

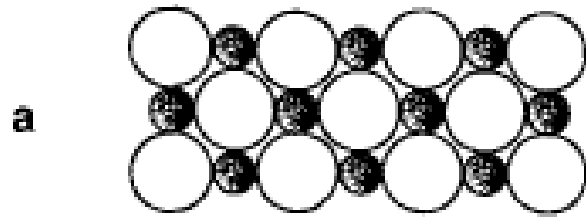
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Geochemie minerálních povrchů

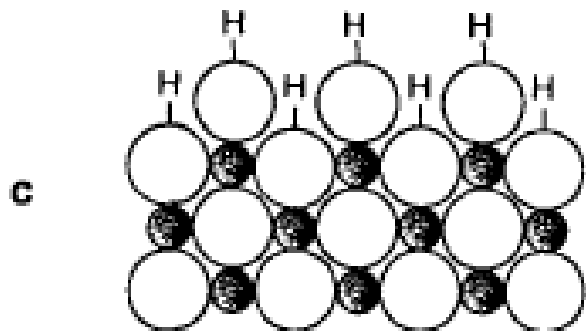
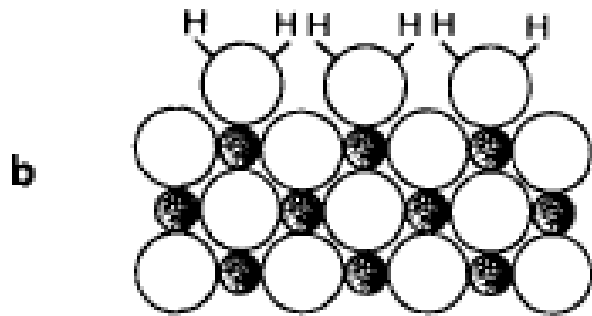
I.

Koordinační geochemie mezifází
oxyhydroxid-voda

Koordinační geochemie mezifází oxyhydroxid-voda



průřez fázovým rozhraním

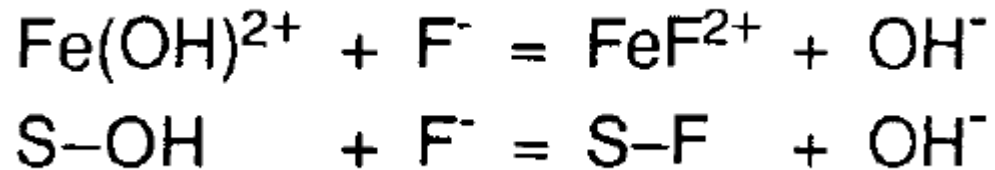
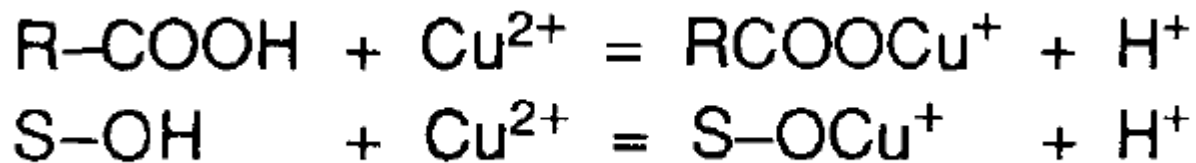


Schematic representation of the cross section of the surface layer of a metal oxide. ●, Metal ions; ○, oxide ions. The metal ions in the surface layer (a) have a reduced coordination number. They thus behave as Lewis acids. In the presence of water the surface metal ions may first tend to coordinate H_2O molecules (b). For most of the oxides dissociative chemisorption of water molecules (c) seems energetically favored.

(From P. Schindler, in *Adsorption of Inorganics at the Solid/Liquid Interface*, Anderson, N. and Rubin, A., Eds., Ann Arbor Science, Ann Arbor, 1981)

Koordinační geochemie mezifází oxyhydroxid-voda

obdoba reakcí ve vodě



Koordinační geochemie mezifází oxyhydroxid-voda

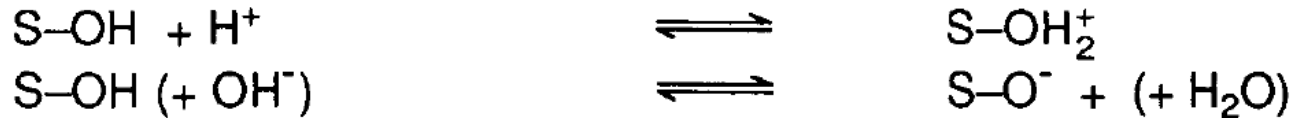
modely

- sorpce na specifických koordinačních místech
- sorpce může být popsána hmotovými rovnicemi
- povrchový náboj je výsledkem sorpčních reakcí
- vliv povrchové náboje na sorpci lze odvodit z teorie elektrické dvojvrstvy

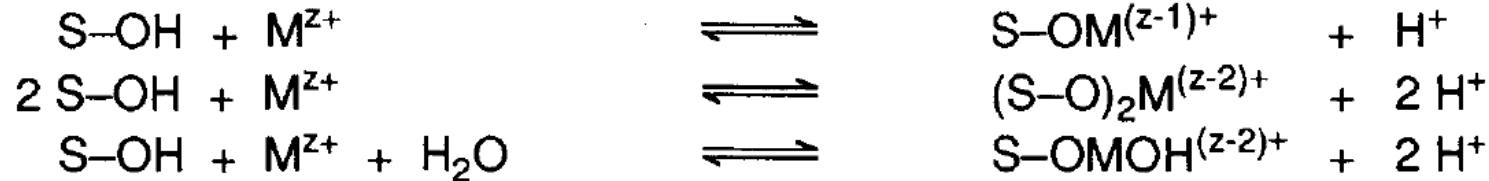
Koordinační geochemie mezifází oxyhydroxid-voda

Adsorption (Surface Complex Formation Equilibria)

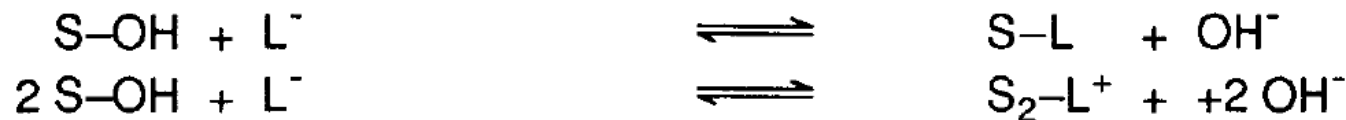
Acid base equilibria



Metal binding



Ligand exchange ($L^- = \text{ligand}$)



Ternary surface complex formation



Koordinační geochemie mezifází oxyhydroxid-voda

acidobazické reakce

$$K_{a1}^s = \frac{\{SOH\} [H^+]}{\{SOH_2^+\}} \text{ mol}/e$$

$$K_{a2}^s = \frac{\{SO^-\} [H^+]}{\{SOH\}} \text{ mol}/e$$

{ }

koncentrace povrchově
sorbované látky mol/kg

$$\langle SOH \rangle = s^{-1} \{SOH\} [\text{mol m}^{-2}]$$

povrchová koncentrace látky,
s – specifický povrch m²

$$[SOH] = a \{SOH\} [\text{mol } e^{-1}]$$

koncentrace rozpuštěné látky,
a – hmotnost oxidu kg/l

Koordinační geochemie mezifází oxyhydroxid-voda

titrační křivka

$$C_A - C_B + [\text{OH}^-] - [\text{H}^+] = [\equiv\text{FeOH}_2^+] - [\equiv\text{FeO}^-]$$

celkový náboj

$$\frac{C_A - C_B + [\text{OH}^-] - [\text{H}^+]}{a} = \{\equiv\text{FeOH}_2^+\} - \{\equiv\text{FeO}^-\} = Q$$

povrchový náboj (C/m^2 , Γ – „adsorpční hustota“)

$$\sigma = QF_s^{-1} = F(\Gamma_{\text{H}^+} - \Gamma_{\text{OH}^-})$$

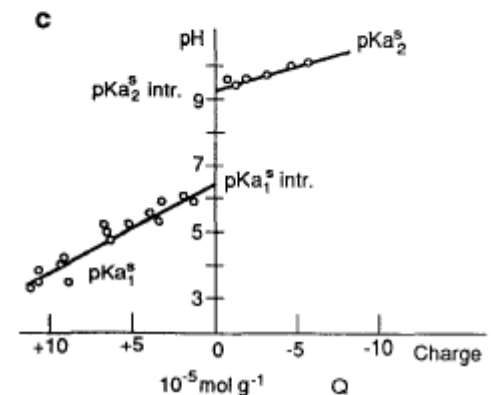
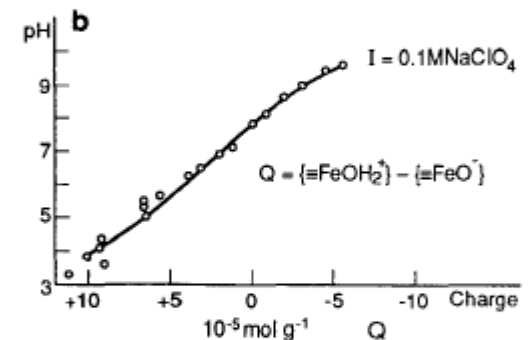
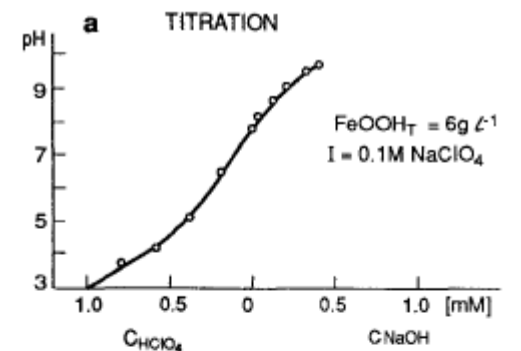
Titration of a suspension of α -FeOOH (goethite) in absence of specifically adsorbable ions.

a) Acidimetric-alkalimetric titration in the presence of an inert electrolyte

b) Charge calculated from the titration curve (charge balance)

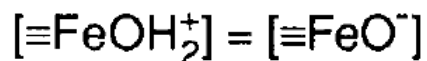
c) Microscopic acidity constants calculated from a) and b). Extrapolation to charge zero gives intrinsic $\text{pK}_{\text{a}1}^{\text{s}}$ and $\text{pK}_{\text{a}2}^{\text{s}}$.

(Data from Sigg and Stumm, 1981)

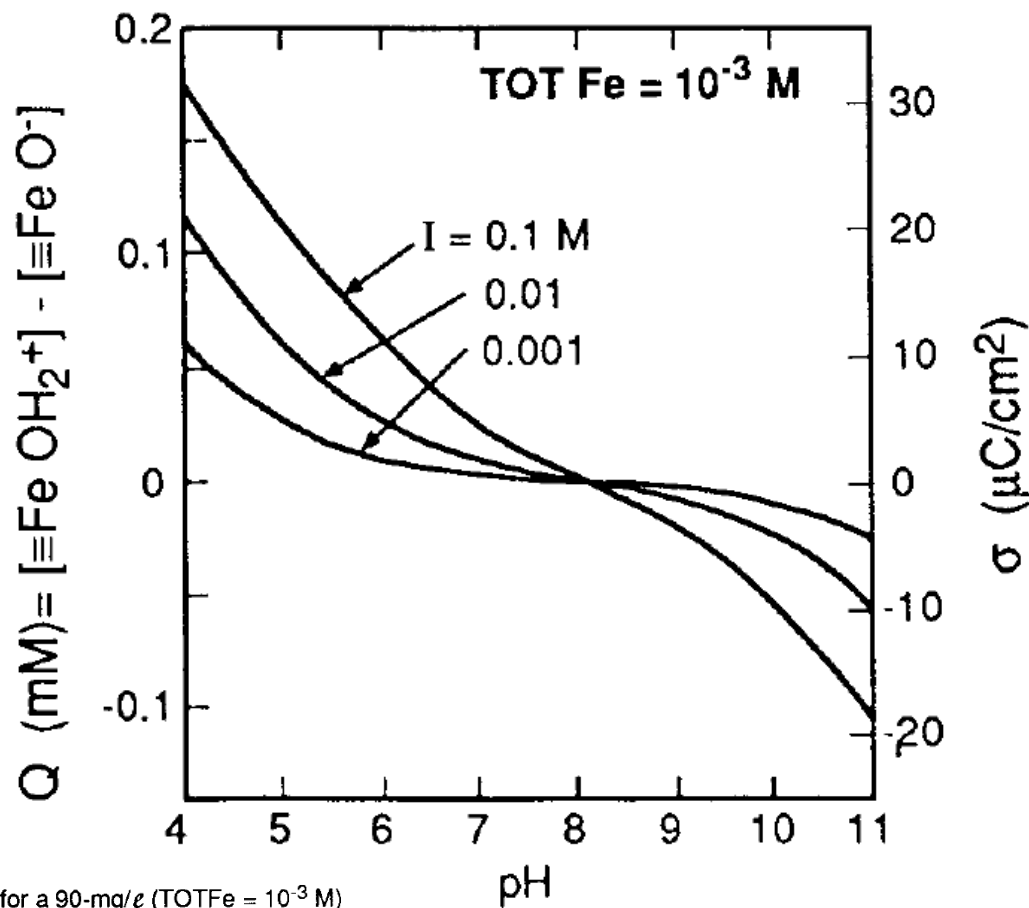


Koordinační geochemie mezifází oxyhydroxid-voda

bod nulového náboje



$$\text{pH}_{\text{pzc}} = 0.5 [\text{pK}_{\text{a1}}(\text{int}) + \text{pK}_{\text{a2}}(\text{int})]$$



Surface charge as a function of pH and ionic strength (1 : 1 electrolyte) for a 90-mg/l (TOTFe = 10^{-3} M) suspension of hydrous ferric oxide.

(From Dzombak and Morel, 1990)

Koordinační geochemie mezifází oxyhydroxid-voda

Point of Zero Charge caused by Binding or Dissociation of Protons ^{a)}

Material	pH _{pznpc}	Material	pH _{pznpc}
α -Al ₂ O ₃	9.1	δ -MnO ₂	2.8
α -Al(OH) ₃	5.0	β -MnO ₂	7.2
γ -AlOOH	8.2	SiO ₂	2.0
CuO	9.5	ZrSiO ₄	5
Fe ₃ O ₄	6.5	Feldspars	2 – 2.4
α -FeOOH	7.8	Kaolinite	4.6
α -Fe ₂ O ₃	8.5	Montmorillonite	2.5
"Fe(OH) ₃ " (amorph)	8.5	Albite	2.0
MgO	12.4	Chrysotile	>10

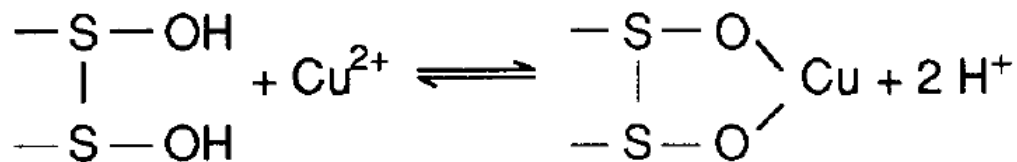
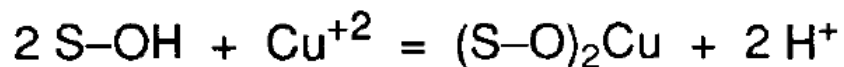
^{a)} The values are from different investigators who have used different methods and are not necessarily comparable. They are given here for illustration.

Koordinační geochemie mezifází oxyhydroxid-voda

povrchové komplexy s kovovými iony



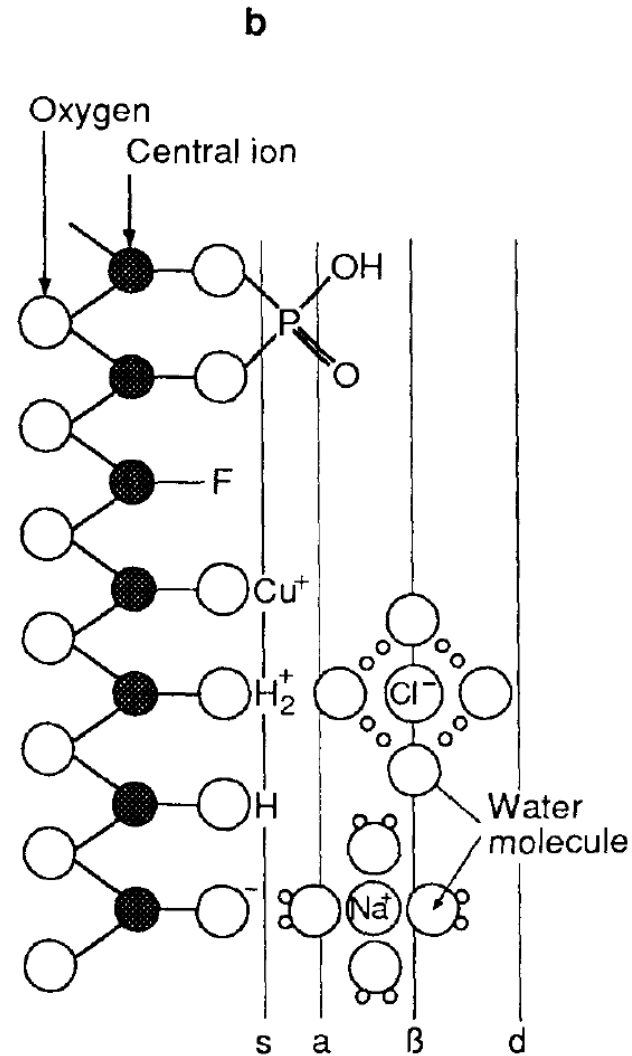
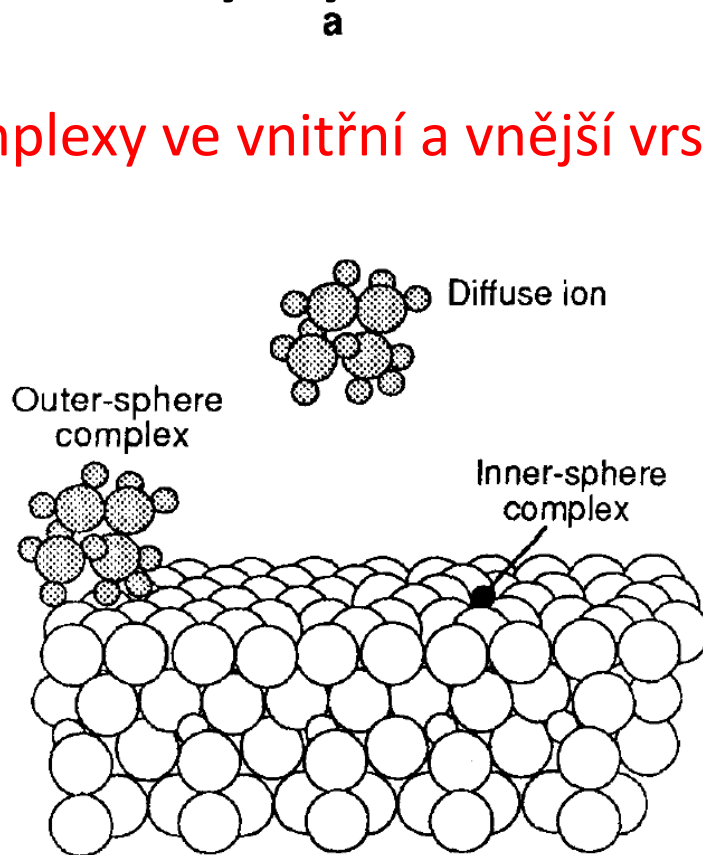
$$K_{\text{Cu}}^{\text{s}} = \frac{\{\text{S-OCu}^+\} [\text{H}^+]}{\{\text{S-OH}\} [\text{Cu}^{2+}]}$$



$$\beta_{2\text{Cu}}^{\text{s}} = \frac{\{(\text{S-O})_2\text{Cu}\} [\text{H}^+]^2}{\{(\text{S-OH})_2\} [\text{Cu}^{2+}]}$$

Koordinační geochemie mezifází oxyhydroxid-voda

povrchové komplexy ve vnitřní a vnější vrstvě

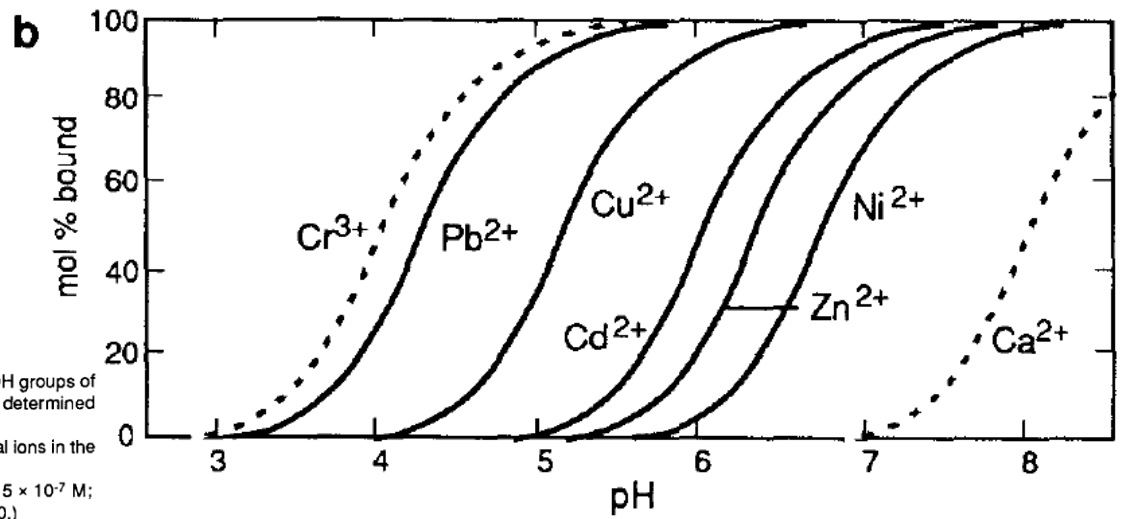
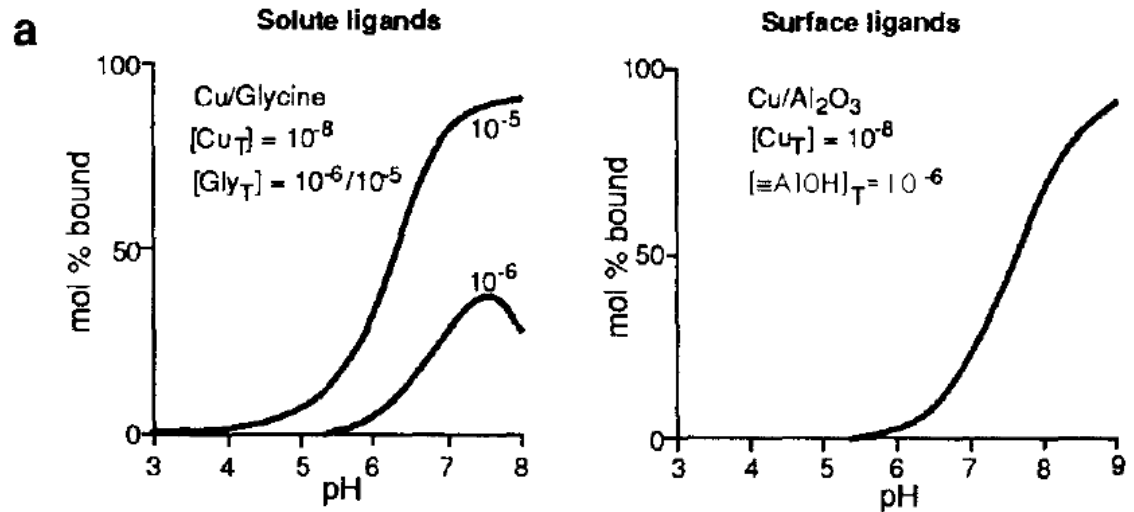


Surface complex formation of an ion (e.g., cation) on the hydrous oxide surface. The ion may form an inner-sphere complex ("chemical bond"), an outer-sphere complex (ion pair) or be in the diffuse swarm of the electric double layer. (From Sposito, 1989)

Fig. b shows a schematic portrayal of the hydrous oxide surface, showing planes associated with surface hydroxyl groups ("s"), inner-sphere complexes ("a"), outer-sphere complexes ("β") and the diffuse ion swarm ("d"). (Modified from Sposito, 1984)

Koordinační geochemie mezifází oxyhydroxid-voda

pH závislost povrchových vazeb



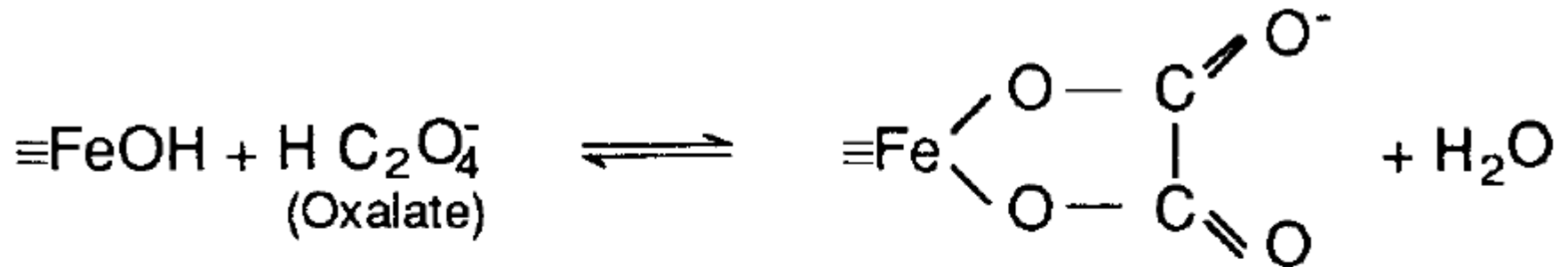
pH-dependence of the binding of metal ions by solute and surface ligands

a) Comparison of the complexation of Cu^{2+} by dissolved ligand (glycine) and by surface OH groups of Al_2O_3 as a function of pH. (The curves are calculated on the basis of experimentally determined equilibrium constants.)

b) Extent of surface complex formation as a function of pH (measured as mol % of the metal ions in the system adsorbed or surface bound).
 $[TOTFe] = 10^{-3} M$ (2×10^{-4} mol reactive sites e^{-1}); Metal concentrations in solution = $5 \times 10^{-7} M$;
 $I = 0.1 M NaNO_3$. (The curves are based on data compiled by Dzombak and Morel, 1990.)

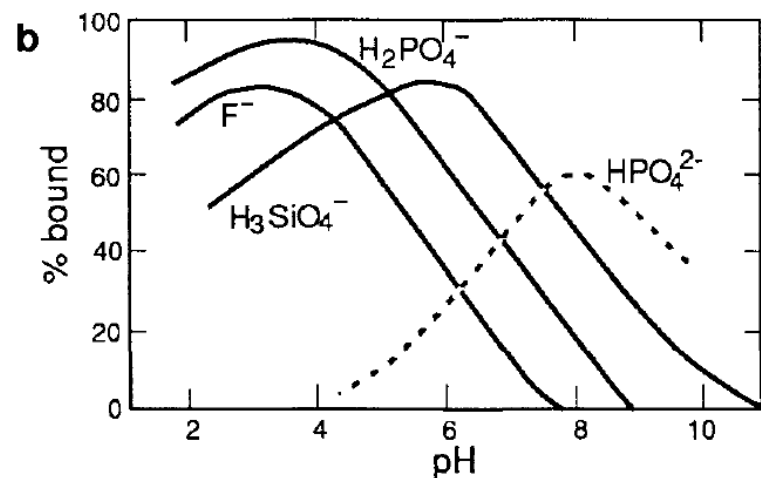
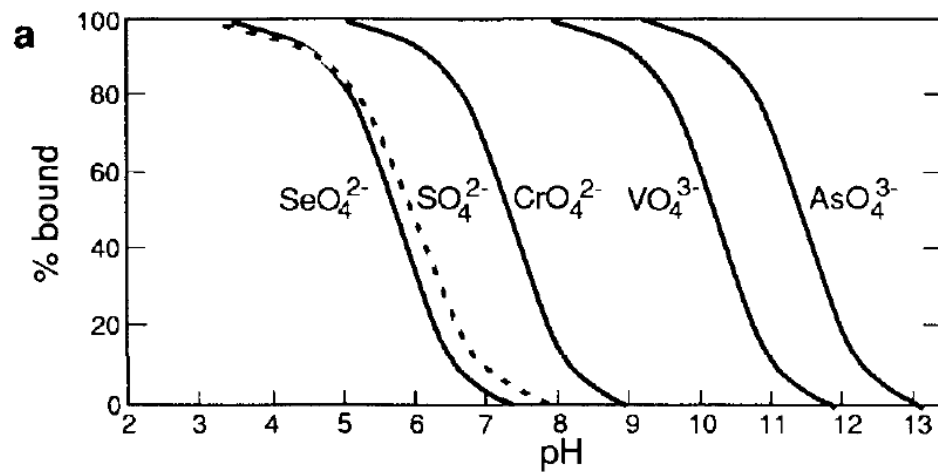
Koordinační geochemie mezifází oxyhydroxid-voda

výměna ligandů, povrchové komplexy anionů a slabých kyselin



Koordinační geochemie mezifází oxyhydroxid-voda

výměna ligandů, povrchové komplexy anionů a slabých kyselin



Surface complex formation with ligands (anions) as a function of pH

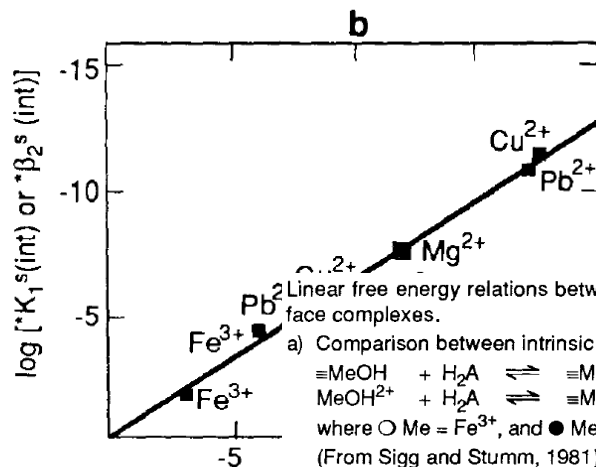
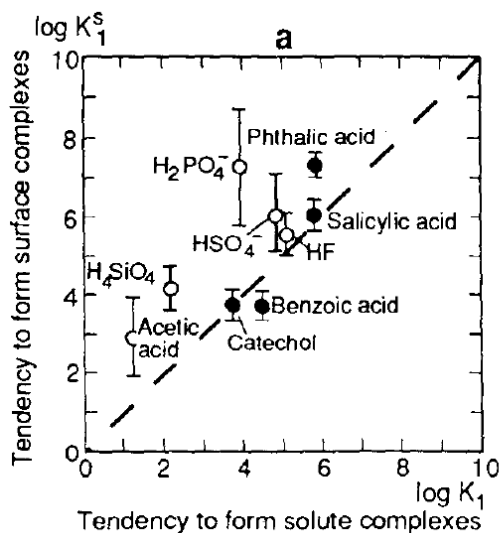
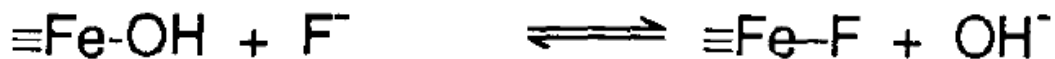
a) binding of anions from dilute solutions (5×10^{-7} M) to hydrous ferric oxide [$\text{TOTFe} = 10^{-3}$ M]. Based on data from Dzombak and Morel, 1990. $I = 0.1$.

b) binding of phosphate, silicate and fluoride on goethite ($\alpha\text{-FeOOH}$); the species shown are surface species. (6g FeOOH per liter, $P_T = 10^{-3}$ M, $\text{Si}_T = 8 \times 10^{-4}$ M.) (Sigg and Stumm, 1981).

(The curves are calculated with the help of experimentally determined equilibrium constants.)

Koordinační geochemie mezifází oxyhydroxid-voda

výměna ligandů, povrchové komplexy anionů a slabých kyselin



Linear free energy relations between the tendency to form solute complexes and corresponding surface complexes.

a) Comparison between intrinsic equilibrium constants of the reactions

$$\equiv\text{MeOH} + \text{H}_2\text{A} \rightleftharpoons \equiv\text{MeHA} + \text{H}_2\text{O} \quad ; \quad K_1^s$$

$$\text{MeOH}^{2+} + \text{H}_2\text{A} \rightleftharpoons \text{MeHA}^{2+} + \text{H}_2\text{O} \quad ; \quad K_1$$

where \circ Me = Fe^{3+} , and \bullet Me = Al^{3+} .
(From Sigg and Stumm, 1981)

b) Correlation of stability constants of surface complexes of amorphous silica with metal ions

$$\equiv\text{SiOH} + \text{Me}^{z+} \rightleftharpoons \equiv\text{SiOMe}^{(z-1)} + \text{H}^+ \quad ; \quad *K_1^s$$

$$2 \equiv\text{SiOH} + \text{Me}^{z+} \rightleftharpoons (\equiv\text{SiO})_2\text{Me}^{(z-2)} + \text{H}^+ \quad ; \quad *\beta_2^s$$

with corresponding hydrolysis reactions

$$\text{H}_2\text{O} + \text{Me}^{z+} \rightleftharpoons \text{MeOH}^{(z-1)+} + \text{H}^+ \quad ; \quad *K_s$$

$$2 \text{H}_2\text{O} + \text{Me}^{z+} \rightleftharpoons \text{Me(OH)}_2^{(z-2)+} + 2 \text{H}^+ \quad ; \quad *\beta_2$$

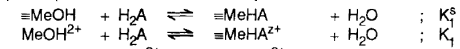
(From Schindler, 1985)

Koordinační geochemie mezifází oxyhydroxid-voda

výměna ligandů, povrchové komplexy
anionů a slabých kyselin

Linear free energy relations between the tendency to form solute complexes and corresponding surface complexes.

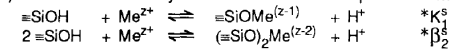
a) Comparison between intrinsic equilibrium constants of the reactions



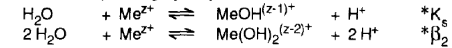
where \circ Me = Fe^{3+} , and \bullet Me = Al^{3+} .

(From Sigg and Stumm, 1981)

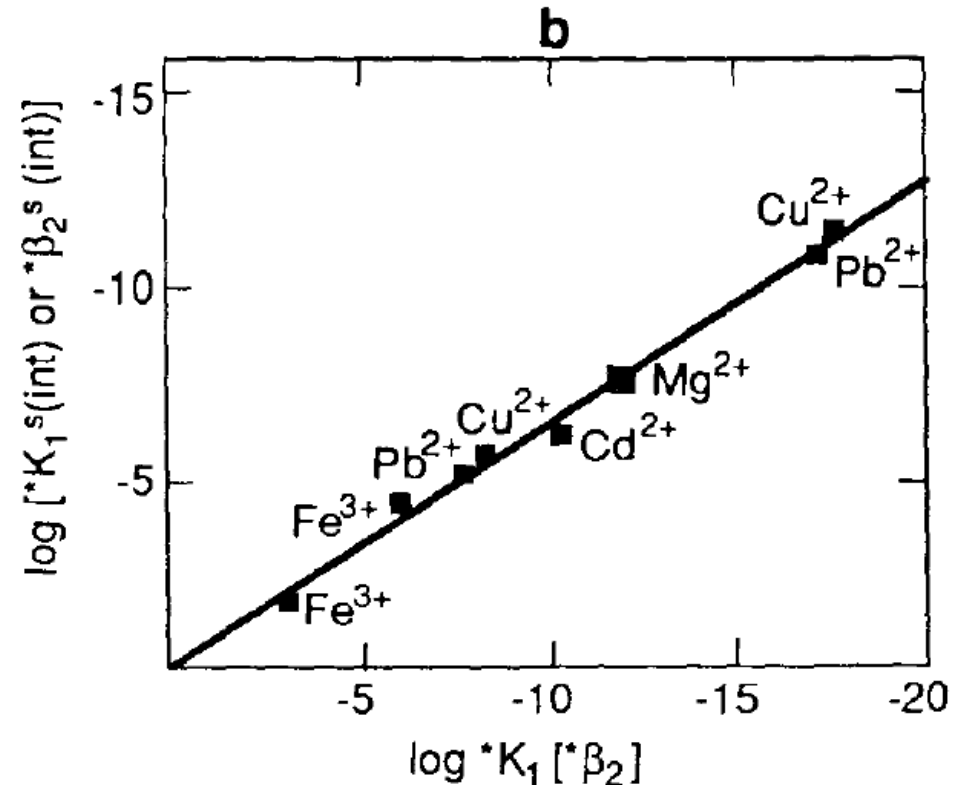
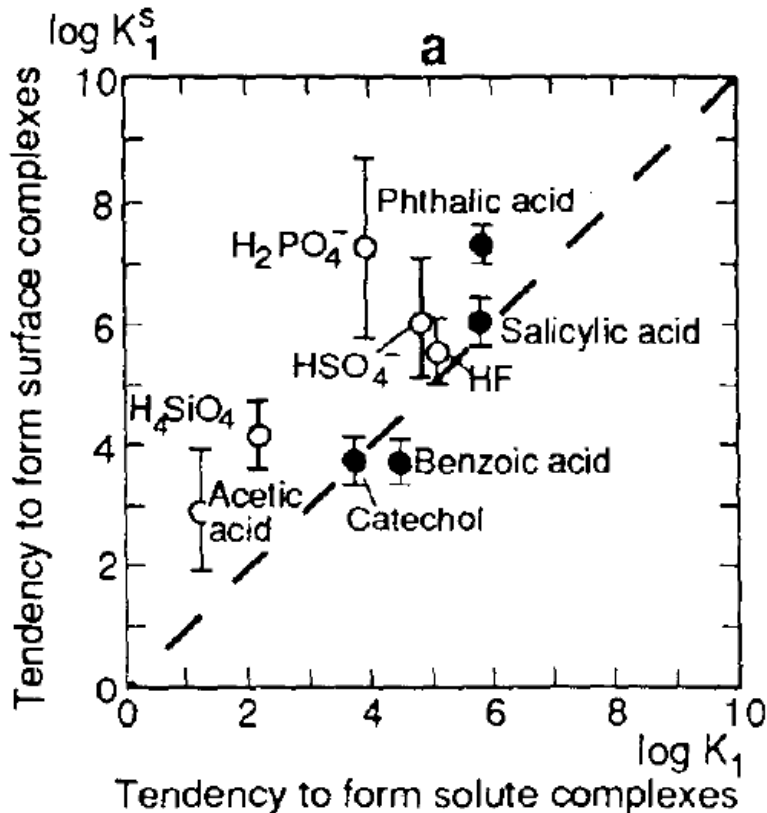
b) Correlation of stability constants of surface complexes of amorphous silica with metal ions



with corresponding hydrolysis reactions

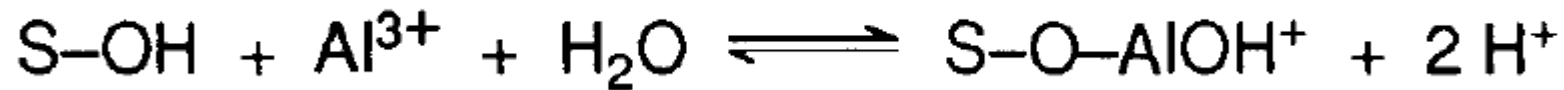
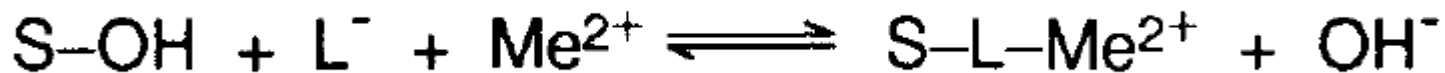
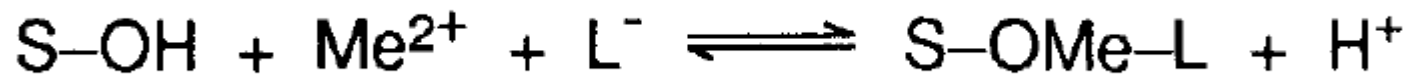


(From Schindler, 1985)



Koordinační geochemie mezifází oxyhydroxid-voda

ternární komplexy



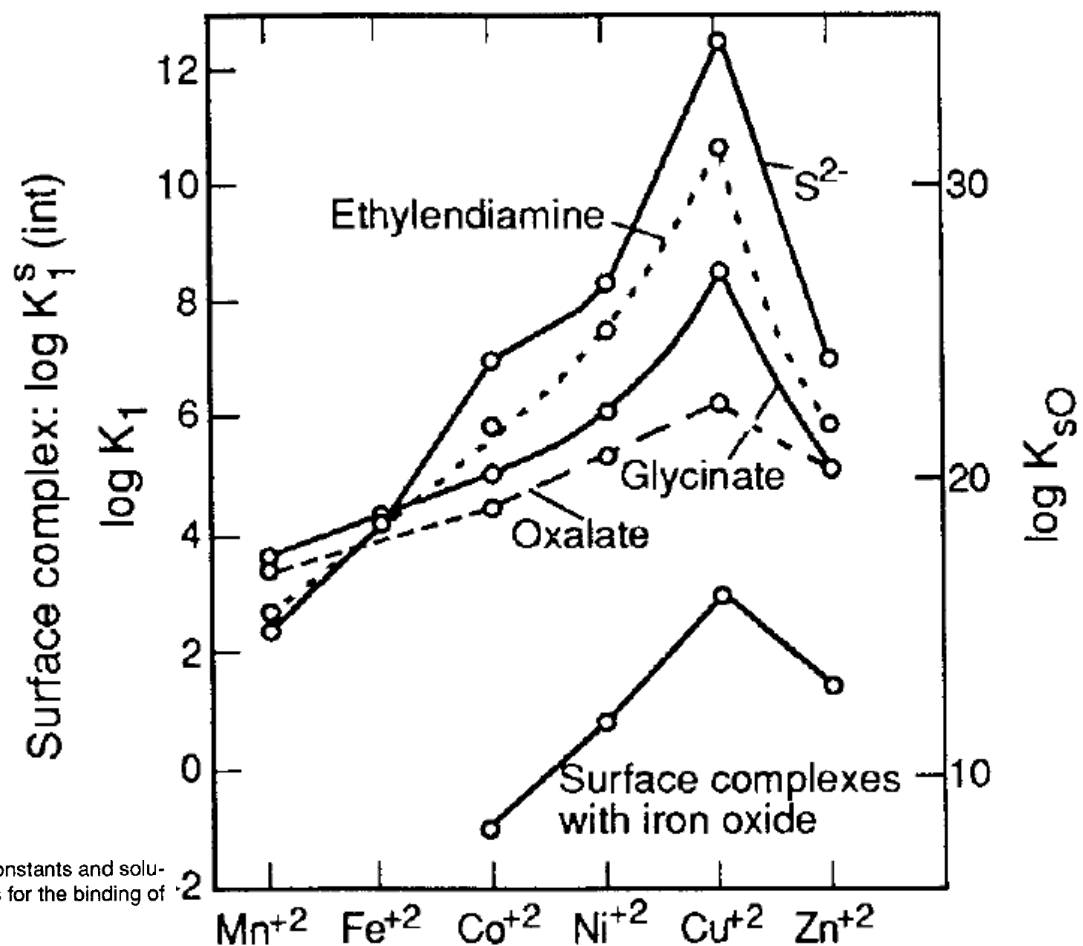
Koordinační geochemie mezifází oxyhydroxid-voda

afinita kationů a anionů ke tvorbě povrchových komplexů

$\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$

$\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$

$\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$



Stability constants (ethylenediamine, glycinate, oxalate), surface complex formation constants and solubility products (sulfides) of transition ions. The surface complex formation constant is for the binding of metal ions to hydrous ferric oxide: $\equiv\text{Fe}-\text{OH} + \text{Me}^{2+} \rightleftharpoons \equiv\text{FeO}\text{Me}^+ + \text{H}^+$; K_1^s .