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Report on theory on the affinity law

SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR WASTE MANAGEMENT

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WP 4 TASK 3

THEORY ON THE AFFINITY LAW

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Abstract

A review of literature data concerning the kinetic properties of some minerals in function of the deviation from equilibrium was carried out in this study. Reported studies combined the Transition State Theory and the Surface Complexation Modeling concept for expressing a rate law in function of solution composition and chemical affinity. It was shown that different classes of rate models are available and no generalized rate equation can be used to model mineral dissolution over the full range of geochemical conditions. It is premature to test affinity law on several minerals at equilibrium due to the lack of coherent and precise data in this range.

Introduction

The present task concerns the theory of the chemical affinity law for dissolution or precipitation of minerals. Numerous experimental observations note that the rate decreases when solution reaches a composition close to the saturation of the mineral. Investigators have also attempted to extrapolate far-from-equilibrium data to near-equilibrium conditions, to predict natural processes like weathering, sometimes with poor results because of the lack of understanding of the dependence of dissolution rate on the Gibbs free energy of the reaction. This study aimed to understand the deviations observed and the roles of surface charge, compositions, surface defect, selective dissolution, etc. on the rate parameters.

Definitions and theoretical background

Several terms had been defined in order to estimate the distance from equilibrium. We can use either the saturation ratio (Ω) which is the quotient between the ion-activity-product (Q) and the thermodynamic equilibrium constant (*K*) (eq. 1) or the chemical affinity which is related to the saturation ratio by its logarithm value (eq. 2).

$$\Omega = \frac{Q}{K} = \exp\left(\frac{\Delta G}{RT}\right) \qquad \text{eq. 1}$$

$$A = -\Delta G = -RT\ln\left(\frac{Q}{K}\right) \qquad \text{eq. 2}$$

ΔG, the Gibbs free energy of the reaction, is the energy driving the reaction towards its products. For an affinity value $A>0$, the solution is undersaturated and dissolution of mineral is observed. For an affinity value $A<0$, the solution is oversaturated and there is precipitation of mineral. For $A=0$, the net rate is zero, there is equilibrium.

The models attempted to describe kinetic of minerals are mostly based upon the Transition State Theory (TST) which defines an intermediate species between reactant and product as an activated complex. Both the forward rate and the backward rate are function of the concentration of this activated complex in solution, which is also considered in equilibrium with a precursor complex. The net rate is the difference between the two processes. The hypothesis of the Transition State Theory is that the activated complex is the same in the two ways (called the principle of detailed balancing), and that there is only one limiting step or one elementary reaction to control the kinetics. This assumption of microscopic reversibility leads to a connection between kinetics and thermodynamics because ratio of forward rate and reverse rate equals the thermodynamic constant *K* when reversibility holds ***(Rimstidt and Barnes (1980),Dove and Crerar (1990))***. This assumption also maintains that processes which increase the rate of a forward reaction can be expected to also increase the rate of the reverse reaction, provided that dissolution and precipitation mechanisms are identical ***(Lasaga (1984))***. In that case only, the net rate can be expressed with eq. 3 ***(Lasaga (1998))***:

$$r_{net} = r_+ - r_- = r_+\left(1-\frac{r_-}{r_+}\right) = k_+ \cdot \prod a_i^{n_i} \times \left(1-\exp\left(-\frac{A^*}{\sigma RT}\right)\right) \qquad \text{eq. 3}$$

where σ is a stoichiometric coefficient inserted to take into account the difference between the composition of the activated complex and the true mineral, defined as the number of moles of precursor complex that can be formed from one mole of mineral. Identically, it is also defined as the ratio of the rate of destruction of the activated complex relative to the overall reaction ***(Lasaga et al. (1994))***. In the mineral precipitation literature, it is rather related to the precipitation mechanism ***(Teng et al. (2000))***.

A^* is the affinity of the reaction involving the activated complex. Generally, A^* refers to the composition of surface layer, which could be different than the bulk mineral composition

(Daux et al. (1997)). A solution can attain equilibrium with the leached surface distinct from that it could attain from the original solid.

The affinity term shows how the overall rate slows down as the driving force ΔG decreases. When a mineral approaches equilibrium, the dissolution rate no longer simply reflects forward dissolution, but is also influenced by the reverse reaction, in which case the rate of dissolution may decrease ***(Wimpenny et al. (2010))***. As $\exp(x) \xrightarrow[x=0]{} 1+x$, the chemical affinity law states that close to equilibrium, the rate will vary linearly with affinity.

The forward rate r_+ can be expressed as $r_+ = k_+ \prod a_i^{n_i}$, a product of a forward rate constant (k_+) and a function of elemental activity of reactant or product, that could catalyze or inhibit the reaction in the near-to-equilibrium region. r_+ corresponds generally to the expression of rate far from equilibrium, at undersaturation conditions.

The sign of the rate (for example positive for dissolution, negative for precipitation) is only a matter of convention.

TST is strictly considered appropriate for an elementary reaction, and one controlling-rate process. This is difficult to assess for minerals with complex structure and several different structural units. However, in the case of multi-step dissolution mechanism, the rate would be controlled by the slowest step. Therefore, if the mechanism of this slowest step is rate limited by an elementary reaction, then TST may be applied to the overall reaction ***(Lasaga (1984))*** and eq.3 can be fitted over the data.

The main difficulty in the study of mineral dissolution (or precipitation) and application of eq. 3 comes from the necessary knowledge (or assumption) of the rate limiting steps in the reaction mechanism and/or the precursor complexes compositions and formation reactions ***(Pokrovsky and Schott (2001))***.

Unfortunately, it arrives that above conditions (of single limiting mechanism) are not satisfied, and studies of dissolution behavior versus large range of chemical affinity led the investigators ***(Nagy et al. (1991),Burch et al. (1993))*** to propose a so-called non linear rate law according to eq. 4a or 4b or even a combination of eq. 4 and eq. 3:

$$r_{net} = r_+\left(1-\exp\left(-n\left(\frac{|A^*|}{RT}\right)^m\right)\right) \qquad \text{eq. 4a}$$

$$r_{net} = r_+\left(1-\exp\left(-n\left(\frac{|A^*|}{RT}\right)\right)\right)^m \qquad \text{eq. 4b}$$

This alternative expression induces a sigmoidal behavior of the rate versus chemical affinity. *n* and *m* are fitted parameters. In that case, investigators generally tried to link the expression with a critical ΔG value, corresponding to a switch of reaction mechanism, and involving the formation of crystal defects such as etch pits ***(Arvidson and Lüttge (2010))***, which are active sites for undersaturated solutions. At near equilibrium conditions, the difference of free energy is insufficient to open etch pits at screw dislocations. Therefore these pits do not form and cannot contribute to the overall dissolution rate ***(Cama et al. (2000),Brantley (2008), Lüttge and Arvidson (2008))***.

However, as both the chemical affinity term and the forward rate (r_+) term may depend on the concentration of reactant and products, it also could happen that a sigmoidal behavior could be represented by an adequate expression of eq.3.

Rate expressions could then be not unique and that shows the complexity to propose correct mechanism. In a recent study, ***Schott et al. (2012)*** tried to reconcile the microscopic observation of surface state and the macroscopic measurement of rate dependence. They proposed that non-linear behavior comes from the low availability of active sites for minerals with low surface area, and that the rate dependence on chemical affinity could be function of the history of treatment before reaction ***(Lüttge (2006),Arvidson (2010))***. On the other hand, minerals with high specific surface area have sufficient reactive sites at the surface, and the reaction could proceed via direct attachment/detachment of reactant, leading to a linear behavior.

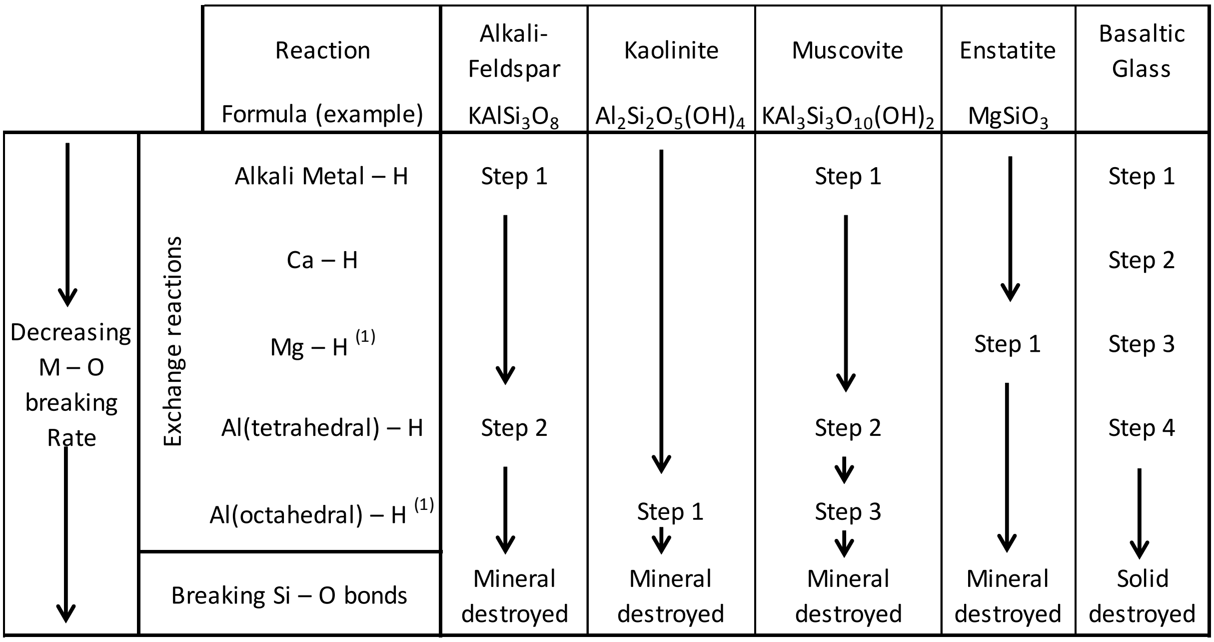
Evaluation of literature data

Literature data on the effect of approaching equilibrium on the kinetic of mineral dissolution had been widely studied by Schott and coworkers ***(Schott et al. (2009))*** and references therein or ***Brantley et al. (2008)***.

Simple oxides or hydroxides, aluminosilicate minerals and glasses, or carbonates have been studied for many years, with respect to their dissolution (or precipitation) behavior as a function of the deviation from equilibrium in solution, at variable conditions of temperature, pH or solution composition. Batch reactor experiments are a simple way to obtain the equilibrium conditions, but in that case, concentration of products and reactants change continually with time and ΔG value is not constant with time over an experiment. Also, interpretation of the rate data may be affected by the precipitation (backward) process. Mixed Flow Reactor experiments are largely preferred to study the variation of rate with chemical affinity, as uniform fluid compositions are easily reached, and reaction rates are straightforwardly deduced from steady state conditions. Moreover this technique avoids diffusion-limited conditions and minimizes accumulation of residual or incongruent product on the surface ***(Dove (1990))***. A wide range of departure from equilibrium can be attained by simply changing the input solution composition and/or flow rate.

The concept of surface speciation (surface complexation modeling) has been combined with TST to understand mineral dissolution rates far from equilibrium ***(Brady and Walther (1990), Schott (2009))*** for oxides, hydroxides or aluminosilicates. Accordingly, the rate law is linked with the formation of leached surface layers on the mineral surface, due to successive breaking of several metal-oxygen bonds upon the proton attack, until no further viable structure remains. This constitutes the rate-controlling precursor complex. The dissolution proceeds by successive removal of metal from the fastest to the slowest breaking bond. The rate limiting step is the destruction of the slowest breaking M-O bond essential for maintaining the mineral structure. In case of aluminosilicates, depending on the pH, this slowest step could be the breaking of Si-O bond (acid pH) or octahedral Al-O bond (basic pH). The leaching of alkali-or alkaline-earth or other cations leaves Si tetrahedra that are still connected to the lattice by bridging oxygen ***(Brantley (2008))***. In the case of simple oxide or hydroxide, only one type of bond is involved in the mechanism.

Figure 1 (From ***(Oelkers (2001))***) illustrates these successive steps and order of importance for several aluminosilicates and basaltic glass at acid pH.



		Reaction	Alkali-Feldspar	Kaolinite	Muscovite	Enstatite	Basaltic Glass
		Formula (example)	$KAlSi_3O_8$	$Al_2Si_2O_5(OH)_4$	$KAl_3Si_3O_{10}(OH)_2$	$MgSiO_3$	
↓ Decreasing M – O breaking Rate ↓	Exchange reactions	Alkali Metal – H	Step 1	↓	Step 1	↓	Step 1
		Ca – H	↓		↓		Step 2
		Mg – H (1)				Step 1	Step 3
		Al(tetrahedral) – H	Step 2		Step 2	↓	Step 4
		Al(octahedral) – H (1)	↓	Step 1	Step 3		↓
	Breaking Si – O bonds		Mineral destroyed	Mineral destroyed	Mineral destroyed	Mineral destroyed	Solid destroyed

(1) Mg – H and Al(octahedral) – H exchange is slower than Si – O bond breaking at **basic** conditions

Figure 1*: Illustration of the dissolution mechanisms of some minerals at acid pH. The slowest rate before the mineral destruction is the rate limiting step (From* ***(Oelkers (2001))****)*

For the simple oxide, the dissolution mechanism proceeds by the formation of a leached layer by proton exchange before its final irreversible destruction. This case is illustrated for minerals brucite, boehmite, or quartz.

Brucite $Mg(OH)_2$

Breaking of one type of bond (Mg–O) is assumed. Accordingly, the rate expression that fitted the data of ***Pokrovsky and Schott (2004)*** for dissolution of $Mg(OH)_2$ (0.2 m^2/g) at 25°C and basic pH (Figure 2) is expressed as eq. 5:

$$R_{diss} = k_{MgOH2+} \cdot \left\{ \equiv MgOH_2^+ \right\}^2 \times \left(1 - \exp\left(\frac{-A}{0.5RT} \right) \right) \qquad \text{eq. 5}$$

In this case, extrapolation of the data and TST appear effective to describe mineral dissolution close to equilibrium.

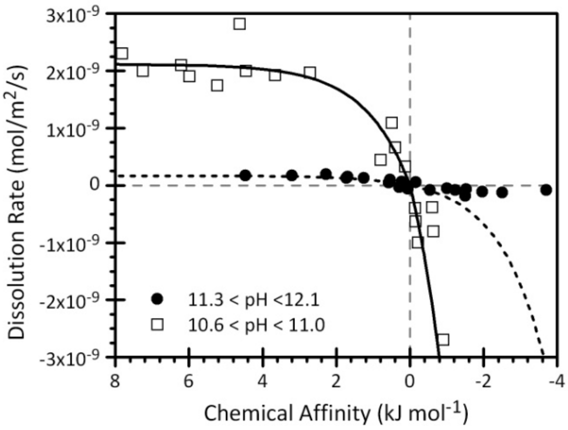


Figure 2*: Application of chemical affinity law on Brucite ($Mg(OH)_2$) dissolution and precipitation at 25°C and basic pH, using eq.5 (From* ***(Pokrovsky and Schott (2004)))***

Boehmite AlOOH

Dissolution and precipitation rates have been expressed as functions of surface speciation ($\equiv AlOH_2^+$, $\equiv AlOH$ or $\equiv AlO^-$ concentration) far from equilibrium and extrapolated to near-equilibrium ***(Schott (2009))***. For example, in neutral to basic solution, the principle of detailed balancing yields the following expression for the overall rate (eq.6):

$$R = k_{OH} \cdot \{OH^-\}\{\equiv AlO^-\} \times \left(1 - \exp\left(\frac{-A}{RT}\right)\right) \qquad \text{eq. 6}$$

This equation is illustrated in Figure 3A for the ratio of boehmite (1.65 m^2/g) dissolution (precipitation) rate at 100°C in neutral to basic solution and OH^- concentration as function of the degree of saturation (From ***(Bénézeth et al. (2008))***)

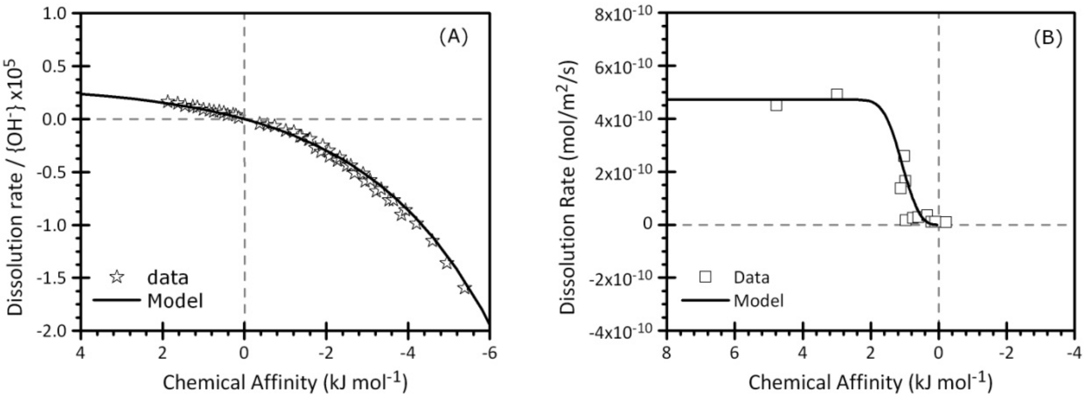


***Figure 3**: A) Boehmite dissolution and precipitation rates as function of chemical affinity at 100°C and neutral to basic pH solution (From **(Bénézeth (2008))**) B) Gibbsite dissolution rate at 80°C and pH 3 (From **(Nagy and Lasaga (1992))**)*

Gibbsite Al(OH)$_3$

Nagy and Lasaga (1992), reported a different behavior for gibbsite dissolution at 80°C in acid solution, with a highly non-linear relation of the rate with chemical affinity (Figure 3B), and a precipitation rate expression which differ from the dissolution rate expression. According to these authors, gibbsite ($Al(OH)_3$) dissolution at 80°C and pH 3 is fitted over the whole range of saturation states studied according to :

$$R_{diss} = k_H \times \left(1 - \exp\left(-8.12\left(\frac{|A|}{RT}\right)^{3.01}\right)\right) \qquad \text{eq. 7a}$$

However, from their data, it is difficult to evaluate the separate effects of pH, aluminum concentration in solution (as catalyst or inhibitor), and chemical affinity in solution near equilibrium. Moreover, the data near equilibrium exhibits large uncertainties.

When estimating rate equation on a narrow range of saturation state (-0.83 to +0.83 kJ/mol), it could appear that rate becomes linear when approaching equilibrium according to:

$$R_{diss} = k_H \times \left(\frac{|A|}{RT}\right)^{1.06} \qquad \text{eq. 7b}$$

This relationship is consistent with TST, and implies that the same reaction mechanism may control both dissolution and precipitation in the close to equilibrium area.

Quartz SiO_2

Quartz is one of the most studied minerals with respect to dissolution-precipitation mechanism. However, there are still some discrepancies between the data, and no generalized rate law is available.

For example, at neutral pH, between 200°C and 300°C ***(Berger et al. (1994))***, the rate-controlling precursor complex is formed by adsorption of H_2O molecules on quartz surface and hydrolysis of Si-O-Si structural unit ***(Brady (1990), Schott and Oelkers (1995))***.

$$(\equiv Si-O-Si\equiv)+H_2O \leftrightarrow (Si-O-Si\circ OH_2)^* \rightarrow 2(\equiv Si-OH)$$

$$nH_2O + \equiv SiOH \leftrightarrow [(\equiv SiOH)(nH_2O)]^*$$

4 Si-O-Si needs to be successively broken, but breaking the first Si-O-Si bond is probably the most energetic step, and the dissolution process is limited by the progress of this intermediate reaction ***(Dove (1990))***.

Dissolution kinetic of quartz has been combined with surface complexation calculations (involving different surface species like $\equiv SiOH_2^+$, $\equiv SiOH$ or $\equiv SiO^-$) to yield an equation of dissolution rate as function of departure from equilibrium ***(Schott (2009))***. In deionized water only, the rate could be expressed as:

$$R = k_{H2O}\{\equiv SiOH\}\times\left(1-\exp\left(\frac{-A}{RT}\right)\right) \qquad \text{eq. 8a}$$

Eq.8a is consistent with eq. 3 and shows a linear dependence on chemical affinity.

This case is illustrated in Figure 4A.

In the presence of electrolyte like ($NaNO_3$, $Pb(NO_3)_2$, NaCl) the observed behavior changed: the rates are no longer linear functions of the solution saturation state. A sigmoidal behavior is then observed (Figure 4B). Electrolytes may accelerate the dissolution rate by increasing the accessibility of water molecules to the siloxane bonds ***(Dove (1990))***. ***Davis et al. (2011)*** observed also a rate dependence not linear with respect to chemical affinity in the near equilibrium region (Figure 4C). However, they were able to fit the data with two separate linear regions (both consistent with eq.8a) that are attributed to two parallel processes of dissolution mechanisms.

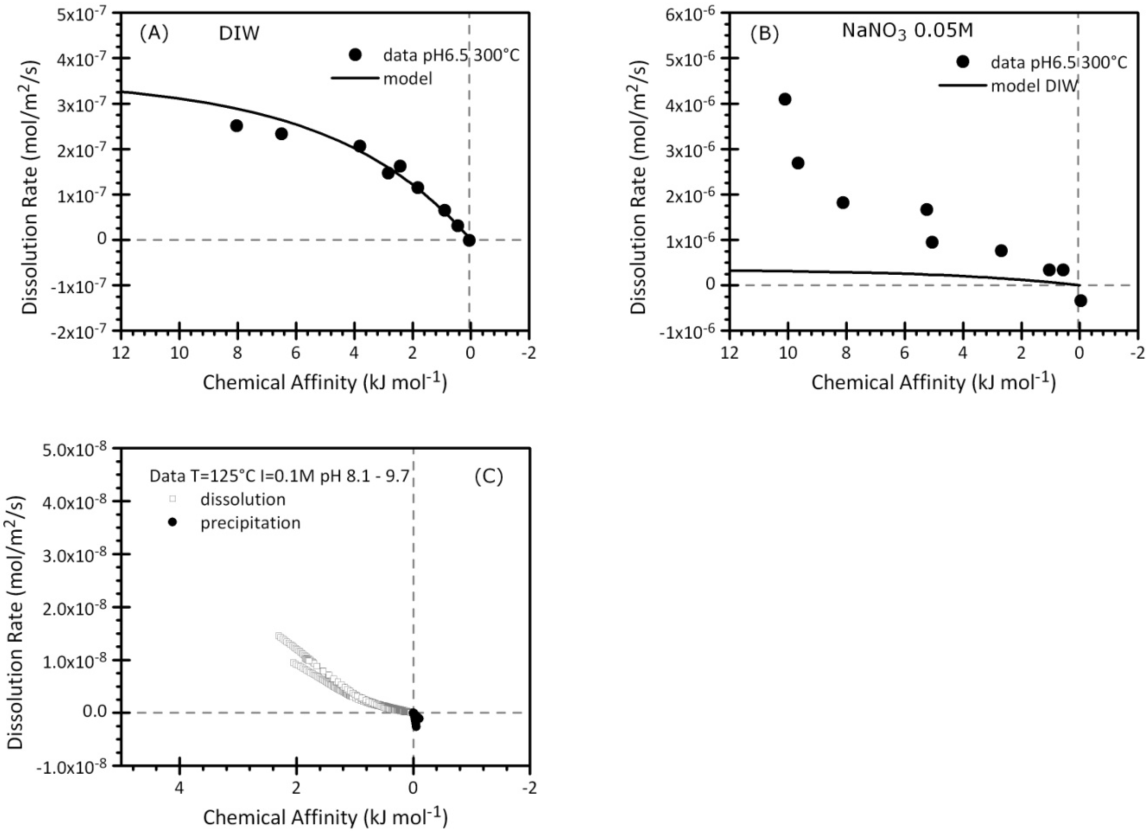


Figure 4*:A) Application of chemical affinity law on Quartz (*SiO_2 *0.31m*^{2}*/g) dissolution in deionized water at 300°C and neutral pH, using eq.8a (From* ***(Schott (2009))*** *and* ***(Berger (1994))****) B) in presence of* $NaNO_3$ *and pH 6.5 (Refitted from* ***(Berger (1994))****with A = -RT ln(*$[H_4SiO_4]/10^{-2}$*)) C) Close to equilibrium data for dissolution and precipitation of quartz (0.26 m*^{2}*/g) at 125°C and pH 8.2-9.6 (From* ***(Davis (2011))****) as function of A.*

In NaCl electrolyte solution, ***Dove and Crerar (1990)*** suggest the following rate law for quartz dissolution between 100 and 300°C:

$$R = \left(k_+ + k_{ad} \frac{K_{Na^+}\left[Na^+\right]}{1 + K_{Na^+}\left[Na^+\right]} \right) \times \left(1 - \exp\left(\frac{-A}{RT} \right) \right) \qquad \text{eq. 8b}$$

Ganor et al. (2005) studied precipitation of quartz (0.06m^2/g) at 180°C and pH 4 in a batch reactor experiment ***(Ganor et al. (2005))***. Data agree with the principle of detailed balancing, and the rate equation consistent with TST is applied satisfactorily. However, the authors state that their data are not sufficient to retrieve a function that uniquely describes precipitation rate dependence on deviation from equilibrium nor to propose a mechanism for the precipitation of quartz.

Aluminosilicates

The successive breaking of metal (alkali-, alkaline-earth, aluminum and silicon)–oxygen bonds results in a partially Al-depleted Si-rich surface layer, which could be considered as the precursor complex.

Schott and Oelkers ***(Oelkers (2001),Schott (2009))*** have generalized a dissolution rate law by incorporating a specific effect for Al inhibition at acidic conditions into the forward rate expression. Inhibitory effect of Al^{3+} could be attributed to a back-reaction of specific precursor surface sites ***(Brantley (2008))***. According to the aluminum coordination in the structure (tetrahedral sites or octahedral sites), the dissolution behavior could depend on the pH conditions. For example, on minerals which contain only tetrahedral Al (Albite, K-Feldspar), the precursor complex is formed by reversible $Al^{3+}/3H^+$ exchange reversible whatever the pH (acid or alkaline) ***(Schott (1995))***. In case of minerals like kaolinite or smectite, with some octahedral Al in their structure, the same exchange reaction forms the precursor complex only at acid to neutral pH. At basic conditions, its formation depends both on aqueous Al and SiO_2. Accordingly, the rate expression may be written as eq. 9a and 9b.

$$R = k_+ \cdot \left(K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right)^n \Bigg/ \left(1 + K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right)^n \right) \right) \times \left(1 - \exp\left(\frac{-A}{\sigma RT} \right) \right) \qquad \text{eq. 9a}$$

$$R = k_+ \cdot K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right)^n \cdot \left(\frac{1}{\{SiO_2\}} \right) \times \left(1 - \exp\left(\frac{-A}{\sigma RT} \right) \right) \qquad \text{eq. 9b}$$

K^* is the equilibrium constant for the Al proton exchange reaction and n is a stoichiometric coefficient for the precursor complex.

This Al inhibition can have an important impact on the dependence of kinetics on chemical affinity, resulting in a sigmoidal behavior analogous to that attributed to the etch pits dislocation control of dissolution.

Equation 9a has been applied on chlorite ($Mg_{2.76}Fe^{2+}_{1.90}Fe^{3+}_{0.07}Al_{0.97}Si_{2.48}Al_{1.52}O_{10}(OH)_8$; $1.41 m^2/g$) with $n=0.27$ ***(Lowson et al. (2005))***, and on muscovite (mica family $KAl_3Si_3O_{10}(OH)_2$) with $n=0.5$ ***(Oelkers et al. (2008))*** both far from equilibrium.

Aluminum speciation in solution has been taken into account to express the rate equation for dissolution of K-Feldspar ($K_{0.81}Na_{0.15}Ba_{0.03}Al_{1.05}Si_{2.96}O_8$) at pH 9 and T=150°C with a modification of eq.9a according to (eq. 9c) :

$$R = 1.7 \cdot 10^{-13} \cdot \left(\frac{1}{\{Al(OH)_4^-\}^{1/3} \cdot \{H^+\}^{1/3}} \right) \times \left(1 - \exp\left(\frac{-A}{3RT} \right) \right) \qquad \text{eq. 9c}$$

with k_+ in mol.m^{-2}s^{-1} ***(Gautier et al. (1994))***. Plot of experimental data is presented on figure 5 in function of chemical affinity.

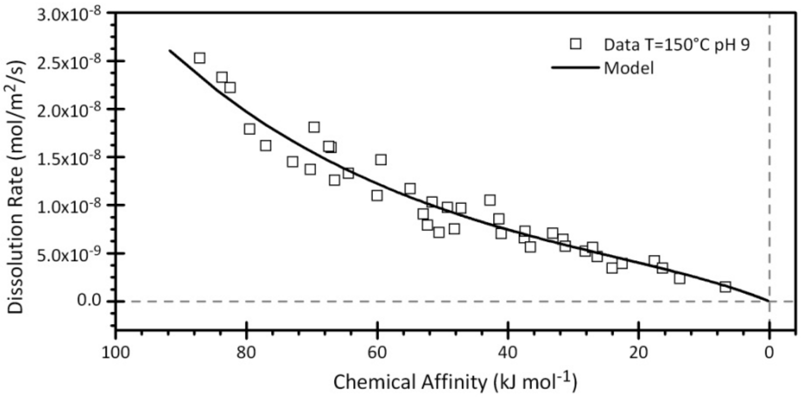


Figure 5*: Application of chemical affinity law on K-Feldspar ($K_{0.81}Na_{0.15}Ba_{0.03}Al_{1.05}Si_{2.96}O_8$) dissolution in deionized water at 150°C and pH 9 (from* ***(Gautier (1994))****)*

However, Lüttge’s critical analysis revealed that the kaolinite rate data from Gautier et al. (1994) cannot be used to distinguish between different kinetics models: a model based on a simple transition state formulation (with various values for σ) for the chemical affinity dependence of the rate or a model based on the statistical theory of crystal defects growth and dissolution ***(Lüttge (2006))***.

Kaolinite ($Al_2Si_2O_5(OH)_4$) had been studied at pH 2-3 and 80°C ***(Nagy (1991))*** or 150°C ***(Devidal et al. (1997))***. Both studies show a non linear behavior of the rate dependence on chemical affinity (Figure 6). ***Nagy et al (1991)*** fitted their data with equation 10a, but also stated that without acquiring more data near equilibrium it was premature to assess validity of the principle of detailed balancing.

$$R = 1.24 \cdot 10^{-12} \times \left(1 - \exp\left(\frac{-A}{1.17 \cdot RT}\right)\right) \qquad \text{eq. 10a}$$

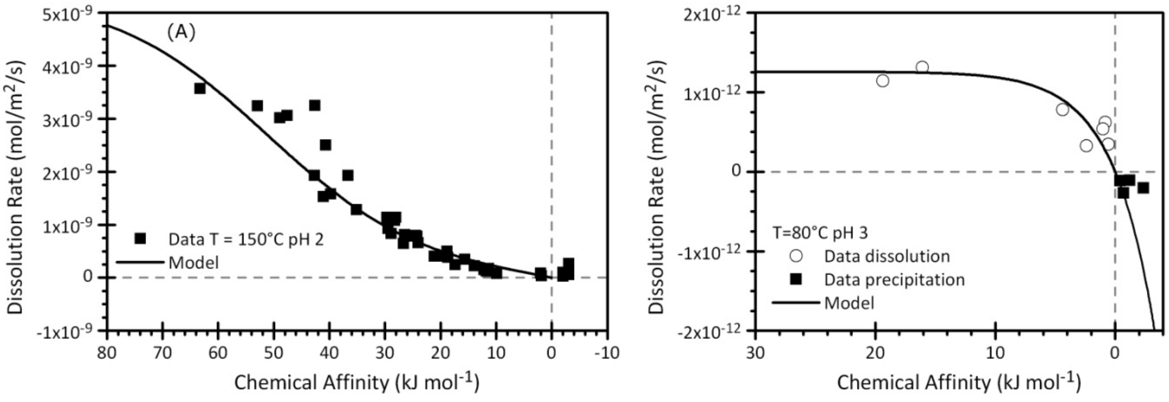


Figure 6**:A) Application of chemical affinity law on Kaolinite ($Al_2Si_2O_5(OH)_4$) dissolution in deionized water at 150°C and pH 2 (3.17m^2/g , from **(Devidal (1997)))** B) at 80°C and pH 3 (From **(Nagy and Lasaga (1990)))

Devidal et al. (1997) tried to improve the rate expression by considering that close to equilibrium, lateral interactions among the precursor complexes on kaolinite in the case of Si-rich or Al-rich solution cannot be neglected. Eq.9a then becomes:

$$R = k_+ \cdot \left(K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right) \middle/ \left(1 + K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right) \right) \right) \times \exp\left(\frac{\omega_1}{RT} \frac{K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right) - 1}{K^* \cdot \left(\frac{\{H^+\}^3}{\{Al^{3+}\}} \right) + 1} \right) \times \left(1 - \exp\left(\frac{-A}{2RT} \right) \right)$$

with ω_1 the interaction energy between two surface species.

Albite ($NaAlSi_3O_8$) has been studied with respect to chemical affinity at basic pH (8.8-10) and 80°C ***(Burch (1993))*** or 150°C ***(Hellmann and Tisserand (2006))***. Both show a sigmoidal behavior non consistent with TST. The rate expression used to represent the data over the full range of chemical affinity reflects the potential presence of two parallel mechanisms, and the presence of a critical ΔG value (eq. 11)

$$R = k_1 \left[1 - \exp\left\{ -\left(\frac{n_1 |A|}{RT} \right)^{m_1} \right\} \right] + k_2 \left[1 - \exp\left\{ -\left(\frac{|A|}{RT} \right) \right\} \right]^{m_2} \qquad \text{eq.11}$$

Generally, values of n_1, m_1 and m_2 are correlated, and several mixed expressions can represent the data equally well. Also, the second term is not well enough constrained by the data. ***Burch et al. (1993)*** also stated that the rate dependence on chemical affinity could be considered linear only in a narrow range of chemical affinity (A<0.9kJ/mol).

Few data are available concerning the dissolution rate of clay minerals as function of saturation state. ***Cama et al. (2000)*** studied smectite dissolution at pH 8.8 and 80°C. They show that their data could equally well be fitted with the two following equations (eq.12a or eq. 12b)

$$R = 8.1 \cdot 10^{-12} \times \left[1 - \exp\left(-6 \cdot 10^{-10} \times \left(\frac{|A|}{RT} \right)^6 \right) \right] \qquad \text{eq. 12a}$$

$$R = 1 \cdot 10^{-10} \times \left[1 - \exp\left(-9 \cdot 10^{-7} \times \left(\frac{|A|}{RT} \right)^3 \right) \right] \qquad \text{eq. 12b}$$

Figure 7 shows the application of these two equations.

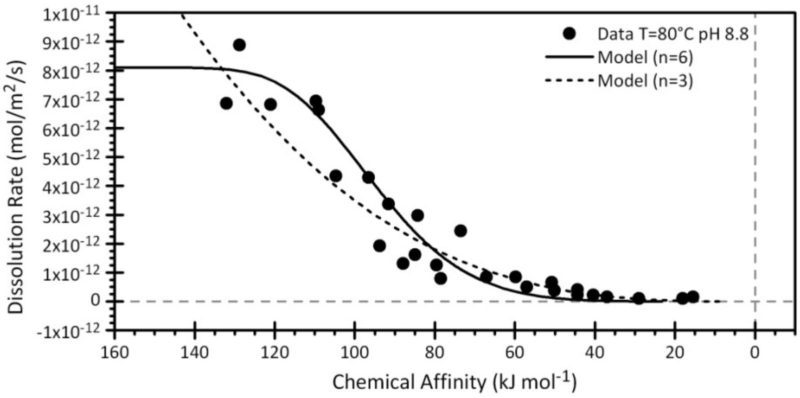


Figure 7*: Application of chemical affinity law on smectite dissolution in deionized water at 80°C and pH 8.8 (62m^2/g data from* ***(Cama (2000))****).*

Taking into account the potential inhibitory effect of silicon, they also proposed eq.12c applicable at least far from equilibrium:

$$R = k_+ \times \left[\frac{K^* \{OH^-\}}{1 + K^* \{OH^-\} + K' \{H_4SiO_4\}} \right] \qquad \text{eq. 12c}$$

Including an affinity term *(1-exp(-A/R/T))* in equation 12c makes no great difference on the fitting of the curve, showing that there is not enough data close to equilibrium to constrain the model.

Illite du Puy dissolution experiments have been carried out by ***Köhler et al. (2003)*** between 5°C and 50°C and pH ranging from 2 to 12 in batch reactors. Their data is not enough detailed to calculate affinity of the reaction and dissolution rate dependence.

Experiments with clay minerals may appear difficult, as they may not reach a steady state due to a modification of the morphology of clay particles during dissolution ***(Köhler et al. (2005))***.

Natural glasses

No thermodynamic equilibrium constant can be defined for glasses since they cannot precipitate from solution. In order to study the approach of equilibrium, affinity term must refer to the leached layer composition. For example, for a basaltic glass, ***Daux et al. (1997)*** estimated the affinity by:

$$A^{*} = RT \cdot \ln\left(\frac{\{H_4SiO_4\}\{Al(OH)_4^-\}^{0.36}\{Fe(OH)_3\}^{0.18}\{OH^-\}^{-0.36}}{8.2 \cdot 10^{-5}} \right) \qquad \text{eq. 13a}$$

At 90°C and pH~8, the data for dissolution rate dependence on chemical affinity show a behavior consistent with TST (Figure 8) and the rate expression is given by eq. 13b ***(Daux (1997))***.

$$R = 3 \cdot 10^{-10} \times \{OH^-\}^{0.39} \times \left(1 - \exp\left(\frac{-A^{*}}{RT}\right)\right) \qquad \text{eq. 13b}$$

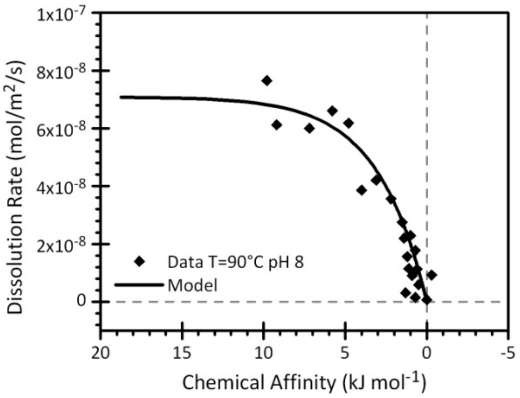


Figure 8*: Application of chemical affinity law for basaltic glass dissolution at 90°C and pH 8 (from* ***(Daux (1997))****).*

As for the aluminosilicate minerals, glass dissolution proceeds by a single mechanism at both low and high pH. This mechanism likely consists of the relatively rapid and complete removal of univalent and divalent cations from the near surface layer, then aluminum-releasing exchange reaction between 3 aqueous protons and Al in the basaltic glass structure, followed by the relatively slow detachment of partially liberated silica ***(Oelkers and Gislason (2001))***. Far from equilibrium, the data on dissolution of a rhyolitic glass (with low Al content) between 40°C and 200°C and pH ranging from 2 to 10 ***(Declercq et al. (2013))*** are modeled with the following equation eq. 13c consistent with eq.9a:

$$R = k_+ \cdot K^* \cdot \left(\frac{\left\{H^+\right\}^3}{\left\{Al^{3+}\right\}} \right)^{1/11.1} \qquad \text{eq. 13c}$$

Carbonates

The surface complexation modeling demonstrated the presence of both carbonate sites and metal cation sites. At neutral pH, the surface sites are all protonated, whereas in alkaline solution, the dissolution is controlled by the hydration of metal cation surface sites ***(Oelkers et al. (2009))***. The dissolution rate could then be expressed according to:

$$R = \left[k_{CO3} \left\{ \equiv CO_3H^+ \right\}^{n_H} + k_{Me} \left\{ \equiv MeOH_2^+ \right\}^{n_{H2O}} \right] \times \left(1 - \exp\left(\frac{-A}{\sigma RT} \right) \right) \qquad \text{eq. 14a}$$

For example, for calcite ($CaCO_3$), n_H =2 and n_{H2O}=1.

The rate depends on both chemical affinity and the activity of aqueous species that control the concentration of $\equiv MeOH_2^+$ precursor species. At 25°C for dolomite ($CaMg(CO_3)_2$, $0.105 m^2/g$), $n_H = n_{H2O} = 2$ and $\sigma = 0.5$ ***(Pokrovsky (2001))***. Above pH 5, dissolution is controlled by the hydration of Mg surface sites and the formation of $\equiv MeOH_2^+$ species. Aqueous calcium and carbonates ions may have an inhibitory effect, resulting in a sigmoidal behavior dependence on chemical affinity (Figure 9).

Saldi et al. (2012) and Shiraki and Brantley (1995) studied precipitation of carbonates (magnesite and calcite). For them, dissolution rate constant and equation cannot be extrapolated to predict precipitation rates ***(Shiraki and Brantley (1995),Saldi et al. (2012))***.

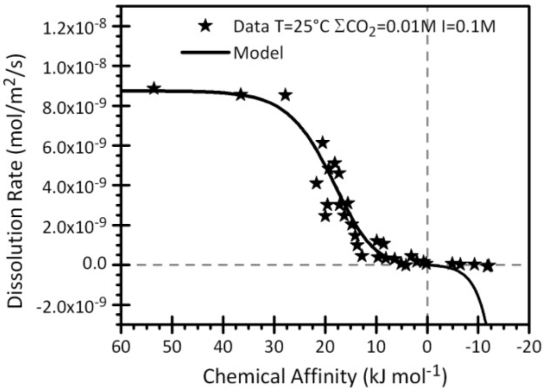


***Figure 9**: Dolomite overall reaction rate at 25°C as a function of chemical affinity at ΣCO_2=0.01M and I=0.1M (From **(Pokrovsky (2001))**)*

Experimental means to study very-close-to-equilibrium rates

Review of literature data has shown that affinity-based models may not be useful or sufficient in modeling dissolution and growth rate over the full range of ΔG. Moreover, the current laboratory data for bulk dissolution rates are not precise enough to derive specific dissolution mechanism very close to equilibrium ***(Lüttge (2006))***, where a linear dependence could be observed (on a narrow range of affinities). A concept to be defined is “how close is “close-to-equilibrium”?”. Usually, this is admitted when $\Delta G << RT$ (i.e. at 25°C ΔG <<2.5kJ). Few data are available for this range.

Recent experimental techniques are developed that allow more precise measurement or observation near equilibrium. For example, Atomic Force Microscopy and Vertical Scanning Interferometry show promise towards the development of a fundamental understanding and comprehensive theory of crystal dissolution ***(Dove et al. (2005),Lüttge (2006))***.

A Hydrogen-Electrode Concentration Cell has been developed and associated with pH jump relaxation technique and permits measurement of pH in solution with an accuracy of 0.002 pH unit, and then lower uncertainty in calculation of chemical affinity ***(Bénézeth (2008),Davis (2011))***.

Isotopic Ratio Measurement: Stable isotopes are powerful environmental tracers that could be used to assess kinetics parameters ***(Gee and Bruland (2002))***. Indeed, whereas the total concentration of an element may be affected by secondary phase precipitation (backward reaction), this is not the case with the isotopic composition, assuming that no fractionation occurs. The solution isotopic ratio decreases with the dissolution of a solid with a lower isotopic ratio. Strontium isotopic composition has been used years ago to calculate the reaction progress of a basaltic glass with an isotopic composition different from the composition of the solution ***(Daux et al. (1994),Daux (1997),Valle et al. (2010))***. More recently, solution enriched (spiked) with one less abundant isotope have been used to study atom exchange or dissolution of mineral having a “normal” isotopic composition. For example, ***Gorski et al. (2012)*** studied iron atom exchange between aqueous Fe^{2+} (spiked with ^{57}Fe) and “normal” magnetite in a batch reactor. The same type of study was carried out with goethite (Figure 10) at pH7.5 and 25°C ***(Handler et al. (2009))***.

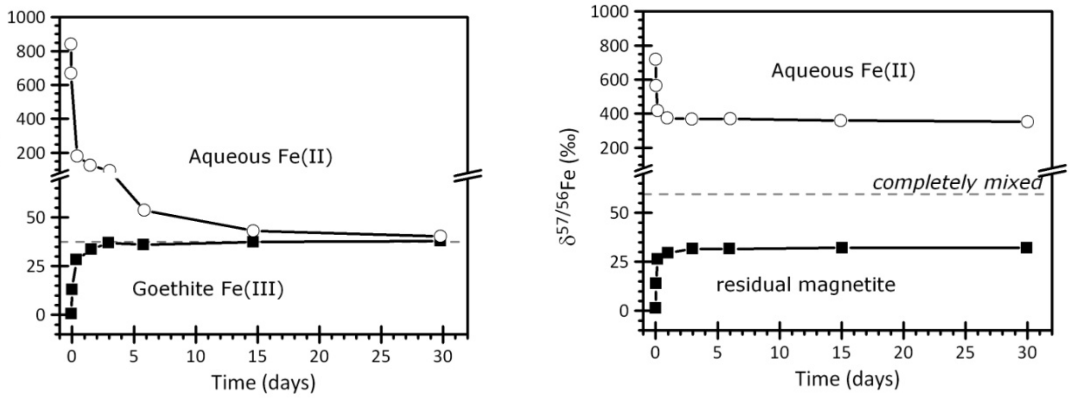


Figure 10*: Illustration of isotopic exchange between spiked ^{57}Fe aqueous solution and iron oxide/hydroxide (goethite or magnetite)* ***(Handler (2009),Gorski (2012))***

An approach with the “three-isotopes method” was applied by ***Li et al. (2011))*** to calculate a fractionation factor between an ^{25}Mg enriched solution at equilibrium with epsomite ($MgSO_4$).

Harpaz et al. (2007) and Gruber et al. (2013) have studied dissolution of albite and kaolinite using a mixed flow reactor and an inflow solution enriched with ^{29}Si, at a total silicon concentration of 200µM and pH~5, T=50°C (far from equilibrium according to PhreeqC calculation). They have shown that calculation of steady state rate with isotopic ratio method is more accurate than the traditional method ***(Harpaz et al. (2007),Gruber et al. (2013))***.

The outflow isotopic ratio depends on the ratio and elemental concentration both of the mineral and the input solution, and of the amount of mineral dissolved.

For example, based on these last studies, in the case of using silicon isotopes (^{29}Si spiked inflow solution), the conservation of mass for each isotope, assuming that fractionation is negligible, leads to the following equation for the steady state rate in a mixed flow reactor:

$$Rate = \frac{Q}{A} \times \left[\frac{\left(\frac{29}{28}\right)_{in} - \left(\frac{29}{28}\right)_{out}}{\left(\frac{29}{28}\right)_{out} - \left(\frac{29}{28}\right)_{rock}} \right] \times \frac{Si_{in}}{Si_{rock}} \times \left[\frac{\left(\frac{29}{28}\right)_{rock} + 1.0335}{\left(\frac{29}{28}\right)_{in} + 1.0335} \right] \qquad \text{eq. 15}$$

where Q = flow rate (m^3/s), A = specific area (m^2), Si_{in} = total concentration of Si in the inflow solution (moL/L), Si_{rock}=molar fraction of Si in the dissolving mineral (mol/mol_{rock}), 1.0335 = $1+(^{30}Si/^{28}Si)$ assumed constant.

Equivalent studies are needed to assess the kinetics of mineral dissolution close to equilibrium and under various solution compositions, where traditional methods lead to large uncertainties.

Conclusions

This study has focused on the literature review for the kinetics of dissolution or precipitation of minerals likes oxides, hydroxides or aluminosilicates, when the evolution with chemical affinity (or saturation state) is available. The knowledge of the exact dependence of rate on chemical affinity is important because in natural systems, reactions occur often close to equilibrium and are strongly influenced by chemical affinity.

Usually, chemical affinity rate law is used as an extrapolation of experiments performed in laboratory to very near equilibrium.

It was shown that, most of the time, a single rate law, based on the Transition State Theory, is poorly or not applicable. It often requires using a succession of different rate laws with parameters with no physical meaning so far. Moreover, experimental data seem to depend on the history of dissolution of the solid, and changes of surface morphology. Different rate laws could equally well fit the data.

Very close to equilibrium, lack of the data and large uncertainties are a real drawback for the study of the impact of saturation state on mineral kinetics. However, new analytical techniques are emerging which would provide precise data in this area, like HECC or isotopic ratio measurements. Recently, isotopic ratio measurements on silicates or iron oxide/hydroxides have been published. More studies of this type need to be compiled in order to refine the effect of approaching equilibrium on the overall reaction rate. Applicability of the principle of detailed balancing to surface reactions consisting of several possible mechanisms on either side of equilibrium is not easy to prove; the data is often non-conclusive. Further work must be carried out to uncover the underlying physical chemistry governing processes the near equilibrium region.

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