The mechanism of dissolution of forsterite, olivine and minerals of the orthosilicate group

F.K. Crundwell *

CM Solutions (Pty) Ltd, Building T5 Pinelands, 1 Ardeer Road, Modderfontein, 1609, South Africa

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A B S T R A C T
The dissolution of forsterite and other minerals of the olivine and phenakite silicate groups are described by a novel mechanism of dissolution. For many of these minerals, the order of reaction with respect to H⁺ is close to 0.5 in the acidic region. The mechanism of dissolution proposed here correctly predicts these orders of reaction without any adjustable parameters. Recent work has shown that 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. Previously proposed models of dissolution cannot predict this change in order of reaction, whereas the mechanism proposed here does predict this change in reaction order, again without any adjustable parameters. The mechanism proposes 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 at higher values of pH. The acceleration of the rate of dissolution by organic acids and the retardation of the rate by dissolved silica and carbon dioxide are also correctly predicted. The mechanism predicts a change in the interfacial potential difference at the same value of pH that the order of reaction changes. This prediction is verified by measurements of the zeta potential, which reflects the predicted change in surface potential at a pH of approximately 6. The proposed mechanism provides a framework for the interpretation of the correlation between the rate of dissolution of the orthosilicates and the exchanges rates of water in the inner sphere of the corresponding metal aqua-ion.

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1. Introduction

The olivine group of minerals, which includes the minerals forsterite (Mg₂SiO₄), fayalite (Fe₂SiO₄), and tephroite (Mn₂SiO₄), has received a lot of recent attention due to their utility for carbon dioxide sequestration and their potential significance for the origin of life (Kump et al., 2000; Kuszuba et al., 2013; Schuiling and Krijgsman, 2006). There is extra-terrestrial interest in the dissolution of olivine, driven by an interest in determining the extent to which the surface of Mars has been weathered by aqueous solutions (Olsen and Rimstidt, 2007).

The dissolution of the olivine minerals also has industrial significance. Olivine weathering results in the formation of the nickel laterites used as the feed material to a number of hydrometallurgical plants around the world (Crundwell et al., 2011). The dissolution of rock-forming minerals is also important in whole-ore leaching operations, and the consumption of acid by gravel and rock layers of the leaching pad of a heap. Willemite (Zn₂SiO₄), a member of the phenakite group, and zinc-containing tephroite are sources of zinc (Terry and Monhemius, 1983). The use of olivine to neutralize industrial acid waste has also been proposed (Jonckbloedt, 1998).

The dissolution of minerals is important in a number of scientific fields, such as mineral weathering, geochemistry, materials science, environmental science and hydrometallurgy. Knowledge of the mechanisms of dissolution is a primary goal of these fields. Such knowledge can aid in the design of operations where dissolution or etching is required. It can be used to understand the behaviour of minerals in rocks to weathering patterns, which are important in understanding climate and climate change.

Knowledge of how forsterite and other minerals of the orthosilicate group dissolve might help to develop a generalized mechanism of dissolution of silicates and understand the interactions between rocks, minerals and aqueous solutions on a more fundamental basis. The broad purpose of this study is to provide the framework for a novel mechanism of dissolution that can describe the kinetics of dissolution of orthosilicate minerals. The general aim of this work is to describe the dissolution of forsterite, which has been studied experimentally in significant detail. The results of more than 768 dissolution experiments are analysed in this paper, and it is shown that all of this data can be described by the dissolution theory presented by Crundwell (Accepted for publication, 2014a, 2014b). These experimental results are reviewed next, after which the specific aims of this work are presented.
1.1. Review of the experimental results for the kinetics of dissolution of orthosilicate minerals

Forsterite and other orthosilicates dissolve in both acidic and alkaline solutions. The overall reaction stoichiometry is given as follows:

\[ \text{Mg}_2\text{SiO}_4 + 4\text{H}^+ \rightarrow 2\text{Mg}^{2+}(\text{aq}) + \text{Si(OH)}_4^{4-}(\text{aq}) \]  

The rate of an irreversible dissolution reaction, such as that given in Eq. (1), is usually expressed mathematically in the following form (Crundwell, 2013; Holmes and Crundwell, 2000):

\[ \text{rate} = k[c]^n \exp\left(-\frac{E_A}{RT}\right) \]  

where \( [c] \) represents the concentration of a reactant, \( k \) the rate constant, \( n \) the order of reaction, \( E_A \) the activation energy, \( R \) the gas constant, and \( T \) the temperature.

The order of reaction, \( n \), indicates how the rate of reaction depends on the concentration of the reactant. If the value of \( n \) is one and the reactant is \( \text{H}^+ \), the reaction is said to be first order in \( \text{H}^+ \). The order of reaction is the key parameter, and it is the goal of chemical kinetics to provide a derivation of the order of reaction based on a proposed mechanism of reaction in which all the individual steps are elementary reactions (Atkins and de Paulo, 2006; Murphy and Helgeson, 1987). In the next section the results for the orders of reaction with respect to \( \text{H}^+ \) for a wide variety of minerals in the acid region are presented. Following that presentation, more detailed results for forsterite are presented for a wider range of pH, and for the inhibition of the reaction by its products.

1.1.1. Orders of reaction of orthosilicate minerals in the acid region

The orders of reaction with respect to \( \text{H}^+ \) in the acidic region are given in Table 1. The values given in this table indicate that the order of reaction with respect to \( \text{H}^+ \) is close to 0.5.

The results given in Table 1 show a remarkable pattern. The activation energies are similar, many of which are between 49 and 62 kJ/mol. This suggests that a similar rate-determining step may control the dissolution for all of these minerals. This is in line with the observation that the orders of reaction have similar values, that is, close to a value of one half. The two biggest outliers are fayalite and phenakite, with values of 0.69 and 0.3, respectively. However, only a limited number of experiments have been reported orders of reactions with respect to \( \text{H}^+ \) for fayalite and phenakite, as shown in Fig. 1. If, for example, the only study of forsterite was that of Grandstaff (1986), the order of reaction with respect to \( \text{H}^+ \) would be reported as 1.0; however, six subsequent studies in which 520 data points were recorded indicates that the order of reaction is between 0.46 and 0.54 in acidic solutions. The point is that the orders of reaction for phenakite and fayalite are probably also close to 0.5.

1.1.2. Orders of reaction for forsterite in acid solutions

The orders of reaction in the acid region at values of the pH less than 4 are shown in Fig. 2 for various temperatures. These results, from Olsen and Rimstidt (2008), show that the order of reaction is independent of temperature and has a value of 0.5.

### Table 1

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mineral formula</th>
<th>Structure</th>
<th>Reaction order wrt H(^+), ( n )</th>
<th>Activation energy, ( E_A ), kJ/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forsterite</td>
<td>Mg(_2)SiO(_4)</td>
<td>Olivine</td>
<td>0.45 to 0.54</td>
<td>HCl</td>
<td>Brantley (2008), Westrich et al. (1993),</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Rimstidt et al. (2012)</td>
</tr>
<tr>
<td>Fayalite</td>
<td>Fe(_2)SiO(_4)</td>
<td>Olivine</td>
<td>0.69</td>
<td>HCl</td>
<td>Wogelius and Walther (1992), Brantley (2008)</td>
</tr>
<tr>
<td>Monticellite</td>
<td>CaMgSiO(_4)</td>
<td>Olivine</td>
<td>0.56</td>
<td>HCl</td>
<td>Westrich et al. (1993)</td>
</tr>
<tr>
<td>Co-olivine</td>
<td>Co(_2)SiO(_4)</td>
<td>Olivine</td>
<td>0.36</td>
<td>HCl</td>
<td>Westrich et al. (1993)</td>
</tr>
<tr>
<td>Tephroite</td>
<td>Mn(_2)SiO(_4)</td>
<td>Olivine</td>
<td>0.47</td>
<td>HCl</td>
<td>Westrich et al. (1993); Casey et al. (1993)</td>
</tr>
<tr>
<td>Ca-olivine</td>
<td>Ca(_2)SiO(_4)</td>
<td>Olivine</td>
<td>0.42</td>
<td>HCl</td>
<td>Westrich et al. (1993)</td>
</tr>
<tr>
<td>Co-Mn olivine</td>
<td>CoMnSiO(_4)</td>
<td>Olivine</td>
<td>0.42</td>
<td>HCl</td>
<td>Westrich et al. (1993)</td>
</tr>
<tr>
<td>Phenakite</td>
<td>Be(_2)SiO(_4)</td>
<td>Phenakite</td>
<td>0.3</td>
<td>HCl</td>
<td>Casey and Westrich (1992); Westrich et al. (1993)</td>
</tr>
<tr>
<td>Willemite</td>
<td>Zn(_2)SiO(_4)</td>
<td>Phenakite</td>
<td>0.45</td>
<td>HCl</td>
<td>Terry and Monhemius (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.49</td>
<td>Terry and Monhemius (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.53</td>
<td>Terry and Monhemius (1983)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.38</td>
<td>Terry and Monhemius (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.40</td>
<td>Terry and Monhemius (1983)</td>
</tr>
</tbody>
</table>
1.1.3. Orders of reaction for forsterite in alkaline solutions

Brantley (2008) and Palandri and Kharaka (2004) presented an empirical analysis of the rate of dissolution of silicate minerals based on separate dissolution paths in acid and alkaline solutions. The interesting observation for forsterite, and presumably the other orthosilicates, is that these minerals do not react with hydroxide ions. This is in contrast to aluminosilicate minerals, where dissolution in acid and hydroxide solutions frequently occurs, with a minimum in the neutral region. While forsterite might not react with hydroxide, the kinetic behaviour in the alkaline region is nevertheless very interesting.

The rate of dissolution of forsterite as a function of pH is shown in Fig. 2. The results plotted in this figure indicate the order of reaction with respect to H⁺ changes from 0.5 in the acidic region to 0.25 in the alkaline region, that is, above a pH of about 6. This change in order of reaction for forsterite was also noted by Rimstidt et al. (2012) in their systematic review of the data reported in the literature for forsterite. The relationships that Rimstidt et al. (2012) identified are as follows:

\[
\text{rate} = 10^{6.02} [H^+]^{0.46} \exp\left( \frac{-70518}{RT} \right) \quad \text{for pH < 5.6} \tag{3}
\]

\[
\text{rate} = 10^{4.07} [H^+]^{0.256} \exp\left( \frac{-66344}{RT} \right) \quad \text{for pH > 5.6} \tag{4}
\]

Both these relationships are valid for the temperature range between 0 °C and 150 °C. Eq. (3) was regressed using 519 data points and Eq. (4) using 125 data points. These relationships are essentially the same as those shown graphically in Fig. 4.

1.1.4. Beneficial effect of organic acids on the orders of reaction

An important feature of the dissolution of forsterite and the orthosilicate minerals is that the rate of reaction increases in the presence of several organic acids and ligands. Grandstaff (1986) found that both EDTA and potassium hydrogen phthalate (KHP) increase the rate of dissolution. The order of reaction with respect to KHP was found to be 0.53. Wogelius and Walther (1991, 1992) reported an order of reaction of 0.45, which is close to the value reported by Grandstaff. The kinetic data presented can be described by the following expression:

\[
\text{rate} = k_0 [H^+]^{0.5} + k_{\text{KHP}}[\text{KHP}]^{0.5} \tag{5}
\]

where \(k_0\) is the rate constant without any KHP, \(k_{\text{KHP}}\) is the rate constant for the KHP reaction and the square brackets represent concentration or activity.

Haenchen et al. (2006) found that citric acid increased the rate of dissolution, and Wogelius and Walther (1991) reported that the rate of dissolution was increased by the presence of ascorbic acid. They reported an order of reaction with respect to ascorbic acid of 0.6.

Olsen and Rimstidt (2008) investigated the effect of oxalate ion on the rate of dissolution of forsterite. Their results at a constant pH are shown in Fig. 5, which is in general agreement with the results of Grandstaff (1986) and Wogelius and Walther (1991, 1992) for KHP and ascorbic acid. Interestingly, Olsen and Rimstidt (2008) investigated the kinetics of reaction in much more detail, and reported that they were affected by the concentrations of both H⁺ and oxalate ions.

Fig. 2. The effect of pH and temperature on the rate of dissolution of forsterite. Data from Rosso and Rimstidt (2000).

Fig. 3. The effect of pH on the rate of dissolution of forsterite, Mg_{1.82}Fe_{0.18}SiO_{4}, at 25 °C. This is a representation of 440 data points analysed. Rimstidt et al. (2012) analysed 637 data points, and reported essentially the same results shown here, that is, there are two regions, one at lower pH with an order of reaction with respect to H⁺ of 0.5 and the other above pH 6 with an order of reaction of 0.25. Data from Pokrovsky and Schott (2000), Rosso and Rimstidt (2000), Wogelius and Walter (1992), Blum and Lasaga (1988), Oelkers (2001a,b), Luce et al. (1972) and Wogelius and Walter (1991).

Fig. 4. The effect of temperature on the rate of dissolution of forsterite. Data from Pokrovsky and Schott (2000b), Rosso and Rimstidt (2000), Oelkers (2001a,b) and Haenchen et al. (2006).
Their experimental results are shown in Fig. 6. They suggested a rate expression of the following form:

\[
\text{rate} = k_H [H^+]^{0.46} + k_{\text{OX}} [\text{OX}]^{0.4} [H^+]^{0.47}
\]

where \(k_{\text{OX}}\) is the rate constant for the reaction with oxalate ions, and \([\text{OX}]\) represents concentration of oxalate ions. Our analysis of the data measured by Olsen and Rimstidt (2008) yields a similar rate expression, except that the orders of reaction are slightly different:

\[
\text{rate} = k_H [H^+]^{0.5} + k_{\text{OX}} [\text{OX}]^{0.5} [H^+]^{0.5}.
\]

1.1.5. Inhibition by dissolved carbon dioxide

Carbon dioxide has been reported to decrease the rate of dissolution of olivine (Wogelius and Walther, 1991). Pokrovsky and Schott (2000a, b) reported the experimental results shown in Fig. 7. The effect of CO2 is to increase the concentration of carbonate ions in solution. It should be noted that Golubev et al. (2005) reported that there is no effect of pCO2 on the rate of dissolution, while Haenchen et al. (2006) showed that the effect of pCO2 might be dependent on the pH.

1.1.6. Inhibition of forsterite by the reaction products, Mg\(^{2+}\) and Si(OH)\(_4\)

Oelkers (2001a,b) measured the rate of dissolution of forsterite as a function of the concentration of MgCl\(_2\) and H\(_4\)SiO\(_4\) in solution. He found that the rate of dissolution was independent of the concentration of MgCl\(_2\) and H\(_4\)SiO\(_4\) in solution in the acidic region. However, Pokrovsky and Schott (2000a,b) found that the concentration of H\(_4\)SiO\(_4\) in solution reduced the rate of dissolution in the alkaline region. The results of Pokrovsky and Schott (2000a,b) are shown in Fig. 8. These results indicate that the rate of dissolution has an order of reaction that is close to \(-0.25\) with respect to dissolved silica.

In the next section we argue that these orders of reaction, be they with respect to H\(^+\), or organic acids, or the inhibition by carbonate ions and reaction products, have not yet been adequately explained.

1.2. Limitations of previously proposed mechanisms of dissolution

A reaction mechanism is the set of elementary steps that correctly describe both the stoichiometry of the overall reaction and the empirically-determined kinetic parameters, primarily the orders of reaction. An elementary reaction step is a single reaction encounter in which the order of reaction for that step reflects the stoichiometry of the step. Particularly challenging is the explanation of orders of reaction that are fractions, like those of leaching and dissolution reactions (Crundwell, 2013). A classic example of one such reaction with...
fractional orders of reaction is the formation of HBr from H₂ and Br₂. A detailed mathematical analysis of the kinetics showed that the reaction proceeded by a chain reaction consisting of several elementary steps (Atkins and de Paulo, 2006). Of course, the problem of fractional orders of reaction cannot be wished away by using fractional stoichiometry.

There are two related models of dissolution that are currently used to interpret the rate of dissolution reactions: (i) the proton-promoted version of the surface-complexation model, and (ii) the precursor-complex version of the surface-complexation model. Each of these models will be discussed next.

1.2. Limitations of the precursor-species model

The precursor-species model proposes the existence of a precursor species that controls the rate of dissolution (Oelkers et al., 1994; Oelkers and Schott, 1995; Brantley, 2008). This precursor species, which is bound to the surface, is in equilibrium with both the reactants and the surface. The precursor species is also in equilibrium with an "activated complex" that breaks down to form the reaction products. Conceptually, this model can be expressed as follows:

\[ \text{surface + aqueous species} \rightleftharpoons \text{precursor} \rightleftharpoons \text{activated complex} \rightleftharpoons \text{products}. \] (9)

In the context of the dissolution of forsterite, this model can be described as follows (Pokrovsky and Schott, 2000a,b). The first step is that in which the surface is protonated with the concomitant release of magnesium:

\[ >\text{Mg}_2\text{SiO}_4(\text{surface}) + 4\text{H}^+(\text{aq}) \rightarrow >4\text{H} \cdot \text{SiO}_4(\text{surface}) + 2\text{Mg}^{2+}. \] (10)

The symbols "\( >\text{Mg}_2\text{SiO}_4(\text{surface}) \)" and "\( >4\text{H} \cdot \text{SiO}_4(\text{surface}) \)" represent the unreacted surface and the protonated surface respectively. This reaction is followed by the critical second step, which is written as follows:

\[ >4\text{H} \cdot \text{SiO}_4(\text{surface}) + n\text{H}^+(\text{aq}) \rightarrow >(4+n)\text{H} \cdot \text{SiO}_4(\text{surface}) \] (11)

The symbol "\( >(4+n)\text{H} \cdot \text{SiO}_4(\text{surface}) \)" represents a surface site or species that has n more protons in addition to the four that are attached in the previous step. Pokrovsky and Schott (2000a,b) propose that the rate of dissolution is proportional to the surface concentration of \( >4\text{H} \cdot \text{SiO}_4(\text{surface}) \) through the formation of a silica dimer, given as \( >\text{Si}_2\text{O}_7^-(\text{H}^+) \).

According to Pokrovsky and Schott (2000a,b), the rate of dissolution can be written as follows:

\[ \text{rate} = k \left( >\text{Si}_2\text{O} \cdot \text{H}^+ \right) \] (12)

where the \( \{ \} \) brackets represent surface concentration or activity, as appropriate, and the designation surface has been omitted to simplify the notation. The surface concentration of \( >\text{Si}_2\text{O} \cdot \text{H}^+ \) is proportional to the surface concentration of the \( >(4+n)\text{H} \cdot \text{SiO}_4(\text{surface}) \) species, so that the rate is given by:

\[ \text{rate} = k \left( >(4+n)\text{H} \cdot \text{SiO}_4 \right) \] (13)

The total concentration of sites on the surface is given by:

\[ \text{C}_T = \{ >\text{Mg}_2\text{SiO}_4 \} + \{ >4\text{H} \cdot \text{SiO}_4 \} + \{ >(4+n)\text{H} \cdot \text{SiO}_4 \}. \] (14)

The equilibrium condition for the initial protonation step, Eq. (10), is given by:

\[ \text{K}_\text{exa} = \frac{\alpha_{\text{Mg}^{2+}}}{\alpha_{\text{H}^+}} \left( >\text{Mg}_2\text{SiO}_4 \right) \] (15)

where \( \alpha_{\text{Mg}^{2+}} \) and \( \alpha_{\text{H}^+} \) represent the solution activities of Mg²⁺ and H⁺, respectively.

The equilibrium condition for the second step, Eq. (11), is given by Pokrovsky and Schott (2000a,b) as:

\[ \text{K}_\text{ads} = \frac{\{ >(4+n)\text{H} \cdot \text{SiO}_4 \}}{\{ >4\text{H} \cdot \text{SiO}_4 \}}. \] (16)

Solving this set of equations, yields the following rate expression:

\[ \text{rate} = \frac{k\text{K}_\text{ads}\alpha_{\text{H}^+}^n}{1 + \text{K}_\text{ads}\alpha_{\text{H}^+}^n + \frac{\alpha_{\text{Mg}^{2+}}}{\alpha_{\text{H}^+}}}. \] (17)

Pokrovsky and Schott (2000a,b) state that the value of \( n \) in Eq. (16) is equal to one-half. However, if this is the case, Eq. (11) is not an elementary step and consequently Eq. (16) is not properly formulated. In other words, if the reaction (Eq. (11)) was an elementary step, then Eqs. (11) and (16) should be written with stoichiometric coefficients that are
whole numbers – in other words the lowest value that n can assume is one, not one half. The assertion of Pokrovsky and Schott (2000a,b) that the value of n is one half effectively means that half a proton reacts with the surface site in the second reaction step, Eq. (11). Clearly, this cannot be true.

An examination of Eq. (11), and the derivation of the mechanism that follows it, shows that Pokrovsky and Schott (2000a,b) have essentially solved the problem of fractional orders of reaction for the dissolution of forsterite by making the stoichiometry fractional. As was mentioned earlier in this section, this violates the concepts of mass action kinetics, molecularity and the notion that a complex reaction is made up of a set of elementary steps. These violated concepts are the foundations of chemical kinetics stretching back to Guldberg and Waage in 1867 (Holland and Anthony, 1979; see also Atkins and De Paula, 2006; Laidler, 1965; and Levenspiel, 1971).

Lasaga (1981) presented a model based on the simultaneous dissociation of both the adsorbed ligand and the adsorption site into two exactly equivalent species. The defence of Eq. (11) by appealing to Lasaga’s model fails, because the derivation by Lasaga requires both the lixiviant and the surface to dissociate into two equal species, which does not occur in Eq. (11). A proton cannot dissociate into two, so this model does not assist. Rosso and Rimstidt (2000) appeal to Lasaga’s model more directly by arguing that water is adsorbed to a silica dimer, and this dissociates as required by Lasaga (1981). However, a water molecule does not dissociate into two equal parts, as required by Lasaga (1981), and consequently this suggestion cannot assist in obtaining orders of reaction that are close to one half.

The precursor formulation of the surface complexation model has been used extensively (Oelkers and Schott, 1995; Hamilton et al., 2001; Schott et al., 2009). In spite of this history, the model is incorrectly formulated, and if formulated correctly would not predict orders of reaction with values that are close to one half with respect to H⁺ ions in solution. The only conclusion that can be drawn is that the correct mechanism of reaction has not yet been identified.

### 1.4. Specific aims of this work

The kinetics of the dissolution of the orthosilicates displays remarkable consistency: the order of reaction, which is the most important of the kinetics parameters, has a value that is close to one-half with respect to H⁺ in the acidic region (Casey and Sposito, 1992; Casey and Westrich, 1992). Other models of dissolution that have been proposed, such as the surface-complexation model and the precursor-species model, do not provide a clear and creditable explanation for this remarkable consistency. Therefore, the specific aim of this work is to provide a novel mechanism that can describe the orders of reaction, the surface potential and the activation energies. A particular challenge for this work is the observation that the order of reaction of forsterite changes at a pH of about 6, which the proposed mechanism meets. In addition, the theory is extended to account for the effect of reaction products, organic ligands and dissolved carbon dioxide.

In order to explain the change in the order of reaction at a pH of about 6, the order of reaction with respect to organic acids, carbonate ions and reaction products, a new theory of dissolution developed by Crundwell (Accepted for publication, 2014a, 2014b) is used. This theory has origins in the work of Vermilyea (1966) and Crundwell and Verbaan (1987). However, a subtle but significant modification is made to that approach, which is discussed on presentation of the theory in Section 3.

### 1.5. Structure of this paper

The paper is structured in the following manner. The structure of the solid–liquid interface is discussed in the next section. Following this, the proposed mechanism of dissolution is presented and shown to describe all of the features of the reaction discussed in Section 1.1. It is then shown that the core proposal of the theory that the dissolution reactions control the charging of the surface is supported by the measurements of the zeta potential made by Pokrovsky and Schott (2000a). The implications of the theory for relating the rates of dissolution across different minerals in the orthosilicate group are then discussed.

### 2. Structure of the solid–solution interface

The surface of the mineral is charged, due to the termination of bonds at the surface and the adsorption of charged species from the solution onto the surface (Morrison, 1980). This charge is distributed across a region close to the surface in the solid and in the solution. The region of most interest is that between the solid surface and the distance of closest approach of solution species. This region is called the Helmholtz layer, and is illustrated in Fig. 9 for the forsterite surface.

There are two sites for adsorption by ions in solution. The first is called non-specific adsorption in which ions from the solution interact with the surface by electrostatic forces (Bard and Faulkner, 1980). Non-specific adsorption occurs at the outer-Helmholtz plane (OHP), as shown in Fig. 9. However, some ions might also adsorb at the inner Helmholtz plane (IHP), also shown in Fig. 9. Such adsorption is called specific adsorption, and occurs when there is a strong interaction...
between the surface and the adsorbed ion. The difference between non-specific adsorption and specific adsorption is analogous to outer-sphere and inner-sphere complexes in aqueous solutions (Bard and Faulkner, 1980).

The electric potential at the interface changes dramatically between the solid and the solution, as shown in Fig. 10. This change in electrical potential occurs primarily across the Helmholtz layer, resulting in a region of high field strength because this layer is so narrow, at most only a few water molecules thick (Bockris and Reddy, 1970).

As a result of this high field strength, the potential difference across the Helmholtz layer has a dramatic effect on the dissolution behaviour of minerals chiefly because dissolution involves the transfer of charge across this layer (Vermilyea, 1966; Bockris and Reddy, 1970; Morrison, 1980). It is the effect of this potential difference across the Helmholtz layer on the kinetics of dissolution that we wish to incorporate in our theory of the dissolution of the orthosilicates. The proposed mechanism of dissolution is discussed next.

3. The proposed mechanism of dissolution of fosterite

3.1. Removal of magnesium from the surface of forsterite

Dissolution involves breaking of bonds with the solid phase, the formation of bonds with the aqueous phase and the concomitant movement of the departing species across the Helmholtz layer. Consider, for example, magnesium on the surface of an orthosilicate mineral, illustrated in Fig. 11. The magnesium at the surface is in thermal motion, which stretches the bonds between the magnesium and the surface oxygen atoms. As these bonds stretch, they become weaker. At the same time, the bonds between the magnesium and water molecules in solution strengthen. The activated state for the removal of magnesium lies between the states of magnesium secure on the surface and magnesium hydrated in solution. Because the reaction coordinate is confined between the surface and the outer Helmholtz plane, the activated state occurs at close to the midpoint of the Helmholtz layer, as shown in Fig. 12.

This reaction, in which the magnesium leaves the surface, can be represented as follows:

\[
\text{Mg}_{\text{lat}} + w\text{H}_2\text{O} \rightarrow \text{Mg}^{2+}(aq) + w^2-
\]

where \(w\) is the stoichiometric coefficient for water in the rate-determining step, the symbol \(\text{Mg}_{\text{lat}}\) represents magnesium in a lattice position on the surface, and \(w^2-\) represents the excess charge on the surface that results from the departure of magnesium from the surface of the solid.

The rate of reaction is given by the transition-state theory as follows (Bard and Faulkner, 1980; Bockris and Reddy, 1970; Miller et al., 1995):

\[
\text{rate} = \kappa \frac{k_B T}{h} [\text{Mg}_{\text{lat}}] [\text{H}_2\text{O}]^w \exp\left(-\frac{\Delta G^\#}{RT}\right)
\]

where \(\kappa\) is the transmission coefficient, \(k_B\) represents Boltzmann’s constant, \(h\) is Planck’s constant, \(R\) is the gas constant, \(T\) is the temperature, and \(\Delta G^\#\) is the free energy for the formation of the activated complex. The symbol \([\text{Mg}_{\text{lat}}]\) represents the surface concentration of lattice sites that participate in the reaction and \([\text{H}_2\text{O}]\) represents the activity of water at the outer Helmholtz plane, which is the same as in the bulk solution.

The rate of removal of magnesium from the surface of forsterite to the solution involves the breaking of the bond with the surface, the formation of a solvation sheath around the ion, and the transfer of the ion to the outer Helmholtz plane, all under the influence of the potential difference across the Helmholtz plane. The effect of potential on the free energy of activation can be expressed as follows (Gerischer, 1970;...

Fig. 11. The removal of magnesium from a position at the surface to a position at the outer Helmholtz plane (which is equivalent to the bulk solution since there are no long range concentration gradients): (a) surface magnesium and water before reaction; (b) the breaking bond with the surface, represented by the dotted arrow, and the formation of the bond with water; (c) the magnesium ion at the outer Helmholtz plane (i.e., in solution) and the excess charge on the surface after the reaction.
\[ \Delta G^\# = \Delta G^\#_{\text{fi}} - \alpha \cdot F \Delta \phi \]  

where the first term on the right-hand side, \( \Delta G^\#_{\text{fi}} \), is the free energy for the chemical component, and the second term is the effect of the change in potential on the free energy of the activated complex. The symbol \( \alpha \) is referred to as the transfer coefficient for the removal of the magnesium, and is expected to have a value close to 0.5, say 0.5 ± 0.1.

An argument for choosing a value of 0.5 for \( \alpha \) is that the activated complex occurs close to the midpoint of the Helmholtz layer (Bard and Faulkner, 1980; Bockris and Reddy, 1970; Miller et al., 1995; Morrison, 1980). The transfer coefficient is also referred to as the symmetry factor, reflecting the symmetrical position of the activated complex in the geometry of the Helmholtz layer, and the symmetry with respect to the reverse reaction.

The substitution of Eq. (20) into Eq. (19) yields the following expression (Marcus, 1964; Gerischer, 1970; Morrison, 1980; Miller et al., 1995; Schmickler, 1995):

\[ \text{rate} = k_\text{fi} \cdot \frac{[\text{H}_2\text{O}]^n}{[\text{Mg$_{\text{lat}}$}]^m} \exp \left( \frac{-\Delta G^\#_{\text{fi}}}{RT} \right) \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right) \]  

By collecting the constant terms together, we get the following form of the rate expression for the removal of a magnesium from the silicate surface:

\[ r_+ = \bar{v}_+ \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right) \]  

The symbol \( \bar{v}_+ \) represents the forward rate constant for the formation of \( \text{Mg}^{2+} \) in solution. The subscript ‘+’ refers to the process that results in the formation of cations in solution.

It is emphasized that at no point in this derivation was it assumed that the surface is metallic or an electrical conductor. Eq. (22) and a similar expression for the removal of silicate ions from the surface form the underlying basis for the development of the kinetic mechanism (compare this with that of Engell (1956) and Vermilyea (1966) for the dissolution of ionic solids). The mechanism of dissolution is developed in the next section.

### 3.2. Mechanism of dissolution of forsterite in the acidic region

The bonds between magnesium and oxygen are significantly weaker than the bonds between silicon and oxygen. Huggins and Sun (1946) estimated the silicon–oxygen bond energy to be about 13 100 kJ/mol, while the magnesium–oxygen bond energy is only about 3816 kJ/mol. This suggests that bonds that are most likely to break during the dissolution of forsterite are the magnesium–oxygen bonds. This implies that the silicate groups, \( \text{SiO}_4^{4-} \), are removed intact from the surface. Therefore, it is proposed that dissolution occurs by the removal of magnesium and silicate groups from the surface.

The reaction is dependent on protons, or \( \text{H}^+ \) ions. It is proposed that \( \text{H}^+ \) ions form an activated complex with the silicate groups as the silicate groups are removed from the surface. Water molecules form an activated complex with magnesium as it is removed from the surface. The rate of removal of both the magnesium and the silicate groups is dependent on the potential difference across the Helmholtz layer, as shown by the derivation of Eq. (22).

The envisaged mechanism of the dissolution of forsterite and other orthosilicate minerals is illustrated schematically in Fig. 13. \( \text{H}^+ \) ions at the outer Helmholtz plane react with silicate groups on the surface, and water molecules react with the magnesium on the surface. The concentration of \( \text{H}^+ \) ions at the outer Helmholtz plane is the same as that in the bulk solution if the concentration of background electrolyte is sufficiently high so that the potential drop across the diffuse layer in solution is small. The position of the \( \text{H}^+ \) ions is important, as this has implications for the change in order of reaction that is considered later.

The silicate groups in the surface structure react with \( \text{H}^+ \) ions at the outer Helmholtz plane (which has the same concentration as the bulk solution):

\[ \text{SiO}_4^{4-} + t\text{H}^+ \rightarrow \text{H}_2\text{SiO}_4^{t-4} (aq) + \text{Mg}^{4+} \]  

where \( \text{SiO}_4^{t-4} \) represents the silicate groups on the surface, \( t \) represents the excess positive charge left due to the departure of the silicate group, and \( t \) represents the number of \( \text{H}^+ \) ions participating in the rate-determining step.

The rate of this reaction is given by:

\[ r_- = \bar{v}_- \left[ \text{H}^+ \right]^t \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right) \]  

where the subscript ‘−’ refers to the silicate groups. The symbol \( t \) represents the number of \( \text{H}^+ \) ions that form an activated complex with the silicate groups.

The rate of removal of magnesium must be half the rate of the removal of silicate by stoichiometry, because the dissolution reaction is congruent and stoichiometric.

\[ r_- = \frac{r_+}{2} \]  

This relationship can be used to obtain the following expression by substituting Eqs. (22) and (24) into Eq. (25):

\[ \bar{v}_- \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right) = 2 \bar{v}_- \left[ \text{H}^+ \right]^t \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right). \]
By solving this expression for $\Delta \phi$, the change in potential difference across the Helmholtz layer, we get the expression:

$$\Delta \phi = \frac{RT}{F(\alpha_+ + \alpha_-)} \ln \left( \frac{2 \bar{\nu}_+ [H^+]^x}{2 \bar{\nu}_- [H^+]^{x-1}} \right). \tag{27}$$

The substitution of Eq. (27) back into Eq. (22) results in the following expression:

$$r = \left( \bar{\nu}_- \right)^{1-x} \left( 2 \bar{\nu}_- \right)^x [H^+]^x \tag{28}$$

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

$$r = k_{rl} [H^+]^x \tag{29}$$

where $k_{rl} = \left( \bar{\nu}_- \right)^{1-x} \left( 2 \bar{\nu}_- \right)^x$.

The values of the transfer coefficients are 0.5 ± 0.1 (as discussed earlier), so the value of $x$ is 0.5 ± 0.1. If the silicate group reacts with only one proton in the rate-determining step, then the value of $x$ is equal to one. The substitution of these values into Eq. (29) gives the following rate expression:

$$r = k_{rl} [H^+]^{0.5} \tag{30}$$

This rate expression agrees with the experimental results for forsterite in the acidic region, as shown in Fig. 1. The proposed mechanism is also in agreement with the orders of reaction presented for other orthosilicates presented in Table 1.

In the next section, the rate of dissolution at values of pH greater than 6 is considered.

3.3. Mechanism of dissolution of forsterite in the pH region above a value of 6

The starting point of this section is the ansatz that the $H^+$ ions are adsorbed specifically at the inner Helmholtz plane. An expression is derived for the adsorption isotherm of $H^+$ ions at the inner Helmholtz plane, and this isotherm is used to derive an expression for the rate of dissolution.

Ions at the outer Helmholtz plane are at the same concentration as the bulk solution; they are non-specifically adsorbed, and are not described by an isotherm. Ions at the inner Helmholtz plane are specifically adsorbed onto the surface, and are described by an adsorption isotherm.

Consider the adsorption of $H^+$ ions at the inner Helmholtz plane, as shown as step (a) in Fig. 14. This adsorption reaction is given as follows:

$$\circ + H^+ = \bullet H^+ \tag{31}$$

The symbol $\circ$ represents an available or unoccupied site, and $\bullet H^+$ represents an occupied site on the silicate group at the inner Helmholtz plane. The proportion of the total surface that is occupied by $\bullet H^+$ is given by $\theta$. The rate of the adsorption and desorption from the surface of $H^+$ ions is dependent on the change in potential difference across the Helmholtz layer. The net rate of adsorption is given by the following expression:

$$r_{ads} = k_{ads} [H^+] \times (1 - \theta) \exp(\alpha_{ads} F \Delta \phi / RT) - k_{ads} \theta \exp(-1 - \alpha_{ads}) F \Delta \phi / RT \tag{32}$$

If the adsorption and desorption of $H^+$ is much faster than dissolution, then the rate of adsorption and desorption of $H^+$ is close to zero. By setting the left-hand side of Eq. (32) to zero, we can derive the following expression for $\theta$:

$$\theta = \frac{k_{ads} [H^+]}{k_{ads} [H^+] + k_{ads} \exp(F \Delta \phi / RT)}. \tag{33}$$

The rate of removal of the silicate group, together with the reacting $H^+$ ion, is dependent on the coverage of surface by the adsorbed proton. The rate expression is given as follows:

$$r_- = \tilde{\nu}_- \theta \exp(-\alpha_F \Delta \phi / RT) \tag{34}$$

where $\alpha_F$ is the charge transfer coefficient for the transferring $HSiO_4^{2-}$ group across the Helmholtz layer.

By combining Eqs. (33) and (34) and assuming that the surface coverage of specifically adsorbed protons is low so that $k_{ads} [H^+]$ is much less than $k_{ads} \exp(F \Delta \phi / RT)$ in Eq. (33), we get the following expression for the rate of removal of the silicate group from the surface:

$$r_- = \tilde{\nu}_- \frac{k_{ads}}{k_{ads} \exp(F \Delta \phi / RT)} \exp(-\alpha_F - 1) \times \exp(-\alpha_F - 1) \frac{F \Delta \phi / RT)}{RT}) \tag{35}$$

The rate of removal of the magnesium and the silicate groups is related by stoichiometry (because dissolution is congruent and stoichiometric), so that

$$r_- = \frac{r_-}{2}. \tag{36}$$
By substituting Eqs. (22) and (35) into Eq. (36), we derive the following expression for $\Delta \phi$:

$$\Delta \phi = \frac{RT}{F(\alpha_+ + \alpha_+ + 1)} \ln \left( \frac{k_{ads}}{k_{-ads}} \right)$$

(37)

Substituting this expression back into Eq. (22), we derive the final rate expression for the dissolution of forsterite in the more alkaline region:

$$r = k_1 [H^+]^{\alpha}$$

(38)

where $y = \alpha_+/(\alpha_+ + \alpha_+ + 1)$, and $k_1 = (\bar{\kappa}_+)^{\alpha_+} (\bar{\kappa}_- k_{ads}/k_{-ads})^{\alpha}$.

The values of the transfer coefficients are expected to be $0.5 \pm 0.1$. This means that the value of $y$ is 0.25. If only one H$^+$ ion forms an activated complex in the rate-determining step, then the value of $t$ is one. This means that the overall order of reaction is 0.25, as follows:

$$r = k_2 [H^+]^{0.25}$$

(39)

This expression derived from the proposed mechanism of dissolution is in agreement with the experimental results above a pH value of about 6, as shown in Figs. 3 and 4, and expressed mathematically in Eq. (4). As the concentration of H$^+$ in solution decreases, the rate of the reaction with protons giving rise to Eq. (30) diminishes. However, protons, even in low concentrations, continue to react with the surface at the inner Helmholtz plane, and Eq. (39) prevails.

3.4. Overall mechanism of dissolution of forsterite

The overall rate of dissolution is given as follows:

(i) $r = k_1 [H^+]^{0.5}$ for pH < 6

(ii) $r = k_2 [H^+]^{0.25}$ for pH > 6.

(40)

The fit of this mechanism to the experimental data is shown in Fig. 3. The values of $k_{H^+}$ and $k_1$ are $2.0 \times 10^{-7} \text{ mol/m}^2/\text{s}/(\text{mol/l})^{0.5}$ and $6.25 \times 10^{-9} \text{ mol/m}^2/\text{s}/(\text{mol/l})^{0.25}$, respectively. Clearly, the proposed mechanism is in agreement with the experimental data.

Therefore, the mechanism of dissolution of the orthosilicates proposed here describes the change in order of reaction with respect to H$^+$ from 0.5 to 0.25. None of the previously proposed models account for the order of reaction of 0.5 with respect to H$^+$ below pH 6, nor do they account for the change in the order of reaction from 0.5 to 0.25 as the pH increases above 6. Since orders of reaction are the key parameters in determining the mechanism of reaction, this agreement between the experimental results and the proposed mechanism is powerful evidence in favour of the proposed mechanism.

3.5. Effect of organic acids on the rate of dissolution

The effect of different acids and possibly different anions in solution is also clearly explained by the proposed theory. The anion forms an activated complex with magnesium in the removal of the metal from the surface. As a result, Eq. (22) is modified as follows:

$$r_+ = \bar{\kappa}_+ [A^-]^t \exp \left( \frac{\alpha F \Delta \phi}{RT} \right)$$

(41)

where $[A^-]$ represents the concentration of the organic anion $A^-$ in solution, and $s$ is the number of organic anions forming the activated complex with magnesium. The other symbols retain their previous meaning.

The use of Eq. (41) in the derivation leads to the following expression:

$$r = k_4 [H^+]^{y} [A^-]^{(1-y)t}$$

(42)

The value of $x$ is 0.5 and $t$ is 1.0, as before. If one organic molecule forms an activated state, then the value of $s$ is 1.0. Therefore, the rate of dissolution is given by:

$$r = k_4 [H^+]^{0.5} [A^-]^{0.5}$$

(43)

This expression shows that the mechanism predicts that the rate of dissolution is one-half order in organic ion. This is in agreement with the results of Grandstaff (1986) and Wogelius and Walther (1991, 1992) for KHP and ascorbic acid. More importantly, Olsen and Rimstidt (2008) showed that the rate of dissolution is dependent on both the H$^+$ ions and the oxalate ions, both with an order of reaction of 0.5. The mechanism proposed here is therefore in agreement with their results as shown in Fig. 6.

The overall rate of dissolution is a combination of Eqs. (42) and (45) in the acidic region:

$$r = k_4 [H^+]^{0.5} + k_4 [H^+]^{0.5} [A^-]^{0.5}$$

(44)

The value of $k_{H^+}$ is $2.0 \times 10^{-7} \text{ mol/m}^2/\text{s}/(\text{mol/l})^{0.5}$ as before, and $k_4$ is $1.41 \times 10^{-6} \text{ mol/m}^2/\text{s}/(\text{mol/l})$.

Eq. (44), representing the proposed mechanism, is in agreement with the empirically-determined Eq. (6). It is important to note that the proposed mechanism provides not only the correct orders of reaction, but also the same functional form as that determined by Olsen and Rimstidt (2008). Therefore, the proposed mechanism successfully describes the effect of organic anions on the rate of dissolution.

3.6. Effect of carbon dioxide and carbonate ions

The effect of increasing the partial pressure of carbon dioxide is to increase the concentration of carbonate ions in solution. Increased concentrations of carbonate ions retard the overall rate of dissolution, as shown in Fig. 7. We propose that the effect of carbonate ions is to block or retard the departure of magnesium from the surface of the reacting solid by adsorbing to magnesium sites. The rate of this reaction is given by:

$$r_c = k_c [CO_3^{2-}] (1 - \theta_c) - k_c \theta_c$$

(45)

where $\theta_c$ is the fraction of magnesium sites occupied by carbonate ions, $[CO_3^{2-}]$ is the concentration or activity of the carbonate ions, and $k_c$ and $k_c$ are the forward and backward rate constants respectively.

If this reaction is fast relative to the other reactions, then $r_c$ is approximately zero, and we get the following expression for the fraction of magnesium sites occupied by carbonate ions:

$$\theta = \frac{k_c}{k_c [CO_3^{2-}] + k_c}$$

(46)

Now the rate of the departure of magnesium from the surface is given by:

$$r_c = k_c (1 - \theta_c) \exp \left( \frac{\alpha F \Delta \phi}{RT} \right)$$

(47)
Combining this with Eqs. (35) and (36), we get the following expression:

$$r = k_1 \left( \frac{[H^+]^{0.25}}{1 + K_C [CO_2^-]} \right)$$

where \( k_1 \) is as defined before and \( K_C \) is given by \( \bar{k}_c / k_c \).

The correspondence between the proposed mechanism given by Eq. (48) using the value of \( k_0 \) of 6.25 \times 10^{-9} \text{ mol/m}^2 \text{s}/(\text{mol/L})^{0.25} \) obtained earlier and the value of \( K' \) of 2000 was shown in Fig. 7 as the model line. The data measured by Pokrovsky and Schott (2000a,b) shown as points. The comparison of theory and data presented in Fig. 7 suggested that proposed mechanism is a good description of the effect of carbonate ions.

3.7. The effect of the activity of water

Olsen (2007) measured the effect of different salts on the rate of dissolution of forsterite in 82 experiments. The effects of Mg\(^{2+}\), SO\(_4^{2-}\), pH, ionic strength, and water activity were investigated. From the detailed statistical analysis of the tests, Olsen (2007) concluded that the concentrations of Mg\(^{2+}\) and SO\(_4^{2-}\) and the ionic strength did not influence the rate of dissolution. However, the water activity, which does not change dramatically under the conditions studied, did influence the rate of dissolution. The rate was described by the following empirical equation in the pH region 1–4:

$$\text{rate} = 1.55 \times 10^{-7} [H^+]^{0.52} [H_2O]^3 \Delta \phi$$

where \([H^+]\) is the concentration of activity of H\(^+\), as before, and [H\(_2\)O] is the activity of water.

The water activity does not vary significantly over the range of conditions for the experiments that have been performed to date. However, one of the principal propositions of the proposed mechanism is that magnesium reacts with water, as shown in Eq. (18). If the activity of water is not considered constant, then Eq. (22) can be re-written from Eq. (21) as:

$$r_+ = \bar{k}_+ [H_2O]^\theta \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right).$$

Using Eq. (50) rather than Eq. (22) in the derivation, we get the following expanded version of Eq. (29):

$$r = k_1 [H^+]^{1/2} [H_2O]^{-1/3} \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right).$$

Since \( x \) is 0.5 and \( t \) is one, as before, the value of \( w \) that is required to agree with Olsen’s (2007) work is six. This value of six seems justified, since it agrees with the coordination number of water molecules in the Mg\(^{2+}\) aqua-ion. Thus, the rate of dissolution is given by:

$$r = k_1 [H^+]^{0.5} [H_2O]^3 \exp \left( \frac{\alpha \cdot F \Delta \phi}{RT} \right).$$

Thus, the proposed mechanism agrees with the empirically determined result, given by Eq. (49). It is again important to note that the proposed mechanism provides not only the correct orders of reaction, but also the same functional form as that determined statistically by Olsen (2007).

3.8. Rate of dissolution at conditions close to equilibrium

Up to this point, the discussion has focused on the forward reaction, in other words, on the dissolution reaction far from equilibrium. In this section, attention is turned to conditions that retard the dissolution reaction because equilibrium conditions are approached.

Limited data is available on the effect of the concentrations of silica and magnesium in solution on the rate of dissolution. Oelkers (2001a, b) found that there was no effect of the concentration of either magnesium or silica on the rate of dissolution at a pH of 2. Pokrovsky and Schott (2000a,b) studied the dissolution kinetics at a pH of 9, where the rate of dissolution is much slower. In this region, they found that only silica affects the rate, as shown in Fig. 8.

As with the forward reaction, we treat the reverse reaction as two coupled steps. The net rate of dissolution of magnesium is given by:

$$r = \bar{k}_- \exp(-\alpha \cdot F \Delta \phi/RT) - \bar{k}_+ \left[ Mg^{2+} \right] \exp \left( 1 - \alpha \cdot F \Delta \phi/RT \right).$$

The net rate of dissolution of silicate is given by:

$$r_- = \bar{k}_- \exp(-\alpha \cdot F \Delta \phi/RT) - \bar{k}_- \left[ SiO_4^{2-} \right] \exp \left( 1 - \alpha \cdot F \Delta \phi/RT \right).$$

In both Eqs. (55) and (56), \( \bar{k} \) represents the forward reaction and \( \bar{k} \) represents the reverse reaction. Since the experimental results presented by both Oelkers (2001a,b) and Pokrovsky and Schott (2000a,b) indicate that the concentration of magnesium in solution does not affect the rate of dissolution, the second term on the right-hand side of Eq. (55) small compared to the left-hand side. Since the rate of removal of cations is in stoichiometric proportion to the rate of removal of anions by Eq. (38), we get the following expression:

$$r_+ \exp(\alpha \cdot F \Delta \phi/RT) = r_- \exp(-\alpha \cdot F \Delta \phi/RT)$$

Using Eq. (33) for \( \theta \) (together with our previous approximation that \( k_{ads}[H^+] \) is much less than \( k_{ads} \exp(F \Delta \phi/RT) \) so that \( 1 - \theta \) is approximately equal to one, and that assumption that the values of \( \alpha \) and \( \alpha_+ \) are close to 0.5), we get the following expression for the potential across the double layer:

$$\Delta \phi = \frac{RT}{2F} \ln \left( \frac{\bar{k}_+ [H^+]}{\bar{k}_- [SiO_4^{2-}]^{-1}} \right).$$

Finally, by substituting this Eq. (56) into Eq. (22), we get an expression for the effect of silica on the rate of dissolution:

$$r = \left( \frac{\bar{k}_+ [H^+]}{\bar{k}_+ [SiO_4^{2-}]^{-1}} \right)^{0.25}$$

This result indicates that the mechanism predicts that the rate of dissolution should have an order of reaction of \(-0.25\) with respect to dissolved silica when \( \bar{k}_- [SiO_4^{2-}]^{-1} \) is much greater than \( \bar{k}_+ \). This is in agreement with the results presented in Fig. 8.

It is important to note that Eq. (57) is not an equilibrium expression, but rather represents the partial equilibrium for silicate removal. Olsen (2007) investigated the effect of Mg\(^{2+}\) up to 4 mol/L, and found that there is no effect of Mg\(^{2+}\) on the rate of dissolution. This suggests that forsterite does not reach true equilibrium at these conditions.

The concept of partial equilibrium is novel and significant. It is possible that many of the dissolution experiments conducted at close to equilibrium conditions might not necessarily be approaching equilibriu, but approaching partial equilibrium.

4. Comparison of the measured surface potential and the theoretical prediction

The interface between the solid and solution is charged. It is universally envisaged that the surface hydroxyl group participates in the hydrolytic reactions that results in the charging of the surface (Healy...
and White, 1978; Duval et al., 2001; Duval et al., 2002). Almost all of the work on the origin of the surface potential of silicates and oxides has assumed that the surfaces are inert (that is, no dissolution) and that only the hydrolytic reactions determine surface charge. These assumptions have been applied to reacting systems without any modification (see, for example, Pokrovsky and Schott, 2000a).

However, the assumption that dissolution does not affect the surface potential or charge cannot be easily defended, because measurements of the surface potential show that the dissolution directly affects the potential difference across the interface. Holmes and Crundwell (2000) demonstrated that the surface potential of pyrite is not dependent on these adsorption reactions but on the mixed potential (Wagner and Traud, 1938), a result of the dissolution reactions occurring on the surface. Similar results have been reported for numerous minerals, such as UO2 (Nicol et al., 1975) and chalcopyrite (Jones and Peters, 1976). Thus, charging of the surface during dissolution is not only a result of hydrolytic adsorption, but must also include the effect of the dissolution reactions themselves.

The zeta potential is a useful measure of the surface potential of insulating minerals. The zeta potential, the potential at the outer Helmholtz plane, is commonly assumed to be the potential at the hydrodynamic shear plane, is commonly assumed to be the potential at the outer Helmholtz plane, $\psi_{ohp}$, measure with respect to the suitable reference, like the potential in the bulk solution (Healy and White, 1978). However, the theory proposed here is dependent on the potential difference across the Helmholtz layer, $\Delta \psi_{ohp}$, which is the difference between the potential at the surface and the potential at the outer Helmholtz plane. Nonetheless, the zeta potential should reflect the changes in potential at about the same value of the pH that the change in the order of reaction with respect to $H^+$ occurs. A comparison of Eqs. (27) and (37) indicates that the proposed theory predicts a change in the slope of the potential difference across the Helmholtz layer, $\Delta \psi_{ohp}$, at the same point that a change in the order of reaction with respect to $H^+$ occurs. In particular, the slope should decrease by a factor of two. This predicted change in slope should be measurable as a change in slope of the plot of the zeta potential against the pH, even though the zeta potential, $\psi_{ohp}$, is not the potential difference, $\Delta \psi_{ohp}$.

The zeta potential of forsterite is plotted against the pH in Fig. 15 for acid-treated forsterite with a background electrolyte consisting of 0.01 M NaCl (Pokrovsky and Schott, 2000a). These results show that the slope of the zeta potential halves at a pH of 5.6 as the pH increases. This is exactly as predicted by the proposed theory. The results shown in Fig. 15 demonstrate that the surface is charged, not by adsorption events, but by dissolution reactions. This result is powerful evidence in favour of the proposed theory.

The importance of this result cannot be emphasized sufficiently. For example, if it assumed that the surface charge and potential are dependent only on adsorption, then one might be able to argue that the activation energy should also be dependent on pH. Such a line of argument was pursued by Casey and Sposito (1992). Because it has been found that there is no dependence of the activation energy on pH (see the temperature dependence in Fig. 4 for example), researchers have abandoned models of dissolution that are dependent on surface potential. However, rejection of the proposed theory based on the false assumption that the surface potential is only dependent on hydrolytic adsorption is incorrect. This work has clearly shown that it is the dissolution reactions themselves that determine the surface potential.

### 5. Activation energy

The effect of temperature was shown in Fig. 4. Rimstidt et al. (2012) analysed the data for the dissolution of forsterite and found that the activation energy for the region below pH 5.6 is 70.5 kJ/mol. In the region above pH of 5.6, they found that the activation energy is 66.3 kJ/mol. These two values are very close together, which suggests that the same basic mechanism applies. As argued in Section 3, the proposed mechanism of dissolution is the similar for both regions; the difference between the regions is the positioning of the reacting $H^+$ ion.

The activation energy below pH 5.6 is a combination of the activation energies for each of the partial reactions. From the definition of $k_f$ in Eq. (29), the overall activation energy is given by a combination of the activation energies of cation and anion partial reactions, expressed as follows:

$$E_a = (1-x) \Delta H^\text{c} + x \Delta H^\text{a}$$

where $x$ is the fraction of the overall reaction that is due to cationic (or anionic) dissolution, $\Delta H^\text{c}$ and $\Delta H^\text{a}$ are the activation energies for the proton adsorption and desorption reactions, respectively.

**Fig. 15.** The effect of the pH on the zeta potential of acid-treated forsterite. Data from Pokrovsky and Schott (2000a).

Since the value of $x$ is close to 0.5 and $y$ close to 0.25, it is expected that there will be a slight difference in the activation energy of
dissolution in the different ranges. The values of $\Delta H^r$ and $\Delta H^\circ$ are expected be in the range of 48 to 96 kJ/mol (Miller et al., 1995). Thus, the activation energy for the overall reaction lies in this region.

It should be clear from this analysis that the theory presented here and by Crundwell (Accepted for publication, 2014a, 2014b) does not anticipate that the activation energy is dependent on the pH of the solution. This is in line with the experimental data; both the data and the proposed theory provide no support for the proposition by Casey and Sposito (1992) that the activation energy is dependent on the pH of the solution.

6. Breaking of bonds during dissolution

The mechanism presented here envisages that the silicate ions remain intact. This implies that metal–oxygen bonds are broken rather than the silicon–oxygen bond. If this is the case, there should be a strong relationship between the rate of dissolution of the orthosilicates and the rates of other reactions that are similarly dependent on the breaking of the metal–oxygen bond. Indeed, several correlations between metal–oxygen bonds and the rate of dissolution of various orthosilicates have been noted: (i) between the rates of dissolution of the orthosilicate and the corresponding metal oxide (Casey, 1991; Casey and Sposito, 1992; Casey and Westrich, 1992), (ii) between the rate of dissolution and the corresponding metal oxide (Velbel, 1999), and (iii) between the rate of dissolution of the orthosilicate and the exchange rate of water in the inner sphere of the corresponding aqua-ion (Casey, 1991; Casey and Sposito, 1992; Casey and Westrich, 1992).

The first of these correlations, in which there is a similarity in the order of reactivity of the orthosilicates and metal oxides, is shown in Fig. 16. This correlation suggests that the mechanism of dissolution of the orthosilicates and the metal oxides has a similar rate-determining step, and that this step is dependent on the bonding between the metal and the oxygen in both structures. Indeed, we propose that the mechanism of these two classes of minerals occurs by the same mechanism presented here (see Crundwell, Accepted for publication-a,b,c).

The close correspondence of the results shown in Fig. 16 provides weight to the proposal that the silicate groups are removed intact.

The correlation between the rate of dissolution and the estimates of the lattice strength is shown in Figs. 17 and 18. The rates of dissolution are plotted against the bond energies estimated by Huggins and Sun (1946) in Fig. 17. This figure indicates that there is a general trend that indicates that the stronger the metal–oxygen bond strength, the lower the rate of dissolution. Another measure of the bond strength is the lattice energy, which is the energy required to completely dissociate the mineral. Westrich et al. (1993) and Velbel (1999) examined the effect of lattice energy (or M-site potential) on the rate of dissolution, and presented results similar to those presented in Fig. 18. The minerals Zn$_2$SiO$_4$ and Be$_2$SiO$_4$ on this figure have the phenakite structure in which the metal atom is four-coordinated. The other minerals are of the olivine structure, in which the metal atom is six-coordinated. This correlation does seem to add weight to the contention that it is the metal–oxygen bond that preferentially breaks. (The correlation that the bond strength influences the rate of dissolution also resonates with general experience in dissolution studies that crystalline solids react more slowly than glassy material of the same chemical composition.)

The proposed mechanism envisages that the magnesium (for forsterite, or the metal component for any of the other orthosilicates) forms an activated complex with water molecules (see Eqs. (18)). Consequently, a correlation between the rates of dissolution and the water–metal bond might be expected. A measure of the water–metal bonding is the rate of exchange of water molecules between the inner coordination sphere of the aqua-ion and the bulk of the water. The correlation between the rate of dissolution and the corresponding rate of water exchange for the aqua-ions is shown in Fig. 19 (Casey, 1991; Casey and Sposito, 1992; Casey and Westrich, 1992). The mechanism
proposed in this paper provides a direct explanation for the correlation shown in Fig. 19: the metal species at the surface reacts directly with water to form aqua-complexes, which is supported by the observations concerning the effect of water activity on the rate of dissolution (see Section 3.7).

As striking as the correlation presented in Fig. 19 is, Nicol (2014) has presented a similar correlation between the exchange current densities for divalent base metals and the rate of water exchange in the corresponding aqua-ion. The exchange current density is related to the rate of the anodic dissolution and cathodic deposition of the particular metal. Nicol’s (2014) correlation is a fascinating result that contains the tantalizing suggestion that the rate of dissolution of the silicates and oxides, through Eqs. (22) and (24), might have a similar rate-determining step to the electrochemical dissolution and deposition of a metal. Clearly, this is an avenue for research in the future.

In the proposed model, the rate of dissolution is also dependent on the potential difference across the Helmholtz layer. It is by accounting for the effect of the potential difference that allows us to derive the expressions for the orders of reaction and the surface potential that are in agreement with the experimental results. Thus the potential difference is the important factor not accounted for by previous models of dissolution mentioned in the introduction. Interestingly, even modelling techniques as sophisticated as ab initio quantum mechanical calculations and Monte Carlo simulations fail to include the effects of the potential difference across the Helmholtz layer on bond breaking and charge transfer (Lasaga, 1995).

Thus, the discussion here points to the importance of three complex phenomena that are incorporated in the theoretical expressions given by Eqs. (22), (50) and (24): (i) the rate is dependent on the interfacial potential difference, represented by \( \Delta \psi \); (ii) the rate is dependent on bond strength, represented by \( k_w \) and \( k_\delta \); and, (iii) rate is dependent on solvation, represented by the term \( [H_2O]^w \).

7. Conclusions

The mechanism of dissolution developed here accounts for data of over 768 dissolution experiments that investigated the effects of pH, Mg\(^{2+}\), SO\(_4^{2-}\), organic acids, carbonate ions, ionic strength, water activity and temperature. Unlike previously proposed models, the theory presented here correctly accounts for the effect of all of these variables on the orders of reaction. It is particularly important to note that the predicted orders of reaction are not adjustable parameters.

Since the key to the mechanism of a reaction is the orders of reaction, the excellent agreement between such a large data set and the proposed mechanism is powerful evidence in favour of the proposed mechanism. In addition, the theory accounts for the effect of the change in the zeta potential at the same value of pH in which the order of reaction with respect \( \psi \) changes.

In particular, the following conclusions are drawn:

1. A novel mechanism of dissolution is presented which describes the order of reaction for forsterite, willemite, and other orthosilicate minerals at pH values of less than 6.
2. This novel theory is based on two parallel steps: the removal of metal species and the removal of silicate groups from the surface.
3. Partial equilibrium might occur if one of the parallel steps, but not the other, reaches equilibrium.
4. The theory accounts for the change in slope observed for forsterite at pH values greater than about 6. The change in slope is caused by a change in position of the adsorbed proton: from the outer Helmholtz plane at pH values less than 6 to the inner Helmholtz plane at pH values greater than 6.
5. The theory correctly accounts for the effect of organic acids, dissolved silica, carbonate ions, and water activity.
6. The theory is corroborated by the results of zeta potential measurements.

Finally, Casey (1991) argued that a predictive model of the dissolution of should account for the changes in solution composition on the rate of dissolution and account for changes in mineral composition for minerals of similar composition (for example, Mg\(_2\)SiO\(_4\), Be\(_2\)SiO\(_4\), Zn\(_2\)SiO\(_4\), etc) on the rate of dissolution. It has been shown that the model presented here is able to fulfill these criteria.

References
