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Surface Complexation and Its Impact on Geochemical Kinetics*

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The weathering of rocks, the formation of soils, the alteration and dissolution of sediments are a consequence of surface reactions. Furthermore, many redox processes such as the oxidation of VO^{2+}, Mn^{2+} and Fe^{2+}, the non-biotic degradation of organic substances and photosensitized processes are catalyzed by surfaces. The electric double layer theory, despite its efficiency in quantifying certain phenomena of colloid stability, has limitations because it neglects chemical speciation at the surface and does not provide information on the chemical structure of the interfacial region. The surfaces of naturally occurring solids are characterized by functional groups, e. g., OH^- groups on the surface of hydrous oxides or on organic surfaces. Specific adsorption of — or interaction with — H^+, OH^-, metal ions and ligands occurs through coordination at the surface; inner-sphere surface complexes can be formed. The form of occurrence of the individual compounds (speciation) needs to be known in order to understand their reactivity; especially the geometry of the coordination shell of surface sites or of reactants at surfaces is a prerequisite for interpreting reaction rates occuring at the particle-water interface.

Some case studies on the oxidation of Mn^{2+} and VO^{2+} and on the dissolution of hydrous oxides and silicates are presented. In each case, the kinetics of the processes and how it is affected by solution variables such as H^+ and ligands (such as oxalate and other di- or hydroxy-carboxylates) are explained by simple mechanistic models that involve the coordination at the mineral-solution interface. Simple rate laws are derived illustrating the rates' dependence on the concentration (activity) of surface species.

1. INTRODUCTION

Almost all the problems associated with understanding the processes that control the composition of our environment concern interfaces, above all the interfaces of water with naturally occurring solids (minerals, soils, sediments, biota and humus). An appreciation of the physical chemistry of these interfaces and the reactions controlled by them is a prerequisit for understanding many of the important processes in natural systems (oceans and fresh waters

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as well as soil and sediment-water systems). The weathering of rocks and the formation of soils as well as the formation, alteration and dissolution of sediments are a consequence of surface reactions. Soil solids are continuously manufactured by the earth's surface by the complicated interactions of rocks and water. The interaction of inorganic physical processes and biological processes is of importance. Organic matter produced from living matter provides ligands and reductants. Furthermore biological surfaces have high affinities for metal ions.[1] The geochemical fate of most trace elements is controlled by the reaction of solutes with solid surfaces; simple chemical models for the residence time of reactive elements in oceans[2] and lakes[3,4] are based on the partitioning of species between soluble and sedimenting aquatic particles.

2. Surface Complexation

2.1. Surface Coordination as a Complement to the Electric Double Layer Theory

For the last decades the electric double layer model has generally been the conceptual framework to interpret many surface chemical phenomena. But, as we have pointed out in the previous conferences[5-8], the fundamental chemical interaction of solutes with natural surfaces occurs through the formation of coordinative bonds. Thus, specific chemical factors need to be considered in addition to the theory of the electric double layer to explain many phenomena in natural systems and to derive rate laws on geochemical processes.

The interaction of a solute with a surface — be it in terms of adsorption or surface complexation — requires a characterization of the physical and chemical properties of the solvent (electrolyte), the solute and the sorbent. In Figure 1 we juxtapose the classical representation of the electric double layer[9] with that of surface complexation. While the surface in the electric double layer model is assumed to be a structureless continuum which interferes with the solution only by its electric charge, the basic concept in the surface coordination model are the surface functional groups formed on all natural inorganic and organic hydrous solids; they are responsible for the surface reactivity (and mechanism of adsorption) of sediments, rocks, soils and biota. These functional groups contain the same donor atoms as found in functional groups of soluble ligands; e. g., the surface hydroxyl group on a hydrous oxide or an organic solid has similar donor properties as the corresponding counterparts in dissolved molecules such as hydroxide ions and carboxylates. We need to consider, however, that the functional groups are bound into a solid framework and their reactivity is, in essence, a cooperative property[10]. In an earlier conference paper[5], we have compared schematically the acid-base and metal-binding properties of simple ligands, their polymers and cross-linked polymers, i. e. solids. Thus, a hydrous oxide particle can be treated like a polymeric oxoacid (or base) which tends to undergo protolysis and to coordinate with metal ions. The metal ions in the surface layer of the

charged surface

solvated positive ion

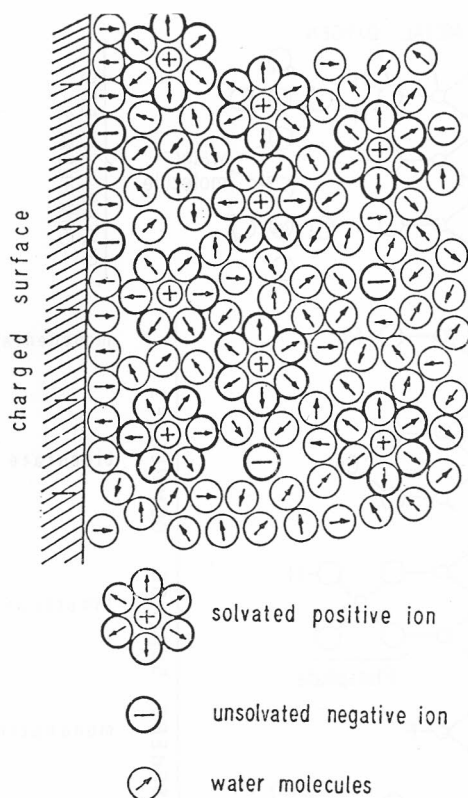unsolvated negative ion

water molecules

a)

Figure 1. Comparison between the models of the Electric Double Layer (a) and of Surface Complexation (b)

a) Electric double layer. The distribution of free charges in the neighborhood of a charged surface is idealized as an electrochemical double layer; one layer of the double layer is envisaged as a fixed charge or surface charge attached to the solid surface while the other layer is distributed more or less uniformely on the electrolyte in contact; the first row is largely occupied by water dipoles. The second row is largely reserved for substrated ions (outer Helmholtz phase). Although the first row is lagerly occupied by H_2O molecules there are some (ionic) species which find their way to the surface. Such ions in »contact adsorption« are said to be specifically adsorbed. (Modified from Bockris and Reddy[9]).

oxide — acting as Lewis acids — can replace their coordinated OH^- ions by ligand exchange reactions with anions or weak acids[11,12].

Surface equilibrium (mass law) constants, experimentally determined, can be used to predict the extent of surface binding (adsorption) and of surface charge as a function of pH and other solution variables.
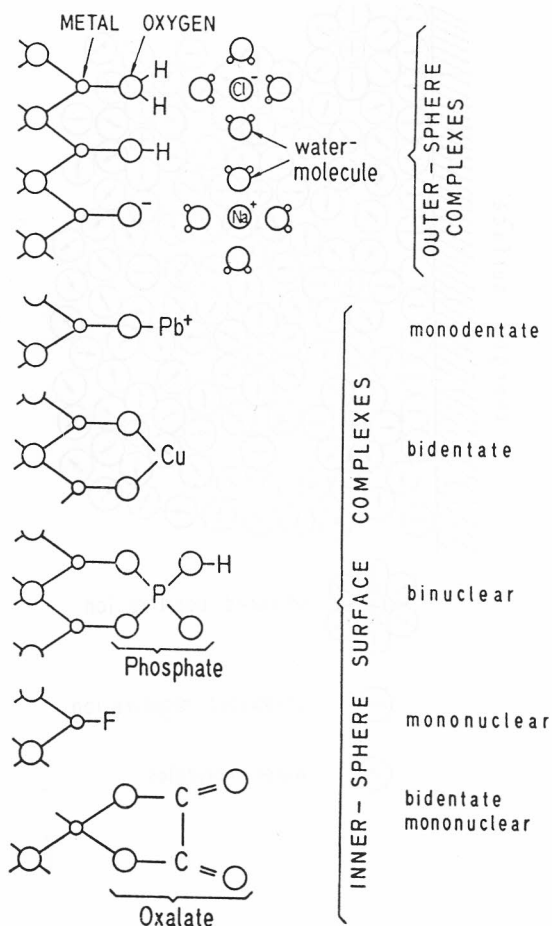
b)

b) Surface complexation. The surface of naturally occurring solids is characterized by functional groups, e. g., OH-groups on the surface of hydrous oxides or on organic surfaces (modified from Sposito[10]). Specific adsorption occurs through coordinative interactions. Two broad categories of surface complexes can be distinguished: inner-sphere complex and outer-sphere complex. Outer-sphere surface complexes involve electrostatic bonding mechanisms and are less stable than inner-sphere surface complexes which involve some covalent bonding.

2.2. Structural Identity of Surface Species

We need to know the form of occurrence of the individual compounds (speciation) in order to understand their chemical and biological reactivity; especially the geometry of the coordination shell of surface sites is a prerequisite for interpreting reaction rates occurring at the particle-water interface

in terms of the basic forces operating between the particular ionic or molecular species. Spectroscopic methods are unfortunately seldom sufficiently sensitive to reveal the structure of surface complexes. Herbert Motschi in our laboratory used electron spin resonance spectroscopy to study Cu(II) surface complexes. Additional studies were carried out with ENDOR (Electron Nuclear Double Resonance Spectroscopy) in order to elucidate structural aspects of surface bound Cu(II), of ternary copper complexes (in which coordinated water is replaced by ligands) and of vanadyl-ions on δ-Al$_2$O$_3$.[13-15] Application of ENDOR spectroscopy allows the resolution of weak interactions between the unpaired electron with nuclei within a distance of ca. 5 Å. From these so-called hyperfine data, structural parameters can be derived, e. g. bond distances of the paramagnetic center to the coupling nuclei of ligands (Figure 2). In the ENDOR-spectrum of adsorbed VO^{2+} on δ-Al$_2$O$_3$, signals caused by
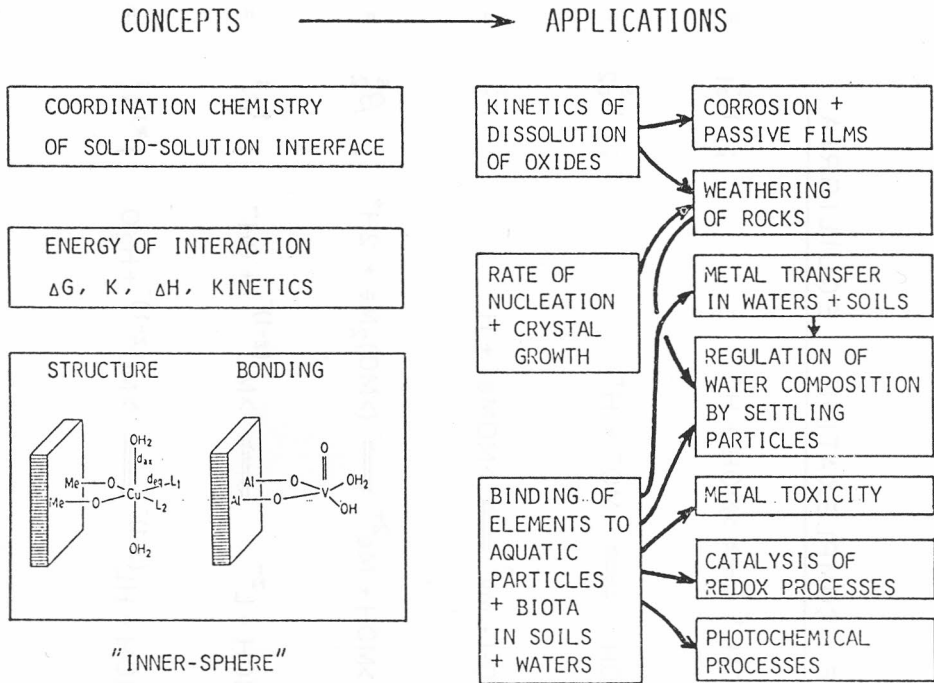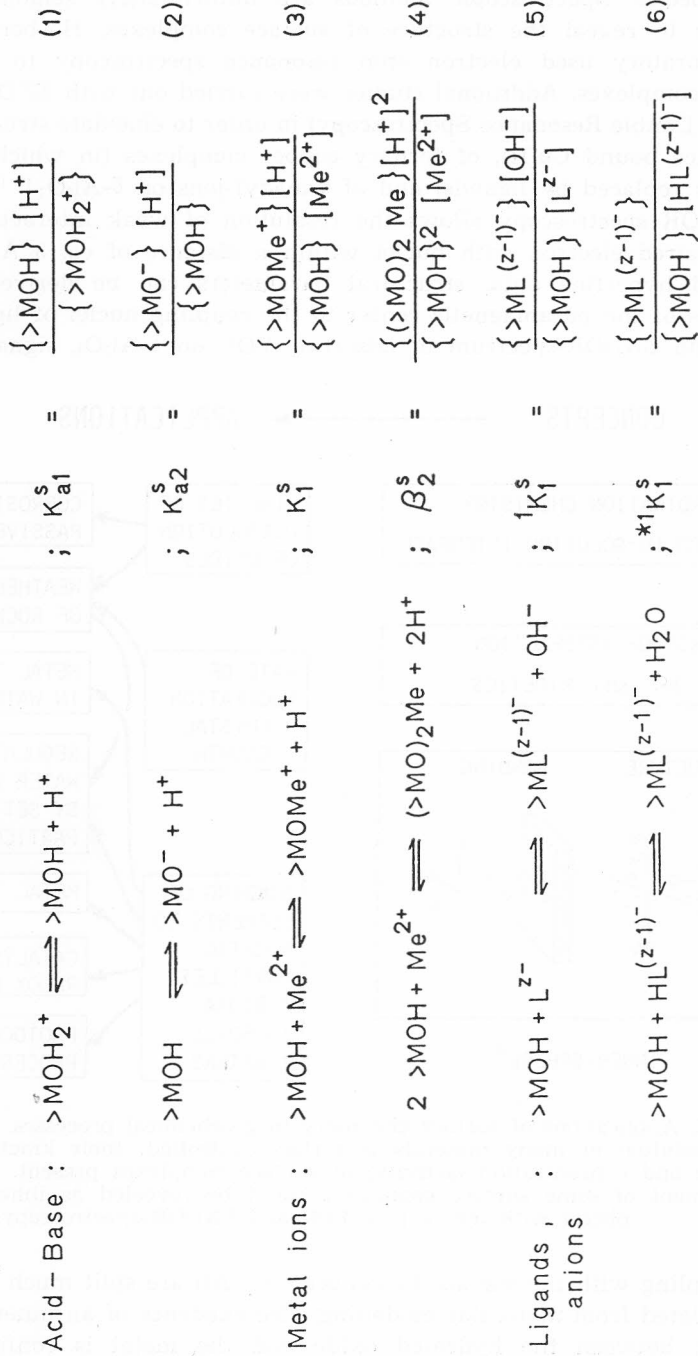

Figure 2. Applications of surface chemistry to geochemical processes. The formation and dissolution of many minerals is surface-controlled; their kinetics depend on the type and concentration (activity) of surface complexes present. The structural arrangement of some surface complexes could be revealed as inner-sphere complexes with the help of EPR and ENDOR-spectroscopy.

the coupling with the surface Lewis center (^{27}Al) are split much stronger than is calculated from molecular modelling. The existence of an inner-sphere coordination between the hydrated oxide and the metal is confirmed experimentally[16].

SURFACE COMPLEXATION EQUILIBRIA

Acid – Base :

$$>MOH_2^+ \rightleftharpoons >MOH + H^+ \quad ; \quad K_{a1}^s = \frac{\{>MOH\}\,[H^+]}{\{>MOH_2^+\}} \qquad (1)$$

$$>MOH \rightleftharpoons >MO^- + H^+ \quad ; \quad K_{a2}^s = \frac{\{>MO^-\}\,[H^+]}{\{>MOH\}} \qquad (2)$$

Metal ions :

$$>MOH + Me^{2+} \rightleftharpoons >MOMe^+ + H^+ \quad ; \quad K_1^s = \frac{\{>MOMe^+\}\,[H^+]}{\{>MOH\}\,[Me^{2+}]} \qquad (3)$$

$$2 >MOH + Me^{2+} \rightleftharpoons (>MO)_2Me + 2H^+ \quad ; \quad \beta_2^s = \frac{\{(>MO)_2Me\}\,[H^+]^2}{\{>MOH\}^2\,[Me^{2+}]} \qquad (4)$$

Ligands, anions :

$$>MOH + L^{z-} \rightleftharpoons >ML^{(z-1)-} + OH^- \quad ; \quad {}^1K_1^s = \frac{\{>ML^{(z-1)-}\}\,[OH^-]}{\{>MOH\}\,[L^{z-}]} \qquad (5)$$

$$>MOH + HL^{(z-1)-} \rightleftharpoons >ML^{(z-1)-} + H_2O \quad ; \quad {}^{*1}K_1^s = \frac{\{>ML^{(z-1)-}\}}{\{>MOH\}\,[HL^{(z-1)-}]} \qquad (6)$$

The characterization of direct interactions between the surface and a surface-bound ligand by vibrational spectroscopy (IR and Raman) is fraught with difficulties. However, in a number of cases, characteristic absorption bonds can be observed with substituents of functional groups of the ligand.

2.3. Equilibrium Constants

The concept of surface complexation permits to handle adsorption equilibria in the same way as equilibria in solution (Table I). The equilibrium constants or quotients are experimentally accessible quantities that can be used to predict the extent of surface binding (adsorption) as a function of pH and other solution variables. These equilibrium quotients are conditional constants where values (at constant temperature, pressure and ionic strength) are — because of the cooperative properties of the functional groups — dependent on the prevailing surface coverage[10,17].

Typically, a relationship

$$K_x^s = K_x^s (\text{intr.}) \exp(-\alpha\{x\}) \tag{1}$$

is encountered: K_x^s is the conditional stability constant of the surface species x; $K_x^s(\text{intr.})$ is the intrinsic constant, which is independent of the surface coverage and α is an empirical constant whose value is dependent on the system under consideration. $\{x\}$ is the surface concentration of the surface-bound (adsorbed) species x, e. g., moles m^{-2}. Eq. (1) illustrates the possibility of evaluating instrinsic constants by linear extrapolation of the experimentally available conditional constants:

$$\log K_x^s = \log K_x^s (\text{intr.}) - \frac{\alpha}{2.3}\{x\} \tag{2}$$

Eqs. (1, 2) may be looked at as empirical relations. Since x is usually a H^+ or a cation or an anion, $\{x\}$ relates to the surface charge density, τ_p.

When the total particle charge is small, it is proportional to the inner potential ψ_s at the surface, the proportionality constant C is the capacitance density:

$$\tau_p = C\psi_s \tag{3}$$

Thus Eq. (1) could also be written as

$$K_x^s = K_x^s (\text{intr.}) \exp(F\psi_s/RT) \tag{4}$$

A comparison of (1) with (4) shows that α corresponds to F/CRT.

The description of the surface complexation reactions by Eqs (1, 2) represents the so-called constant capacitance model (Stumm, Huang, Jenkins,[5] Westall and Hohl,[18]). Eqs. (1) or (4) are essentially adsorption isotherms with two parameters (constants).

In the constant capacitance model, the complex-bound ions are positioned geometrically in the surface layer, in the same plane as H^+ and OH^-. Various models, differing primarily on how the adsorption energy is separated into chemical and electrostatic contributions, have been proposed[18]. As shown by

Westall and Hohl[18], all models can be used to describe experimental data. But a good fit does not prove that the model gives a correct physical description at the interface. For a compilation of surface coordination equilibrium constants, see Schindler and Stumm[17].

2.4. *Comparing Surface Coordination with Solution Coordination*

The tendency to form surface complexes is correlated with the tendency to form complexes in solution.
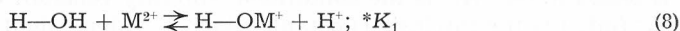
$$S\text{—}OH \rightleftharpoons S\text{—}O^- + H^+; \qquad K^s_{a_2} \text{ (intr.)} \qquad (5)$$
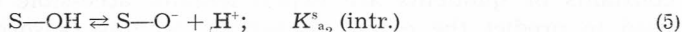
correlate with the corresponding solute acidity constants

$$S\text{—}(OH)_z \text{ (aq)} \rightleftharpoons S(OH)^-_{z+1} + H^+; \; K \qquad (6)$$

Constants for metal complex formation such as

$$S\text{—}OH + M^{2+} \rightleftharpoons S\text{—}OM^+ + H^+; \quad {}^*K^s_1 \text{ (intr.)} \qquad (7)$$

correlate with the corresponding hydrolysis constants

$$H\text{—}OH + M^{2+} \rightleftharpoons H\text{—}OM^+ + H^+; \; {}^*K_1 \qquad (8)$$

Similarly, in ligand exchange surface reactions such as

$$> FeOH + H_2A \rightleftharpoons \; > FeHA + H_2O; \quad {}^*K^s_1 \qquad (9)$$

show similar tendencies to form surface complexes are observed as the tendency to form complexes in solution[12]

$$FeOH^{2+} + H_2A \rightleftharpoons FeHA^{2+} + H_2O; \quad {}^*K_1 \qquad (10)$$
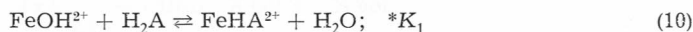
Linear Free Energy Relations. — The correlations observed between the stability of (inner-sphere) complexes in solution with the stability of corresponding surface complexes are additional support for the existence of inner-sphere surface complexes. Such linear free energy relations (LFER) can help to predict surface chemical behavior of metal ions and ligands exploiting the large amount of available complex forming constants in aqueous solutions.

The correlations observed and the stability of surface complex formation (Eq. (7)) with those of the corresponding hydrolysis constants (Eq. (8)) are the basis for the well known coincidence of adsorption and hydrolysis and the ensuing controversy. The sum of the reactions

$$M^{2+} + H_2O \rightleftharpoons MOH^+ + H^+$$

$$S\text{—}OH + MOH^+ \rightleftharpoons S\text{—}OM^+ + H_2O$$
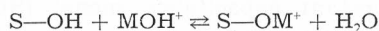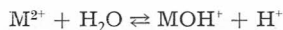
can stoichiometrically or thermodynamically not be distinguished from

$$S\text{—}OH + M^{2+} \rightleftharpoons SOM^+ + H^+ \qquad (7)$$

but kinetic studies of Hachiya et al.[19] support the model of the surface complex formation with the free metal ion.

3. *Application of Surface Coordination to Geochemistry*

Figure 2. illustrates some of the applications of surface chemistry to geochemical processes. In geochemical cycling of the elements, usually the surface to volume ratios of the materials in the various systems of the earth are large and thus many of the materials exchanges are regulated by processes at the interface.

3.1. *Redox Processes*

Many pertinent redox processes such as the oxidation of certain metal ions by oxygen, the non-biotic degradation of organic substances and photosensitized processes are catalyzed by surfaces. The rate of abiotic reactions, R, that involve catalytic or photosensitizing sites on the particle surface which form a reactive complex with the reactant x, can be described by

$$R = \frac{k_s \, [\text{sites}] \, [x]}{K + [x]} \tag{11}$$

where k_s is the rate constant for the catalyzed reaction on the surface, K is a constant and $[x]$ the molar concentration of the reactant[20]. The hyperbolic rate law (similar to the rate laws of enzyme-catalyzed reactions) reflects that the reactant need to be adsorbed onto the functional groups of a surface. Because the surface concentration $\{x\}$ is related to $[x]$ by a Langmuir type relation, the areal rate law could be formulated simply as

$$R' = k_s' \{x\} \tag{12}$$

where R' is the rate per unit area.

Oxidation of metal ions. — Recent studies on the rate of oxidation of Mn^{2+} and VO^{2+}, respectively, in the presence of interfaces were interpreted in terms of surface-controlled reactions using rate laws solely dependent on surface concentration parameters. Figures 3.a) and b) illustrate some results on the oxidation of Mn^{2+} in aqueous solutions at pH = 8.4. At this pH, representative of that of natural waters, and in the absence of microbial or efficient surface catalysts, dissolved Mn(II) is not oxidized over years. Small concentrations of particles cause eventually the oxidation within periods of more than four years (Diem and Stumm,[21]). In the presence of 10 m mol/l of α-FeOOH, however (Figure 3b), oxidation occurs within a few hours (Davies,[22]). The rate law for the oxidation reaction can be written in terms of the bidentate surface complex of Mn(II)

$$-\frac{d\,[Mn(II)]}{dt} = k\,\{(>FeO)_2\,Mn\} \tag{13}$$

A representative example on the oxidation of VO^{2+} by dissolved oxygen is given by Figure 4. At low concentrations of total vanadium (~ 10 μM) the homogeneous oxidation of vanadyl follows the rate law

$$-\frac{d\,[V(IV)]}{dt} = k_1 \cdot [V(IV)] \cdot [H^+]^{-1} \cdot p_{O_2} \tag{14}$$
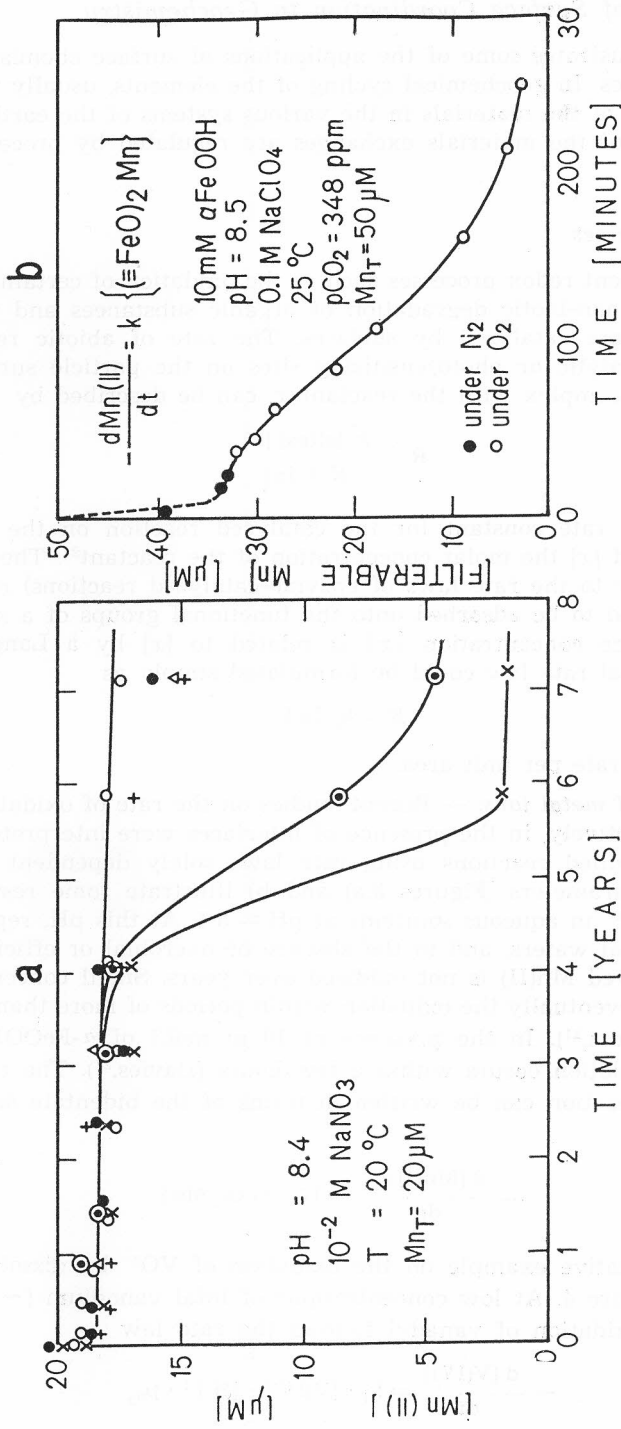
Figure 3. Heterogeneous oxidation of Mn(II). In the absence of surfaces, the abiotic oxidation of Mn(II) does not occur within time spans of years (Figure 3a), (from Diem and Stumm[21]) while in the presence of relatively high concentrations of α-FeOOH, oxidation occurs within hours (Figure 3b), (from Davies[22]).

which implies that the oxidation occurs via the hydroxo-complex VO (OH)$^+$. If the V(IV) is completely adsorbed on TiO$_2$ (anatase), the rate law becomes independent of pH:

$$-\frac{d\,[V(IV)]}{dt} = k_2 \cdot [V(IV)]_{adsorbed} \cdot p_{o_2} \tag{15}$$

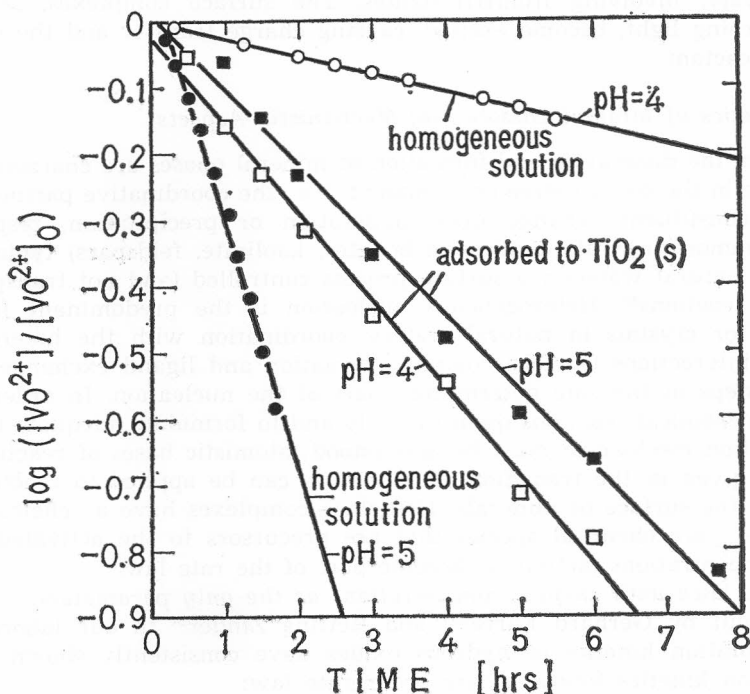Thus, the inner-sphere surface complex of vanadyl shows a similar reactivity towards oxygen as the species VO (OH)$^+$ [23].

Figure 4. Oxidation of vanadyl, VO^{2+}, by dissolved O$_2$ (p_{o_2} = 0.2 atm) in homogeneous solution and in presence of TiO$_2$ (Wehrli and Stumm.[23]) The oxygenation rate, -d [V(IV)]/dt) is proportional in homogeneous solution to [VOOH(aq)$^+$] and in the heterogeneous system (presence of TiO$_2$) to the concentration of the surface complex {> Ti—O—VO$^+$}.

Reductive dissolution of oxides. — The oxides of iron and manganese are among the major components of the earth crust. The metals Fe and Mn play important roles in geochemical cycles, in the chemistry of the lithosphere and natural waters. The dissolution of the (hydr)oxides of Fe(III) and Mn(III, IV) is facilitated under reducing conditions and is influenced by complex forming organic ligands. As shown by Zinder, Furrer and Stumm[24], the chemical reduction of Fe(III) or Mn(III, IV) (fast electron transfer) precedes the rate determining release of the Fe(II) or Mn(II) complex into the solution, i. e., the dissolution of solid iron(III) or manganese(III, IV) phases is critically dependent on the coordinative interactions on these surfaces[24,25].

Photo-assisted reactions. — Reductive dissolution of iron(III) and manganese(III, IV) (hydr)oxides by organic surface ligands, especially when photo--assisted, are most likely of importance in regulating small concentrations of bioavailable soluble Fe(II) and Mn(II)[26,27] in natural aerobic waters. Semiconductor surfaces provide special pathways for ligand-promoted photochemical reactions.

Faust and Hoffmann[28], Waite and Morel[27] and Waite et al.[29] have described heterogeneous photo-assisted reactions, the oxidation of sulfide or citrate respectively, involving iron(III) oxides. The surface complexes, $> Fe(III)x$, by absorbing light, become excited, causing charge transfer and the oxidation of the reactant.

3.2. *Kinetics of Mineral Dissolution; Mechanistic Aspects*

Both, the dissolution and formation of mineral phases are characterized by a change in the coordinative environment, i. e., the coordinative partners of the crystal constituents change upon dissolution or precipitation, respectively. Most common minerals (oxides, carbonates, kaolinite, feldspars) typically dissolve in natural waters via surface process controlled (and not transport controlled) reactions[30]. Heterogeneous nucleation is the predominant formation process for crystals in natural waters; coordination with the heterogeneous surface interactions (surface complex formation and ligand exchange) are essential steps in the rate determining part of the nucleation. In order to describe geochemical reactions quantitatively and to formulate adequate rate laws the reaction mechanism must be understood; atomistic bases of reaction rates, such as given in the transition state theory, can be applied to reactions that occur at the surface of minerals. If surface complexes have a »chemical identity«, i. e., are chemical species that are precursors to the activated species, their concentrations (activities) become part of the rate law.

Rate laws with surface concentrations as the only parameters. — Studies carried out by Gerhard Furrer[31] and Bettina Zinder[24] in our laboratory on the dissolution kinetics of hydrous oxides have consistently shown that the dissolution kinetics follow a zero order rate law:

$$R_i = d\,Q_i/dt = k \qquad (16)$$

or, integrated

$$Q_i = Q_i^0 + kt \qquad (17)$$

where Q_i^0 = the concentration of (dissolving) species i at $t = 0$; Q_i = the concentration of species i at t; k = the reaction rate constant [mol per unit area per time]; R = rate of release by the dissolution of the oxide; and $t =$ = time.

Figure 5. shows examples of the results obtained[31] on the dissolution of δ-Al_2O_3 and of BeO. In batch experiments where pH is kept constant with an automatic titrator, the concentration of Al(III) (aq) and of Be(II) (aq), respectively, is plotted as a function of time. The linear dissolution kinetics observed for every pH is in accord once with Eqs. (16), (17) and compatible with a process whose rate is controlled by a surface reaction. The rate of dissolution is obtained from the slope of the plots. If the rate were controlled by transport (diffusion), a curve parabolic vs. time would be observed.
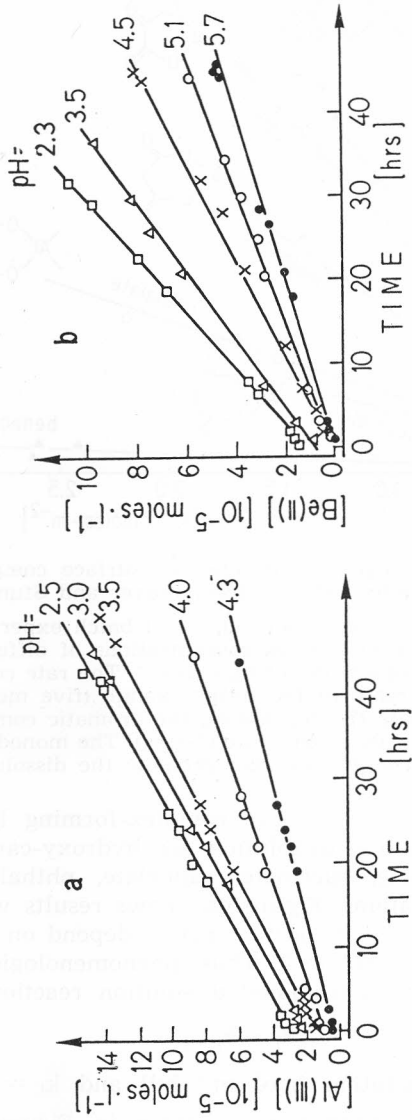
Figure 5. The linear dissolution kinetics observed for the dissolution of δ-Al$_2$O$_3$ (a) and BeO (b) is representativ for processes whose rates are controlled by a surface reaction and not by a transport step (data from Furrer and Stumm[31]).

Although the results have already been published[8,31], we illustrate here, both phenomenologically and atomistically, (1) the influence of a complex former (ligand), and (2) the effect of H^+ on the dissolution of δ-Al_2O_3.
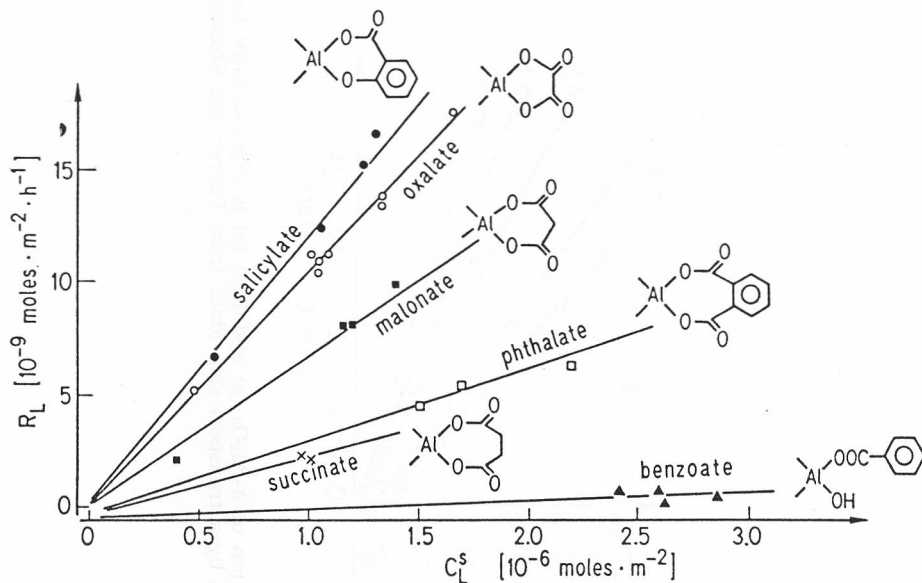
Figure 6. Dissolution of δ-Al_2O_3 in presence of surface complex-forming ligands. (Data and interpretation from Furrer and Stumm[31]).
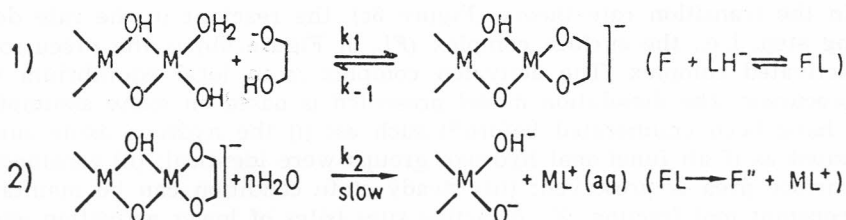
A) Dissolution rates (as measured from individual batch experiments carried out at constant pH in the presence of various concentrations of different ligands) are dependent on the surface concentration of ligands C_L^s. The rate constants of the ligand catalyzed reactions, k_L, decrease in the series oxalate (five membered chelate ring) malonate (6-ring) to succinate (7-ring) among the aromatic complex formers, salicylate (6 ring) is more efficient than phthalate (7-ring). The monodentate benzoate, even at high coverage, does not promote the dissolution.

Effect of ligands. — The surface complex-forming ligands that have a large effect in enhancing the dissolution are hydroxy-carboxylates or dicarboxylates such as oxalate, succinate, salicylate, phthalate, i. e., bidentate ligands with two donor atoms. Figure 6a. shows results which illustrate that the rates of dissolution — at a constant pH — depend on the surface concentration of the ligand C_L^s [mol m^{-2}]. Thus, phenomenologically, we can write the rate law for the ligand-promoted dissolution reaction as

$$R_L = k_L C_L^{\,s} \tag{18}$$

where R_L = rate of dissolution [mol m^{-2} h^{-1}] and k_L = rate constant [h^{-1}].

A plausible reaction mechanism is given in Figure 6b. Although the schematic representation of the reactant moieties does not account for individual crystallographic structures, the scheme given attempts to illustrate a typical sequence of the reaction steps which occur on the surface. The fast surface binding (adsorption) is followed by the slow detachment step in which the surface-complexed central ion becomes transferred to the solution. Even-

1) $\begin{array}{c}\text{(structure with OH, OH}_2\text{, -O, HO)}\end{array} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \begin{array}{c}\text{(structure with OH, O)}\end{array}^{-}$ $(F + LH^{-} \rightleftharpoons FL)$

2) $\begin{array}{c}\text{(structure with OH, O)}\end{array}^{-} + nH_2O \xrightarrow[\text{slow}]{k_2} \begin{array}{c}\text{(structure with OH}^{-}\text{, O}^{-}\text{)}\end{array} + ML^{+}(aq)$ $(FL \longrightarrow F'' + ML^{+})$

B) Schematic representation. In a fast step (1) a ligand surface complex is formed; subsequently a slow detachment (2) is the rate determining step; the surface site is regenerated by a subsequent fast surface protonation.

REACTION COORDINATE ⟶
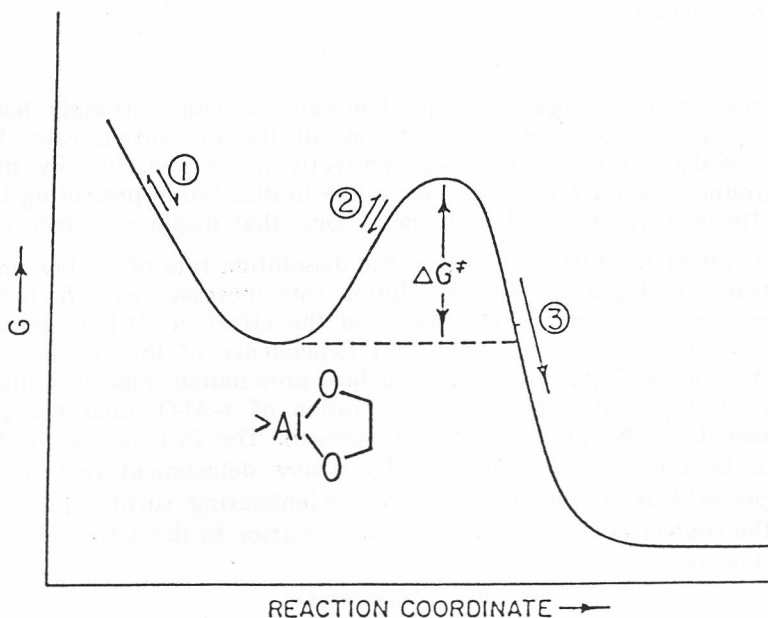
C) In the transition state theory, the high energy species FL (in reaction 2 of Figure 6b) is the precursor to the activated complex.

tually, the surface is regenerated. Thus, a steady state sequence (with respect to the surface phase) is established, i. e.,

$$\frac{d\{F\}}{dt} = \frac{d\{FL\}}{dt} = \frac{d\{F''\}}{dt} = 0 \tag{19}$$

The rate of the ligand-promoted reaction, R_L, in accordance with Eq. (18), is described by

$$R_L = k_2\{FL\} \tag{20}$$

The detachment is the rate determining step. Since the binding of the ligand is faster than the detachment, the concentration of ligands at the surface is in equilibrium with the solution.

In the transition rate theory (Figure 6c), the reactant in the rate deter-mining step, i. e., the surface complex (*FL* in Figure 6b) is the precursor to the activated complex. The activated complex is in local equilibrium with the precursor. The dissolution model presented is based on many assumptions (that have been enumerated before[32]) such as: (i) the hydrous oxide surface is treated as if all functional hydroxo groups were identical; (ii) constancy of the surface area is preserved; (iii) steady state condition can be maintained if a constant mol fraction, X_a, of active sites (sites of lower activation energy caused by surface defects such as steps, kinks, pits etc.) to total sites is maintained, i. e., if active sites are continuously regenerated; iv) the back reaction can be neglected if far away from solubility equilibrium.

Similar results have been obtained with other ligands[31]. The sequence of the rate constants, k_L is

$$k_{oxalate} > k_{malonate} > k_{succinate}.$$

One may note in Figure 6a that benzoate, although strongly bound to the oxide surface, does not accelerate at all the dissolution rate. It thus serves as model substance that acts indirectly as an inhibitor by blocking surface groups which are no larger accessible to dissolution-promoting ligands. Similar effects were observed with metal ions, that displace surface protons.

The effect of H^+: Effects of pH on the dissolution rate of δ-Al$_2$O$_3$ and BeO are illustrated in Figure 5. The dissolution rate increases with $[H^+]$, but the dependence on $[H^+]$ is not first order; and the effect of $[H^+]$ becomes small at pH < 3.5. An explanation of the pH dependence of the reaction rate is obtained by considering the extent of surface protonation. Figure 7. illustrates schematically the proton promoted dissolution of δ-Al$_2$O$_3$ (and the possible rearrangement of the protons by tautomerism). The fast successive binding of protons by the surface is followed by a slow detachment step. The deta-chable species 4 is surrounded by three neighbouring surplus protons that weaken the control bonds. Species 4 is the precursor to the activated complex; the rate law is

$$R_H \propto \{Species\ 4\} \tag{22}$$

As has been explained by Furrer and Stumm[31] and will be illustrated below, the activity of the reactive species in case of δ-Al$_2$O$_3$ is related to $(C_H^s)^3$:

$$\{Species\ 4\} \propto (C_H^s)^3 \tag{23}$$

where C_H^s is the surface protonation (in excess of relative to the point of zero proton charge). In case of BeO, the reactive species is proportional to $(C_H^s)^2$.

Thus, the proton promoted dissolution rate R_H is

$$R_H = k_H (C_H^s)^n \tag{24}$$

where $n = 3$ for δ-Al$_2$O$_3$ and $n = 2$ for BeO, corresponding to the oxidation numbers of the central ion of the respective oxide (Figure 8.). Further experiments with other oxides are necessary in order to find out how gene-ralizable equation (24) is.
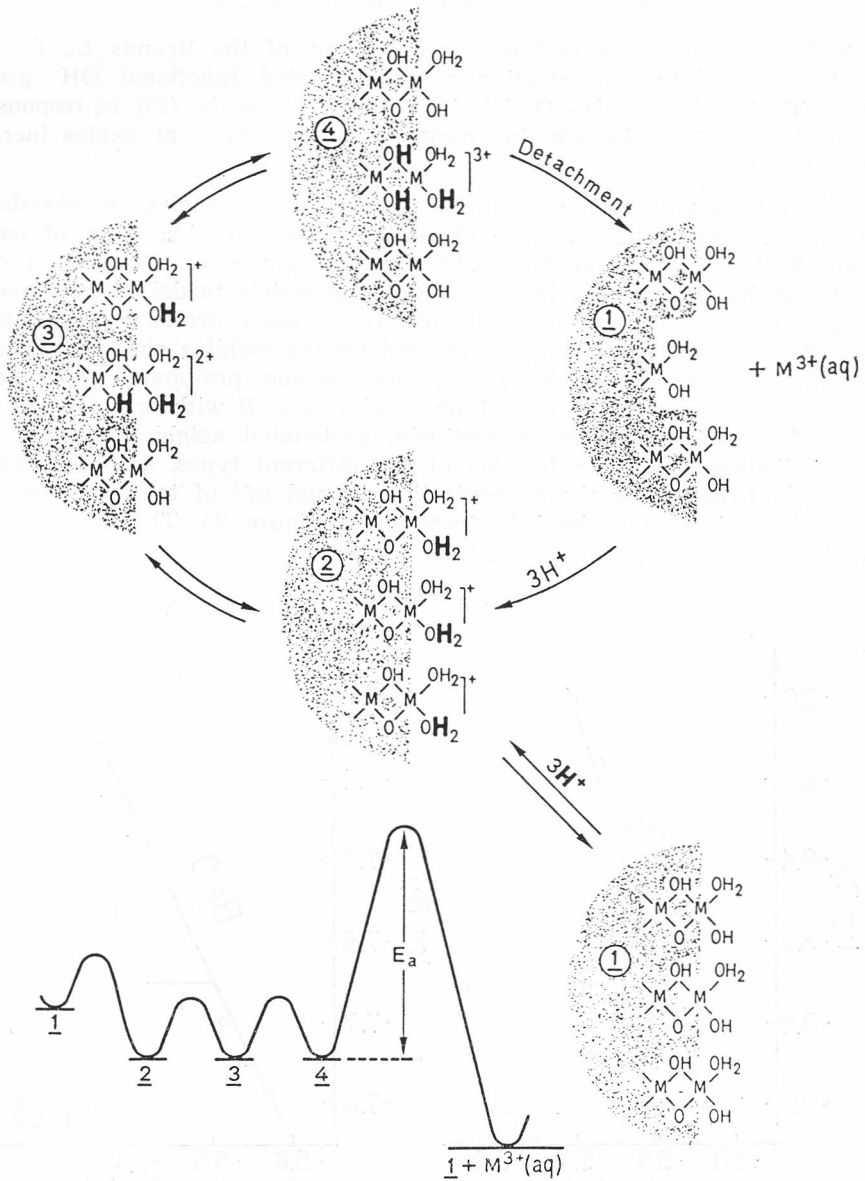
Figure 7. In acid promoted dissolution of trivalent oxides, fast surface protonation leeds to highly polarized interatomic bonds in the immediate vicinity of a surface central ion. (The migration of surface bound protons can be interpreted as tautomeric reactions). Protonation is followed by slow (rate determining) detachment of the central ion into solution. In transition state theory, species 4 is the precursor to the activated complex. The dissolution rate is postulated to be proportional to the concentration of species 4 (modified from Furrer and Stumm,[31]).

Most generally we can establish a dissolution rate of the type

$$R = k_H (C_H{}^s)^n + k_1 C_{L_1}{}^s + k_2 C_{L_2}{}^s + k_3 C_{OH}{}^s \qquad (25)$$

where $C^s{}_{L_1}$, $C^s{}_{L_2}$ are the surface concentrations of the ligands L_1, L_2; and $C^s{}_{OH}$ is the surface concentration of deprotonated functional OH^- groups ($>Me{-}OH + OH^- \rightleftarrows >Me{-}O^- + H_2O$). The last term in (25) is responsible for the fact that in the alkaline range dissolution rates of oxides increase with pH.

The two-dimensional distribution of interface species: a chessboard model. — A mechanistic picture of proton promoted dissolution of oxides (Figure 9) by Wehrli and Wieland[33] shows a precursor site with 2 or 3 nearest neighbour protons. Here a simple geometric model is proposed to estimate the concentration of such different excess proton configurations. The surface metal centers are represented by the »white« chessboard fields; the hydroxo groups (»black« fields) can become protonated at random. Different metal center sites (i. e., type A with zero, B with one, C with two, D with three, E with four, respectively, protonated neighboring sites) can now be distinguished. The fraction of the different types, as a function of $\Theta_H = C_H{}^s/S$ (where S is the concentration in mol m^{-2} of total surface sites) can be derived from probability theory (see Figure 9.). The dissolution of Al_2O_3 is characterized by the rate law
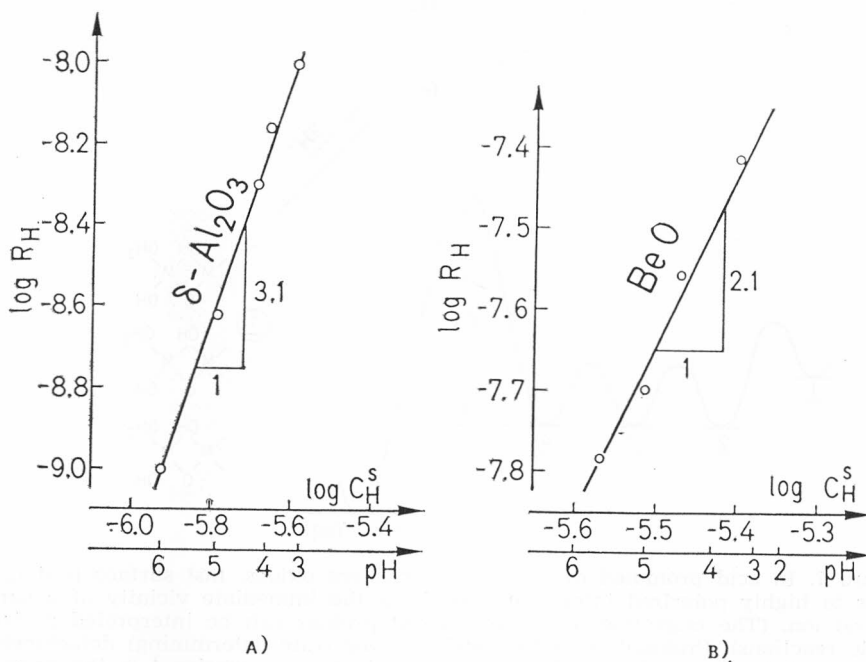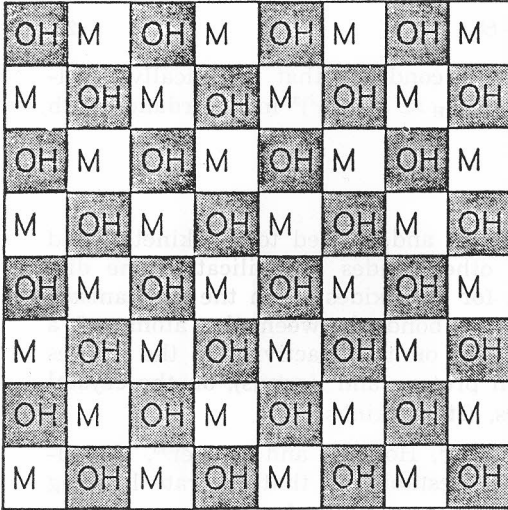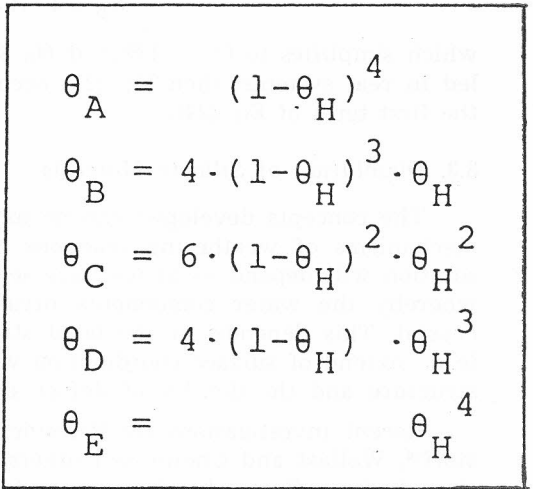
$$R_H = kS\Theta_D \qquad (26)$$

Figure 8. The dependence of the rate of proton-promoted dissolution of δ-Al_2O_3 (a) and BeO (b) respectively, R_H (moles m^{-2} h^{-1}), on the surface concentration of protons, $C_H{}^s$ (moles m^{-2})[31].
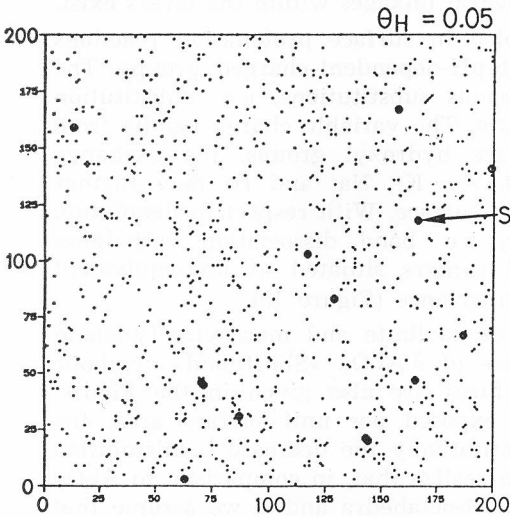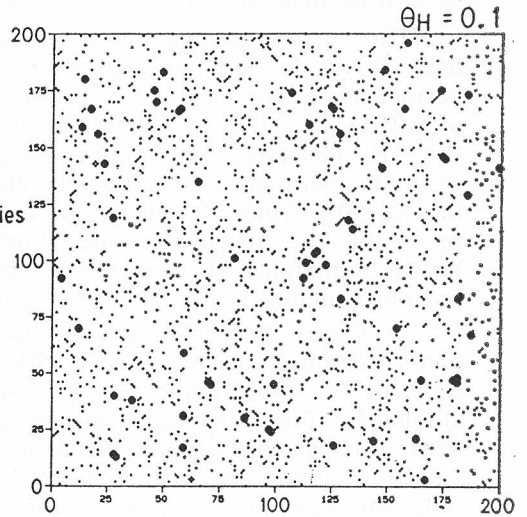
Random distribution

$$\theta_A = (1-\theta_H)^4$$

$$\theta_B = 4 \cdot (1-\theta_H)^3 \cdot \theta_H$$

$$\theta_C = 6 \cdot (1-\theta_H)^2 \cdot \theta_H^2$$

$$\theta_D = 4 \cdot (1-\theta_H) \cdot \theta_H^3$$

$$\theta_E = \theta_H^4$$

a

b

$\theta_H = 0.05$

Species D

$\theta_H = 0.1$

c

d

Figure 9 a), b) Chessboard Model: θ_A, θ_B, θ_C, θ_D, θ_E are the density of metal centers (white fields) surrounded by zero, one, two, three, four protonated hydroxy groups respectively. Probability theory gives the density of species A, B, C, D, E as a function of θ_H, the total density of protonated hydroxo groups.

c), d) Simple Monte Carlo simulations illustrate that the (relative) concentration of species D — marked with dots — increases with θ_H^3.

where Θ_D is the fraction of sites D. $S\,\Theta_D$ corresponds to {species 4} in Figure 7 and in Eq. (22).

$$\Theta_D = 4 \cdot (1 - \Theta_H) \cdot \Theta_H{}^3 \qquad (27)$$

which simplifies to $\Theta_D \approx 4\,\Theta_H{}^3$, if $\Theta_H \ll 1$, (a condition that is typically fulfilled in real systems) then Eq. (25) becomes $R_H \approx k_H\,(C_H{}^s)^3$ in accordance with the first term of Eq. (24).

3.3. *Dissolution of Silicate Minerals*

The concepts developed can be extended and applied to the kinetics and mechanisms of weathering reactions of other oxides and silicates. The dissolution will depend — as we have seen for the oxides — on the mechanisms whereby the water components break the bonds between the atoms of a crystal. This depends on the bond strength, on the reactivity of the solutes (e. q., extend of surface coordination with protons and ligands), on the crystal structure and the density of defect sites, (steps, kinks etc.).

Recent investigations by Petrovic et al.[34], Holdren and Berner[35], Grandstaff[36], Wollast and Chou[37] and others have established that the rate limiting step during silicate dissolution is related to a surface phenomenon.

Dissolution of layer silicates: kaolinite, muscovite. — The mechanistic interpretation of the dissolution of aluminosilicates is more involved than with oxides. Different layers consisting of different types of surface groups as well as different octahedral and tetrahedral linkages within the layers exist.

The surface groups which are involed in surface protonation reactions have to be divided into permanent and pH-dependent-charged groups. The permanent charge results from isomorphous substitutions, i. e., substitution of Al(III) for Si(IV) in the lattice structure. The variable charge results from the pH dependent protonation of surface hydroxyl groups. Ion exchange reactions between lattice bound cations, i. e. K^+, Na^+ and H^+ may further increase the proton density at the mineral surface. With respect to dissolution processes, the thermodynamic stability, i. e. bond dissociation enthalpies, lattice enthalpies of the various metal centers situated at non-equivalent positions in the lattice structure is of importance (Figure 13).

In Figure 10, the dissolution rates of kaolinite and muscovite (Wieland and Stummm[39]) are compared with those of $\delta\,Al_2O_3$. »Shorthand« symbolic schemes for the Al and Si layer structures are also given in the Figure. Obviously, the more Al octahedra are exposed per unit surface area, the greater is the dissolution rate. Semiquantitatively the decrease in dissolution rate of kaolinite can be understood if we realize that, in comparison to Al_2O_3, only one layer of the surface consists of Al-octahedra and if we assume that the dissolution of the Al is rate determining. Support for this assumption comes from the observation that oxalate (which is not bound to the silica surface to any significant extent) accelerates the kaolinite dissolution. A further clue is obtained by studying the surface protonation of kaolinite. As Figure 12 suggests, surface protonation occurs with decreasing pH first at the edges and only below pH $\sim$ 4.5 at the gibbsite type surface layer. The dissolution rate, as measured by the release of H_4SiO_4 into solution (Figure 10) reflects the differential surface protonation.
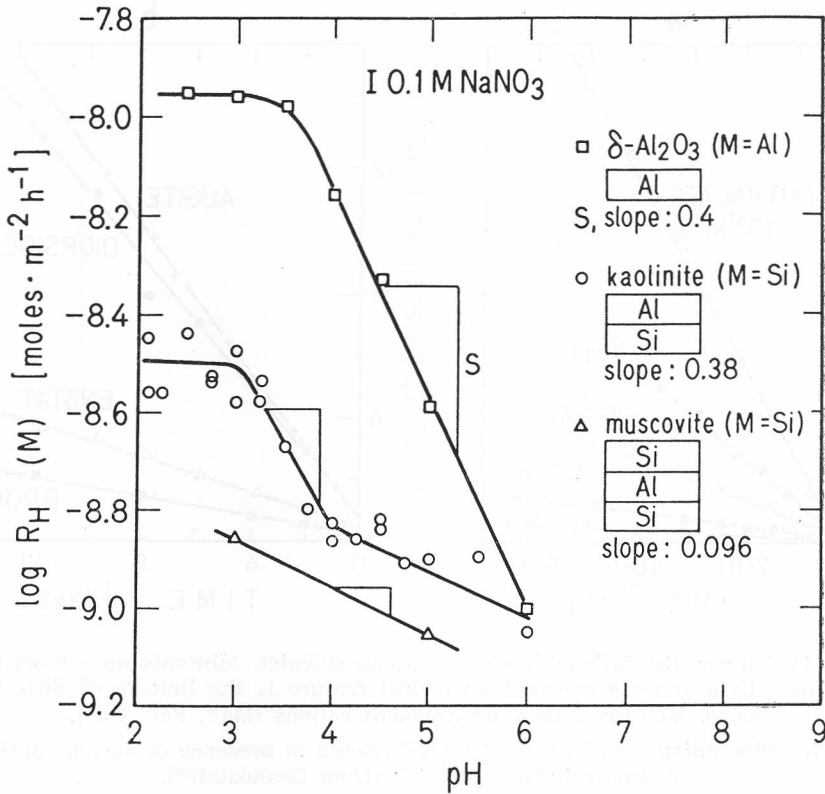
Figure 10. Proton promoted dissolution of δ-Al$_2$O$_3$, kaolinite and muscovite. The dissolution rate decreases with decreasing exposure of Al-octahedra. The rates are measured by Al(III) release in the case of δ-Al$_2$O$_3$ and by Si(IV) release in the case of kaolinite and muscovite, respectively. The slopes are defined by interpreting dissolution rates in terms of pH: $\log R_H = \log k_H - s \cdot pH$. In lower pH range the dissolution rate of kaolinite varies with pH in a similar pH dependence as was observed for δ-Al$_2$O$_3$ (surface protonation of Al—OH groups). In the pH > 4.5 range the edges become protonated and the dissolution occurs at the edge surface of kaolinite and muscovite.

With muscovite, the small increase in the dissolution rates between pH 5 and pH 3 indicates that the reaction mainly occurs at the edge surface which is only a minor part for the total surface. In order to elucidate the role of H$^+$ in a dissolution mechanism and to describe dissolution rates in terms of surface proton coverage it is important to determine experimentally the surface protonation occurring at the edges and the planar surface of sheet silicates.

Grandstaff[36] has shown for olivine that phthalate, oxalate and EDTA enhance the dissolution rate of fosteritic olivine. The linear dissolution reported by him (Figure 11a.)

$$R_T = R_{KCl} + k_{org} \, a_L^{\,n} \tag{23}$$
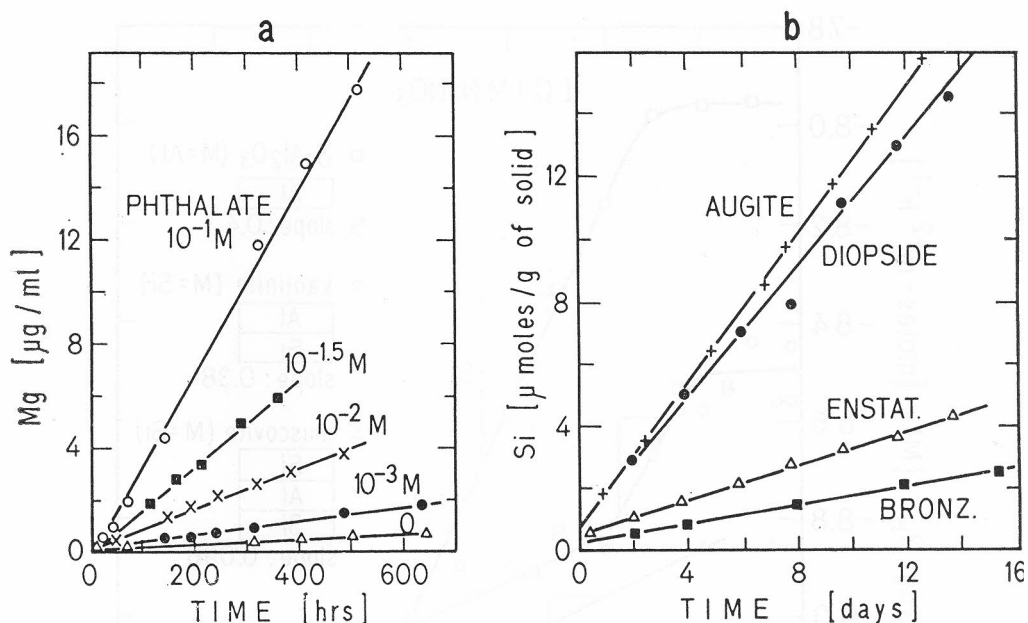
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Figure 11. Linear dissolution kinetics of frame silicates. Minerals used were pyro-
xenes and olivines; their essential structural feature is the linkage of SiO_4 tetra-
hedra, laterally linked by (bivalent cations (Mg^{2+}, Fe^{2+}, Ca^{2+}).

a) Olivine dissolution, as measured by Mg^{2+} release in presence of various phthalate
concentrations at pH 4.5; (from Grandstaff[36]).

b) Plot of amount of silica released vs time for the dissolution of etched enstatite,
bronzite ($p_{O_2} = 0$) diopside and augite at pH 6 ($T = 20\,°C$ for bronzite; 50 °C for the
other minerals; (from Schott and Berner[38]).

where a_L is the activity of the ligand in solution. The exponent n is ca.
00.5. Such a rate law is compatible with a surface ligand promoted dissolution.
An adsorption isotherm of the Freundlich type would show $\{L\} \cong k\,[L]^{0.5}$);
subsequent to the surface complexation, the surface central ion, in this case
$>MgL$, detaches into solution. The pH dependence of the ligand effect
observed by Grandstaff can be readily explained by the pH-dependence of
the extent of surface complex formation.

Schott and Berner[38] have found linear rates of silica release from iron-
free pyroxenes and olivines (Figure 11b). Their rates show a dependence on
H^+ activity (pH 2—6) corresponding to $a_H^{0.6-0.8}$. These authors and Grandstaff
have determined activation energies in the order of 38—150 kJ mol^{-1}. These
high values rule out a control of dissolution by a solution transport mechanism.
As Schott and Berner point out, these activation energies on the other hand
are lower than those expected for breaking bonds in crystals (The bond
dissociation energies, as given in Figure 13, are between 400 and 800 kJ
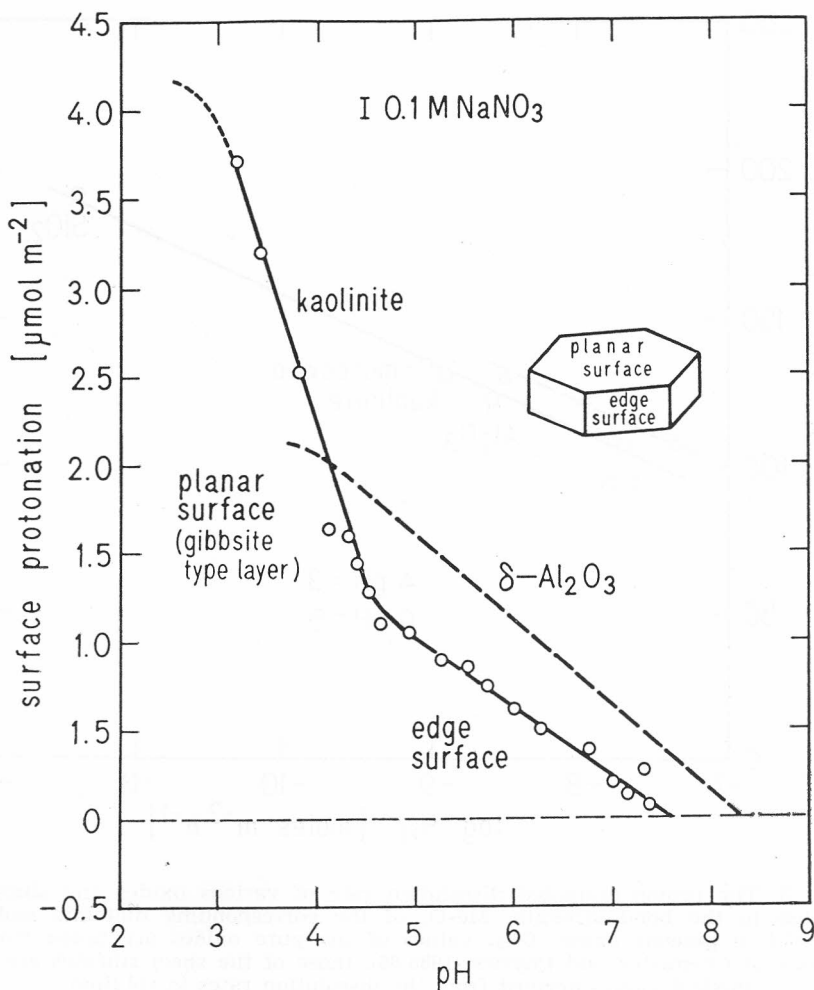
Figure 12. Effect of pH on the kaolinite dissolution may be explained by considering the structure specific surface protonation. The edges are already protonated in the neutral and weak pH range; the gibbsite type layer is protonated at pH < 4.5. The surface protonation is equal to a net proton density on the kaolinite as the total proton density surface was corrected by the ion exchange reaction between H^+ and Na^+ occuring at the siloxane planar surface[39].

mol^{-1}). This catalytic effects of surface bound protons and ligands must reduce the activation energy to an intermediate level.

Wollast and Chou[37] report for the steady state dissolution of the feldspar albite the empirical rate law

$$R = 10^{-16 \cdot 15} + 10^{-1 \cdot 69}\, a_H^{0 \cdot 49} + 10^{-18 \cdot 15}\, a_H^{-0 \cdot 3} \tag{29}$$

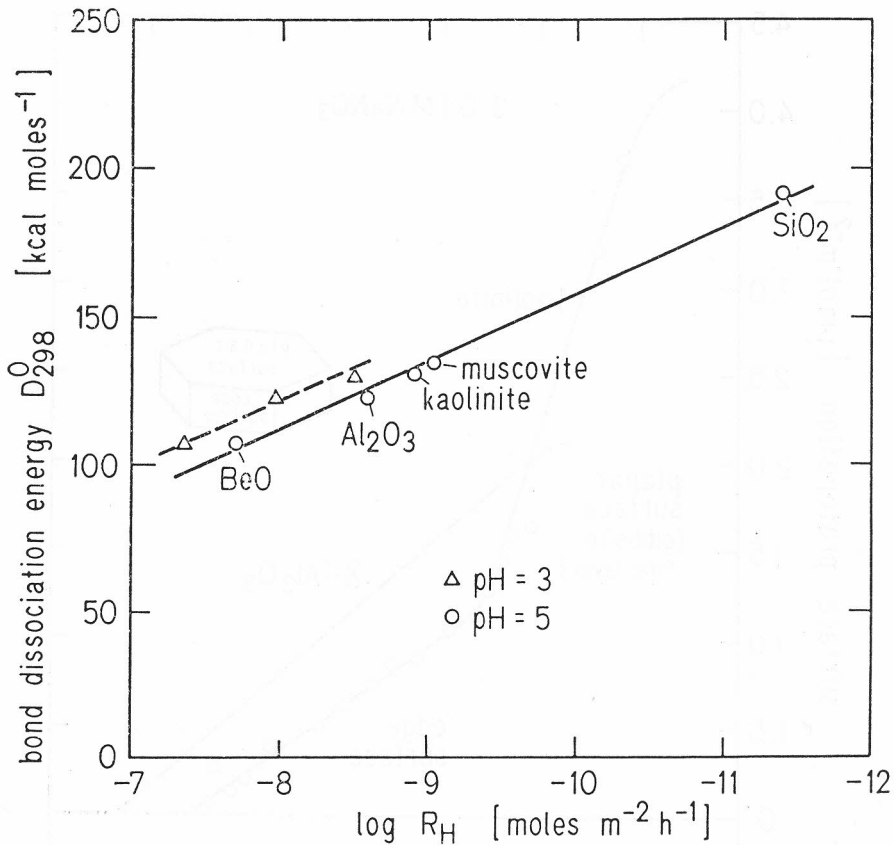This is, in principle, compatible with the general rate law given by Eq. (25).

Figure 13. The proton-promoted dissolution rate of various oxides and silicates is correlated to the bond strength, Me-O, of the corresponding diatomic molecules dissociated in gaseous phase. D^0_{298} values of the pure oxides are taken from the Handbook of Chemistry and Physics (1985/86), those of the sheet silicates are hypothetical values derived from the dissolution rates in solution.

3.3. Weathering in Natural Systems

Effect of Biota on Weathering. — As we have seen, the rate of dissolution of rocks is enhanced by H^+ ions, by surface complex forming substances and, in case of reducible minerals, by reductants. All these accelerations are provided by living matter: (i) microbial respiration of organic matter produces CO_2 and increases H^+; (ii) organic matter released by plants and microorganisms contain ligands such as oxalates, citrates and other polyhydroxy carboxylates.

Complex forming ligands by increasing the solubility of secondary minerals, also change the domain of congruent dissolution, i. e., higher concentrations of Al(III) and Fe(III) can be built up before a new plate is formed.

Relatively high numbers ($10^4 - 10^6$ colony forming units per gram) of bacteria actinomyces and fungi have been reported in the surface layers of various rocks[40]. Oxalic, citric or lactic acid may be excreted by bacteria and especially by fungi, occasionally also by plants. In one study of a natural environment, the top layer of a forest soil contained an average of 7 mg/g oxalate; or of 10^{-5} to 10^{-4} M in soil waters. Degradation products of biota, humic and fulvic acids will also affect the dissolution rate. However, the higher molecular weight humics, by becoming adsorbed, as a consequence of the hydrophobic effect, rather than by surface coordination with their functional groups may act more like an inhibitor. Microorganisms affect weathering in most instances indirectly by releasing organic solutes and by creating acidity, there is perhaps also the possibility that microorganisms are able to attack minerals and rocks directly.

Acid deposition. — The processes by which acid rain is neutralized are closely related to the process of normal chemical weathering. An understanding of the processes of chemical weathering is thus essential for predicting the effects of acid deposition (Schnoor and Stumm,[41]). Two effects need consideration: (i) Increase in [H^+]: Since the increase in weathering rate (rate of acid neutralization) upon increase in [H^+] is not linear — a tenfold increase in [H^+] nearly doubles the weathering rate (Eqs. (24), (25) — increased acidification resulting from atmospheric input cannot be fully compensated by an increased neutralization rate in the watershed. (ii) Increase in ligands: Rain water often contains oxalate and fluoride in concentrations as high as 10^{-6} M; SO_4^{2-} is present in concentrations 100 to 1'000 times larger. Since SO_4^{2-} forms surface complexes with Al_2O_3 surfaces, its accelerate effects on the dissolution are now being investigated[42].

4. *Outlook*

The action of water on minerals is one of the most important processes which produces extremely high surface area and reactive materials in the surface environment. The characterization of such materials is becoming one of our great challenges in understanding the chemistry of natural systems.

Solution chemists have learned that speciation (the form of occurrence of solutes) is the key to understand the reactivity and bioavailabilty of the solutes. The atomistic basis of the solid-solution interface is equally important to appreciate the basic forces operating in interfacial processes. The electric double layer theory, despite its efficiency in quantifying certain phenomena of colloid stability, has serious limitations because it neglects chemical speciation at the surface and does not provide information on the chemical structure of the interfacial region.

The electric double layer theory needs to be supplemented by the concept of surface complexation. Rate laws are expediently written in terms of the chemical entities participating in the reactions. Inner-sphere complexes are such chemical entities. Outer-sphere complexes (i. e. those in the outer Helmholtz plane) that are adsorbed by electrostatic bonds have, in comparison to inner-sphere complexes, little or no effect on the dissolution rate[43].

How can we predict the dissolution rate of different minerals? Three parameters, at least are necessary:

(1) The strength of the bond between the atoms of the crystal, specifically the strength of the bond between the metal center and oxygen (Figure 13.);

(2) the interaction of the solutes, e. g., H^+, OH^-, ligands with the surface of the crystal, i. e., the surface coordination equilibria. Surface protonation and surface complexes polarize the bonds around the surface central ions and induce the breaking of the interatomic bonds;

(3) structural surface factors for a given mineral, above all the density of defect sites (pits, steps, kinks).

The coordination chemistry of the solid-solution interface provides a general framework to project the interpretations given here to other oxides, minerals and ligands and to develop some important predictions for geo-chemical processes.

REFERENCES

1. M. d L. S. Goncalves, L. Sigg, M. Reutlinger, and W. Stumm, *Metal ion binding by biological surfaces; voltammetric assessment in presence of bacteria.* W. Nuernberg Spec. Issue, Sci. Tot. Env., in print.
2. M. Whitfield and D. R. Turner, *The role of particles in regulating the composition of seawater.* In: Aquatic Surface Chemistry. W. Stumm ed., Wiley-Interscience, New York, in press.
3. L. Sigg (1985), *Metal transfer mechanisms in lakes; the role of settling particles.* In: Chemical Processes in Lakes. W. Stumm ed., Wiley-Interscience New York, 283—307.
4. L. Sigg, M. Sturm, and D. Kistler, *Vertical Transport of heavy metals by settling particles in Lake Zürich.* Limnol. Oceanogr., in press.
5. W. Stumm, C. P. Huang, and S. R. Jenkins, Croat. Chem. Acta **42** (1970) 223.
6. W. Stumm, H. Hohl, and F. Dalang, Croat. Chem. Acta **48** (1976) 491 (Proc. IV. Internat. Summer Conf. on *Chemistry of Solid/Liquid Interfaces*, June 1975. Cavtat/Dubrovnik, Yugoslavia.
7. W. Stumm, R. Kummert, and L. Sigg, Croat. Chem. Acta **53** (1980) 291.
8. W. Stumm, G. Furrer, and B. Kunz, Croat. Chem. Acta **56** (1983) 593.
9. J. O'M. Bockris and A. K. N. Reddy (1970), *Modern Electrochemistry,* Vols. **1** and **2**, Plenum, New York.
10. G. Sposito (1984), *The Surface Chemistry of Soils.* Oxford University Press, Oxford.
11. R. Kummert and W. Stumm, J. Colloid. Interface Sci. **75** (1980) 373.
12. L. Sigg and W. Stumm (1981), *Colloids and Surfaces* **2** (1981) 101.
13. H. Motschi, Adsorption Sci. Technol. **2** (1985) 39.
14. H. Motschi and M. Rudin, Colloid. Polymer Sci. **262** (1984) 579.
15. H. Motschi, Naturwiss. **70** (1983) 519.
16. H. Motschi, *Aspects of the molecular structure in surface complexes; Spectroscopic investigations.* In: Aquatic surface chemistry, W. Stumm ed., Wiley-Interscience, New York, in print.

17. P. W. Schindler and W. Stumm, *The surface chemistry of oxides, hydroxydes and oxide minerals.* In: *Aquatic Surface Chemistry.* W. Stumm ed., Wiley-Interscience, New York, in print.

18. J. Westall and H. Hohl, *Advan. Colloid Interface Sci.* **12** (1980) 265.

19. K. Hachiya, M. Sasaki, T. Ikeda, N. Mikami, and T. Yasunaga, *J. Phys. Chem.* **88** (1984) 27.

20. R. G. Zepp and N. L. Wolfe, *Abiotic transformation of organic chemicals at the particle-water interface.* In: *Aquatic Surface Chemistry.* W. Stumm, ed., Wiley-Interscience, New York, in print.

21. D. Diem and W. Stumm, *Geochim. Cosmochim. Acta* **48** (1984) 1571.

22. S. H. R. Davies (1985), *Mn(II) oxidation in the presence of metal oxides.* Doctoral Thesis. CALTECH Pasadena, Ca. U.S.A.

23. B. Wehrli and W. Stumm, to be published.

24. B. Zinder, G. Furrer, and W. Stumm, *Geochim. Cosmochim. Acta* **50** (1986) 1861.

25. A. T. Stone and J. J. Morgan, *Reductive dissolution of metal oxides.* In: *Aquatic Surface Chemistry,* W. Stumm ed., Wiley-Interscience New York, in print.

26. W. G. Sunda and S. A. Huntsman, *Limnol. Oceanogr.* **28** (1983) 924.

27. T. D. Waite and F. M. M. Morel, *Environ. Sci. Technol.* **18** (1984) 860.

28. B. C. Faust and M. R. Hoffmann, *Env. Sci. Techn.* **20** (1986) 943.

29. T. D. Waite, A. Torikov, and J. D. Smith, *J. Colloid Interface Sci.* 2 Vol. **112** (1986) 412.

30. R. A. Berner, *Kinetics of weathering and diagenesis.* In: *Kinetics of Geochemical Processes.* A. C. Lasaga, R. J. Kirkpatrick, eds. *Reviews in Mineralogy,* **8** (1981) 11—134.

31. G. Furrer and W. Stumm, *Geochim. Cosmochim. Acta* **50** (1986) 1847.

32. W. Stumm and G. Furrer, *The dissolution of oxides and aluminum silicates; examples of surface coordination-controlled kinetics.* In: *Aquatic Surface Chemistry.* W. Stumm ed., Wiley-Interscience, New York, in print.

33. B. Wehrli and E. Wieland, *The chessboard — A model for two-dimensional distributions of interface species.* EAWAG-News **20/21** (1986) 9—12.

34. R. Petrovic, R. A. Berner, and M. B. Goldhaber, *Geochim. Cosmochim. Acta* **40** (1976) 548.

35. G. R. Holdren and R. A. Berner, *Geochim. Cosmochim. Acta* **43** (1979) 1161, 1173.

36. D. E. Grandstaff, *The dissolution rate of forsteritic olivine from Hawaiian beach sand.* In: *Rates of Chemical Weathering of Rocks and Minerals.* S. M. Colman and D. P. Dethier, eds. Academic Press Inc. Orlande Fla. U.S.A., 1986, 41—59.

37. R. Wollast and L. Chou, *Kinetic study of the dissolution of albite with a continuous flow-through fluidized bed reactor.* In: *The Chemistry of Weathering.* J. I. Drever ed., NATO ASI SERIES C, 149 (1985) 75—96.

38. J. Schott and R. A. Berner, *Dissolution mechanism of pyroxenes and olivines during weathering.* In: *The Chemistry of Weathering.* J. I. Drever ed., NATO ASI SERIES C, **149** (1985) 35—53.

39. E. Wieland and W. Stumm, in preparation.

40. F. E. W. Eckhardt, *Solubilization, transport, and deposition of mineral cations by microorganisms — efficient rock weathering agents.* In: *The Chemistry of Weathering.* J. I. Drever ed., NATO ASI SERIES C, 149 (1985) 161—173.

41. J. L. Schnoor and W. Stumm, *Schweiz. Z. f. Hydrologie,* in print.

42. L. Charlet and W. Stumm, in preparation.

43. R. Grauer and W. Stumm, *Colloid and Polymer Sci.* **260** (1982) 959.

SAŽETAK

Površinsko kompleksiranje i njegov utjecaj na geokemijsku kinetiku

W. Stumm, B. Wehrli i E. Wieland

Trošenje stijena, stvaranje tla, promjena i otapanje sedimenata posljedica su površinskih reakcija. Mnogi redoks-procesi, npr. oksidacija VO^{2+}, Mn^{2+} i Fe^{2+}, abiotska degradacija organskih tvari te fotosenzitivirani procesi, katalizirani su površinama. Teorija električkog dvosloja, usprkos njezinu uspjehu u kvantifikaciji nekih fenomena stabilnosti koloida, ima ograničenja stoga što zanemaruje kemijsku specijaciju na površini i stoga što ne daje informaciju o kemijskoj strukturi u međufaznom sloju. Površine prirodnih čvrstih tvari karakterizirane su funkcionalnim skupinama, kao npr. OH^- na površinama hidratiziranih oksida ili na površinama organskih tvari. Specifična adsorpcija (ili interakcija sa) H^+, OH, metalnim ionima i ligandima zbiva se putem koordinacije na površini; na taj se način mogu stvarati površinski kompleksi unutarnje sfere. Potrebno je poznavati oblik postojanja individualnih vrsta (specijacija) kako bi se mogla razumjeti njihova reaktivnost. U svrhu pretskazivanje brzina reakcija na granici faza čestica/voda potrebno je poznavati geometriju koordinacijskih ovojnica površinskih mjesta ili površinskih reaktanata.

U radu su prikazani neki primjeri oksidacije Mn^{2+} i VO^{2+}, te otapanja hidratiziranih oksida i silikata. U svakom se od tih primjera kinetika procesa i njihova ovisnost o varijablama u otopini (H^+ ili ligandi poput oksalata ili drugih di-, ili hidroksi-karboksilata) objašnjena je jednostavnim mehanističkim modelima koji uključuju koordinacijsku vezu na granici faza mineral-otopina. Izvedene su jednostavne kinetičke zakonitosti koje pojašnjavaju ovisnost brzine reakcije o koncentraciji (aktivitetu) površinskih vrsta.