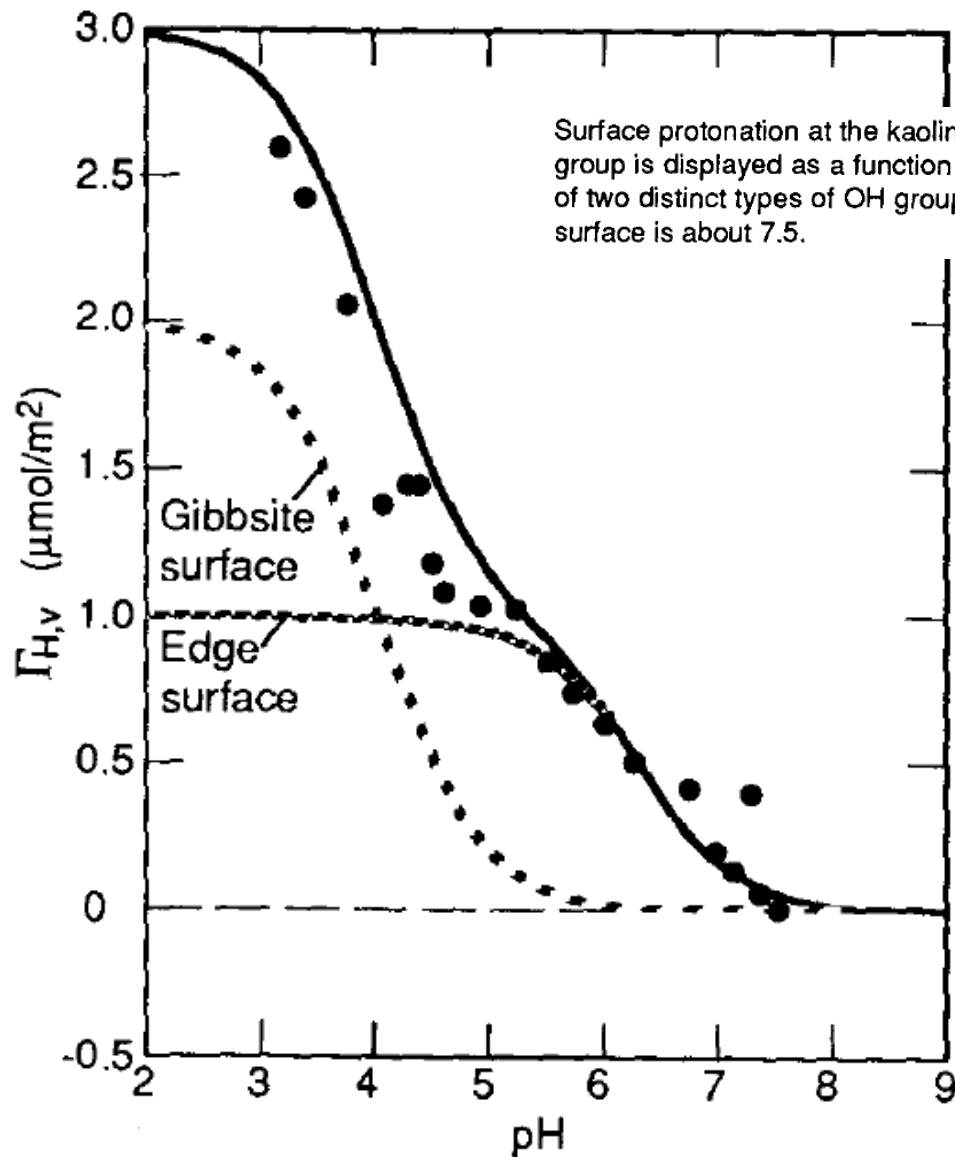# Povrchový náboj

Inner-sphere surface complex:
K⁺ on vermiculite

Outer-sphere surface complex:
Ca (H₂O)₆²⁺ on montmorillonite

Surface complexes between metal cations and siloxane ditrigonal cavities on 2:1 phyllosilicates, shown in exploded view.

Povrchový náboj

Surface protonation at the kaolinite surfaces. The excess proton density, $\Gamma_{H,V}$, at the surface hydroxyl group is displayed as a function of pH. Surface protonation is interpreted as a successive protonation of two distinct types of OH groups localized at the gibbsite and edge surfaces. The pH_{pzc} of the edge surface is about 7.5.

Povrchový náboj

Apatit: $pH_{pzc} = 8{,}15$

$$\equiv Ca - OH_2^+ \quad \text{and} \quad \begin{array}{c} \equiv Ca - O \diagdown \\ P \diagup O^- \\ \equiv Ca - O \diagup \diagdown O \end{array}$$

$$\equiv P-O^- \;+\; H^+ \;=\; \equiv P-OH \qquad\qquad ; \; \log K^s \;=\; 6.6$$

$$\equiv Ca-OH_2^+ \qquad = \; \equiv Ca-OH \;+\; H^+ \quad ; \; \log K^s \;=\; -9.7$$