

CCA-1400

YU ISSN 0011-1643

UDC 541.123

*Invited Conference Paper*

## The Role of Surface Coordination in Precipitation and Dissolution of Mineral Phases\*

Werner Stumm, Gerhard Furrer and Bruno Kunz

Federal Institute for Water Resources and Water Pollution Control (EAWAG)  
Swiss Federal Institute of Technology, Zürich, Switzerland

Received December 10, 1982

In precipitation and dissolution of minerals, the coordinative partners of the crystal-forming ions are changed. In heterogeneous nucleation, these ions interact coordinatively (surface complex formation and ligand exchange) with the surface sites of the heteronuclei or template. The dissolution of oxides too depends on the influence of surface complex-forming ligands and on the degree of surface protonation. A specific rate law for the dissolution of  $\delta$ - $\text{Al}_2\text{O}_3$  as influenced by  $[\text{H}^+]$  and [oxalate] is given. Generalized ideas on the effect of surface coordination in accelerating or inhibiting the dissolution of hydrous oxides and its relevance in the chemistry of rock weathering and metal corrosion are discussed.

### INTRODUCTION

Our research on the chemistry of solid-liquid interfaces has to a large extent been motivated by our interest in natural waters. In these multiphase systems, most important processes occur at phase discontinuities. The properties of the phase boundary between the solid surface and the electrolyte solution are of particular importance; they are dependent (i) on the forces operating on ions (and other solutes) and on  $\text{H}_2\text{O}$  molecules by the electrified surface; and (ii) on the forces operating on the solid surface by the electrolyte. Energies of interactions include electrostatic and chemical contributions. In the preceding conferences we have attempted to show that specific chemical factors need to be considered in addition to the theory of the electric double layer in order to explain most of the phenomena pertinent for solid-electrolyte interfaces occurring in natural systems.<sup>1-3</sup> Specifically we interpret the interaction of hydrous oxide surfaces with  $\text{H}^+$ ,  $\text{OH}^-$  with cations and with anions and weak acids and the concomitant influences upon surface charge as surface coordination (complex formation and ligand exchange) reactions.<sup>4-6</sup>

Surface complexes are especially important in the precipitation (heterogeneous nucleation) and dissolution of mineral phases. Both of these processes essentially consist in a change of the coordinative environment. For example in the formation and dissolution of  $\text{CaCO}_3$ , the coordinative partners

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\* Based on an invited lecture presented at the 6th »Ruder Bošković« Institute's International Summer Conference *Chemistry of Solid/Liquid Interfaces*, Cavtat/Dubrovnik, Croatia, Yugoslavia, June 1982.

of  $\text{Ca}^{2+}$  ( $\text{H}_2\text{O}$ ,  $\text{CO}_3^{2-}$ ) become exchanged; or, the dissolution of a metal oxide is accompanied by a change of the ligands of the metal ions.

The objectives of this paper are:

- (1) to illustrate that surface coordination plays a pertinent role in the precipitation and dissolution of mineral phases; specifically
- (2) to show that in heterogeneous nucleation, the coordinative interactions of crystal-forming ions (surface complex formation and ligand exchange) with the surface sites of the heteronuclei or template, accompanied by partial or full dehydration of the surface complex bond ions, are essential in determining the rate of nucleation; and
- (3) to exemplify how the dissolution of oxides depends on the concentration of surface complex-forming anions (ligands) and on the degree of surface protonation, and provide some generalized insight into surface chemical factors that may cause an acceleration or an inhibition of the dissolution; and
- (4) to relate some of these findings to the chemistry of weathering and corrosion.

#### SURFACE COORDINATION OF HYDROUS OXIDES

An oxide surface, covered in presence of water with amphoteric surface hydroxyl groups,  $\text{>Me-OH}$ , can be looked at as a polymeric oxo-acid or base. The surface OH group has a complex forming O-donor atom that coordinates with  $\text{H}^+$  and metal ions. The underlying central ion in the surface layer of the oxide — acting as a Lewis acid — can exchange its structural  $\text{OH}^-$  ions against other ligands (anions or weak acids) (Figure 1).

The extent of surface coordination and its pH dependence can be explained by considering the affinity of the surface sites for metal ion or ligand and the pH dependence of the activity of surface sites and ligands (Figure 2).

The tendency to form surface complexes may be compared with that to form corresponding solute complexes (Figure 3a). Correspondingly, the tendency of surface hydroxyl  $\text{>MOH}$  groups to form complexes with metal ions is similar to that of  $\text{HOH}$  to form with metal ions hydroxocomplexes (Figure 3b).

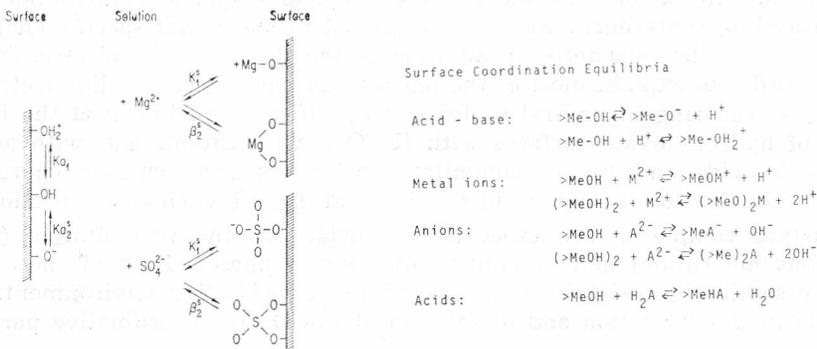


Figure 1. Interaction of hydrous oxides with acid base and with cations and anions, exemplified for the specific adsorption of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ , is interpreted in terms of surface complex formation and ligand exchange equilibria.

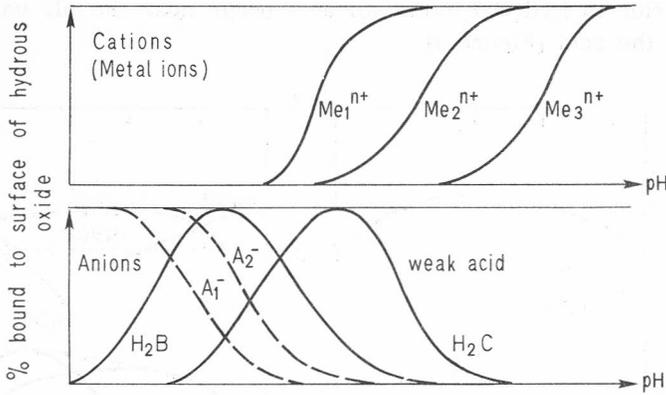


Figure 2. Schematic representation of pH dependence of specific adsorption (surface coordination) of cations, anions and acids on hydrous oxide surfaces. This dependence is in accord with mass law equations describing the surface coordination equilibria.

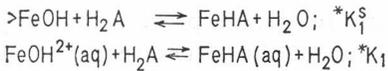
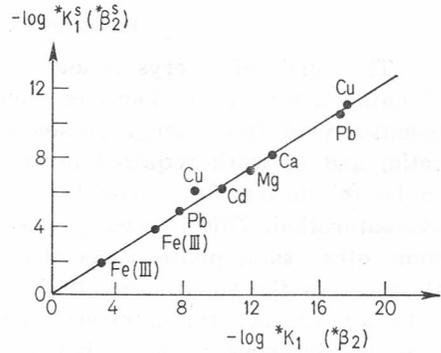
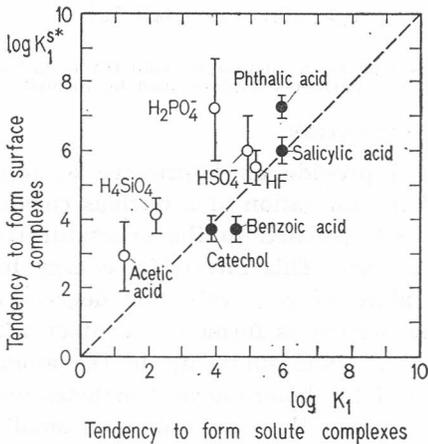


Figure 3. Comparison of the tendency to form surface complexes [ $*K_1^S$ ] with that to form solute complexes [ $*K_1$ ].  
 a) Data on  $\delta$ -FeOOH and  $FeOH^{2+}$  and on  $\delta$ - $Al_2O_3$  and  $AlOH^{2+}$  respectively (from Sigg and Stumm<sup>5</sup>);  
 b) Comparison of cationic surface complexes on amorphous  $SiO_2$  with hydroxo complexes (from Schindler et al., *J. Colloid Interface Sci.* 55 (1976) 469).

Surface equilibrium constants, either experimentally determined or estimated from corresponding complex formation constants in solution, can be used to predict extent of adsorption (surface binding) and resulting surface charge. For example, simple mass law considerations show that optimum

binding of acids to hydrous oxide surfaces occur near the  $pK$  value for the protolysis of the acid (Figure 4).

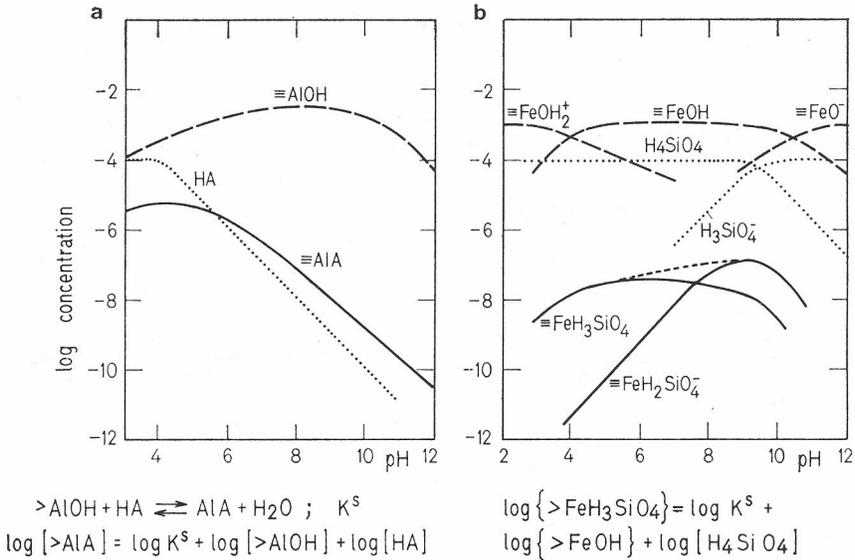


Figure 4. Prediction of the extent of surface coordination for a monoprotic acid HA (e. g. benzoic acid) as a function of pH. For silicic acid, two surface complexes can be formed.

#### HETEROGENEOUS NUCLEATION

The birth of a crystal and its growth provide an impressive example of nature's selectivity. The free energy of the formation of a nucleus consists essentially of free energy gained from bonds (related to the oversaturation ratio) and of work required to create a surface. This interfacial energy has to be minimized for nucleation to take place at relatively low degrees of oversaturation. This is accomplished if the nucleus is formed in contact with some other solid phase, especially if there is some similarity in the atomic structure of the two phases. If the surface of the heteronucleus matches well with the crystal, the interfacial energy between the two solids is smaller than the interfacial energy between the crystal and the solution.<sup>7-10</sup> Such a *heterogeneous nucleation* is the predominant formation process for crystals in natural waters. In addition to the matching of the structures of the surfaces, adsorption or chemical bonding of nucleus constituents to the surface of the substrate (heteronucleus) enhances the nucleation. The coordinative interactions, surface complex formation and ligand exchange of crystal-forming ions with the surface sites of the substrate or template, their partial or full dehydration and structural realignment (inner sphere surface complexes), and perhaps the formation of ternary surface complexes, are essential steps in the rate-determining part of the heterogeneous nucleation process. A critical surface concentration of crystal components, i. e. a two-dimensional solubility product, must be exceeded on the surface before a nucleus is being formed.

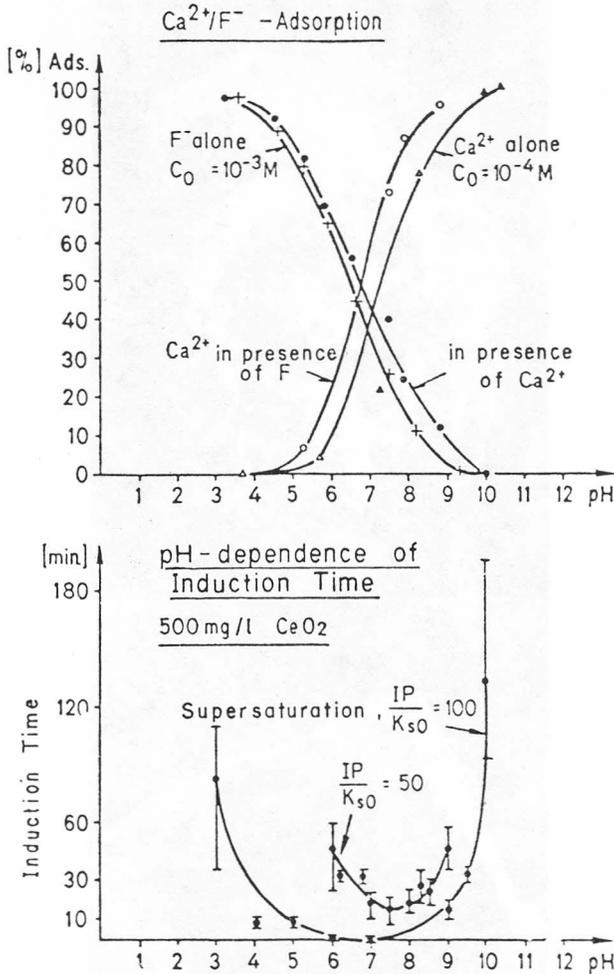


Figure 5. Heterogeneous nucleation of CaF<sub>2</sub> on CeO<sub>2</sub>. It occurs only in pH range where Ca<sup>2+</sup> and F<sup>-</sup> are specifically bound to the CeO<sub>2</sub> surface. This surface coordination, accompanied by partial dehydration of the ions, is a prerequisite for the nucleation.

### Nucleation of CaF<sub>2</sub> or CeO<sub>2</sub>

R. Giovanoli and H. Hohl called our attention to the fact that CeO<sub>2</sub> has the same crystalline structure and lattice distances as CaF<sub>2</sub>. Both Ca<sup>2+</sup> and F<sup>-</sup> are, within certain pH ranges (cf. Figure 2), specifically bound to CeO<sub>2</sub> (Figure 5). The CeO<sub>2</sub> substrate enhances the nucleation of CaF<sub>2</sub> only within the pH range where both Ca<sup>2+</sup> and F<sup>-</sup> are specifically bound to the CeO<sub>2</sub> surface.<sup>11</sup> It is also possible that in this pH range ternary surface complexes (>CeOCaF or >CeFCa) are formed. As shown in Figure 5, induction times (time necessary to form a nucleus — cf. Figure 6 —) depend on the concentration of the surface complexes formed (Figure 6). The same type of results has been

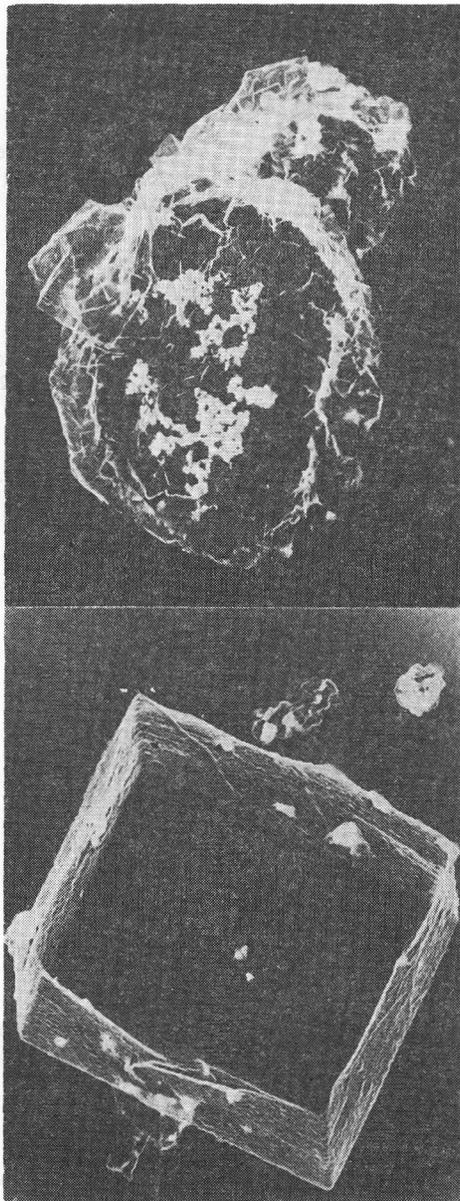


Figure 6. Electron-microscopic investigations of  $\text{CaF}_2$  crystals nucleated by  $\text{CeO}_2$ . At pH 6, many small crystals are formed (upper half); at pH 4, only a few large crystals are formed (lower half). The nucleation is strongly linked to the adsorption behavior of the crystal constituents (electron-microscopic investigations by R. Giovanoli, crystals grown by H. Hohl).

obtained by Hohl in our laboratory for the nucleation of  $\text{MgF}_2$  on  $\text{TiO}_2$ . He also showed that the heterogeneous nucleation rate can be retarded by cations and ligands that are competitively bound to the oxide surfaces.

Heterogeneous Nucleation of CaCO<sub>3</sub> (calcite)

In natural waters calcite nucleation occurs heterogeneously. Many surfaces (algae, biomass, aluminum silicates, aluminum oxides) may serve as heteronuclei. δ-Al<sub>2</sub>O<sub>3</sub> is an excellent substrate for the nucleation of calcite (Figure 7). The Ca<sup>2+</sup> binding to the δ-Al<sub>2</sub>O<sub>3</sub> increases with pH, becoming measurable only above pH = 7. HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> bind also specifically to the δ-Al<sub>2</sub>O<sub>3</sub> surface. In the slightly acidic pH range HCO<sub>3</sub><sup>-</sup> surface complexes are favored; the tendency to form carbonate complexes is, according to our preliminary measurements, especially pronounced in the slightly alkaline pH range.<sup>12</sup> The influence of pH on the calcite nucleation rate on δ-Al<sub>2</sub>O<sub>3</sub> (Table I) is compatible with the pH dependence of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> binding to these surfaces.

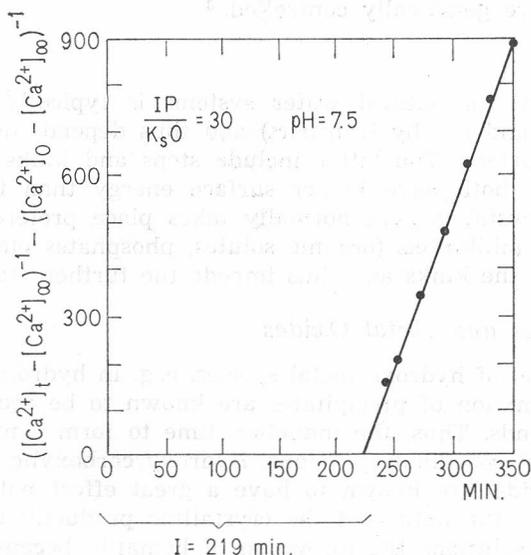


Figure 7. Heterogeneous nucleation of CaCO<sub>3</sub> on δ-Al<sub>2</sub>O<sub>3</sub>. Example for the sequence of nucleation (induction time) and subsequent crystal growth. The latter is plotted as a 2nd order reaction (as is typical for screw dislocation catalysis).

TABLE I

Induction Times (min) for the Nucleation of Calcite on δ-Al<sub>2</sub>O<sub>3</sub> from Solutions that Millimolar in Ca<sup>2+</sup>

IAP	pH:	Induction times (min)					
		7.5		8		8.5	
K <sub>s</sub> O	δ-Al <sub>2</sub> O <sub>3</sub> mg/1:	13.4	4.5	13.4	4.5	13.4	4.5
30		146	273	33	45	15	35
40				28	40		
50				15	20		

### *Nucleation Induced by Organisms*

Organisms are capable of forming a diverse array of minerals.<sup>13</sup> The formation is often intracellular. Nucleation occurs in most instances on the surface of an organic framework having a reasonably selective surface sites matrix (template) on to which the appropriate ions become surface complex bond and thus induced to form the nucleus. This organic mold constructed by the organisms, often enables nucleation and subsequent crystal growth to occur under conditions of low supersaturation. (Nucleation outside the organism may not occur because suitable heterogeneous surfaces are not available which can catalyze the nucleation at these low supersaturations; or the extracellular solution is undersaturated; i. e. the cell maintains on the inside an oversaturation). »Biologically-induced« nucleation can be extremely selective; the mineral type, the crystallographic orientation etc., depend on the matrix and are genetically controlled.<sup>13</sup>

### *Crystal Growth*

Crystal growth in natural water systems is typically controlled by a surface reaction (and not by transport) and thus depends on the topography of the mineral surface. The latter include steps and kinks often caused by screw dislocation; both have higher surface energy than the atoms in the plain surfaces. Crystal growth normally takes place preferentially at kinks. So-called growth inhibitions (organic solutes, phosphates etc.) are thought to bind primarily to the kinks and thus impede the further attachment of ions.<sup>9</sup>

### *Metal Hydroxides and Metal Oxides*

Polymerization of hydroxo metal species, e. g. in hydrolysis leading eventually to the formation of precipitates are known to be accelerated by complex-forming ligands. Thus, the induction time to form a nucleus is reduced by the presence of coordinating anions. Hydroxy carboxylic acids (e. g., citric, tartaric, lactic acids) are known to have a great effect both on the rate of crystallization and the nature of the crystalline product.<sup>14</sup> Certain acids can induce in Fe(III) solutions the formation of hematite because they contain a group which acts as a template for the nucleation of hematite.<sup>14</sup>

#### SURFACE REACTION CONTROLLED DISSOLUTION OF SOLID PHASES

Berner<sup>8</sup> has shown that most common minerals (calcite, SrCO<sub>3</sub>, feldspar, opaline silica, apatite) typically dissolve in natural waters via surface reaction-controlled kinetics. Transport control (diffusion) is often observed in the laboratory for minerals that are typically more soluble than the examples given above.

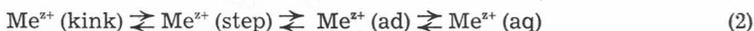
Knowledge of the solid water interface, especially the topography of the mineral surface and its coordination chemistry aid the understanding of the dissolution kinetics. The chemical properties of surfaces is significantly determined by specific adsorption or coordination of solutes to this surface; dissolution may be inhibited or accelerated. For example, the dissolution of passive Al- or Fe-oxides in HNO<sub>3</sub> is accelerated by traces of phosphates; on the other hand phosphates are known to be efficient inhibitors of corrosion. The coordination chemistry of oxide surfaces and its effects on the dissolution kinetics of hydrous oxides have been reviewed recently by Grauer and Stumm.<sup>15</sup>

### The Effect of Surface Coordination on the Dissolution of Oxides

As pointed out before, the dissolution of a metal, or metalloid oxide means a change of the ligands of the metal or metalloid ions. As pointed out by Valverde and Wagner<sup>16</sup> one has in essence the scheme



This may be refined by introducing the following consecutive steps

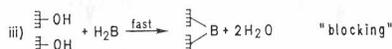
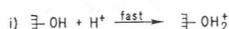


In comparing dissolution with the vaporization of a metal into a vacuum, Valverde and Wagner assume that the rate-determining step is essentially characterized by the release of ions from kinks into the adjacent solutions.

TABLE II

OXIDE DISSOLUTION (Simple Hypothesis on Rate-Determining Step)

1.) Surface coordination reactions



2.) Surface controlled dissolution reactions



Dissolution Rate

$$\text{Related to } \{ \text{≡-OH}_2^+ \}^m, \{ \text{≡-LH} \}, \{ \text{≡-L} \}$$

Far away from dissolution equilibrium, back reaction is negligible

Table II and Figure 8 illustrate in a simplified way, how acids and ligands affect the oxide surface  $\text{>MeOH}$  groups and polarize the  $\text{Me-O}$  binding (they also modify the surface charge which in turn modifies the acidity of the  $\text{>MeOH}_2$  groups). In a ligand exchange reaction, the nucleophilic ligand, L, binds to an Me center and replaces an OH group. This also polarizes the particular  $\text{Me-O}$  bonds. Furthermore, the surface complex formation is typically accompanied by a decrease in surface charge. (A positive surface charge hinders the approach of  $\text{H}^+$  to the surface).

The weakening of the  $\text{Me-O}$  bonds by the protonation of surface OH groups and the formation of (inner sphere) surface complexes with suitable ligands enhance the subsequent detachment of a  $\text{Me} \cdot \text{H}_2\text{O}$  or a  $\text{MeL}$  group. This detachment is rate-determining. The deprotonation or additional hydroxylation of the surface OH groups, as it may occur under alkaline conditions, facilitates the detachment into the solution of a hydroxo-Me group. Thus, the dissolution rate, R, must be a function of the degree of surface protonation and the concentration of ligand surface complexes.

$$R = f(\{ \text{≡-OH}_2^+ \}^m, \{ \text{≡-LH} \}, \{ \text{≡-L} \}, \{ \text{≡-O}^- \}^n) \quad (3)$$

Probably a more refined interpretation can be given if the structure of the surface and its double layer characteristics are better known.

Because we are usually far away from a dissolution equilibrium, the back

reaction can be neglected. In Table III some literature data on oxide dissolution by acids is referred to, where effects of surface complex forming anions on

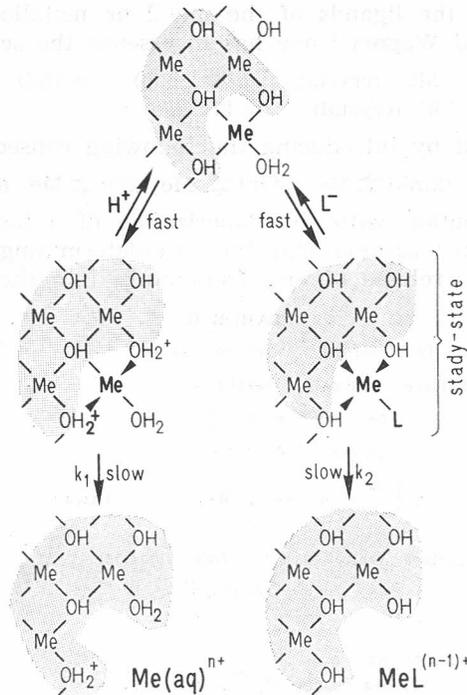


Figure 8. Surface reaction controlled dissolution of solid phases. (Compare Table 2). The polarization of the Me-O bonds by the protonation of surface OH groups and the formation of surface complexes with suitable ligands enhance the subsequent detachment of the Me · H<sub>2</sub>O or MeL group. This detachment is rate-determining.

TABLE III

Reaction Orders for the Dissolution of Oxides by Acids (from Grauer and Stumm<sup>15</sup>)

Solid phase	Solution	Proportionality of dissolution rate	Ref.
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	HCl < 1M > 3M	[H <sup>+</sup> ] [Cl <sup>-</sup> ] [H <sup>+</sup> ]	28
$\alpha$ -FeOOH	HClO <sub>4</sub> HCl < 2M	[H <sup>+</sup> ] [H <sup>+</sup> ] [Cl <sup>-</sup> ]	27
Fe(OH) <sub>3</sub> -Gel	various acids	HClO <sub>4</sub> + HCl $\frac{[\text{Cl}^-]}{K + [\text{Cl}^-]}$	29
Cr(OH) <sub>3</sub> -Gel	various acids	[H <sup>+</sup> ] <sup>0.48</sup> ; [ClO <sub>4</sub> <sup>-</sup> ] <sup>0</sup> ; [NO <sub>3</sub> <sup>-</sup> ] <sup>0.3</sup> [SO <sub>4</sub> <sup>2-</sup> ] <sup>0.37</sup> ; [Cl <sup>-</sup> ] <sup>0.72</sup>	30
BeO	H <sub>2</sub> SO <sub>4</sub> HCl	C <sup>0.7</sup> C <sup>0.5</sup>	26

the dissolution rate were observed. As will be shown later, the proportionality to  $[H^+]^x$  and  $[L]^y$ , (where  $x, <1, y <1$ ) for the dissolution rate is compatible with (3).

*Inhibition.* As indicated in Table II (reaction 1, *iii*) a specifically adsorbing solute may block, preferentially at a kink or step site, the surface-OH groups and shield them from attack by  $H^+$  and ligands. Such inhibitions may be hydrophobic substances or amphipatic surfactants (containing a hydrophilic and a bulky hydrophobic part) that accumulate preferentially at interfaces or polar substances which interact chemically with more than one of the surface sites and thus are capable of forming *multinuclear surface complexes*,<sup>15</sup> on that participate in the formation of a new surface phase. As has also been suggested by Matijević,<sup>17,19</sup> the energy involved in the simultaneous detachment from the surface of more than one  $>Me$  center is much larger than that needed to dislocate from the surface a mononuclear  $>MeL$  group.

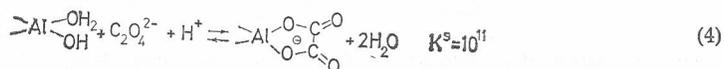
The known corrosion inhibitors with exception to those that act as oxidizing passivators) — e.g. phosphates and phosphate group containing substances, silicates, polysilicates and phenolates — have, within certain pH ranges, the properties given above. As shown by Sigg,<sup>5,20</sup> such substances (partially because they are present in various deprotonated forms) bind typically to iron oxide surfaces over a wide pH range. The inhibitory action of phosphates and silicates is enhanced by  $Zn^{2+}$  and  $Ca^{2+}$ . The formation of ternary surface complexes<sup>18</sup> or synergistic coadsorption may explain such phenomena.<sup>15</sup> Matijević's observations<sup>19</sup> that the dissolution of  $\beta$ -FeOOH is retarded by EDTA at pH values below 8.5 and accelerated at higher pH values are explainable because EDTA specifically adsorbs to  $\beta$ -FeOOH at pH values below 8.5 while EDTA at higher pH values increases the saturation equilibrium concentration of Fe.

#### *A Case Study: The Effect of Oxalate on the Dissolution of $\delta$ -Al<sub>2</sub>O<sub>3</sub>*

In *weathering processes*, it is commonly assumed<sup>7</sup> that complex formers, released from organisms and plants, may preferentially »leach« out certain lattice constituents and thus enhance the rock disintegration. The presence of water-soluble anions of organic acids of low molecular weight, i. e. malic, malonic, acetic, succinic, tartaric, vanillic and p-hydroxy benzoic acids has been demonstrated in top soils in concentrations as high as  $10^{-5}$  M to  $10^{-4}$  M, oxalate being the most abundant.<sup>21</sup>

Oxalate forms complexes with  $Al^{3+}$  in solution and on the surface of  $Al_2O_3$ . Figure 9 illustrates how solute complex formation of oxalate with  $Al^{3+}$  increases the solubility of  $\delta$ - $Al_2O_3$ . The inset of Figure 9 shows the pH dependence of the specific »adsorption« of oxalate on hypothetically non-dissolving  $\delta$ - $Al_2O_3$  surfaces.

The formation of oxalate surface complexes can be given as



In making dissolution experiments with hydrous oxides, special attention must be devoted to the properties of the surface. Parabolic rate laws have

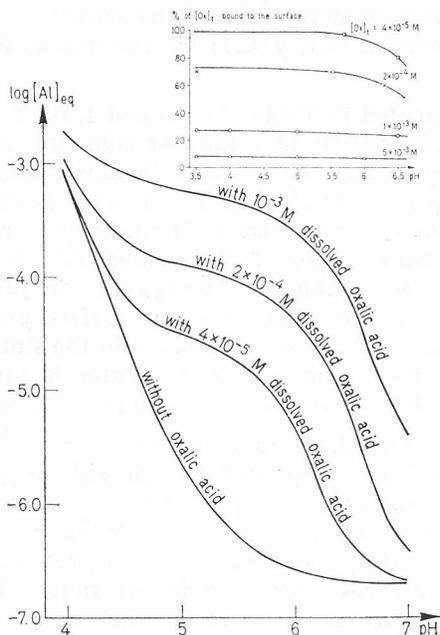


Figure 9. Equilibrium solubility of  $\delta\text{-Al}_2\text{O}_3$ . Effect of oxalate on solubility of  $\delta\text{-Al}_2\text{O}_3$ . Total solubility is enhanced by presence of oxalate. Calculations made for  $25^\circ\text{C}$ ;  $I = 0.1\text{ M}$ . Inset: Extent of specific binding of oxalate on a hypothetically non-dissolving  $\delta\text{-Al}_2\text{O}_3$ . Drawn out curves calculated by equilibrium constant given in eq. (4).

been observed as being typical in the dissolution of minerals. As shown by Berner and his collaborators and by Petrović,<sup>8,22-24</sup> parabolic dissolution rates are experimentally found primarily because of the heterogeneity in the surface properties (different phases, different surface energies, different particle size). We also observed parabolic rate laws (Figure 10) for unwashed

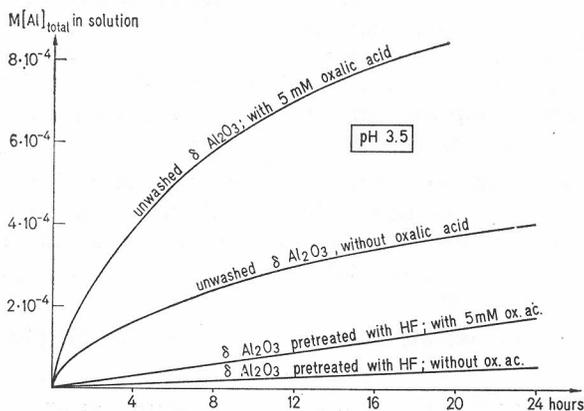


Figure 10. Effect of oxalate and surface heterogeneity upon  $\delta\text{-Al}_2\text{O}_3$  dissolution rate at  $\text{pH } 3.5$ ;  $25^\circ\text{C}$ ;  $I = 0.1\text{ M}$ . Parabolic curves are obtained for unwashed dispersions containing partially amorphous surface layers. Linear rate laws are obtained for dispersions that have been pretreated with HF. The dissolution rate is controlled chemically by reactions at the surface and is increased by oxalate.

dispersions containing partially amorphous surface layers. Pretreating the dispersions with HF, followed by washing with H<sub>2</sub>O, apparently renders the surface properties sufficiently homogeneous so that linear rate laws are obtained. The dissolution rate is controlled chemically by the reactions at the surface and is increased by oxalate.

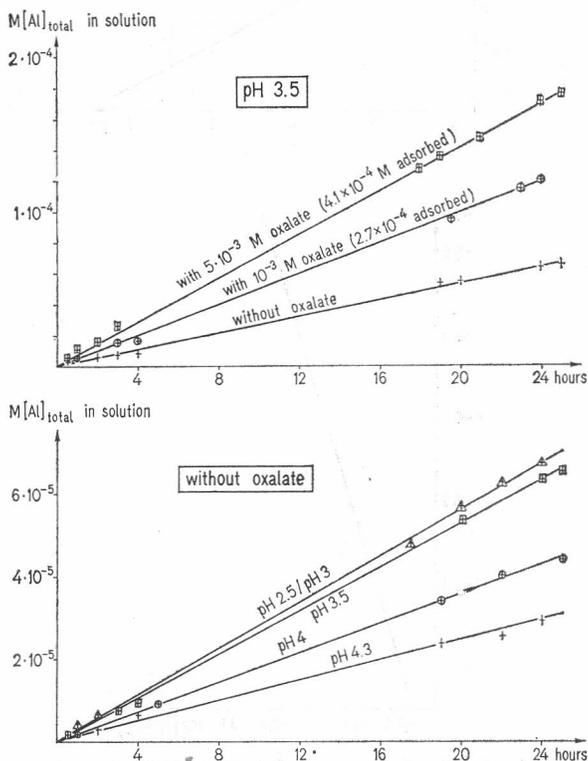


Figure 11. Effect of hydrogen  $[H^+]$  and [oxalate] on the dissolution rate of  $\delta$ -Al<sub>2</sub>O<sub>3</sub>. Constant surface area (2.2 g  $\delta$ -Al<sub>2</sub>O<sub>3</sub>/l)

Representative results obtained (25 °C) at various pH values in presence and absence of oxalate are given in Figure 11a and b. The rate of dissolution increases with increasing  $[H^+]$  reaching a plateau at  $pH < 3.5$  and with increasing oxalate concentration,  $[Ox_T]$ .

The  $[H^+]$  ion dependence observed (Figure 12a),  $rate = \text{prop } [H^+]^{0.4}$ , can be reinterpreted in terms of the degree of surface protonation,  $q$ . The dissolution rate depends on  $q^3$  or on  $\{\exists-OH_2^+\}^3$  (Figure 12b). This exponent of 3 may be explained statistically by considering that three  $H^+$  are needed on the surface per Al center.

Finally, the results obtained for the dissolution rate,  $R$ , at different pH values (2.5–6) and with various oxalate concentrations can be generalized into the rate law (Figure 13)

$$R = k_1 \{\exists-OH_2^+\}^3 + k_2 \{\exists<Ox\} \quad (5)$$

This rate law is in accordance with (3). The interpretation given to the results obtained in this case study is of a more general nature and can be extended

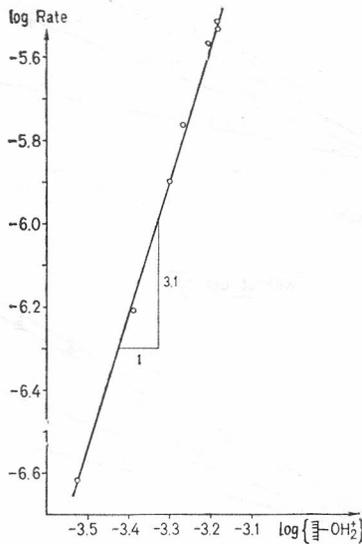
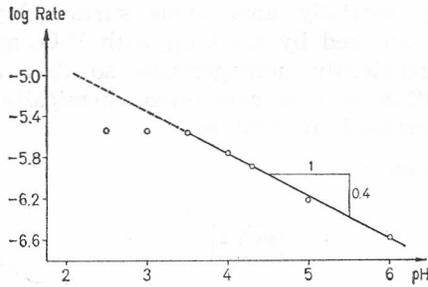


Figure 12. Effect of pH on the dissolution rate of  $\delta\text{-Al}_2\text{O}_3$ . This dependence (Figure a) can be reinterpreted in terms of a 3rd order dependence of  $\{\text{Al}(\text{OH})_2^+\}$  (Figure b). (cf. Eq. 5).

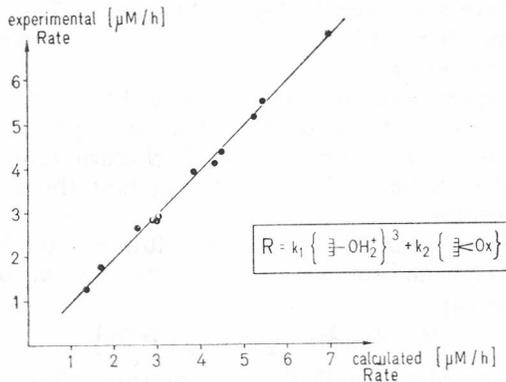


Figure 13. Experimental data are compared with those calculated from the rate law (eq. 5).

to systems involving other ligands, other oxides, aluminum silicates and other minerals.<sup>33</sup> Some recent treatments in the kinetics of geochemical reactions,<sup>34,35</sup> are, in this context, of great interest.

*Fractional Reaction Orders for Oxide Dissolution Rates Indicative of Surface-Controlled Reactions\**

In Table III, some previous results on oxide dissolution were summarized. A reinterpretation of these results and those of other researchers show that the dissolution kinetics usually can be accounted for by surface-controlled reaction rates.<sup>15</sup> The fractional reaction orders on H<sup>+</sup> and ligand (anion) that have often been reported (Table III) are compatible with a direct dependence on the concentration of surface species.

The equations given on the top of Figure 14 illustrate that the mass law expressions for surface ligand exchange or surface protolysis can be rewritten and plotted in the form of Langmuir adsorption type equations. If the same relations ( $[>ML]$  vs  $[L]$  and  $[>MOH_2^+]$  vs  $[H^+]$ ) are plotted in a double log-

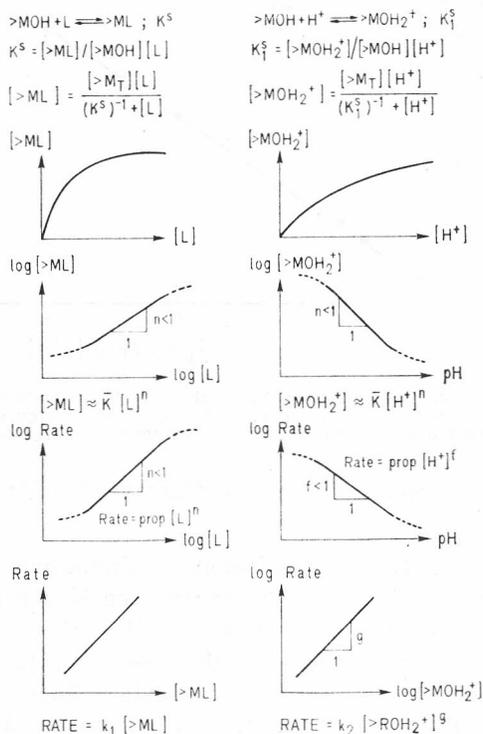


Figure 14. Scheme illustrating that surface complex formation reactions can be plotted in terms of Langmuir adsorption equations. A fractional reaction order for the dissolution is often indicative of a reaction rate that is proportional to the concentration of a surface complex.

arithmic plot (like one were to plot a Freundlich adsorption isotherm), a significant part of the curve will be linear, having a slope of  $n < 1$ . This is a

\* The arguments summarized here are taken in part from Grauer and Stumm.<sup>15</sup>

reaction rate dependence on  $[L]^n$  or  $[H^+]^n$ , where  $n < 1$  can be reinterpreted in terms of a reaction rate dependence on  $[>ML]$  or on  $[>MOH_2^+]$ .

In Figure 15, results of the effect of phosphate on the dissolution rate of aluminum hydroxide<sup>32</sup> are reported. As indicated in Figure 15, the plot can be derived from a Langmuir adsorption isotherm.

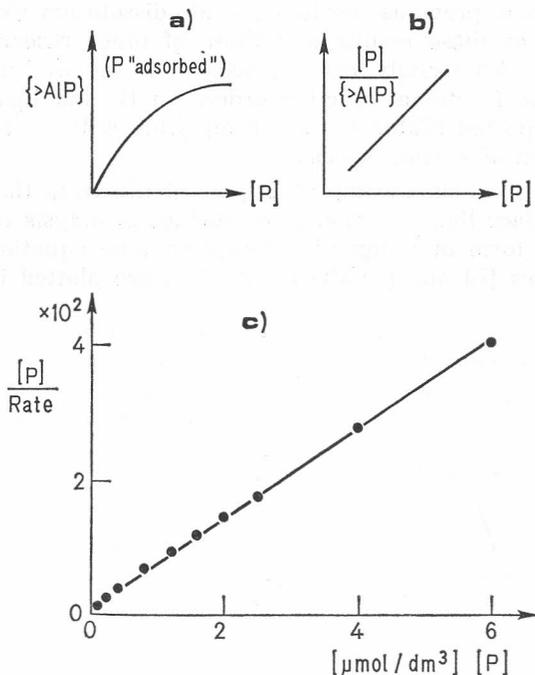
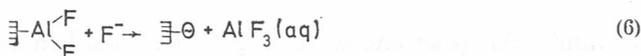


Figure 15. Effect of phosphate concentration, P, on the dissolution rate of aluminum hydroxide in 0.2 M HCl. The results given by Tartar et al.<sup>32</sup> are plotted (Figure c). This plot can be derived from a Langmuir adsorption isotherm (Figures a and b).

### Effect of Surface Complexation on the Rate of Anodic Dissolution of Aluminum Oxide

Observations of the anodic dissolution of aluminum disc electrodes<sup>25</sup> in presence of  $F^-$  are compatible with the generalized idea presented above. The anodic (corrosion) current density is related to the dissolution of the passive aluminum oxide layer. In presence of  $F^-$  the dissolution rate depends not only on the potential dependent concentration of surface fluoro complexes but also linearly on the concentration of  $F^-$  in solution. Wiedmer and Grauner<sup>25</sup> explained this behavior in terms of the reaction



The addition of oxalate and of other oxyanions causes a partial displacement of the fluoride bond to the surface.<sup>36</sup> Because the anodic dissolution of

FLUORIDE - OXALATE EFFECT ON  
Al / Al<sub>2</sub>O<sub>3</sub> DISSOLUTION at pH=4.0

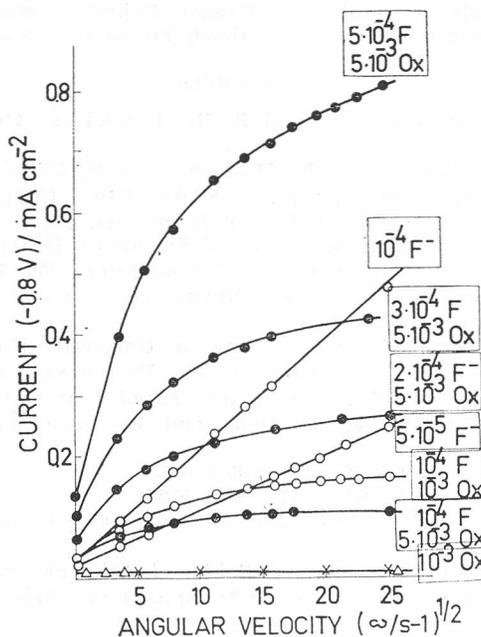


Figure 16. Effect of oxalate and fluoride ions on anodic dissolution of hydrous alumina. The dissolution current is plotted against the square root of rotation rate. Linear dependence is characteristic of a transport-controlled process ( $5 \times 10^{-5}$  M and  $10^{-4}$  M  $F^-$ ), and independence of the transport parameter (no complexing ligands (x) and  $10^{-3}$  M oxalate ( $\Delta$ )) is typical of a surface-controlled process. All other compositions (indicated on the corresponding curves) resulted in mixed transport surface controlled dissolution (from Zutic and Stumm<sup>36</sup>).

the Al-electrode is not as fast in the presence of oxalate as in the presence of  $F^-$ ,  $F^-$  displacement causes a reduction in the corrosion current<sup>36</sup> (Figure 16).

#### CONCLUDING REMARKS

Almost all the problems associated with understanding the rate processes that control the composition of our environment concern interfaces. Oxides especially those of Si, Al, Fe and Mn are abundant component of the earth's crust. Oxides are also of importance in passive films. The oxygen donor atoms present on the hydrous oxide surfaces tend to undergo protolysis to form complexes with metal ions, and to become exchanged for other ligands (anions or weak acids). Many of these surface complexes are believed to be of an inner sphere nature, i. e. they are not in the outer Helmholtz plane or diffuse part of the double layer but are coordinatively bound to the surface. The rates of processes occurring at the hydrous oxide surface, such as precipitation (heterogeneous nucleation on oxide surfaces) of minerals and dissolution of mineral phases — of importance in the weathering of rocks, in the formation of soils and sediments, in the corrosion of metals and their inhibition — are critically dependent on the coordinative interactions taking place on these surfaces.

*Acknowledgement.* — We are indebted to Rudolf Giovanoli for providing the photograph of Figure 6 and to Herbert Hohl for permitting us to use the data given in Figure 5. During this research, the authors enjoyed the assistance and valuable advice given by Rudolf Giovanoli, Rolf Grauer, Robert Kummert, Laura Sigg and Vera Žutić. The support by the Swiss National Foundation is acknowledged.

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**SAŽETAK****Uloga površinske koordinacije pri taloženju i otapanju mineralnih faza**

*W. Stumm, G. Furrer i B. Kunz*

Tijekom taloženja i otapanja minerala mijenjaju se koordinativni partneri iona koji grade kristal. U slučaju heteronukleacije ti se ioni koordiniraju s površinskim mjestima heteronukleusa, dajući površinske komplekse ili razmjenjujući ligande. Na otapanje oksida također utječu ligandi koji tvore površinske komplekse, a uz to i stupanj protonacije površine. Dan je poseban izraz za brzinu otapanja  $\alpha\text{-Al}_2\text{O}_3$  koja ovisi o koncentraciji  $\text{H}^+$  i oksalat-ionu. Raspravlja se i o općim osnovama ideje o utjecaju površinske koordinacije na ubrzavanje i inhibiciju otapanja (hidro)oksida. Razmatran je odnos prema kemiji trošenja stijena i koroziji.