

# Dissolution kinetics of rock–water interactions and its implications

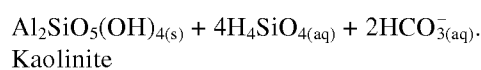
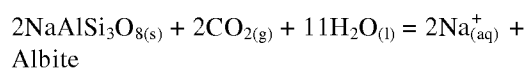
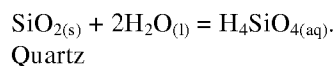
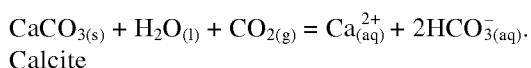
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**Chemical dissolution of bed rock/minerals plays a central role in determining the geochemistry of natural waters. The major source of dissolved species to natural water is the rocks coming in contact with water. As soon as the rocks come into contact with water, water–rock reaction starts and moves forward towards equilibrium by dissolving or leaching bedrock minerals into the solution. By this mechanism, major cations, anions, silica and other essential nutrients are released into the hydrosphere. The solute concentration in the water system is proportional to the reactivity of the bedrock minerals constituting the catchment. Thus, the chemical composition of natural waters is a direct indication of the geology of their catchment. Dissolution kinetics of rocks and minerals is important in understanding different rates of chemical weathering of various lithologies, development of soils, production of secondary porosity in the rocks, triggering of landslides and sequestration of atmospheric carbon dioxide. Recent studies on mineral weathering phenomena in inter-terrestrial materials and under space weathering conditions reveal the differences in chemical weathering under different physical and chemical conditions.**

**Keywords:** Chemical weathering, dissolution rate, equilibrium kinetics, water–rock interactions.

DISSOLUTION refers to the complete or partial alterations of composition of the mineral due to leaching of its components. The terms ‘dissolution’ and ‘chemical weathering’ can be used interchangeably; however, chemical weathering includes both hydrolysis and dissolution phenomena<sup>1</sup>. The forward reaction of the water–rock system results in the dissolution of the constituents of rock-forming minerals, whereas the backward reaction implies precipitation mechanism. Dissolution may occur as congruent or as incongruent reaction. Simple dissolution of a mineral into its constituent ions is known as congruent dissolution, and dissolution with formation of secondary minerals is known as incongruent dissolution<sup>1</sup>. Most common example of congruent dissolution is the weathering of calcite and quartz and that of incongruent dissolution is albite<sup>1</sup>.



Minerals of olivine, pyroxene and amphibole group are rarely found in equilibrium with the natural waters at surface pressure and temperature regime, and undergo irreversible congruent dissolution releasing their constituents in the water. Some primary minerals, mainly calcite, orthoclase and gypsum initially undergo congruent dissolution to release their respective ions into the water till equilibrium is achieved. Once equilibrium is achieved, their dissolution reaction becomes reversible, forming the respective secondary minerals. However, the major difference among the dissolution reactions of the various minerals lies in their dissolution rates and mechanisms. For example, the complete dissolution of 1 mm sphere of calcite, albite and quartz takes approximately  $0.1$ ,  $575 \times 10^3$ , and  $34 \times 10^6$  years respectively, in laboratory-simulated condition<sup>2</sup>. However, field weathering rates are generally observed to be up to five orders of magnitude slower than laboratory dissolution rates, and there is no definite clarification for this behaviour<sup>3</sup>. A large amount of work has been done in the laboratory using batch reactors and mixed flow-through reactors to know the dissolution kinetics of minerals<sup>4,5</sup>. Laboratory dissolution studies are an important tool in deriving models of dissolution kinetics of minerals and thus help in understanding environmental phenomena such as formation of soils and saprolites, sequestration of atmospheric  $\text{CO}_2$ , acid-mine drainage, and causes of mass movements facilitated by natural and anthropogenic activities.

## Factors controlling dissolution rates

### Temperature

Dissolution rate increases exponentially with increasing temperature. This is furnished by Arrhenius equation<sup>6–8</sup>,

$$k = A \cdot e^{(-E_a/RT)}$$

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where  $k$  is the dissolution rate constant,  $A$  is the temperature-independent pre-exponential factor,  $E_a$  (kcal mol<sup>-1</sup>) is the activation energy,  $R$  is gas constant, and  $T$  is the absolute temperature in Kelvin. Transformation of reactants to products usually passes through some intermediate stage of higher energy than the reactants.  $E_a$  is the minimum amount of energy required to ensure a reaction to happen. The 'energy hump' defines the limit of  $E_a$  (Figure 1).

The activation energy  $E_a$  for the rate constant  $k$  of an overall reaction is the sum of all elementary reactions constituting the reaction mechanism. Activation energy  $E_a$  of the overall reaction which is dependent on temperature, can also be defined by the equation<sup>5,9</sup>:

$$E_a = -R\{d\ln k/d(1/T)\}.$$

Hence, values of  $E_a$  can be determined from the slope of the straight line by plotting  $\ln k$  versus  $1/T$ .  $E_a$  values (in kcal mol<sup>-1</sup>) for diopside, enstatite, augite, forsterite, calcite and quartz (crystalline) are 12–36, 12, 19, 9.1, 8.4 and 16–18 respectively<sup>2</sup>.

## pH

Far from equilibrium, the dissolution rates of most silicate minerals have the form shown below (Figure 2)<sup>10–13</sup>.

In the acid region, due to proton-promoted dissolution, the rate increases exponentially with increasing hydrogen ion concentration, or

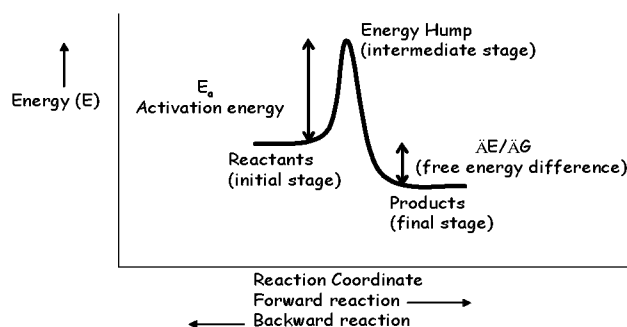


Figure 1. Activation energy ( $E_a$ ) of a reaction<sup>6–8</sup>.

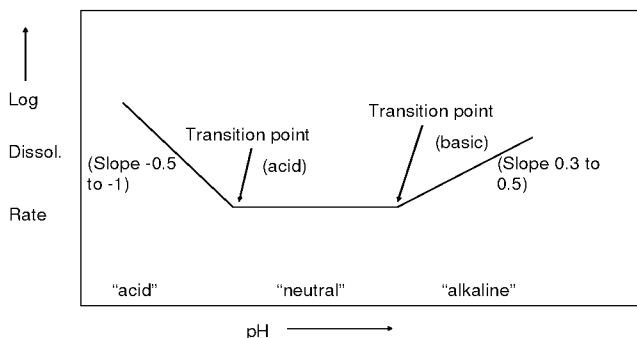


Figure 2. Silicate dissolution rates (far from equilibrium) as a function of pH<sup>10–13</sup>.

$$(\text{Rate})_H = k_H[H^+]^n, \quad (\text{acid region})$$

where  $k_H$  is a rate constant;  $[H^+]^n$  is the activity of  $H^+$  in the solution, and  $n$  is an exponent that is different for different minerals and typically has a value between 0.3 and 1.

Above some transition pH, typically about 4 and 5, dissolution rates are generally independent of pH, or

$$(\text{Rate})_{\text{neutral}} = k_N. \quad (\text{neutral region})$$

In the alkaline region, at pH values above 8, we have hydroxyl-promoted dissolution and the rate increases with increasing pH

$$(\text{Rate}) = k_{OH}[OH^-]^m, \quad (\text{basic region})$$

where  $m$  typically has a value of about 0.3 to 0.5.

Hence, the total dissolution rate can be expressed as the sum of the individual rates

$$(\text{Rate})_{\text{total}} = k_H[H^+]^n + k_N + k_{OH}[OH^-]^m.$$

## Organic acids and ligands

The principal acids produced by soil microorganisms are carbonic and sulphuric acids and decomposition of plants produces humic acids and a host of various organic acids. These acids are high molecular weight compounds which play an active role in the chelation process by getting associated with heavy metals. These acids also provide hydrogen ions which replace cations on mineral surfaces, thus bringing about disintegration of the rocks. Also, some organic acids react with specific elements, particularly Al contained in the mineral to form chelates/ligands or metal–organic complexes. Adsorbing organic ligands may accelerate the dissolution rates of silicates by forming organo-complexes with metals, particularly iron and aluminium, on the mineral surface, thereby weakening the bonds between the metal and the solid. The ligand-promoted rate is proportional to the concentration of adsorbed ligand, which will be a function of the activity of the ligand in solution. Thus ligand-facilitated dissolution rate can be given as<sup>14</sup>:

$$(\text{Rate})_{\text{ligand}} = k_L[\text{ligand}]^p.$$

Then, total dissolution rate can be represented as the sum of the individual rates, i.e.

$$(\text{Rate})_{\text{total}} = k_H[H^+]^n + k_N + k_{OH}[OH^-]^m + k_L[\text{ligand}]^p.$$

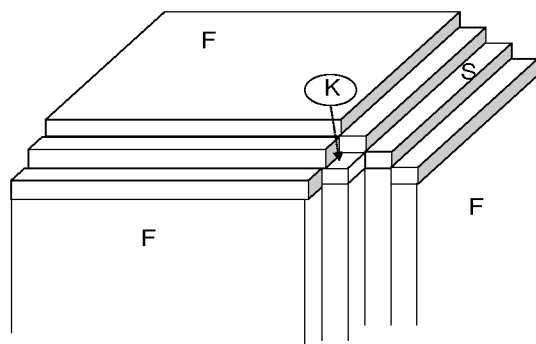
The exponent  $p$  reflects the stoichiometry of the complex and the relationship between adsorbed concentration and concentration of species in the solution. Thus, organic acids may affect mineral weathering rates through changing solution pH or by forming metal–organic complexes at the mineral surface<sup>10,11</sup>.

### Crystal dislocation

Far from equilibrium condition, the rate of dissolution reaction is often controlled by the surface morphology of the crystals<sup>13</sup>. The crystal surface is rarely uniform and shows various imperfections called dislocations, in which one part of the crystal is offset relative to another. Dislocations are rows of atoms in crystals that are slightly displaced and therefore are highly energetic. The rate of dissolution is thus regulated by the type and density of the dislocations present. The dislocations normally include 'steps' and 'kinks'. Kinks have three 'sides' exposed to the solution, steps have two, and planar surfaces have only one (Figure 3). During dissolution, the atoms with highest energy detach most rapidly from the surface. Because kinks are points of high surface energy, they are favoured locations for the adsorption of species from the solution. During the course of time, the adsorbed species may form a leached layer and 'block' or immobilize the dislocation site and thus result in lowering of dissolution rate. Such species are called inhibitors or surface poisons<sup>15</sup>. For example, even a minor concentration (a few  $\mu\text{mol/kg}$ ) of phosphate hinders the dissolution of calcite in sea water. As a result of the selective dissolution, etch pits form on the mineral surfaces, which reflect the crystal structure of the underlying mineral and therefore are regular in shape and aligned in definite directions.

### Dissolution mechanism

The overall process of dissolution of rock-forming minerals exposed to an aqueous solution is controlled either by transport or by surface chemical reactions. Dissolution occurs whenever undersaturation of the bulk solution is present; in other words, where  $\Omega < 1$  (the parameter  $\Omega$  is defined as the actual ion activity product (IAP) divided by the equilibrium or solubility product ( $K_{\text{eq}}$ ), i.e.  $\Omega = \text{IAP}/K_{\text{eq}}$ ). IAP in excess of  $K_{\text{eq}}$  leads to precipitation and  $\text{IAP} < K_{\text{eq}}$  denotes dissolution reaction. In the case of dissolution, controlled by surface-reaction mechanism, selective dissolution of the surface results in the formation of



**Figure 3.** Cubical model of a crystal surface illustrating dislocation-type: face (F), step (S), and kink (K).

large, well-developed etch pits. This results because of the fact that major dissolution originates only at specific points of excess energy on the surface, such as dislocation outcrops. In the case of transport-controlled dissolution, attack of the surface is so rapid and non-specific that the etching occurs virtually everywhere, and, as a consequence, only general rounding results<sup>5</sup>.

In the laboratory, experiments to determine dissolution rates of rocks and/or minerals is generally carried out at 'far from equilibrium' conditions<sup>7,9,13</sup>. By definition, for a simple reaction  $A \leftrightarrow B$ , at equilibrium,  $R_+ = R_-$ , where  $R_+$  is the rate of forward reaction (dissolution), and  $R_-$  is the rate of backward reaction (precipitation). As the chemical reaction approaches equilibrium, the rate of backward reaction tends to be finite. Thus the net rate of reaction decreases and ultimately becomes zero at equilibrium. However, this is a controversial question and has not been fully resolved in the literature. When the reaction approaches chemical equilibrium, the dependence of dissolution rate on the chemical affinity can be derived in terms of the Transition State Theory (TST)<sup>5</sup>, which states that the dissolution rate is controlled by the desorption kinetics of an activated complex formed at the surface. For a simple elementary dissolution reaction, TST gives

$$R_{\text{net}} = k_+[1 - \exp(\Delta G_R/\sigma RT)],$$

where  $R_{\text{net}}$  denotes the overall dissolution rate (mol/surface area/time),  $k_+$  is the apparent forward rate constant for dissolution at a given temperature and pressure,  $\sigma$  is a 'stoichiometric number', conventionally set equal to 1,  $R$  is the gas constant and  $T$  the temperature in Kelvin.  $\Delta G_R$ , chemical affinity or free energy difference having unit kcal/mol or kJ, can be regarded as the difference between the energy of the initial stage and the energy of the final stage.

Wollast<sup>15</sup> was one of the first workers on chemical weathering kinetics, who experimented with the dissolution of ground K-feldspar placed in buffered aqueous solution and measured the release of silica with time. He found that the rate of release of silica to the solution declined over time and explained this decrease in terms of the formation of a protective layer on the surface of feldspar. This layer was protective in the sense that, it strongly inhibits the migration of dissolved species to and from the surface of K-feldspar. In due course of time as dissolution proceeds, the thickness of the layer increases. The protective layer was assumed to be either a precipitate of aluminium hydroxide and/or clay minerals, or 'feldspar' in which the cations have been replaced by hydrogen (or hydronium) ions. Subsequent workers expanded Wollast's theory and described the release of silica from alkali feldspar in terms of 'parabolic' kinetics, where concentration of the solute in solution builds up in direct proportion to the square root of time. Such experiments typically show an approximately parabolic curvature, indicating that dissolution rate of the mineral decreases with time according to the relationship<sup>5,13</sup>

$$Q = kt^{1/2},$$

where  $Q$  is amount in solution,  $k$  is a constant and  $t$  the time (in hours). This behaviour is called parabolic rate law. After a sufficiently long time, the increase in concentration may become linear, giving a linear rate law as shown Figure 4.

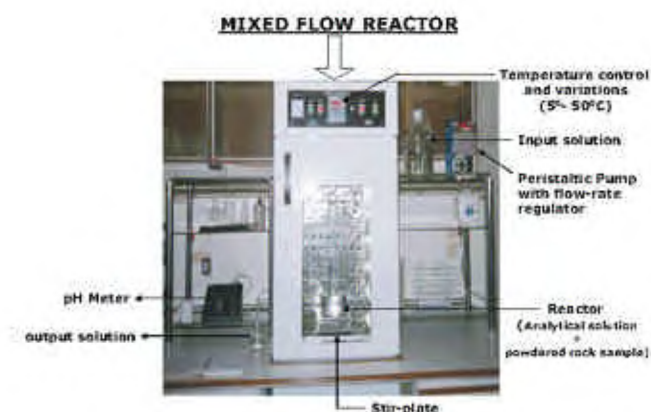
### Experiments in mixed-flow reactors

Mineral weathering rate experiments are carried out in batch experiments with different minerals and solutions. Dissolution of rocks and minerals in natural conditions can be simulated in the laboratory by mixed flow-through reactors. Steady state dissolution rate ( $R$ , mol/cm<sup>2</sup>/s) in the laboratory can be computed by measuring solution composition using the equation<sup>16</sup>:

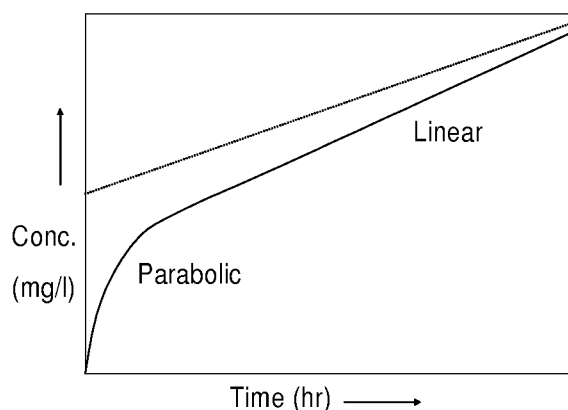
$$R_{\text{Si}} = -q \cdot \Delta[\text{SiO}_{2(\text{aq})}]_{\text{tot}}/s,$$

where  $q$  is the fluid flow rate,  $\Delta[\text{SiO}_{2(\text{aq})}]_{\text{tot}}$  is the change in input and output silica concentrations, and  $s$  refers to the total mineral surface area. The laboratory-measured reaction rates of minerals are mostly an order or more faster in magnitude compared to the natural dissolution rates. Mixed-flow reactors offer more options for temperature, pressure conditions and also a continuous and regulated flow of the solutions. One such reactor devised and manufactured in the Geochemistry Laboratory, IIT Roorkee is shown in Figure 5. A 500 ml polyethylene reaction vessel with desired solution is kept inside the reactor and is continuously stirred with a floating teflon-coated magnetic stirrer. Stirring is controlled by a stir plate located inside the main chamber of the reactor. About 1–4 g of the powder (100–150  $\mu\text{m}$ ) sample (of known surface area measured by BET surface area analyser) is put into the reaction vessel and constantly fluidized by the input solution at a fixed rate. The input solution is kept in a 5–10 l glass beaker placed outside the reactor and is injected

into the reaction-vessel using a peristaltic pump with flow rates ranging from 0.01 to 10 ml/min. About 10% of the reaction solution leaves the reactor at regular intervals through a 5  $\mu\text{m}$  pore size Ti filter and is subsequently filtered through a 0.45  $\mu\text{m}$  acetate filter. A pH-electrode hangs through the reactor to measure *in situ* pH at different time intervals. The electrode is periodically calibrated with standard pH solution at 25°C. Either changing the flow rate or the composition of the input solution can regulate the fluid composition of the reaction vessel. Input solution of distinct composition and pH comprised of CO<sub>2</sub>-free degassed H<sub>2</sub>O, analytical reagent grade HCl, NaOH, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaCl<sup>16,17</sup>. In any one run, experimental conditions are held constant for sufficient time so that steady-state condition can be achieved. After steady-state condition is reached, dissolution rate is evaluated and the stirring speed and/or flow rate are changed to achieve a different steady state. Steady-state dissolution rates can be calculated from the Ca, Mg or Si concentrations of the output solution.



**Figure 5.** Photograph of mixed-flow reactor in the Geochemistry Laboratory, IIT Roorkee (with funding from a DST project).



**Figure 4.** Dissolution rate showing parabolic curve initially which becomes linear after a long time<sup>13</sup>.

**Table 1.** Approximate time for a hypothetical 1 mm sphere of various minerals to dissolve in dilute solution at 25°C and pH 5 (ref. 2)

Mineral	Log dissolution rate (mol m <sup>-2</sup> s <sup>-1</sup> )	Lifetime (yr)
Quartz	-13.39	34 m
Kaolinite	-13.28	6 m
Muscovite	-13.07	2.6 m
Epidote	-12.61	0.923 m
Microcline	-12.50	0.921 m
Albite	-12.26	0.575 m
Enstatite	-10.00	10 k
Diopside	-10.15	6.8 k
Forsterite	-9.0	2.3 k
Dolomite		1.6
Calcite		0.1

### *Dissolution rates in laboratory versus natural (field) conditions*

A large amount of data exist on the kinetics of dissolution of various minerals in laboratory experiments. Table 1 gives dissolution rate and approximate time taken by important minerals to dissolve in laboratory-simulated conditions<sup>2</sup>. However, extrapolation of laboratory-derived dissolution rates to field-dissolution rates shows deviations. Field weathering rates are generally observed to be up to five orders of magnitude slower than laboratory dissolution rates, and there is no definite clarification on the reasons for these deviations<sup>3</sup>. However, possible explanations for the deviations are: (i) differences in dissolution mechanism between the laboratory and field; (ii) lack of steady-state attainment; (iii) differences in solution chemistry (inhibition in the field or acceleration in the laboratory); (iv) differences in solution chemistry (chemical affinity effects); (v) improper estimation of reactive surface area; (vi) differences or variability in temperature and (vii) biological effects<sup>3,18</sup>. By definition, extrapolation of kinetics requires that the mechanism of reaction should be the same in both field and laboratory systems, but improper understanding of reaction mechanism in this regard has been attributed to be the major cause of deviation. In the laboratory, experiments on mineral dissolution are carried out till the attainment of steady state; however, many researchers have admitted that reaction rates decrease with time at such a slow rate that true steady state may not occur. Whether steady-state dissolution occurs in natural systems is also unknown. Therefore, laboratory 'steady-state' rates may really be maximum estimates of field-dissolution rate. Differences in solution chemistry, including the presence of inhibitors or accelerators, or differences in chemical affinity may also affect the rates in either the laboratory or the field. For example, dissolved cations or salts have been shown to accelerate the dissolution of quartz, but inhibit the dissolution of feldspar. Differences and fluctuation of temperature in the field will also cause deviations in rates with respect to laboratory rates. Researchers have estimated that such differences may account for a factor of five discrepancies for most weathering studies. Undermining biological effects may also cause such deviations. Also, one of these discrepancies is that most dissolution experiments are conducted using a single mineral, whereas most silicate rocks are composed of several major minerals. To minimize the gap in the results of field dissolution rates and laboratory dissolution rates, the following variables should at least be clearly known: (i) mechanism of dissolution, (ii) reactive surface area, (iii) mineral composition, (iv) pH and temperature of dissolution, (v) chemical affinity of dissolving solution, (vi) crystal dislocation, (vii) biological parameters, (viii) hydrological parameters and (ix) duration of dissolution<sup>3</sup>.

The importance of mountain upliftment to the weathering of silicates has been emphasized recently<sup>19</sup>. Uplift results in rugged relief and cold temperatures at high elevations. This also results in the start of a new cycle of erosion. These altogether result in enhanced physical erosion and greater exposure of primary silicates to chemical dissolution. There will be accelerated dissolution if the precipitated water is charged with humic acid produced from decay and decomposition of organic matter, atmospheric CO<sub>2</sub> and that produced from soil-biota respiration. In considerable period of geologic time, the dissolution reactions will produce secondary porosity in the form of karst in carbonate rocks and other rock types. If the catchment is facing timely neotectonic activities, then the rocks will slide and creep along the planes weakened by dissolution reactions. The area will face frequent landslides if the rate of dissolution is faster. Thus determination of the kinetics and mechanism of rock dissolution is fundamental to the successful application of the preventive measures to control landslides.

Chemical weathering of basic silicates consumes twice the amount of atmospheric CO<sub>2</sub> compared to that of carbonate rocks, and thus predominantly regulates the global CO<sub>2</sub> cycle. CO<sub>2</sub> in the atmosphere has been varying over geologic time, one major factor being the non-uniform distribution of land surface during geologic timescales and weathering intensity. Hence, knowledge of kinetics and mechanism of silicate dissolution is important to rigorously sequester CO<sub>2</sub> of the atmosphere. This can help in modelling the atmospheric CO<sub>2</sub> concentration over the past and future geologic time, thereby predicting the global climatic change<sup>3,20</sup>.

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