



The mechanism of dissolution of minerals in acidic and alkaline solutions: Part II Application of a new theory to silicates, aluminosilicates and quartz



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ABSTRACT

The kinetics of the dissolution of silicates, aluminosilicates and quartz is described by a novel theory of dissolution. The experimental data for the rate of dissolution of these minerals shows a remarkable pattern: for many of these minerals, the order of reaction with respect to H^+ is close to 0.5 in the acidic region, and the order of reaction with respect to OH^- is close to 0.5 in the alkaline region. It is proposed that the site of bond breaking in the rate-determining step of dissolution is the weakest bond, and this is frequently the metal–oxygen bond because of the higher bond energy of silicon–oxygen bonds. Alternatively, the least number of silicon–oxygen bonds is broken. This means that silicate groups react intact as a unit. Both metal atoms and silicate groups react and are removed independently. The rates of these independent processes are coupled by the potential at the surface. In the acid region, H^+ reacts with silicate groups at the surface. In the alkaline region, OH^- ions react with the metal atom at the surface. The proposed theory of dissolution correctly predicts the observed orders of reaction with respect to H^+ ions and OH^- ions in solution. The order of reaction of forsterite with respect to H^+ changes from 0.5 in the acidic region to 0.25 in the region above a value of pH of approximately 6. The proposed mechanism suggests that the reason for the change in order of reaction is that the H^+ needs to be positioned at the inner Helmholtz plane to be effective in alkaline solutions.

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1. Introduction

The dissolution of minerals in acidic and alkaline solutions is of interest in a large number of fields, including geochemistry, minerals processing, hydrometallurgy and materials science. The dissolution of rock-forming minerals is important in establishing an understanding of many geochemical processes. The dissolution of protective films on materials continues to be of interest in materials science. The dissolution of minerals that contain valuable metals is the key process in hydrometallurgy. The study of dissolution and leaching continues to drive much of the research interest in hydrometallurgy.

The dissolution of silicate ores to recover valuable metals is not frequently practised in hydrometallurgy. One notable exception is in the recovery of zinc. Zinc is recovered at the Skorpion mine in Namibia from saucanite and hemimorphite minerals, which are silicate minerals (Borg et al., 2003). Another possibility, although economically unattractive at present, is the dissolution of clay minerals such as kaolinite, which has been investigated as an alternative source of aluminium (Ford, 1991).

For hydrometallurgists, though, the dissolution of silicates is important in the whole-ore processing of other minerals. Silicates are almost

always present in economic ores because they are such an abundant mineral group. During leaching, the silicates may not be inert, and can contribute to the impurities that need to be removed from solution. For example, aluminosilicates contribute aluminium, colloidal silica and other metal ions to whole-ore and heap-leaching circuits. Aluminium needs to be removed from copper plants in Zambia and the Democratic Republic of Congo by precipitation to prevent build-up in the circuit. Silica in solution and colloidal silica may contribute to crud formation in solvent extraction plants.

Fractional orders of reaction, particularly with respect to H^+ and OH^- , are frequently observed for silicate minerals. A general mechanism for the dissolution of minerals in non-oxidizing solutions was proposed by Crundwell (2014). This mechanism accounts for the effect of the potential difference across the interface between the mineral and the solution, which leads to the fractional orders of reaction reported for the silicates.

The purpose of this paper is to apply the proposed mechanism of dissolution to the kinetics of dissolution of the silicate and aluminosilicate minerals and quartz. In particular, this paper demonstrates that the mechanism of dissolution derived by Crundwell (2014) describes the dissolution of the silicates.

The paper is structured in the following manner. In the next section, classification of the silicates based on their structure will be presented.

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The types of dissolution behaviour will be described next. Following this, the experimental results reported by others are summarized. Finally, the proposed theory of dissolution is applied to the dissolution of these minerals.

2. Classification of the silicates

Silicon forms a tetrahedral unit with four oxygen atoms, SiO_4^{4-} , in silicate minerals. These tetrahedral units can be arranged in several different ways by sharing the oxygen atoms on the corners of the tetrahedral structure, resulting in the six classes of silicates that are shown in Table 1.

The silicates present a wide range of structural arrangements, from independent tetrahedra, through ring, chain and sheets to a continuous three-dimensional polymer.

The behaviour of these structures during dissolution is discussed in the next section.

3. Dissolution behaviour of the silicates

The dissolution of silicates in acid or alkaline solutions results in either (i) the complete breakdown of the silicate structure, (ii) the partial breakdown of the structure, usually experienced as the dissolution of the cations leaving a siliceous residue behind, or (iii) no dissolution (Terry, 1983b,1983c).

The dissolution of silicates, particularly in the context of weathering, is frequently classified as congruent or incongruent. Congruent dissolution occurs when no new phases are formed; incongruent dissolution occurs when new solid phases form with dissolution. Incongruent dissolution implies the formation of a partially leached zone or an alteration layer.

One of the earliest models for the dissolution of silicates is the proposal that the rate of dissolution is controlled by the diffusion of ions through an alteration layer. Alteration layers, of several Angstroms thick, have been observed on the surface by XPS and other studies, which presumably supported the observation of parabolic kinetics (Brantley, 2008; Tsomaia et al., 2003). The diffusional view is no longer predominant. The evidence against the diffusional view is two-fold: (i) the observed orders of reaction are close to one-half, whereas diffusional processes can only be first order; and (ii) the dissolution often becomes congruent at longer reaction times, particularly at conditions far from equilibrium.

Even if diffusion through the alteration layer does not control the rate of dissolution, alteration layers are present on the surface, particularly at lower pH values. Such alteration layers may be the result of preferential leaching leading eventually to a layer of constant thickness at

steady state, or due to the re-precipitation of material after dissolution (Brantley, 2004).

This study is focused on the dissolution of the silicates under conditions where dissolution is congruent and the products are in the same stoichiometric ratio as in the mineral. Oelkers (2001) and Oelkers and Gislason (2001) argue that the partial breakdown of the silicate structure is part of the initial stages of dissolution, a “provisional part of the dissolution process” that continues until congruent dissolution is established. In other words, this study is not concerned with the initial processes where non-stoichiometric dissolution might dominate prior to dissolution under stoichiometric conditions. The rates of dissolution of the silicates are frequently determined by measuring the concentration of Si in solution, which implies the measurement of the complete breakdown of the silicate structure.

Generally, the dissolution reactions are assumed to be dependent on the phenomena occurring at the interface, rather than on the diffusion of material through the alteration layer. One model of the reaction pathway envisages the dissolution occurring in four steps as the bridging bonds between the Si are broken by reaction with protons. This means that the silicon tetrahedral with four oxygen atoms departs from the surface by breaking bonds with other Si atoms. This possible pathway is shown in Fig. 1 (Brantley, 2008; Tsomaia et al., 2003).

The pathway shown in Fig. 1 seems plausible; however, like all proposals concerning chemical pathway, it does not describe the kinetics of dissolution. In other words, the pathway does not indicate how the rate of reaction is increased or retarded, or the factors that influence the rate of reaction. In contrast, the aim of a kinetic mechanism is to identify the step or steps that are the slowest in the reaction pathway. These slow steps ‘control’ the rate of the overall reaction. As is argued later, these rate-controlling phenomena have not been satisfactorily identified for the dissolution of silicates.

The kinetic factors that influence the rate of dissolution are discussed in the next section.

4. Kinetics of dissolution of silicate minerals

The rate of dissolution is affected by the concentration of the reagent in solution and the temperature (Crundwell, 2013). This dependence is usually expressed mathematically in the following form for an irreversible reaction:

$$\text{rate} = k[c]^n \exp(-E_A/RT) \quad (1)$$

where $[c]$ represents the activity or concentration of a reactant, k the rate constant $[\text{mol}/(\text{mol}/\text{m}^3)^{-n}/(\text{m}^2/\text{s})]$, n the order of reaction $[-]$, E_A the activation energy $[\text{kJ}/\text{mol}]$, R the gas constant $[\text{kJ}/\text{mol}/\text{K}]$, and T the temperature $[\text{K}]$. The units of rate are $\text{mol}/\text{m}^2/\text{s}$.

Table 1
Classification of silicates (Terry, 1983a).

Class	Structural arrangement	Si:O ratio	Silicate group	Example
Nesosilicates (orthosilicates)	Independent tetrahedra	1:4	SiO_4^{4-}	Forsterite, Mg_2SiO_4 Willemite, Zn_2SiO_4
Sorosilicates (pyrosilicates)	Two tetrahedral that share a common oxygen atom	2:7	$\text{Si}_2\text{O}_7^{6-}$	Hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$
Cyclosilicates (ring silicates)	Closed rings of tetrahedral sharing two oxygen atoms each	1:3	$\text{Si}_3\text{O}_9^{6-}$	Beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$
Inosilicates (chain silicates)	Pyroxene group: continuous single chain of tetrahedral each sharing two oxygen atoms	1:3	$(\text{Si}_2\text{O}_6^{4-})_n$	Enstatite, MgSiO_3 Diopside, $\text{CaMgSi}_2\text{O}_6$
	Amphiboles: continuous double chain of tetrahedral alternately sharing two and three oxygen atoms	4:11	$(\text{Si}_4\text{O}_{11}^{8-})_n$	Anthophyllite, $(\text{Mg}, \text{Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$ Hornblende, $(\text{Ca}, \text{Na})_{2-3}(\text{Mg}, \text{Fe}, \text{Al})_5\text{Si}_6(\text{Al}, \text{Si})_2\text{O}_{22}(\text{OH})_2$
Phyllosilicates (sheet silicates)	Continuous sheets of tetrahedral each sharing three oxygen atoms	2:5	$(\text{Si}_2\text{O}_5^{2-})_n$	Chrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ (serpentine) Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ Biotite, $K(\text{Mg}, \text{Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
Tectosilicates (framework silicates)	Continuous framework of tetrahedral each sharing all four oxygen atoms	1:2	$(\text{SiO}_2)_n$	Quartz, SiO_2 K-feldspar, KAlSi_3O_8 Albite, $\text{NaAlSi}_3\text{O}_8$

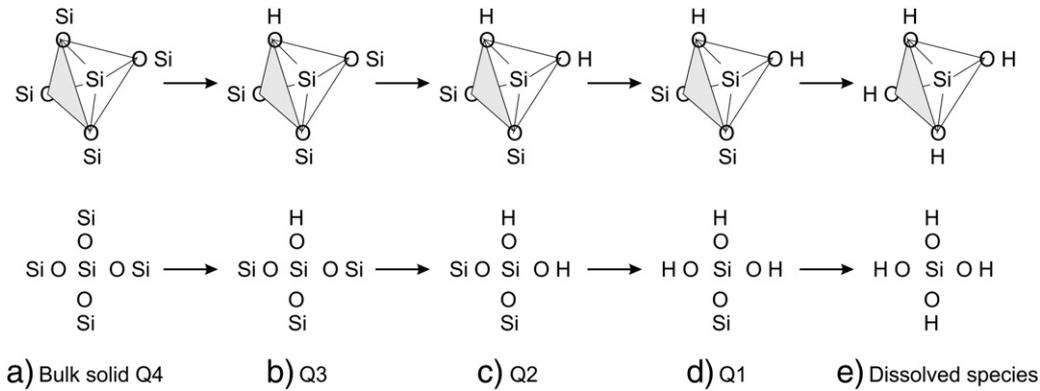


Fig. 1. Reaction pathway proposed for the dissolution of silica, showing the stagewise breaking of silicon–oxygen bonds to form H_4SiO_4 (Brantley, 2008): (a) the Q^4 site represents a central silicate tetrahedron bonded to four silicons; (b) Q^3 , a silicon–oxygen bond is replaced with a hydrogen ion; (c) Q^2 , two silicon–oxygen bonds are replaced with two hydrogen ions; (d) Q^1 , three silicon–oxygen bonds are replaced with three hydrogen ions; and (e) final dissolved species in solution.

The key parameter from the point of view of interpreting kinetics is the order of reaction. The order of reaction indicates how the rate of reaction depends on the concentration of the reactant. If the value of n is one and the reactant is H^+ , the reaction is said to be first order in H^+ .

Brantley (2008) presented an analysis of the rate of dissolution of silicate minerals based on the following empirical equation:

$$\text{rate} = k_H [\text{H}^+]^n + k_{\text{OH}} [\text{OH}^-]^m \quad (2)$$

where k_H represents the rate constant for the dissolution reaction with acid, and k_{OH} represents the rate constant for the dissolution reaction

with hydroxide. The terms $[\text{H}^+]$ and $[\text{OH}^-]$ represent the concentration or activity of the H^+ and OH^- ions, respectively.

The values for the orders of reaction compiled by Palandri and Kharaka (2004), Bandstra and Brantley (2008) and Brantley (2008) from the literature are given in Table 2.

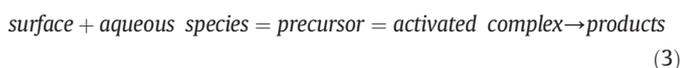
The orders of reaction presented in Table 2 are remarkable. If the outliers, (the two high values for bytownite and anorthite and the two low values for kaolinite and jadeite) are removed from the data set, the mean of the orders of reaction is 0.45 ± 0.12 . The clustering of these values suggests that a general mechanism is responsible for the dissolution of all the silicate minerals.

The mechanism of dissolution of the silicate minerals has not been described in a satisfactory manner. The previously proposed models

Table 2
Orders of reaction for the dissolution of silicate minerals.

Silicate group	Mineral	Mineral formula	n , reaction order wrt H^+	m , reaction order wrt OH^-	Reference	
Orthosilicates	Forsterite	Mg_2SiO_4	0.37		Bandstra and Brantley (2008)	
	Fayalite	Fe_2SiO_4	0.69		Brantley (2008)	
	Willemite	Zn_2SiO_4	0.40–0.5		Terry (1983c)	
	Monticellite	CaMgSiO_4	0.56		Westrich et al. (1993)	
	Co-olivine	Co_2SiO_4	0.36		Westrich et al. (1993)	
	Tephroite	Mn_2SiO_4	0.47		Westrich et al. (1993)	
	Ca-olivine	Ca_2SiO_4	0.42		Westrich et al. (1993)	
	Co–Mn olivine	CoMnSiO_4	0.42		Westrich et al. (1993)	
	Tectosilicates	Quartz	SiO_2	0.31	0.41	Bandstra and Brantley (2008)
		K-feldspar	KAlSi_3O_8	0.5	0.82	Palandri and Kharaka (2004), Brantley (2008)
Albite		$\text{NaAlSi}_3\text{O}_8$	0.40–0.46	0.38–0.57	Bandstra and Brantley (2008), Palandri and Kharaka (2004)	
Oligoclase		$\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$	0.46		Palandri and Kharaka (2004), Brantley (2008)	
Andesine		$\text{Na}_{0.6}\text{Ca}_{0.4}\text{Al}_{1.4}\text{Si}_{2.6}\text{O}_8$	0.54		Palandri and Kharaka (2004), Brantley (2008)	
Labradorite		$\text{Na}_{0.4}\text{Ca}_{0.6}\text{Al}_{1.6}\text{Si}_{2.4}\text{O}_8$	0.63		Palandri and Kharaka (2004), Brantley (2008)	
Bytownite		$\text{Na}_{0.2}\text{Ca}_{0.8}\text{Al}_{1.8}\text{Si}_{2.2}\text{O}_8$	1.02		Palandri and Kharaka (2004), Brantley (2008)	
Anorthite		$\text{CaAl}_2\text{Si}_2\text{O}_8$	0.99–1.41		Bandstra and Brantley (2008), Palandri and Kharaka (2004)	
Phyllosilicates		Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	0.24		Brantley (2008)
		Phlogopite	$\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	0.4		Brantley (2008)
	Muscovite	$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	0.14		Brantley (2008)	
	Biotite	$\text{K}(\text{Mg,Fe})_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$	0.36		Bandstra and Brantley (2008)	
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	0.13	1.02	Bandstra and Brantley (2008)	
	Chlorite	$(\text{Mg,Fe})_3(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$	0.5		Smith et al. (2013)	
	Inosilicates	Enstatite	MgSiO_3	0.6		Palandri and Kharaka (2004)
Wollastonite		CaSiO_3	0.4		Brantley (2008)	
Rhodonite		MnSiO_3	0.27		Brantley (2008)	
Spodumene		$\text{LiAlSi}_2\text{O}_6$	0.64		Brantley (2008)	
Jadeite		$\text{NaAlSi}_2\text{O}_6$	0.18		Brantley (2008)	
Anthophyllite		$(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$	0.44		Palandri and Kharaka (2004)	
Glaucophane		$\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{22}(\text{OH})_2$	0.64		Brantley (2008)	
Hornblende		$(\text{Na,Ca})_{1-2}(\text{Mg,Fe,Al})_5\text{Si}_6(\text{Al,Si})_2\text{O}_{22}(\text{OH})_2$	0.37		Bandstra and Brantley (2008)	
Sorosilicates		Epidote	$\text{Ca}_2(\text{Al,Fe})_3\text{O}(\text{SiO}_4)(\text{Si}_2\text{O}_7)(\text{OH})$	0.34		Palandri and Kharaka (2004)

have been discussed in Part I (Crundwell, 2014). Brantley (2008) has recognized the difficulties associated with the surface-complexation model, and suggested that the precursor-complex form of the surface complexation model offers a possible solution. This alternative version of the surface-complexation model proposes the existence of a precursor species, which is on the surface and is in equilibrium with both the reactants and the surface (Oelkers, 2001). The precursor species is also in equilibrium with an activated complex, and this activated complex breaks down to form the reaction products. Conceptually, this model can be expressed as follows:



This model was briefly reviewed by Crundwell (2014), who identified that at a critical juncture in the derivation, it is simply assumed that the surface species are in equilibrium with half a proton, and this gives rise to the half-order kinetics. This is tantamount to solving the problem of fractional orders of reaction by making the stoichiometry fractional (see Eq. (2)a and b in Pokrovsky and Schott, 2000; and Eqs. (24) and (25) of Schott et al., 2009). As a result, the precursor model is not a satisfactory description of the dissolution of silicates because it is incorrectly formulated. Even if the formulation were corrected it would not predict the observed order of reaction with respect to H^+ correctly.

The theory of dissolution proposed by Crundwell (2014) represents a significant departure from the surface-complexation models. In the next section, the proposed mechanism of dissolution is applied to the dissolution of the silicates.

5. Application of the proposed mechanism to the dissolution of silicates

The purpose of this paper is to demonstrate that proposed mechanism of dissolution, derived by Crundwell (2014), can describe the dissolution of the silicates. First, the dissolution of the nesosilicates (orthosilicates), like forsterite, Mg_2SiO_4 , is discussed. After this, the mechanism dissolution of quartz, SiO_2 , the feldspars, and the phyllosilicates is developed.

5.1. Mechanism of dissolution of orthosilicate minerals

5.1.1. Measured orders of reaction for the dissolution of orthosilicate minerals

The orthosilicate minerals dissolve according to the following reaction, written in this case for forsterite:



The rate of dissolution of forsterite and similar olivine minerals has been examined extensively. The orders of reaction for eight different orthosilicates are given in Table 2. The average of these values is 0.46 ± 0.1 . This value is close to the value of 0.5 predicted using the proposed mechanism of dissolution. Terry and Monhemius (1983) studied the dissolution of willemite, Zn_2SiO_4 , in hydrochloric, perchloric, nitric and sulphuric acids. They found that the order of reaction in these solutions was 0.45, 0.4, 0.38 and 0.5, respectively, in accordance with the proposed theory.

The effect of pH on the rate of dissolution of forsterite is shown in Fig. 2. While previous researchers fitted a single reaction order to this data, it is clear from the data that there are two regions:

1. at values of pH below 6, has an order of reaction with respect to H^+ of 0.5; and,
2. at values of pH above 6, has an order of reaction with respect to H^+ of 0.25.

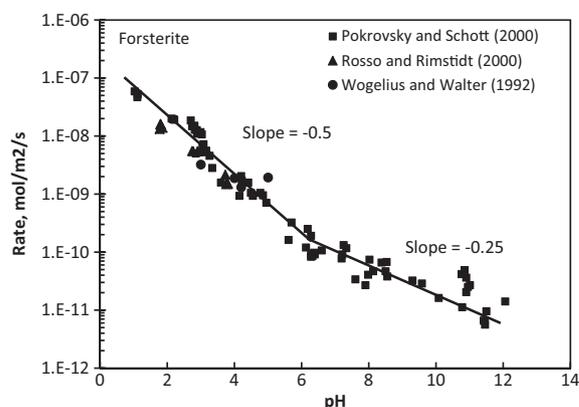


Fig. 2. The effect of pH on the rate of dissolution of forsterite, $Mg_{1.82}Fe_{0.18}SiO_4$, at 25 °C. Data from Pokrovsky and Schott (2000), Rosso and Rimstidt (2000) and Wogelius and Walter (1992).

Rimstidt et al. (2012) have recently re-evaluated the published rate data. They also concluded that there is a change in order of reaction from 0.5 to 0.25 as the value of the pH increased above 5.6. No explanation for these orders of reaction, or the change from 0.5 to 0.25, has yet been advanced.

5.1.2. Proposed mechanism

The bonds of forsterite that are broken are those between magnesium and the oxygen atoms. The silicon–oxygen bond energy, with a value of about 13 100 kJ/mol, is significantly higher than the magnesium–oxygen bond energy, which has a value of 3816 kJ/mol (Huggins and Sun, 1946). Dissolution would favour the breaking of the weaker bond. Thus, the magnesium dissolves to form Mg^{2+} and the silicon dissolves to form silicate, SiO_4^{4-} . The mechanism of dissolution is illustrated in Fig. 3, which shows the separate parallel processes that result in the formation of silicate and magnesium ions in solution. In acidic solutions, the departing silicate group forms an activated complex with protons and that the departing magnesium forms an activated complex with water. Surface magnesium and silicate species move across the interface at equal rates during congruent, stoichiometric dissolution.

This proposed theory of dissolution accounts for the breaking of bonds and the transfer of charged species across the potential difference that exists at the mineral interface (Crundwell, 2014). The premises of the theory are: (i) the breaking of the bond with the surface and the re-organization of the solvation sheath around the ion are dependent on the potential difference across the Helmholtz layer; (ii) the dissolution processes for the constituents of the solid that eventually become anions and cations occur separately in parallel; and (iii) the separate cation and anion processes are linked by the potential difference across the interface. The proposed mechanism is applicable to all solids, and is not restricted to either ionic or covalent solids.

As shown in Fig. 3, the mechanism of dissolution changes with changes in pH. In the acidic region, H^+ ions are present in abundance in the bulk solution. If the rate of dissolution is slow relative to the rate of diffusion and the solution is well stirred, the concentration of H^+ ions at the outer Helmholtz plane is equal to the concentration of H^+ ions in the bulk. These conditions are generally met in the case of the studies reported on the dissolution of silicate minerals. Thus in the acidic region, the H^+ ions that react with the silicate component of forsterite are positioned at the outer Helmholtz plane, as shown in Fig. 3(a).

As the pH increases, the concentration of H^+ in solution becomes very low, and hence its concentration at the outer Helmholtz plane becomes very low. As a result, there is a slight change in mechanism: the H^+ that reacts with silicate is not positioned at the outer Helmholtz plane; instead, it is positioned at the inner Helmholtz plane as a specifically adsorbed ion (see Fig. 3(b)). Because of this, there is change in the kinetics of dissolution.

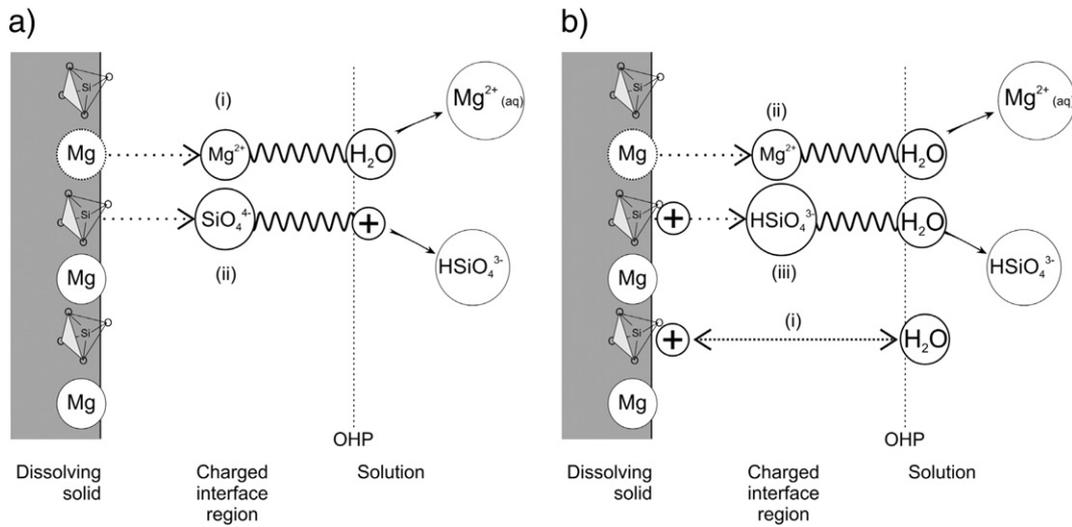


Fig. 3. The proposed mechanism for the dissolution of orthosilicate minerals: (a) in acidic solutions H⁺ ions at the outer Helmholtz plane react with silicate tetrahedra at the surface to form SiO₄⁴⁻ (aq) in solution and magnesium reacts to form Mg²⁺ (aq); (b) in neutral and alkaline solutions, H⁺ ions first adsorb at the inner Helmholtz layer before reacting with the silicate tetrahedra to form SiO₄⁴⁻ (aq) in solution.

The rate expression corresponding to these two situations is derived next.

5.1.3. Derivation of the rate expression for the dissolution of forsterite in acidic solutions

The rate of the removal of magnesium from the solid lattice to form metal ions in solution, r_+ [mol/m²/s], is given by the following expression:

$$r_+ = k_+[H_2O]^w \exp(\alpha_+F\Delta\phi/RT) \quad (5)$$

where the symbols with their units in parentheses are as follows: k_+ is the rate constant (mol/m²/s), α_+ is the transfer coefficient (–), F is Faraday’s constant (C/mol), $\Delta\phi$ is the potential difference between the surface and the outer Helmholtz layer [V], R is the gas constant (J/mol/K), and T is the temperature. The [] brackets in Eq. (5) represent activity (–), and w is the stoichiometric coefficient with respect to water for the rate-determining step in the removal of magnesium (–). The subscript ‘+’ refers to the process that results in the formation of the cation in solution.

The silicate groups in the structure react with protons, which are positioned at the outer Helmholtz plane. The rate of this reaction is given by:

$$r_- = k_-[H^+]^t \exp(-\alpha_-F\Delta\phi/RT) \quad (6)$$

where the subscript ‘-’ refers to the anion, and t represents the stoichiometric coefficient in the rate-determining step in the removal of silicate ions from the surface.

Since the rate removal of silicate groups, r_- , is equal to twice the rate of removal of magnesium, r_+ , for stoichiometric dissolution, an expression for the potential across the Helmholtz layer, $\Delta\phi$, can be derived by equating Eq. (5) to twice Eq. (6). This expression can then be substituted back into Eqs. (5) or (6) to yield the following rate expression:

$$r = (k_+[H_2O]^w)^{1-x} (2k_-)^x [H^+]^{xt} \quad (7)$$

where $x = \alpha_+ / (\alpha_+ + \alpha_-)$. The constant terms can be combined to give the following expression:

$$r = k[H^+]^{xt} \quad (8)$$

If the values of the transfer coefficients are close to each other, then the value of x is 0.5. If the silicate group reacts with only one proton in the rate-determining step, then the value of t is equal to one. The substitution of these values into Eq. (8) gives the following rate expression:

$$r = k[H^+]^{0.5} \quad (9)$$

This rate expression agrees with the experimental results for forsterite and the other orthosilicates in the acidic region (see orders of reaction listed in Table 2). A rate expression that so clearly agrees with the experimental results has not been presented before for forsterite or the orthosilicates.

The interesting feature for forsterite is the identified change in reaction order with increasing values of pH shown in Fig. 2. The rate expression based on the explanation of the mechanism given in Section 5.1.2 for the neutral and alkaline region is derived next.

5.1.4. Derivation of the rate expression for the dissolution of forsterite in neutral and alkaline solutions

The mechanism of dissolution of forsterite, and presumably the other orthosilicates, changes as the concentration of H⁺ ions becomes extremely low. The mechanism proposed for the acidic region envisages the H⁺ ions as positioned at the outer Helmholtz plane, which represents non-specific adsorption. The concentration of H⁺ ions at the outer Helmholtz plane is the same as that in the bulk solution.

As the value of pH increases above 6, the reaction continues but with H⁺ ions that are now positioned at the inner Helmholtz plane. In other words, these H⁺ ions are specifically adsorbed.

The specific adsorption of H⁺ given by the following reaction:



where \circ represents an available or unoccupied site, and $\bullet H^+$ represents an occupied site on the surface at the inner Helmholtz plane.

The fraction of the surface area that is occupied by $\bullet H^+$ is given by θ . The rate of the adsorption and desorption from the surface is dependent on the potential across the Helmholtz plane because the H⁺ ions move across this region. This rate is given by the following expression:

$$r_{ads} = k_{ads}[H^+](1-\theta) \exp(\alpha_{ads}F\Delta\phi/RT) - k_{-ads}\theta \exp(-(1-\alpha_{ads})F\Delta\phi/RT) \quad (11)$$

If it is assumed that the adsorption and desorption of H^+ are faster than dissolution, then the rate of this reaction is close to zero. If the surface coverage is low, the following expression for θ is obtained:

$$\theta = \frac{k_{ads}[H^+]}{k_{-ads} \exp(F\Delta\phi/RT)} \quad (12)$$

The rate of formation of the silicate ion is given as follows:

$$r_- = k_{-a}\theta \exp(-\alpha F\Delta\phi/RT) \quad (13)$$

where α is the charge transfer coefficient for the silicate group in the form of $HSiO_4^{3-}$.

The substitution of Eq. (12) into Eq. (13) gives the following expression for the rate of removal of silicate from the surface:

$$r_- = k_{-a} \frac{k_{ads}}{k_{-ads}} [H^+] \exp\{-\alpha, -1)F\Delta\phi/RT\} \quad (14)$$

By combining Eqs. (14) and (5) using the same method described in Section 5.1.3, we can obtain the rate expression:

$$r = k_2 [H^+]^{x_2 t} \quad (15)$$

where $x_2 = \alpha_+ / (\alpha_+ + \alpha_- + 1)$.

The rate expression is similar to that derived earlier as Eq. (8); however, the order of reaction is different. If the values of the transfer coefficients are all close to 0.5, then the value of x_2 is 0.25, rather than 0.5 in the acidic region. If one proton reacts in the rate-determining step with the silicate ion, the value of t is one. Therefore, the rate of reaction in the neutral and alkaline region (pH greater than 6) is as follows:

$$r = k_2 [H^+]^{0.25} \quad (16)$$

Overall, the order of reaction is 0.25, in agreement with the experimental results in the neutral and alkaline region. As the concentration of H^+ becomes lower, only specifically adsorbed H^+ ions are capable of participating in the rate-determining step. Consequently, the order of reaction changes from 0.5 to 0.25 with increasing values of pH. No previously proposed model accounts for this change in the order of reaction.

5.1.5. General nature of non-oxidative dissolution

Casey (1991) noted a correlation between the rate of dissolution of the orthosilicates and the rate of dissolution of the corresponding

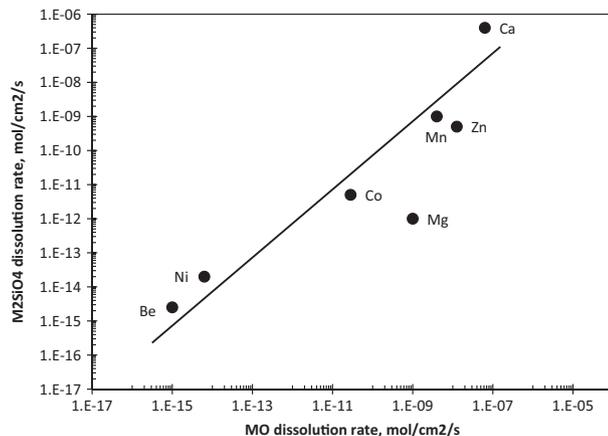


Fig. 4. The correlation between the rates of dissolution of metal oxides (MO) and orthosilicates (M_2SiO_4). This correlation suggests that the breaking of the metal–oxygen bond is bond broken during dissolution of both classes of minerals. Data from Casey (1991).

metal oxide, which is shown in Fig. 4. This correlation suggests that an important step in the dissolution of both metal oxides and silicates is the breaking of the metal–oxygen bond. This is consistent with the mechanism of dissolution proposed here, where the metal departs from the surface as an ion without any oxygen atoms, and the silicon departs as a silicate anion.

In order for the cations and anions ions to form during dissolution of metal oxides and metal silicates, the metal–oxygen bond needs to break. The rate of dissolution is dependent on the ease of breaking this bond, which accounts for the correlation shown in Fig. 4.

An interesting feature is that the orders of reaction for the dissolution of MgO, ZnO and a number of other oxides are also close to 0.5 (see, for example, Table 1 in Crundwell, 2014). The rate expression for the mechanism of dissolution proposed here also predicts a reaction order of one half for these oxides. This suggests that the theory proposed by Crundwell (2014) is a general description of the kinetic mechanism of non-oxidative dissolution reactions.

In summary, the mechanism proposed here appears to be a good description of the kinetics of dissolution of the orthosilicates. The site of dissolution is the metal–oxygen bond, which results in the formation of the metal ion and silicate ion. The important factor not accounted for by previous work was the effect of the potential difference at the surface on the rate of reaction of these bond-breaking reactions. The proposed mechanism accounts for this effect of potential on the rate of bond breaking at the surface.

In the next section, the theory proposed by Crundwell (2014) is applied to the dissolution of quartz.

5.2. Proposed mechanism of dissolution of quartz, SiO_2

Quartz lies at the opposite end of the structural spectrum to the orthosilicates. Orthosilicates consist of unit tetrahedra of the silicate group, SiO_4^{4-} with metal ions separating the tetrahedra from one another. In quartz, oxygen atoms are shared by all silicate tetrahedra, without any metal ions separating the silicate tetrahedra. However, in spite of these structural differences, it is argued in this section that the proposed mechanism is also applicable to quartz.

5.2.1. Measured orders of reaction for the dissolution of quartz

The dissolution of quartz has been studied extensively, although it can be challenging to measure these rates with confidence due to the low rates of dissolution. The results reported by Knauss and Wolery (1988) for the dissolution of quartz at 70 °C and by Brady and Walther (1992) at 60 °C are shown in Fig. 5. Both sets of results show that the rate of dissolution increases with increasing pH, with a slope of 0.5. This implies that the rate of dissolution is proportional to $[OH^-]^{0.5}$.

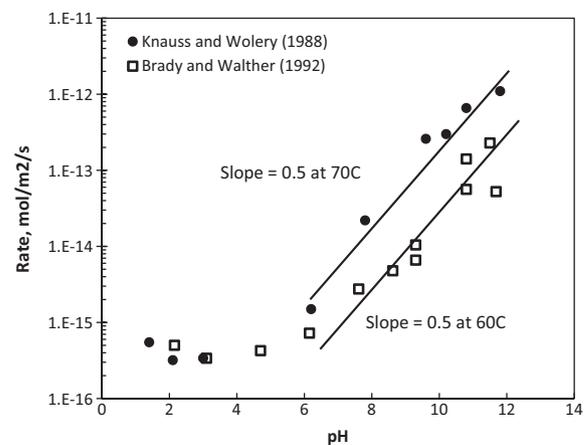


Fig. 5. The dissolution of quartz at 60 and 70 °C, showing the order of reaction is close to 0.5 with respect to OH^- ions. Data from Knauss and Wolery (1988) and Brady and Walther (1992).

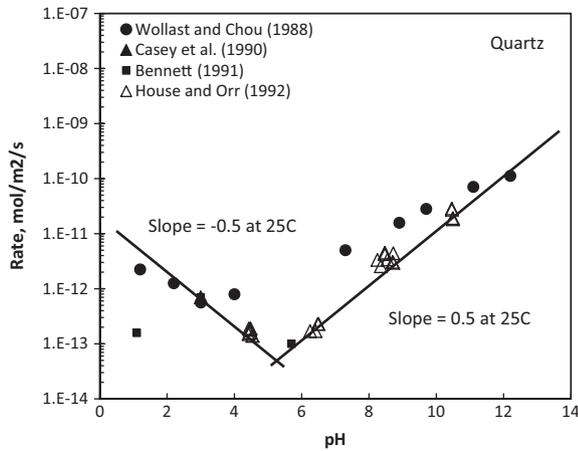


Fig. 6. The effect of pH on the rate of dissolution of quartz at 25 °C, showing the order of reaction with respect to H⁺ and OH⁻. Data from Wollast and Chou (1988), Casey et al. (1991), Bennett (1991) and House and Orr (1992).

The rates of dissolution of quartz at 25 °C reported by a number of different research teams are shown in Fig. 6. These results suggest that quartz dissolves both in the acidic and in the alkaline region. The order of reaction is 0.5 with respect to H⁺ in the acidic region, and 0.5 with respect to OH⁻ in the alkaline region.

Bandstra and Brantley (2008) fitted Eq. (2) to a selected set of data reported in the literature and concluded that the order of reaction is 0.41 ± 0.03 with respect to OH⁻ in the alkaline region and 0.31 ± 0.08 with respect to H⁺ in the acidic region. The reason for the difference between the orders shown in Fig. 6 and those of Bandstra and Brantley (2008) is probably because Bandstra and Brantley (2008) restricted the data that collected at 25 °C.

5.2.2. Proposed mechanism of dissolution of quartz in alkaline solutions

The proposed mechanism of dissolution of quartz in alkaline solutions is illustrated in Fig. 7. Silicon–oxygen bonds are broken at the surface to produce a range of hydrated silicon–oxygen products. SiO₄⁴⁻ (aq) and SiOH³⁺ (aq) entities have been illustrated in Fig. 7, but these could be replaced with hydrated SiO₃²⁻ (aq) and SiOOH⁺ (aq) species as intermediate products.

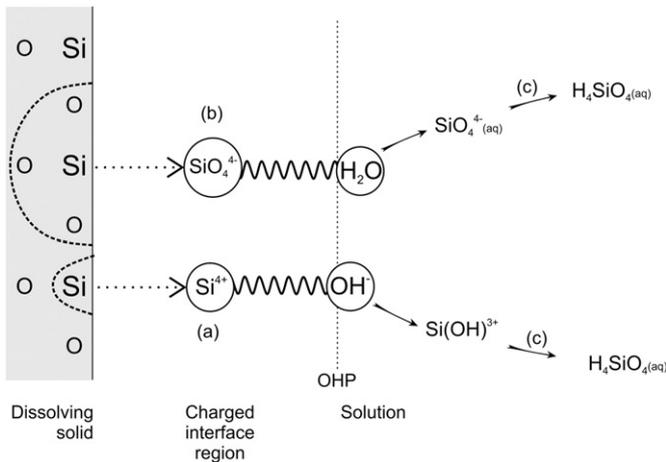


Fig. 7. The proposed mechanism of dissolution of quartz in alkaline solutions in three steps: (a) individual silicon atoms at the surface react with hydroxide ions across the Helmholtz layer; (b) silicate tetrahedra at the surface depart intact, and (c) the products of the previous two steps react with species in solution to form the final product. Steps (a) and (b) are rate-determining. The bond-breaking may produce hydrated SiO₃²⁻ and SiOOH⁺ entities in the rate-determining steps, rather than the hydrated SiO₄⁴⁻ and Si⁴⁺ entities shown here.

In alkaline solutions, hydroxide ions attack the silicon–oxygen bonds to form a potential-dependent activated complex with Si⁴⁺ [alternatively SiO²⁺ (aq)] within the Helmholtz layer. The SiO₄⁴⁻ [alternatively SiO₃²⁻] sites react with water to form a potential-dependent activated complex within the Helmholtz layer.

While these steps represent the proposed rate-determining step, this does not imply that these are the final products of the reaction in solution. There are further reactions at the outer Helmholtz plane between the products of the rate-determining steps and species in solution that result in the final products.

The rate of formation of cations from the surface in the rate-determining step is given by:

$$r_+ = k_{a,+} [OH^-]^{t_{OH}} \exp(\alpha_+ F \Delta \phi / RT) \tag{17}$$

where t_{OH} is the stoichiometric coefficient for the elementary step of hydroxide ions reacting with silica sites on the surface. The rate of formation of anions from the surface in the rate-determining step is given by:

$$r_- = k_{a,-} \exp\{-\alpha_- F \Delta \phi / RT\} \tag{18}$$

Since the dissolution is congruent and stoichiometric, the rate of formation of cations is equal to the rate of formation of anions. Therefore, Eqs. (17) and (18) can be combined to give an expression for the potential of the dissolving surface. If the resulting expression for the potential is substituted back into either Eq. (17) or (18), the following rate expression is obtained:

$$r = k_{OH} [OH^-]^{t_{OH}(1-x_{OH})} \tag{19}$$

where x_{OH} = α₊ / (α₊ + α₋).

If one OH⁻ ion reacts with Si⁴⁺ in the rate determining step, then the value of t_{OH} is one. Since the value of x_{OH} is expected to be equal to one half as before, the order of reaction is 0.5, and the rate expression is given as follows:

$$r = k_{OH} [OH^-]^{0.5} \tag{20}$$

Therefore, the proposed mechanism of dissolution, as illustrated in Fig. 7, predicts that the rate of dissolution is a one-half order in OH⁻, which is what is observed experimentally.

This mechanism accounts for the observed orders of reaction. In contrast, the surface-complexation model has to assume that the concentration of surface sites is proportional to [OH⁻]^{0.5} in order to obtain the observed order of reaction. The precursor species model makes the error of using fractional stoichiometric coefficients as the orders of reaction in the rate expression. In addition to the surface-complexation and the precursor-species models, Dove et al. (2005) have advocated a model that views dissolution of quartz as the opposite of crystallization. However, the view that dissolution is crystallization in reverse does not account for the observed order of reaction.

The feature of the proposed mechanism of dissolution that results in the correct orders of reaction is the breaking of the rate-determining bond under the influence of the potential difference across the Helmholtz layer. None of the previous models account for the effect of the potential difference at the surface.

The dissolution of quartz in acidic solutions is discussed in the next section.

5.2.3. Proposed mechanism of dissolution of quartz in acidic solutions

The mechanism that is proposed for the mechanism of dissolution in acidic solutions is shown in Fig. 8. The silicon–oxygen bonds are broken to form anions as either HSiO₄⁻ or HSiO₃⁻, and cations as either Si⁴⁺ or SiO²⁺ in separate parallel reactions.

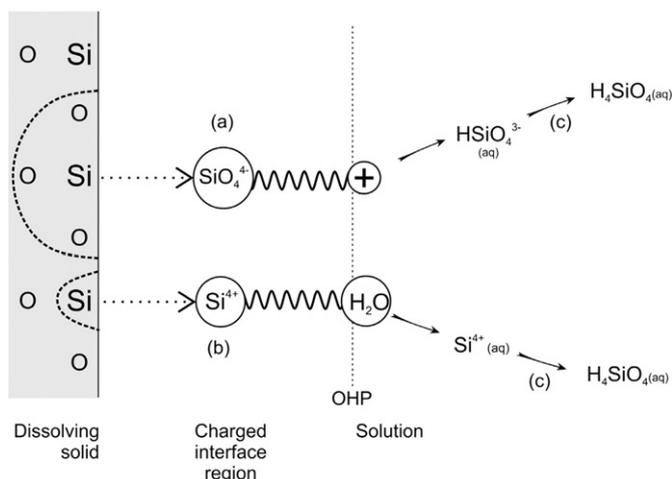


Fig. 8. The proposed mechanism of dissolution of quartz in acidic solutions in three steps: (a) silicate tetrahedra at the surface react with H^+ ions across the Helmholtz layer; (b) individual silicon atoms at the surface react with water across the Helmholtz layer; and (c) the products of the previous two steps react with species in solution to form the final product. Steps (a) and (b) are rate-determining. The bond-breaking may produce hydrated $HSiO_3^-$ and SiO_2^{2+} entities in the rate-determining steps, rather than the hydrated SiO_4^{4-} and Si^{4+} entities shown here.

The H^+ ion attacks the SiO_4^{4-} or SiO_3^{2-} sites to form a potential-dependent activated complex in the Helmholtz layer. In a parallel 'partial' reaction, Si^{4+} or SiO_2^{2+} sites form an activated complex with water molecules in solution. Once these activated complexes break down into products, they subsequently react with species at the outer Helmholtz plane to form the final products in solution.

The rate of dissolution in acidic solutions is the same as that presented for the dissolution of forsterite, and is given by Eq. (8):

$$r = k_H [H^+]^{x_H t_H} \quad (21)$$

The order of reaction for this rate expression is $x_H t_H$, the value of which is calculated as follows. The value of t_H is one because only one H^+ ion is envisaged as forming an activated complex with the SiO_4^{4-} and SiO_3^{2-} sites. The value of x_H is one half, because the value of both transfer coefficients is close to 0.5. Consequently, the calculated order of reaction, $x_H t_H$, is 0.5, in agreement with the experimental values.

In summary, the proposed mechanism appears to be a good description of the rate-determining processes in dissolution of the quartz. In the next section, the proposed mechanism is applied to the dissolution of the feldspar minerals.

5.2.4. Overall rate of dissolution of quartz

The dissolution of quartz in both alkaline and acidic conditions is the sum of the rate expressions for the acid mechanism and that for the alkaline mechanism. As a result, the rate expression can be written as follows:

$$r = k_H [H^+]^{x_H t_H} + k_{OH} [OH^-]^{t_{OH} (1 - x_{OH})} \quad (22)$$

where the subscript H refers to the acid dissolution mechanism, and the subscript OH to the alkaline mechanism.

The substitution of the calculated values of x_H , t_H , x_{OH} , and t_{OH} yields the following expression for the overall rate of dissolution:

$$r = k_H [H^+]^{0.5} + k_{OH} [OH^-]^{0.5} \quad (23)$$

It is clear that not only does this rate expression describe the rate of dissolution of quartz over the entire pH region, but it also provides a

theoretical underpinning to the empirical expression used by Brantley (2008) and Bandstra and Brantley (2008), given as Eq. (2).

The dissolution of the feldspar group of minerals is discussed next.

5.3. Mechanism of dissolution of feldspar minerals

The feldspars are rock-forming minerals in the series $KAlSi_3O_8$ (K-feldspar)– $NaAlSi_3O_8$ (albite)– $CaAl_2Si_2O_8$ (anorthite). This series might be represented by the general formula $XAl(Al,Si)_2O_8$, where X is potassium, sodium, or calcium. These tectosilicate minerals are regarded as amongst the most abundant of the minerals that make up the earth's crust. Although the origin of the name 'feldspar' implies that these minerals have no contained metals of value, feldspars are mined for use in the glass-making and ceramics industries, and are a crucial ingredient in the manufacture of porcelain.

As indicated by the general formula for feldspars, some of the aluminium occupies tetrahedral sites. The structure of the feldspars consists of double chains of SiO_4^{4-} and AlO_4^{5-} tetrahedra with aluminium, potassium, sodium and calcium balancing the charge between these tetrahedra.

5.3.1. Measured orders of reaction for the dissolution of feldspar minerals

The feldspars dissolve in both acidic and alkaline solutions. The effect of pH on the rate of dissolution of two of the end-member feldspars, albite and K-feldspar, is shown in Figs. 9 and 10, respectively. These results show that the order of reaction with respect to H^+ is 0.4 for albite and 0.5 for K-feldspar, and the order of reaction with respect to OH^- is 0.38 for albite, and 0.5 for K-feldspar.

The average of the values for the orders of reaction given in Table 2 for plagioclase feldspars albite, oligoclase, andesine, and labradorite is 0.51 in acidic conditions.

The values shown in Figs. 9 and 10 are slightly different to those in Table 2, because Bandstra and Brantley (2008) restricted their data to values collected at 25 °C. However, it is clear that the orders of reaction in both the acid and alkaline regions are close one-half.

5.3.2. Proposed mechanism of dissolution of feldspar minerals in acidic solutions

The feldspars are more complex in chemical composition and structure than the other silicate minerals discussed previously in this paper. This makes it more difficult to identify the bonds that break in the rate-determining step during dissolution.

The rate of dissolution of the plagioclase feldspars is known to be dependent on the aluminium content of the mineral. Casey et al. (1991) studied the plagioclase minerals (that is, the solid solution series from albite to anorthite). Their dissolution results are plotted in Fig. 11 as a function of the fraction of aluminium that substitutes for silicon in

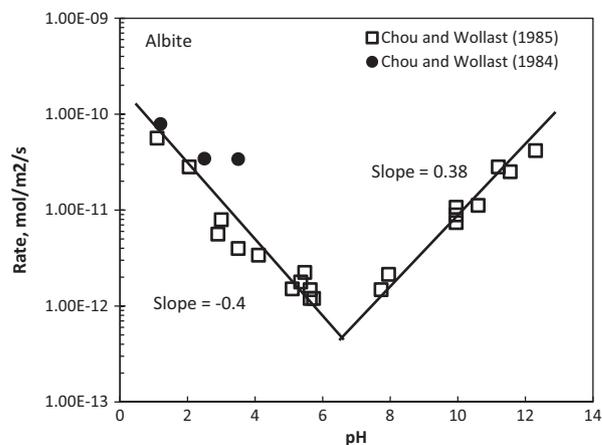


Fig. 9. The effect of the pH of the solution on the rate of dissolution of albite at 25 °C. Data from Chou and Wollast (1984, 1985).

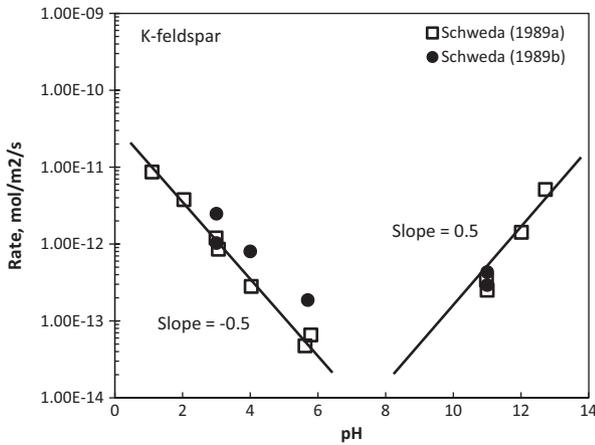


Fig. 10. The effect of the pH of the solution on the dissolution of K-feldspar at 25 °C. Data from Schweda (1989a, 1989b).

tetrahedral sites. The results shown in this figure indicate that the rate of dissolution is exponentially dependent on the aluminium content. In other words, the Gibbs free energy of activation is linearly dependent on the aluminium content of the mineral.

These results suggest that the breaking of the aluminium–oxygen bonds critically affects the rate of dissolution. It is proposed that both the aluminium–oxygen bonds and the silicon–oxygen bonds need to break to form the activated complexes. If this is the case, the oxygen atoms remain with the silicon to form the anions as SiO_4^{4-} and the cations are Na^+ and Al^{3+} .

The proposed mechanism of dissolution is shown in Fig. 12. Water forms an activated complex with the Al^{3+} sites, and H^+ ions form the activated complex with the SiO_4^{4-} sites, resulting in dissolution of the mineral. The formation of these activate complexes during the breaking of the critical bonds with surface atoms represents the rate-determining step during dissolution.

This mechanism is similar to that discussed in Section 5.1.3 for the rate of dissolution of forsterite in acidic solutions. The derivation is the same as that which led to Eq. (8):

$$r = k_H [H^+]^{x_H t_H} \quad (24)$$

The order of reaction from this rate expression is given by $x_H t_H$. The calculation of the order of reaction is as follows. The value of x is 0.5 ± 0.1 , because the value of both transfer coefficients is taken as 0.5 ± 0.1 . The value of t is one because only one H^+ ion is envisaged as forming an activated complex with the SiO_4^{4-} site. Therefore, the

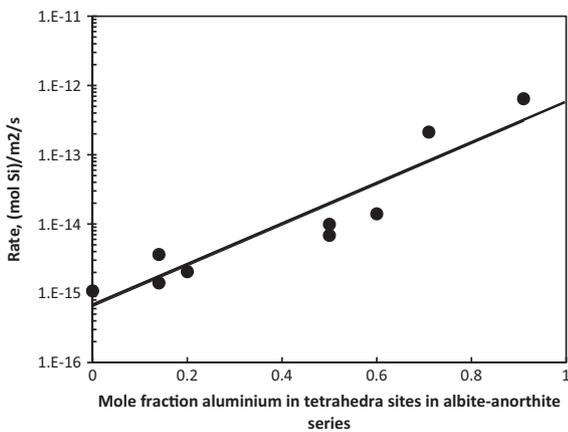


Fig. 11. Rate of dissolution of plagioclase feldspars (albite to anorthite solid solution series) with increasing amounts of aluminium in tetrahedral positions. Data from Casey et al. (1991).

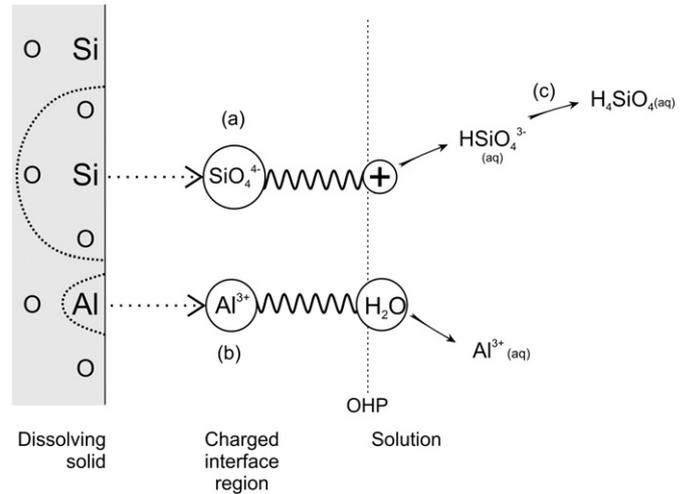


Fig. 12. The proposed mechanism of dissolution of feldspar in acidic solutions in three steps: (a) silicate tetrahedra at the surface react with H^+ ions across the Helmholtz layer; (b) individual aluminium atoms at the surface react with water across the Helmholtz layer; and (c) the products of the previous two steps react with species in solution to form the final product. Steps (a) and (b) are rate-determining.

order of reaction is 0.5 ± 0.1 , which is consistent with the experimental measurements.

The agreement between the theory and the measured results suggests that the proposed mechanism describes the rate-determining steps during the dissolution of feldspar minerals.

The dissolution of feldspar minerals in alkaline solutions is discussed in the next section.

5.3.3. Proposed mechanism of dissolution of feldspar minerals in alkaline solutions

The proposed mechanism of dissolution for the dissolution of feldspar minerals in alkaline solutions is shown in Fig. 13. The critical bonds that are broken during dissolution are the aluminium–oxygen and silicon–oxygen bonds. Water molecules form an activated complex with SiO_4^{4-} sites, while hydroxide ions form an activated complex with Al^{3+} sites.

This mechanism is similar to that discussed in Section 5.2.2 for the rate of dissolution of quartz in alkaline solutions. The derivation

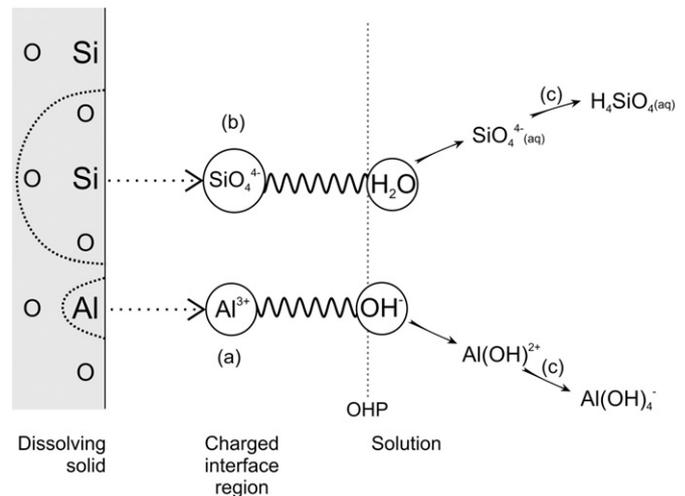


Fig. 13. The proposed mechanism of dissolution of feldspar in alkaline solutions in three steps: (a) individual aluminium atoms at the surface react with hydroxide ions across the Helmholtz layer; (b) silicate tetrahedra at the surface depart intact, and (c) the products of the previous two steps react with species in solution to form the final product. Steps (a) and (b) are rate-determining.

presented in that section led to Eq. (19). The value of x_{OH} is 0.5 ± 0.1 , because the value of both transfer coefficients is taken as 0.5 ± 0.1 . The value of t_{OH} is one because only one hydroxide ion is envisaged as forming an activated complex with the Al^{3+} sites.

$$\vec{r} = k_{OH}[OH^-]^{t_{OH}(1-x_{OH})} = k_{OH}[OH^-]^{0.5} \quad (25)$$

As a result, the calculated order of reaction is 0.5 ± 0.1 , in agreement with the experimental results.

5.3.4. Overall rate of dissolution of feldspar minerals

Based on the arguments presented here, the overall rate of reaction for the feldspar minerals is described by the following rate expression:

$$r = k_H[H^+]^{0.5} + k_{OH}[OH^-]^{0.5} \quad (26)$$

This agrees with the empirical rate expression presented by Brandley (2008) and Bandstra and Brantley (2008).

5.4. Mechanism of dissolution of phyllosilicate minerals

Phyllosilicate minerals have a structure in which the silicate tetrahedra form sheets. Cations, which balance the charge, are positioned between the sheets. The mechanism of dissolution is similar to the feldspars, and is examined in the sections that follow.

5.4.1. Measured order of reaction for the dissolution of phyllosilicate minerals

The dissolution of phyllosilicate minerals follows a similar pattern to that established in previous sections. The mineral dissolves both in acid and alkaline solutions, with a minimum in the region between these

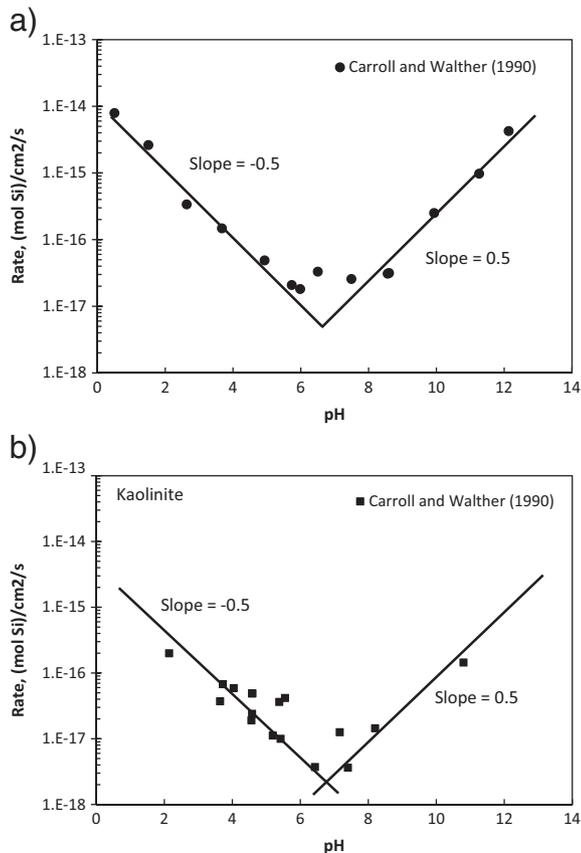


Fig. 14. The effect of pH on the rate of dissolution of kaolinite at (a) 80 °C and (b) 60 °C.

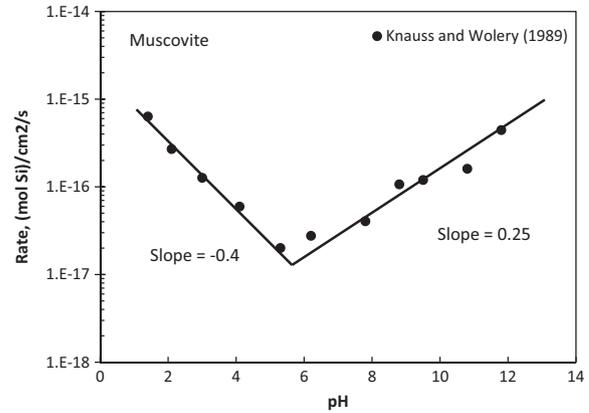


Fig. 15. The effect of pH on the rate of dissolution of muscovite at 70 °C. Data from Knauss and Wolery (1989).

two. The effect of pH on the rate dissolution of kaolinite and muscovite is shown in Figs. 14 and 15, respectively.

For kaolinite, the order of reaction is close to 0.5 with respect to H^+ in the acidic region, and with respect to OH^- in the alkaline region. For muscovite, the order of reaction is 0.25 with respect to the OH^- .

5.4.2. Proposed mechanism of dissolution of phyllosilicate minerals in acidic and alkaline solutions

The proposed mechanism of dissolution for the phyllosilicate minerals is the same as that proposed for the feldspar minerals, and shown in Fig. 12 and 13. It follows from this mechanism proposed that the orders of reaction calculated from the proposed mechanism of dissolution are 0.5 with respect to H^+ and 0.5 with respect to OH^- . This mechanism is consistent with the experimental results. The order of reaction with respect to OH^- for muscovite can be described by a mechanism in which the OH^- ions react at the inner Helmholtz plane.

6. Discussion

A mechanism of dissolution has been proposed here that describes the dissolution of an incredibly wide range of minerals, both in composition and structure. Some generic patterns are observed from the data, and from the proposed mechanism of dissolution. There is a strong suggestion from the data that the empirical rate expression is as follows:

$$rate = k_H[H^+]^{0.5 \pm 0.1} + k_{OH}[OH^-]^{0.5 \pm 0.1} \quad (27)$$

The recognition of this pattern in the data is significant in its own right. This expression seems to apply to all the silicates except the orthosilicates, where, at least for forsterite, no dissolution by hydroxide was observed; instead a change of order of reaction with respect to H^+ ions occurs.

The application of the proposed mechanism to the dissolution of the silicates is based on the following elementary steps for silicate dissolution:

Acidic solutions:

- (i) the metal atoms which react with water to form solvated cations; and,
- (ii) silicate groups are attacked by H^+ to form hydrated anions.

Alkaline solutions:

- (i) the metal atoms which react with hydroxide ions form hydrolyzed cations; and,
- (ii) silicate groups react with water to form hydrated anions.

The site of the breaking of the bond is two-fold:

- a. between the silicate group and the solid lattice, and
- b. between the metal atom and the solid lattice.

This proposed mechanism predicts that the order of reaction will have values close to either 0.25, 0.5 or 1, depending on the number of H^+ or OH^- ions that form the activated complex within the Helmholtz layer and whether the H^+ is position at the inner or outer Helmholtz plane. For silicate minerals, it appears that the number of H^+ or OH^- forming an activated complex with the Helmholtz layer is one, so that the order of reaction is close to 0.5 for most of the silicates.

7. Conclusions

The following conclusions are drawn:

1. The dissolution of the silicate minerals is of fractional order with respect to H^+ in acidic solutions. The value of the order of reaction with respect to H^+ is frequently found to be close to 0.5.
2. The dissolution of the silicate minerals is of fractional order with respect to OH^- in alkaline solutions. The value of the order of reaction is close to 0.5.
3. The mechanism of dissolution proposed here is able to account for these observed orders of reaction.
4. The mechanism of dissolution proposed here can describe the change in order of reaction from 0.5 to 0.25 with respect to H^+ that occurs at a pH of about 5.6 for the orthosilicate mineral forsterite.

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