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Organic ligands and feldspar dissolution

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Abstract—Organic compounds can both enhance and inhibit the rates of feldspar dissolution in the laboratory and presumably in field settings where organic matter is abundant. Organic acids can directly enhance dissolution by either a proton- or a ligand-mediated mechanism. They can also indirectly enhance dissolution by the formation of complexes in solution with reaction products and as a consequence increase the chemical affinity for the overall dissolution reaction. The former mechanism is likely to be important at high chemical affinities and the latter at lower chemical affinities. The direct ligand-mediated mechanism involves the adsorption of ligands to Al sites on the feldspar surface, the formation of Al-organic complexes at the surface site, and the subsequent leaching of Al into solution. The degree of dissolution enhancement by the direct ligand-mediated mechanism is dependent on the structure and concentration of the ligand, the composition of the feldspar, the composition of the solution, and the temperature. However, overall dissolution rates are not a simple function of these factors. Organic polymers can either inhibit dissolution by irreversibly binding to the mineral surface and reducing the effective reactive surface area (i.e. the number of reactive sites) of the mineral or enhance dissolution by a ligand-mediated mechanism. The experimental determinations of the impact of a wide variety of organic ligands on feldspar dissolution rates provide evidence of multiple mechanisms of mineral ligand interaction that can impact the dissolution process. This literature is reviewed in light of conceptual models of the dissolution process.

1. INTRODUCTION

The dissolution of primary rock-forming minerals, the release of ions to solution, and the formation of secondary minerals take place in all earth-surface environments where rocks and water coexist. Weathering is an important process in the creation of soils and the maintenance of soil productivity, the evolution of ground- and surface-water compositions, the denudation of continents, the flux of continental solids and solutes to the ocean, the maintenance of seawater composition and productivity, and the regulation of atmospheric composition and global climate. Secondary porosity generated by mineral dissolution contributes to the success of petroleum migration and recovery, and may also impact the transport of solutions and solutes through aquifers. Weathering reactions involving feldspars are particularly important since they are the most abundant rock-forming mineral at the earth's surface and represent a potentially important source of non-carbonate calcium that controls the long-term concentrations of atmospheric carbon dioxide, and therefore regulates the global heat balance (Berner, 1991; Brady, 1991).

Traditionally, silicate and alumino-silicate weathering has been viewed by geochemists as an abiotic, acid-mediated, hydrolysis process initiated by the reaction of primary minerals with water and dilute inorganic acids, typically carbonic acid (H_2CO_3), but also nitric (HNO_3) and sulfuric acid (H_2SO_4) in some geological settings (Garrels and Mackenzie, 1971). Increasingly, however, it is recognized that the weathering process can be further mediated by organisms and their metabolites. Respiration by plant roots and microbial degradation of organic matter can elevate carbonic acid concentrations in soils and groundwater, leading to an increase in the weathering rates of minerals (Chapelle et al., 1987; Hendry et al., 1992; Keller and Wood, 1993). In addition to carbonic acid (carbon dioxide and water), plants, bacteria, and other microorganisms produce other compounds (such as other inorganic acids, alkaline compounds, low- and high-molecular-weight organic compounds, oxidants, and reductants) which can affect mineral weathering reactions (Huang and Schnitzer, 1986; Ehrlich, 1990; Drever and Vance, 1994; Barker et al., 1997; Stone, 1997). Ligand-mediated dissolution represents one of the additional mechanisms by which minerals dissolve (hydroxyl-mediated and redox-mediated dissolution are two others). Ligands can affect feldspar weathering rates by complexing with ions at the mineral surface or in solution. Ligands may also inhibit feldspar dissolution rates under some conditions (Welch and Vandevivere, 1994; Welch et al., 1999). The impact of these ligand-mediated reactions on the rates of mineral weathering must be considered, particularly in near-surface environments where microbes are present and where microbially produced metabolites and/or organic contaminants may be abundant. They also may be important in oilfield reservoir systems or at contaminated sites where partial oxidation of petroleum compounds can also lead to high levels of organic ligand production (Kharaka et al., 1986; Fisher, 1987; Bennett and Siegel, 1987; Cozzarelli et al., 1994).

In this review we consider primarily the effect of naturally occurring organic ligands on feldspar dissolution rates. Increasingly, however, organic contaminants and their decomposition products are found in natural waters and many of these may have the capacity to influence silicate and alumino-silicate dissolution (e.g., Bennett and Siegel, 1987). Less is known, however, about these compounds and their impact on mineral weathering reactions. For the purpose of this review, we also presume that the principal effect of organisms on feldspar dissolution rates is due to the production and excretion of compounds to the solution. There is, however, increasing evidence that direct contact between bacteria and minerals may be important in mineral alteration reactions, as microbial surfaces can also complex with metal ions (Ferris et al., 1988; Daughney et al., 1998; Fein et al., 1997). Microorganisms attached to mineral surfaces can also create micro-environments where concentrations of ligands, acidity, and redox activity can be substantially elevated compared to the bulk solution, thus affecting mineral exchange reactions (Hiebert and Bennett, 1992; Barker and Banfield, 1996, 1998; Rogers et al., 1998a,b; Barker et al., 1998). The impact of direct contact between organisms and mineral surfaces on mineral weathering reactions is not addressed here.

It is clear from a large number of studies that feldspar dissolution rates are a strong function of pH (Blum and Lasaga, 1988, 1991; Brady and Walther, 1989; Drever and Vance, 1994; Blum and Stillings, 1995). Rates are lowest in near-neutral solutions (pH ≈ 5 to 8) and then increase dramatically at low and high pH due to proton-mediated and hydroxyl-mediated mechanisms, respectively. The direct effects of ligands on the dissolution process are of secondary importance except when protons and hydroxyl concentrations are at their minimum. However, at these near-neutral pHs, which correspond to the pHs of many natural environments, ligands may significantly enhance dissolution rates by up to an order of magnitude (Wogelius and Walther, 1991; Welch and Ullman, 1993,1996; Stillings et al., 1998). The mechanism by which ligands interact with the dissolving mineral, the degree of dissolution enhancement or inhibition, the effect of ligand structure and concentration on the degree of enhancement, and the interactions between ligand-mediated and other dissolution mechanisms are the important questions that need to be addressed in order to make reasonable predictions of chemical weathering rates on a local, regional, or global scale.

The objective of this review is to summarize the existing experimental results concerning the role of organic ligands in the feldspar weathering process, both as dissolution enhancers and inhibitors, as compared to the rates of dissolution due to proton- or hydroxyl-mediated feldspar dissolution alone. The dependence of ligand-mediated dissolution rates on mineral chemistry, solution compositions, and physical factors, principally temperature, are also considered. We consider primarily feldspars because of their abundance in crustal rocks. However, results from other mineral systems are also useful in interpreting feldspar weathering rates, and a sampling of such studies are included in this review. We also evaluate the simple empirical and thermokinetic models of the dissolution process that have been found to reproduce the experimental results and discuss the extrapolation of laboratory results to field settings.

The overall weathering process, however, is complicated. It is not possible to consider all of the possible combinations and permutations of dissolution and precipitation reactions involving all of the phases and components that may occur in field settings. It is also not entirely clear how the various rate-controlling factors interact to obtain the overall rates of mineral dissolution observed in the laboratory or in the field. We therefore focus only on the general trends in the primary dissolution of feldspars, a single, but important group of minerals. These trends, however, provide a useful blueprint for the conditions under which ligand-mediated dissolution enhancement and inhibition may be significant, and therefore this review should prove useful for those interested in interpreting or predicting the rates of mineral alteration in field settings where organic ligands are important participants in the weathering process.

2. A CONCEPTUAL MODEL OF FELDSPAR DISSOLUTION

Feldspars are tectosilicate minerals in which a regular three-dimensional network of Si and Al tetrahedra provides the structural framework, and alkali and alkaline earth metals in interstitial positions balance the net charge of this structure (Smith and Brown, 1988). The charge-balancing cations are known to easily exchange with cations in solution (especially with H^+), resulting in a leached near-surface layer that is amorphous and stable (Petrovič, 1973; Chou and Wollast, 1985; Casey and Bunker, 1990; Stillings and Brantley, 1995). For this reason, most studies of feldspar dissolution, including this one, are focused on the release rates of the structural cations, Al and Si.

2.1. Dissolution in Ligand-Free Aqueous Solution

In a ligand-free aqueous solution, the stoichiometry of a generalized overall feldspar dissolution reaction can be described as a sum of three types of reactions. In neutral solutions, the feldspar hydrolysis (HD) reaction predominates and is given by:

$$(K_xNa_y)Ca_{(1-x-y)}Al_{(2-x-y)}Si_{(2+x+y)}O_8 + 8H_2O \rightarrow (2+x+y)Si(OH)_4{}^o + (2-x-y)Al(OH)_3{}^o + (2-x-y)OH^- + xK^+ + yNa^+ + (1-x-y)Ca^{2+} \quad (1)$$

The principal feldspar dissolution reaction in acidic solutions is an acid hydrolysis (proton-mediated: PMD) reaction and can be given as:

$$(K_xNa_y)Ca_{(1-x-y)}Al_{(2-x-y)}Si_{(2+x+y)}O_8 + 4(x+y)H_2O + 4(2-x-y)H^+ \rightarrow (2+x+y)Si(OH)_4{}^o + (2-x-y)Al^{3+} + xK^+ + yNa^+ + (1-x-y)Ca^{2+} \quad (2)$$

In basic solution, the feldspar hydroxylation (hydroxyl-mediated: HMD) reaction can be written as:

$$(K_xNa_y)Ca_{(1-x-y)}Al_{(2-x-y)}Si_{(2+x+y)}O_8 + (6-x-y)H_2O + (2+x+y)OH^- \rightarrow (2+x+y)SiO(OH)_3{}^- + (2-x-y)Al(OH)_4{}^- + xK^+ + yNa^+ + (1-x-y)Ca^{2+} \quad (3)$$

The above reactions and stoichiometries reflect a conceptualization and simplification of the overall reactions that actually take place through a series of elementary reaction steps involving, at the molecular scale, direct electronic interaction between reactants and formation and/or destruction of molecular bonds (Lasaga, 1981; Brezonik, 1994).

Much of the interesting weathering behavior of feldspar is not reflected in these conceptual stoichiometries. For example, initial rates of feldspar dissolution are usually not stoichiometric and non-stoichiometric release of component ions may persist even after steady dissolution rates are achieved in longer experiments. Casey and Bunker (1990) suggest that this behavior is the result of multipathway leaching during which each element is subjected to a different set of solubilization reactions. Also, some of the reaction products may react with each other or with some of the reactants to form different solute phases or secondary solids. Secondary clays are a common product of feldspar weathering reactions (Garrels and Mackenzie, 1971) and the nature of these secondary reactions and phases plays an important role in soil development and fertility.

The three reactions given by Eqns. 1-3 have different stoichiometric dependencies with respect to the concentrations of H^+ and OH^- and therefore predominate at different ranges of pH. The rates of hydrolysis in neutral solution are known to be exceedingly slow, accounting for the long-term geological stability of feldspars in many near-neutral environments. The net effect of these inorganic reactions on feldspar dissolution rates, R_{inorg}, can be described as a linear sum of the three mechanisms:

$$R_{inorg} = R_{PMD} + R_{HD} + R_{HMD} \quad (4)$$

where R_{HD}, R_{PMD}, and R_{HMD} are the contributions due to the hydrolytic (Eqn. 1), proton-mediated (Eqn. 2), and hydroxyl-mediated (Eqn. 3) dissolution mechanisms to the overall surface-normalized dissolution process in the absence of ligands. The pH dependence of the three mechanisms and overall dissolution behavior in the absence of ligands, R_{inorg}, is shown schematically in Fig. 1.

The acid hydrolysis and hydroxylation mechanisms of feldspar dissolution are far more rapid than the hydrolysis reaction and are often described using catalytic terminology (proton-promoted and hydroxyl-promoted dissolution), in spite of the consumption of protons and hydroxyls by the overall reaction (Eqns. 2 and 3). Protons and hydroxyls may have catalytic effects on specific elementary reactions in the silicate dissolution process (Xiao and Lasaga, 1994,1996). We have, however, adopted a less controversial terminology (proton-mediated dissolution, PMD, and hydroxyl-mediated dissolution, HMD) to describe the increase in the rate of dissolution above the hydrolytic dissolution rate (HD), but this terminology is synonymous with the catalytic terminology used in most of the papers that we have reviewed.

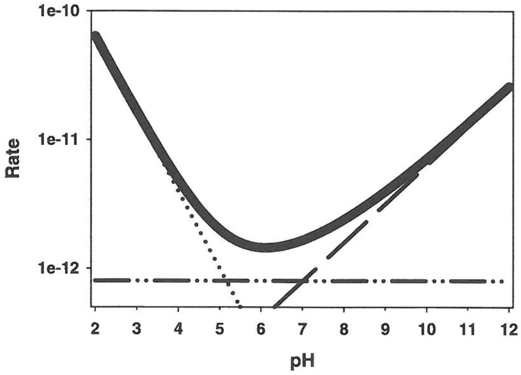

Fig. 1. A schematic view of the relative importance of proton-mediated feldspar dissolution (PMD; ·······), hydrolytic dissolution (HD; — ·· —), and hydroxyl-mediated dissolution (HMD; —— ——). The net effect of these processes as a function of pH (Eqn. 10) is given by (———). At near neutral pH, there is a region where the dissolution rate is at a minimum and it is within this region where ligand-mediated dissolution (LMD) influences rates most dramatically (Eqn. 18). Rate in moles/m^2/sec.

2.2. Dissolution in Ligand-Containing Aqueous Solutions

This review concerns the importance of a fourth reaction, the ligand-mediated dissolution (LMD) reaction that can be written for a single hypothetical monovalent ligand, L^-, in neutral solution as:

$$\begin{aligned}&(K_xNa_y)Ca_{(1\text{-}x\text{-}y)}Al_{(2\text{-}x\text{-}y)}Si_{(2+x+y)}O_8 + 8H_2O +\\&(2\text{-}x\text{-}y)L^- \rightarrow (2+x+y)Si(OH)_4{}^{o} + (2\text{-}x\text{-}y)AlL^{2+} +\\&4(2\text{-}x\text{-}y)OH^- + xK^+ + yNa^+ + (1\text{-}x\text{-}y)Ca^{2+}\end{aligned} \quad (5)$$

There are a wide variety of possible ligands with a wide range of chemical reactivities that may either enhance feldspar dissolution rates or inhibit dissolution. In nature, it is likely that many ligands will be present in solution and each will react with feldspars according to Eqn. 5. Under these conditions, the overall rates of LMD will be some function of the relative concentrations of the contributing ligands and the impact of each ligand individually on dissolution. There are only few controlled experiments involving multiple ligands and feldspar dissolution, and therefore the nature of this function, whether additive, multiplicative, or more complicated, is, as yet, uncertain. Some inferences concerning ligand-ligand and other ligand-solute interactions and their effect on LMD are discussed below.

Ligands can be either inorganic or organic, but this review focuses primarily on the effect of organic compounds on the dissolution process. Polyvalent ligands may have slightly different stoichiometries than given above. An analogous reaction can be written for LMD in acidic or basic solutions, but there is little experimental evidence that this process is important at higher pH.

The stoichiometry of Eqn. 5 does not require that ligands be involved in any of the fundamental steps in the dissolution process. Equation 5 could be described as a stepwise reaction involving first HD and subsequent reaction to form ligand complexes with the reaction products ($Al(OH)_3{}^{o}$) of the HD reaction subsequent to dissolution. There is, however, sufficient experimental evidence to indicate that the overall rate of feldspar dissolution into solution containing ligands, R_{total}, given conceptually by

$$R_{total} = R_{inorg} + R_{LMD} = R_{HD} + R_{PMD} + R_{HMD} + R_{LMD} \quad (6)$$

increases with ligand concentration when the reaction conditions and composition of the reacting solutions are held constant. This suggests that LMD, like PMD and HMD, involves an important rate-controlling process in feldspar dissolution and represents a mechanism that is independent of, or at least, partially independent of the other contributing reactions. Recent experimental work and *ab initio* modeling suggest that direct interaction of ligands and silicate surfaces does occur and that organic ligands can disrupt the aluminum-silicate structure leading to dissolution (Kubicki et al., 1997, 1999)

3. SOURCES, FUNCTIONS, AND CONCENTRATIONS ORGANIC LIGANDS

Although mineral weathering reactions can occur in a wide variety of geochemical environments, the importance of ligand-mediated reactions will certainly depend on the amounts and types of organic compounds that are present. It is therefore instructive to review the processes responsible for organic ligand production, the types of ligands produced, and the ranges of concentrations that may be achieved in contrasting geochemical settings.

3.1. Sources and Functions

Low-molecular-weight organic anions are commonly found in natural waters (Table 1). Microbes, plants, and animals produce organic acids as a result of their metabolism due to the anabolic synthesis or catabolic breakdown of larger organic compounds (Brock and Madigan, 1988). In the absence of other electron acceptors, anaerobic and facultative anaerobic microorganisms ferment the available organic carbon compounds and produce ligands such as formate, acetate, propionate, lactate, and butyrate (Gottschalk, 1986; Maeda and Kuwaii, 1988). Under extremely reducing conditions, microbes can produce organic anions (primarily acetate) from inorganic carbon (Brock and Madigan, 1988). Oxidative microbial degradation of macromolecules (such as polysaccharides and proteins) can result in the production of low-molecular-weight organic acids (Thurman, 1985). Bacteria can also produce and excrete high concentrations of organic acids when grown under conditions of nutrient stress, relatively high carbon availability, but limited availability of other nutrients, such as N and P (Neijssel and Tempest, 1975; Tempest and Neijssel 1992; Linton 1990). A number of ligands, notably oxalate, but also pyruvate, citrate, succinate, malate, gluconate, lactate, fumarate and formatel, have been detected in soils and on weathered rock colonized by fungi and bacteria (e.g., Fox and Comerford, 1990; Palmer et al., 1991; Baziramakenga et al., 1995; Krzyszowska et al., 1996). Ectomyccorrhizal organisms are known to produce soluble organic compounds that affect mineral weathering reactions (Jones 1998; Paris et al., 1995, 1996; Leyval et al., 1990). Plants produce and excrete organic ligands through their roots as well (Ochs et al., 1993; Laheurte et al., 1990). It is difficult to differentiate between compounds produced directly by the plants and those produced by their ectomyccorhizal communities (Laheurte et al., 1990; Paris et al., 1995).

Bacteria, fungi, and plants also produce other soluble compounds that are capable of interacting with mineral surfaces and altering mineral reaction rates. Under conditions of Fe limitation, organisms produce a specific class of soluble ligand, siderophores, that bind very strongly to Fe^{3+}, solubilizing normally insoluble iron compounds and making the iron available to the organism. Siderophores can also bind with other metals, particularly Al^{3+}, and can therefore, by the LMD mechanism, affect alumino-silicate mineral solubility and dissolution rates (Ochs et al., 1993; Bennett et al., 1998; Rogers et al., 1998a,b).

Although low-molecular-weight ligands are thought to dominate the interaction between rocks and solution in biologically mediated rock weathering, organisms produce other higher molecular-weight compounds, such as cell surfaces and extracellular polymers, that can affect the rates of mineral/water exchange reactions. Biopolymers can function as attachment or protective structures, food-storage reservoirs, or colonization substrates for other potential food organisms (Christensen and Characklis, 1990). Microbial extracellular polymers are typically comprised of sugars (including oxidized sugars such as gluconate or uronic acids) or amino acids. These compounds create microenvironments around attached organisms on mineral surfaces where they may play a role in mineral-water exchange reactions. All cell surfaces also have reactive functionality (carboxylic acids, teichoic acids, etc.) that can similarly bind either to metals at mineral surface or to metals released from the minerals to solution, and thus potentially affect mineral diagenesis and mineral-water exchange (Fein et al., 1997; Daughney et al, 1998).

3.2. Concentrations

Acetate is typically the most abundant organic anion in natural systems (Sansone and Martens, 1982; Sansone, 1986; Surdam et al., 1984; Fisher, 1987; Talbot et al., 1990; Martens, 1990; Kawamura and Nissenbaum, 1992; Table 1). Acetate concentrations greater than 10,000 ppm (160 mM) have been measured and acetate has been detected at temperatures up to 200 °C in sedimentary basins (Surdam et al., 1984; Kharaka, et al., 1986). Acetate can be produced by both abiotic and biological processes (Shock, 1988). Oxalate is also abundant in soils where it is often found to precipitate as metal-oxalate salts. Hydrated Ca-oxalate ($Ca(C_2O_4) \cdot H_2O$, whewellite) and its non-crystalline form are common constituents of soil litter (Graustein et al. 1977; Lapeyrie et al., 1990).

The total concentration of low-molecular-weight organic anions in natural waters associated with petroleum can exceed 1 g/L. Short chained aliphatic organic ligands (acetate, propionate, butyrate, and valerate) are typically the most abundant single ligands detected in these waters, although difunctional ligands (such as oxalate, malonate, and succinate) and aromatic compounds have also been observed in appreciable quantities (Peltzer and Bada, 1981; Kharaka et al., 1986; Fisher, 1987; MacGowan and Surdam, 1988; Cozzarelli, et al., 1994; see Table 1). Maximum organic ligand concentrations tend to be found in the 70 to 120 °C range, above the temperature (~70 °C) where microbial uptake commonly depletes organic concentrations (although low levels of microbial activity have been found in deep subsurface environments at elevated temperatures, Onstott et al., 1998), and below the temperatures where thermal decarboxylation consumes these compounds (Kharaka et al, 1986; Fisher, 1987; MacGowan and Surdam, 1988). Because of thermal decarboxylation of potential ligands, ligand-mediated dissolution is likely to be less important at hydrothermal temperatures (> 100 °C; Stoessel and Pitman, 1990).

The total concentration of organic carbon (dissolved + particulate) in soils typically ranges up to 6% (Brady and Weil, 1996). Most of this is the relatively refractory, high-molecular-weight residue of the degradation of plant and animal material (Thurman, 1985). However, microbial degradation of this material produces a myriad of soluble low-molecular-weight organic ligands that can potentially react with minerals. The low-molecular-weight ligands that are extremely common in relatively organic-poor environments, such as acetate, oxalate, etc., are also common in soils. Aromatic organic compounds have also been detected in natural waters where concentrations can range from μM to mM levels (see Table 1). In the rhizosphere, the microenvironments surrounding plants roots that include the ectomycorrhizal community, organic acid concentrations can be up to 1 to 2 orders of magnitude higher than in bulk soils. Grierson (1992) measured mg/L levels of maleic, fumaric, malic, acontitic, and citric acids in leachates from the rhizosphere of *Banksia integrifolia*. The concentrations of these compounds were approximately an order of magnitude lower in leachates of the surrounding soil and leaf litter. In a similar study, Fox and Comerford (1990) found up to 1mM of oxalate in the soil rhizosphere. Similar concentrations of oxalate, 10 to 100 μM of leachate, were measured at an Antarctic lichen community (Johnston and Vestal, 1993).

Table 1. Low molecular weight organic ligands in natural settings and some of their thermodynamic properties. All thermodynamic data from Smith and Martell (1998).

Ligand (Acid Formula)	**Concentrations**	**pK_a^***	**Al Complexes****
	Aliphatic Monocarboxylic Acids		
Formate ($HCOOH$)	Few hundred nmol/g in stone (a); 5 to 174 μM in soil (b); 10 to 20 μM in beech forest soil (d); Few hundred nmol/g in soil extract (e); 10 to 50 μM in groundwater (f); 0.2 to 1.4 μM in forest floor solution (g); 50 to 300 μmol/kg in soil leachate (k)	3.75	log $\beta_1 = 1.36$ log $\beta_2 = 2.02$ other complexes I = 1
Acetate (CH_3COOH)	10 to 20 μM in beech forest soil (d); 140-1000 nmol/g in soil extract (e); 10 to 50 μM in groundwater (f); 0 to 50 μM in forest floor solution (g); 50 μM to 250 mM in formation water (h,j); 5 to 800 μmol/kg in soil leachate (k)	4.76	log $\beta_1 = 1.51$ other complexes I = 1
Propionate (CH_3CH_2COOH)	Few μM in beech forest soil (d); 30 μM to 24 mM in formation water (h,j); 5 to 800 μmol/kg in soil leachate (k)	4.87	log $\beta_1 = 1.69$ other complexes I = 1
Butyrate ($CH_3(CH_2)_2COOH$)	Up to 169 μM in formation water (h,j); up to 10 μmol/kg in soil leachate (k)	4.82	log $\beta_1 = 1.58$ (I = 1)
Valarate ($CH_3(CH_2)_3COOH$)	Up to 7 μM in formation waters (j)	4.83	No data
	Aliphatic Dicarboxylic Acids		
Oxalate ($HOOCCOOH$)	Few tens nmol/g in stone (a); 25 to 1000 μM in soil (b); 20 to 100 μmol/g dry sediment in reducing marine sediment (c); Few μM in beech forest soil (d); 40-100 nmol/g in soil extract (e); 1-5 μM in forest floor solution (g); up to 5 mM in formation water (j); up to 200 μmol/kg in soil leachate (k)	1.25, 4.27	log $\beta_1 = 5.97$ log $\beta_2 = 10.93$ log $\beta_3 = 14.88$ (I = 0.5)
Malonate ($HOOCCH_2COOH$)	Up to 25 mM in formation water (j); up to 200 μmol/kg in soil leachate (k)	2.85, 5.70	log $\beta_1 = 6.26$ log $\beta_2 = 11.11$ log $\beta_3 = 13.3$ (I = 0.15)
Succinate ($HOOC(CH_2)_2COOH$)	Few tens nmol/g in stone (a); Few tens μmol/g dry sediment in reducing marine sediment (c); 2 to 500 μM in formation water (h); up to 200 μmol/kg in soil leachate (k)	4.21, 5.64	log $\beta_1 = 3.20$ other complexes (I = 0.5)
Fumarate ($HOOC\text{-}CH{=}CH\text{-}COOH$)	Few tens nmol/g in stone (a); up to 30 μmol/kg in soil leachate (k)	3.02, 4.48	No data
Malate ($HOOCCH_2CHOHCOOH$)	Few μM in beech forest soil (d); Few nmol/g in soil extract (e); 8 to 30 nmol/ml in soils and root leachate (l); up to 30 μmol/kg in soil leachate (k)	3.46, 5.10	log $\beta_1 = 4.60$ log $\beta_2 = 7.62$ other complexes (I = 0.15)
	Aliphatic Tricarboxylic Acids		
Citrate ($COOH\text{-}CH_2\text{-}C(OH)COOH\text{-}CH_2\text{-}COOH$)	Few nmol/g in stone (a); trace in soils (b); Few tens (5 to 25) nmol/g in soil extract (e); 0-0.13 μM in forest floor solution (g); 70 to 600 nmol/ml in soils and root leachate (l); up to 30 μmol/kg in soil leachate (k)	3.13, 4.76, 6.40	log $\beta_1 = 7.14$ log $\beta_2 = 12.9$ other complexes (I = 0.1)
Isocitrate ($COOH\text{-}CH_2\text{-}CH(COOH)$ – $CHOH\text{-}COOH$)	Few μM in beech forest soil (d)	3.05, 4.30, 5.74 (I = 0.1)	No data
Aconitic ($HOOC\text{-}CH{=}C\text{-}(COOH)CH_2\text{-}COOH$)	Few μM in beech forest soil (d); Few nmol/g in soil extract (e); 1 to 20 nmol/ml in soils and root leachate (l)	2.8 4.5	No data

	α-Hydroxy- and α-Keto-carboxylic Acids		
Glycolate (CH_2OH-COOH)	<1 μmol/g dry sediment in reducing marine sediment (c); up to 250 μmol/kg in leachate (k)	3.83	No data
Pyruvate ($CH_3CHOCOOH$)	Few tens nmol/g in stone (a); Few μM in beech forest soil (d); up to 40 μM/kg in soil leachate (k)	2.48	No data
Lactate ($CH_3CHOHCOOH$)	Few tens nmol/g in stone (a); <1 μmol/g dry sediment in reducing marine sediment (c); to 400 μmol/kg in soil leachate (k)	3.86	$\log \beta_1 = 2.36$ $\log \beta_2 = 4.42$ $\log \beta_3 = 5.8$ other complexes (I = 0.5)
Gluconate ($HOCH_2(CHOH)_4$ COOH)	Very reactive. Not reported in nature.	3.46, I = 0.1	$\log \beta_1 = 1.9$ (I = 0.5)
α-Ketoglutarate (HOOC-$(CH_2)_2$-(C = O)-COOH)	Very reactive. Not reported in nature.	1.9, 4.44, I = 0.5	No data
	Aromatic Carboxylic Acids		
Salicylic Acid (2-Hydroxybenzoic Acid)	2 - 5 nmol/g in rhizosphere (e); 0 to 0.5 mM in formation waters (j)	13.7	$\log \beta_1 = 13.7$ $(I \le 0.1)$ $\log \beta_2 = 24.8$ $(I \le 0.5)$
p-Hydroxybenzoic Acid	5 - 60 nmol/g in rhizosphere (e)	4.58, 9.46	No data
Protocatechuic Acid (3,4-Dihydroxybenzoic Acid)	1 – 5 nmol/g in rhizosphere (e)	4.49, 8.75, 13.0	$\log \beta_1 = 16.8$ $\log \beta_2 = 29.8$ $\log \beta_3 = 38.5$ other complexes (I = 0.1)
Caffeic Acid (3-(3,4-Dihydroxyphenyl) Propanoic Acid)	No concentration data found.	4.62, 9.07, 12.5, I = 0.1	No data
Gallic Acid (3,4,5-Trihydroxybenzoic Acid) (Note: Dissociation and stability constants refer to the singly protonated ligand. Full deprotonation is not observed)	No concentration data found.	4.4 9.11 11.4 $(I \le 0.1)$	$\log \beta^*_1 = 6.4$ $\log \beta^*_2 = 9.0$ $\log \beta^*_3 = 7.4$ $(I \le 0.1)$
Vanillic Acid (4-Hydroxy, 3-Methoxy-benzoic Acid)	1-14 nmol/g in rhizosphere (e)	No data	No data
	Other Aromatic Compounds		
Catechol (1,2-Dihydroxybenzene) (Note: Also forms strong complexes with Si; Smith and Martell, 1998)	No concentration data found.	9.45, 13.3	$\log \beta_1 = 16.7$ $\log \beta_2 = 30.35$ $\log \beta_3 = 39.4$ other complexes $(1 \le 0.1)$

• Acid dissociation constants at 25 °C and I = ionic strength = 0 unless noted

** Association constants for complexes of the form AlL_n where $\beta_n = [AlL_n]/[Al^{3+}][L]^n$. The stabilities of complexes of differing form (other complexes) are described in Smith and Martell (1998).

Concentrations reported by:
a) Palmer et al., 1991
b) Fox and Comerford, 1990
c) Peltzer and Bada, 1981
d) Shen et al., 1996
e) Baziramakenga et al., 1995
f) McMahon and Chapelle, 1991
g) Krzyszowska et al., 1996
h) Kharaka et al., 1986
i) Grierson, 1992
j) MacGowan and Surdam, 1988, 1990
k) Cordt and Kussmaul, 1992

Below the soil zone, dissolved organic carbon concentrations on the order of a few to few 10's of mg/l are found in sediments and groundwater. Most of this material consists of relatively refractory high-molecular-weight humic and fulvic material (Thurman, 1985). In shallow anoxic ground water, up to tens of μM of fermentation products (acetate, butyrate, formate, and lactate) have been measured (Welch, unpublished). McMahon and Chapelle (1991) also measured low concentrations (tens of μM) of acetate and formate in an oxic aquifer. They hypothesized, however, that these organic acids were produced by microbial fermentation in the adjacent anoxic aquitard and that microbial uptake of these compounds was rapidly consuming them in the oxic groundwater solution.

4. INTERACTION OF ORGANICS WITH MINERAL SURFACES

The first step in the interaction of organic ligands and the mineral surface, by analogy with PMD and HMD, must involve adsorption of the ligand to the surface (Kubicki et al., 1997). Adsorption will depend on ligand structure, speciation, and charge, as well as the speciation and charge of the surface and the concentrations of other cations and anions competing for the ligand or reactive sites at the mineral surface. Soluble ions in solution may impact the activity of the ligand in solution and may compete with ligands for adsorption sites at the mineral surface. Adsorption and solution equilibria will have additional dependencies on temperature.

A number of investigators have studied the pH dependence of surface charge and the availability of surface exchange sites on alumino-silicate minerals. Blum and Lasaga (1988, 1991) concluded on the basis of acid and base titrations of albite and a simple Langmuir model that, under acidic conditions, feldspar surface charge is primarily controlled by the Al sites on the mineral surface and that the isoelectric point of the mineral was therefore similar to that of tetrahedral surface Al (Parks, 1967; Brady and Walther, 1992). Brady and Walther (1989, 1992) and Blum and Lasaga (1991) proposed that surface Si sites, although three times more abundant than surface aluminum sites based on the bulk albite stoichiometry, play a negligible role in PMD of this mineral. Oxburgh et al. (1994) further demonstrated that proton adsorption increases with An content of the feldspar from An_{12} to An_{75}. Several experimental studies have demonstrated that feldspar dissolution rates under acidic conditions increase dramatically with increasing Al content (Manley and Evans, 1986; Casey et al., 1991, Welch and Ullman 1992; 1996). This is an additional indication that, at least for PMD, Al content of the mineral and the relative abundance of Al-sites at the mineral surface play an important role in the first step in the dissolution process.

Brady and Walther (1989, 1992) suggest, based on the similarity of the pH dependence of HMD for a number of classes of minerals, that deprotonation of silica sites may play an important role in silicate dissolution in basic solutions, as well. Blum and Lasaga (1991), however, prefer a model dependent on the protonation and deprotonation of Al sites that also reproduces the observed pH dependence. More complex models involving multiple site adsorption (Stillings et al., 1992) and constant capacitance, double- and triple layer models (Sverjensky and Sahai, 1996) do not substantially alter the qualitative interpretations based on these simple models.

The one problem with the direct application of the Blum and Lasaga (1991) model to ligand adsorption is that it predicts that more proton adsorption occurs on feldspar than there are Al-sites on the surface. They propose that this is due to more than one proton or hydroxyl adsorbing to a given Al site (see also Stillings et al., 1998), a condition that may be realistic for the extremely fine-grained, and presumably stressed, surface of their experimental mineral. Alternatively, proton and hydroxyl adsorption may be occurring at some depth below the surface layer (Brantley and Stillings, 1996). While small protons may be able to penetrate into the feldspar surface to react with the bulk mineral, it is unlikely that larger ions or molecules, such as complexing organic ligands, will be able to do the same. As a result of this size constraint, ligand adsorption and therefore ligand-mediated reactions, are likely limited to the surface-most layer of the dissolving aluminum silicate and to one or fewer ligands per reactive surface site. Stillings et al. (1998), however, demonstrated that a Freundlich isotherm model that does not presume a fixed number of adsorption sites does a better job of describing oxalate adsorption to feldspar surfaces and LMD rates than a Langmuir isotherm that limits adsorption to a fixed number of surface sites. Both of these models suggest that one or more ligands adsorb at each Al site, if adsorption at Si sites is presumed negligible.

The condition of the surface is not the only factor influencing the adsorption of organic ligands to the mineral surface, and therefore LMD rates. The speciation of the attacking ligand is also important (Kubicki et al., 1997). Ligand speciation is controlled by pH and the concentration of other ions that form stable complexes in solution. If the charge of the dominant ligand species in solution is neutral or of the same sign as the surface, adsorption will be inhibited due to electrostatic repulsion (Morel and Hering, 1993). Thus, the expectation is that ligand adsorption and LMD rates should be greatest in those regions of pH where surface and ligand charges are predominantly of opposite sign and where there are few ions that form stable complexes with the ligand in solution. Figure 2 schematically shows the speciation of oxalic acid and its dissociated anions as a function of pH. Below pH = 1.25, neutral oxalic acid ($H_2Ox^o = H_2(COO)_2{}^o$) predominates in solution and above pH = 4.27 , oxalate ion ($Ox^{2-} = (COO)_2{}^{2-}$) is dominant. Over this same range of pH, a typical feldspar surface changes from a net positive charge to a net negative charge. Measurements of proton adsorption indicate that the pH (or point) of zero net proton charge (PZNPC) for feldspar is somewhere in the region of 5.2 to 7.5 (see discussions in Brantley and Stillings, 1996; Chen and Brantley, 1997). Above the PZNPC it is unlikely, because of charge similarities, that HOx^- ($= H(COO)_2{}^-$) or Ox^{2-}, the dominant ionic forms of oxalate in this range of pH, will significantly adsorb to the feldspar surface, and if adsorption is an important step in the LMD dissolution process, oxalate will have little or no impact on overall dissolution rates.

The presence of organic ligands in solution is only one of the requirements for LMD of feldspars. PMD and HMD predominate as dissolution mechanisms where protons and hydroxyls are in substantial concentration and where they compete with ligands for adsorption sites. Although ligands can affect the dissolution reaction over a wide range of pH, their major positive impact on feldspar dissolution occurs in the near-neutral pH range where proton and hydroxyl concentrations are at a joint minimum. The composition of the bulk feldspar and the feldspar surface also affects the number and type of reactive sites available to attacking protons, hydroxyls, and ligands, and therefore influence dissolution rates. Temperature may also influence the strength of interactions between ions in solution and on surfaces, and therefore potentially affects both the mechanism and the rates of mineral/solute interactions. It is therefore necessary to consider the impact of all of these processes on the LMD mechanism in order to identify the general trends that may be useful in modeling the stability of feldspar or other minerals under the wide range of conditions that may be found on the Earth's surface.

5. EXPERIMENTAL RESULTS

The results of experimental work summarized in Table 2 represent the best information available to date from which to infer the effects of ligands in solution and on surfaces on the rates of feldspar dissolution. For each experiment, we give the range of rates and some of the experimental conditions under which the rates were determined.

There is a great deal of variability in the rates that have been determined, although most of the rates at a given temperature and pH for the same mineral are within an order of magnitude of each other (Welch and Ullman, 1996). This variability is probably due to differences in experimental methods and materials. This variation reflects: (1) the choice of experimental minerals; (2) the preparation of the minerals for experiments; (3) the presence of trace contaminants and compositional intergrowths in the experimental minerals; (4) the assignment of specific surface areas to the reacting phases; (5) differences in the types of reactors used in the experiments; (6) the length of the experiment. As a result of these differences in experimental protocols, it has often been difficult to compare the results from one laboratory to those of another, and such comparisons, when made, are often not reliable in detail. Intra-laboratory comparisons, with common experimental constraints, are better suited for examining trends with respect to solution composition, mineral chemistry, and other parameters, and these general trends are often confirmed from laboratory to laboratory. These trends provide the basis of our understanding of the effect of ligands on feldspar dissolution rates and the mechanism of LMD reactions.

In Eqn. 6, we conceptually described the overall dissolution rate, R_{total}, as a sum of contributions from HD, PMD, HMD, and LMD, even though it is not clear how the factors controlling these reactions interact. Each of these mechanisms involve the same limited mineral surface and therefore it is likely that a simple sum of contributions will not adequately reproduce observations in an experimental situation where more than one mechanism contributes to dissolution. A more general equation describing the overall reaction rates as a function of the solution and mineral surface composition, the physical conditions of the reaction, and which allows for the possibility of interaction between the various dissolution mechanisms, can be given as:

$$R_{total} = f(L, S, M, T) \tag{7}$$

where L describes the ligand or ligands, their chemical characteristics, and concentration; S describes the composition of other components of the solution and includes the effect of protons and hydroxyls on dissolution, as well as the saturation state of the solution with respect to any primary or secondary minerals (note that L could conceptually be included in this term, but we have chosen not to do so because of our focus on the ligand-mediated mechanism of dissolution); M is a parameter describing the chemical, mineralogical, and textural characteristics of the dissolving mineral and mineral surface; and T describes the physical conditions of the experiment, principally temperature. In typical laboratory experiments, one of these parameters is varied while the other three remain approximately fixed. However, these factors are not entirely independent as, for example, temperature can alter equilibria, or solution composition can affect mineral surface characteristics. We will, nonetheless, attempt to discuss these variables one at a time.

5.1. Ligand Composition and Concentration

Table 2 indicates that a wide variety of organic ligands have been found to affect feldspar dissolution rates. These results universally demonstrate that ligands can enhance dissolution rates compared to controlled experiments in the absence of ligands. Generally, it has been found that low-molecular-weight ligands capable of forming strong complexes with Al^{3+} in solution (Table 1), and therefore, by analogy, with Al-sites on the mineral surface, have the greatest positive impact of dissolution rates (Furrer and Stumm 1986; Welch and Ullman, 1993). The best example of this effect is oxalate ion. Al^{3+} forms strong bidentate inner-sphere complexes with many multifunctional organic ligands (such as oxalate) in solution, and many of these ligands dramatically affect feldspar dissolution rates (Martell and Motekaitis, 1989; Bennett and Casey, 1994). In a survey of aliphatic ligands, Welch and Ullman (1993) found that equimolar amounts of the polyfunctional ligands that form strong, stable complexes with Al^{3+} (and possibly with $Si(OH)_4$; Bennett 1991) in solution, such as oxalate, citrate, succinate, α-ketoglutarate, and pyruvate, enhanced dissolution rates to a larger extent than the monofunctional acids acetate and propionate, although both classes of ligands enhanced dissolution over the rates found in inorganic solutions. This order of effectiveness of dissolution enhancement follows, approximately, the order of the strength of the first aluminum/ligand complex in solution (log β_1 in Table 1). However, the strength of this first association cannot be the only controlling factor. Many of the aromatic ligands studied, which form extremely strong complexes with Al in solution, are not as effective at promoting LMD as oxalate and citrate (Manley and Evans, 1986). Apparently other characteristics of the association of the ligand with the Al sites on the feldspar surface are also important (Bennett and Casey, 1994).

The observation that LMD rates appear to be higher in the presence of ligands that strongly complex Al in solution further suggests that the LMD mechanism is acting primarily at the Al sites or at Al-O-Si bonds (Kubicki et al., 1997) at the feldspar surface, in support of other lines of evidence. For example, in complexing organic acid solutions at near neutral pH and low temperature, feldspar dissolution is more rapid than HD alone and approximately stoichiometric (Fig. 3; Welch and Ullman, 1993; 1996; Stillings et al., 1996; Schweda, 1989; Mast and Drever, 1987; Schenk et al., 1989). In contrast, in similar inorganic solutions, where overall dissolution rates are low, Si is often released preferentially to Al and Al may not be detected in solution (Fig. 3; Welch and Ullman, 1993; Manley and Evans, 1986). However, Bennett et al. (1988) observed LMD of quartz, suggesting that, in the absence of Al sites on the mineral surface, ligands can interact with Si sites in much the same way in which they interact with Al sites on feldspar surfaces. Inorganic ligands may also contribute to LMD; experiments have shown that fluoride can enhance feldspar dissolution by a LMD mechanism as well (Amrhein and Suarez, 1988; Shotyk and Nesbitt, 1992).

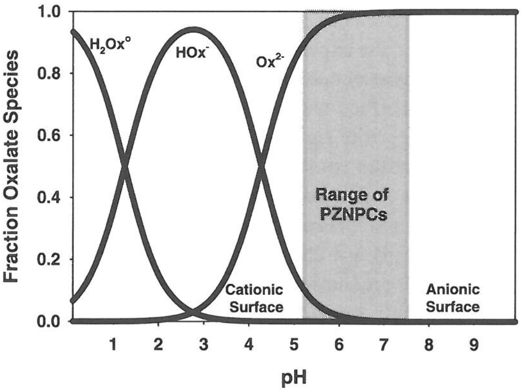

Fig. 2. The importance of ligand and surface charge on dissolution rates. In the pH region below the point of zero net proton charge (PZNPC) the average charge on the feldspar surface is positive. In this range of pH, the adsorption of anionic organic ligands (oxalate is given as an example), which is the first step in the ligand-mediated dissolution (LMD) reaction mechanism, is favored. Above the PZNPC, the anionic surface will electrostatically inhibit ligand adsorption, and therefore LMD as well. The PZNPC is given as a range of values (stippled) in this diagram.

Manley and Evans (1986) found that salicylic, protocatechuic, gallic, p-hydroxybenzoic, vanillic, and caffeic acids enhanced feldspar dissolution and that the degree of enhancement increased with the Al content of the feldspar and with the strength of the organic acid (pK_a, Table 1). However, they could not distinguish between the impact of LMD and PMD in their experimental design. A number of authors have also demonstrated that complex organic solutions

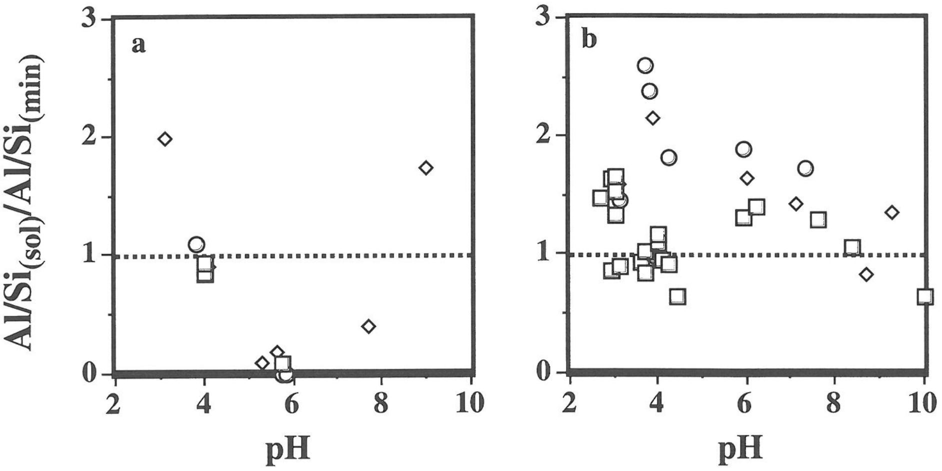

Fig. 3. The ratio of Al/Si released to solution during dissolution normalized to the Al/Si ratio of the dissolving feldspar. (Bytownite = □; Labradorite = ◊, ○ ; data from Welch and Ullman, 1993). (a) The Al/Si release ratio in the absence of organic ligands is a strong function of pH, reflecting the solubility of Al(III) species in solution. (b) The addition of ligands that form strong and stable complexes with Al(III) in solution, and therefore, presumably at the mineral surface as well, leads to a dramatic increase in the Al/Si release ratio and the rates of mineral dissolution (Welch and Ullman, 1993). This is strong evidence of the direct interaction of ligands with Al sites or perhaps Al-O-Si bonds at the mineral surface leading to LMD.

such as stream water and peat, soil, and leaf extracts can also enhance the dissolution rates of feldspars by a LMD mechanism (Tan, 1980; Lundström and Öhman, 1990; Heyes and Moore, 1992). Although these experiments with complex organic materials are difficult to interpret, Lundström and Öhman (1990) suggest that the impact of their mixtures on dissolution rates is due to an easily metabolizable fraction of the mixtures, suggesting that lower molecular weight and/or multifunctional components of the mixture are responsible for the observed LMD enhancement.

At higher temperatures, Bevan and Savage (1989) and Blake and Walter (1996, 1999) demonstrated that both acetate and oxalate are effective at enhancing dissolution rates compared to inorganic controls at 70 - 100 °C. At 100 to 160 °C, acetate and oxalate also enhance dissolution rates (Surdam et al., 1984; Stossel and Pittman, 1990; Manning et al., 1992; Gestsdóttir and Manning, 1992; Hajash et al, 1992, 1998; Huang and Longo, 1992; Franklin et al., 1994). This is in spite of the suggestion, based on low-temperature studies, that the relative importance of LMD compared to PMD may decrease with increasing temperatures (Welch and Ullman, 2000). These observations suggest that there may be some unexplored details of the LMD mechanism that change as a function of temperature. Many of the qualitative observations of LMD at low temperature, however, appear to be consistent with the higher temperature observations.

There are a number of experiments that demonstrate that the ligand-mediated rate of dissolution, where and when observed, increases monotonically with ligand concentration (Fig. 4). Welch and Ullman (1992) demonstrated that the oxalate-mediated dissolution rate of bytownite feldspar (An_{75}) was linearly proportional to total oxalate concentration up to 1 mM, but that the constant of proportionality was a function of pH. The absolute enhancement of dissolution was greatest at pH = 3 and decreased with increasing pH, suggesting that oxalate-mediated dissolution was linearly dependent on HOx^- concentration, or that there is some other synergy between LMD and PMD mechanisms. Stillings et al. (1996) found that the oxalate-mediated dissolution rate of andesine (An_{47}) was approximately linear with total oxalate concentration up to 8 mM at pH = 3 and pH = 4 (Fig. 4c), but that oxalate apparently inhibited dissolution at high total oxalate concentrations (greater than 2 mM) at neutral pH. These results were used to suggest that the effect of oxalate on LMD is dependent on the changing speciation of oxalate in solution (see Fig. 2), and that dissolution rates should be best described in terms of the activities of the ionic oxalate species HOx^- and Ox^{2-}. Stillings et al. (1996) suggest that an alternative non-linear, but nonetheless monotonically increasing function of the total free ionic oxalate activity ($\{HOx^-\} + \{Ox^{2-}\}$) better fits the data at these high total oxalate concentrations. This empiri-

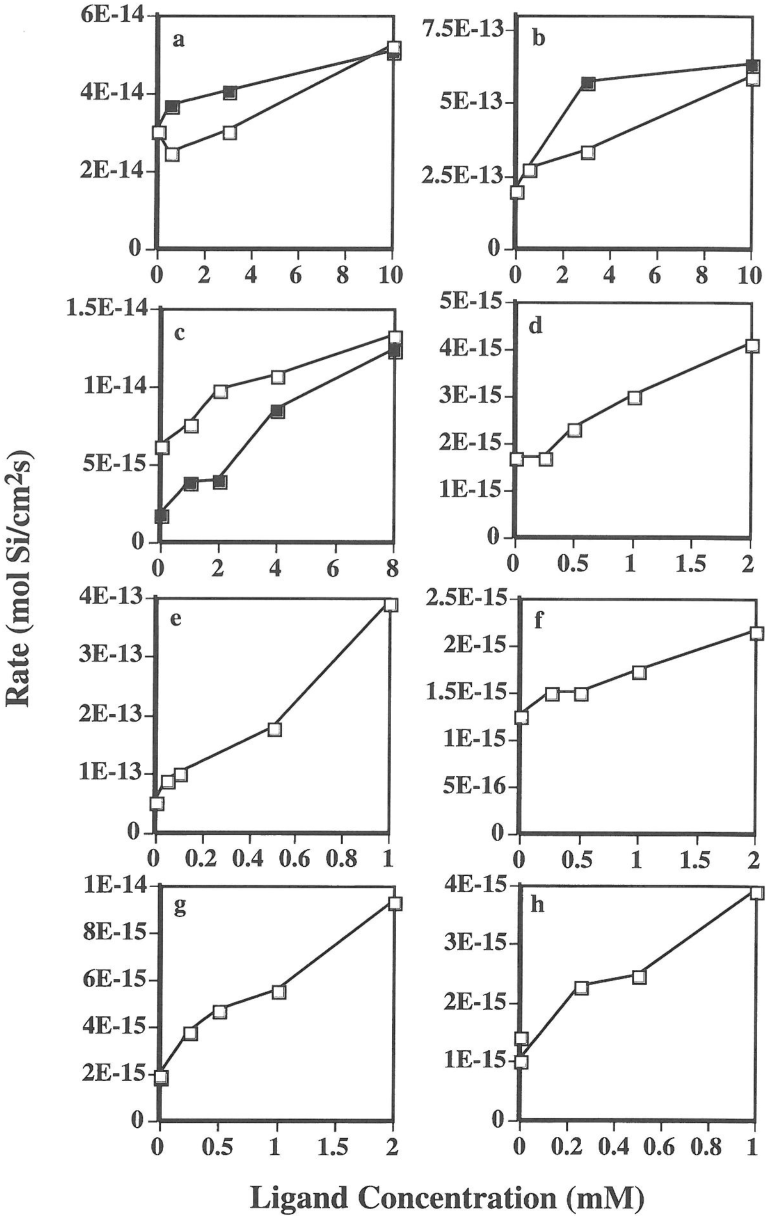

Fig. 4. Feldspar dissolution rates (as quantified by silica release rates) in the presence of low-molecular weight ligands are a monotonic function of ligand concentrations when other factors are held constant. The same ligands that enhance dissolution at lower concentrations may inhibit dissolution rates at high concentrations (>1-2 mM under some experimental conditions; Stillings et al., 1996; Ullman and Welch, unpublished). (a) Orthoclase dissolution in batch reactors at pH 6 and 80 °C (oxalate = ❒; citrate = ■; data from Blake and Walter, 1999); (b) Labradorite dissolution in batch reactors at pH 6 and 80 °C (oxalate = ❒; citrate = ■; data from Blake and Walter, 1999); (c) oxalate-mediated dissolution of andesine in a flow-through reactor (pH 3 = ❒; pH 4 = ■; data from Stillings et al., 1996); (d) gluconate-mediated dissolution of bytownite in a flow-through reactor at neutral pH (Vandevivere et al., 1994); (e) oxalate-mediated dissolution of bytownite in a flow-through reactor at pH ≈ 4.5; (f) oxalate-mediated dissolution of albite in a flow-through reactor at pH ≈ 4.5; (g) oxalate-mediated dissolution of andesine in a flow-through reactor at pH ≈ 4.5; (h) oxalate-mediated dissolution of albite in a flow-through reactor at pH ≈ 6.0 (e - h, data from Ullman and Welch, unpublished).

cal relationship may be the result of the non-linearity of adsorption behavior at high total oxalate concentration and the ultimate dependence of dissolution rate on this adsorption step (Amrhein and Suarez, 1988). Vandevivere et al. (1994) found that the gluconate-mediated rate of bytownite (An_{75}) dissolution was also linearly proportional to total ligand concentration at pH = 6 (Fig. 4d). Blake and Walter (1999) indicate that LMD rates at 80 °C increase monotonically but non-linearly with oxalate and citrate concentration and similarly conclude from these results that adsorption of the ligand is an important step in the LMD process (Figs. 4a and 4b). Knauss and Copenhaver (1995) also observed a monotonic but non-linear rate increase due to malonate-mediated dissolution.

Mixtures of ligands also tend to enhance dissolution compared to PMD alone. Franklin et al. (1994) found that the addition of oxalate to a solution of acetate at 100 °C enhanced LMD rates by comparison with the acetate solution alone. However, Huang and Longo (1992) note that mixtures of ligands may also lead to dissolution inhibition. The addition of EDTA or oxalate to solutions of catechol lead to overall LMD rates less than rates measured in catechol solution alone. This observation suggests that there are competitive reactions between dissolution enhancing species that may be important in field settings where many different ligands with different dissolution enhancing properties may play a role.

Not all ligands enhance dissolution rates. Welch and Vandevivere (1994) and Welch et al. (1999) demonstrated that several acidic polysaccharides (alginate, gum xanthan, and pectin) inhibited feldspar dissolution rates in near-neutral solutions. Inhibition was a function of the concentration of the polymer in solution and the abundance and orientation of carboxylic acid functional groups on the polymer chain. In addition, a high-molecular-weight fraction of polyaspartate (26kD) inhibited dissolution, while a lower molecular-weight fraction (6kD) had no effect on dissolution rates. A number of other polysaccharides had no impact on dissolution rates. However, under mildly acidic conditions, several of the acidic polysaccharides greatly enhanced feldspar dissolution compared to the controls. The maximum enhancement occurred near the pH of the pK_a of the carboxylate groups of the polymers and not at the pH of maximum Al-organic complexation in solution (Welch et al., 1999). On the basis of these results, Welch et al. (1999) suggest that the enhancement of Al leaching from the feldspar surface, and therefore the overall feldspar dissolution rate, is related not only to the strength of the Al-L complex, but also to the solubility and stability of this complex once formed.

Some bacterially produced polysaccharides enhanced dissolution compared to buffered controls, but inhibited dissolution rates in the presence of gluconate, a dissolution-enhancing ligand (Welch and Vandevivere, 1994). This dual nature of polymers can be explained by considering the competition between polymer complexation in solution and polymer adsorption and binding to the mineral surface. At near-neutral pH, the carboxylic groups of the polymers are deprotonated and bind irreversibly to multiple sites on the mineral surface, thereby inhibiting the dissolution reaction by a reduction in the number of reactive sites or reactivity of the adsorption sites. Under mildly acidic conditions, only a fraction of the carboxyls are deprotonated. Under these conditions, the polymers can bind to the surfaces, but less strongly, and protons are also available to react with the mineral surface and release ions by the PMD reaction. Once reaction products have been released to solution, these can react with the polymers to further reduce the activity of the carboxylic sites on the polymer and therefore the strength of surface adsorption and binding, thus further enhancing the PMD reaction. It may be difficult to distinguish between this combined PMD and LMD mechanism and a mechanism where the primary effect of protons is to change the solubility of a multiply-bound ligand-aluminum surface complex allowing dissolution by a primarily LMD mechanism.

Low-molecular-weight ligands can also have this dual dissolution-enhancing and inhibiting nature. In feldspar dissolution experiments, pyrocatechol violet initially increased feldspar dissolution compared to controls (Schenk et al., 1989; Petersen et al., 1992). However, long-term dissolution rates were inhibited by this ligand due to irreversible adsorption to the surface. Subsequent experiments with these mineral samples showed that this inhibition could be reversed by pyrolytic removal of the adsorbed organic layer.

What is clear from these results is that the impact of ligands on the feldspar dissolution process will require consideration of the thermodynamic and steric competition between protons and ligands for Al sites at the mineral surface and between Al and protons (and perhaps other cations) for the charged functional groups of the ligand. Some of the models, discussed below, attempt to integrate these competitive processes into estimates of overall dissolution rates.

5.2. Effect of Overall Solution Composition

Mineral/water exchange is a function of solution and surface speciation, both of which are strong functions of solution pH, and to a lesser extent a function of redox potential, ionic strength, and the ionic composition of the solution. In addition, solution composition may affect the saturation states with respect to dissolving primary phases, reactive intermediates, and secondary precipitating phases which can also affect mineral dissolution rates.

5.2.1. pH dependence of dissolution

The pH dependence of mineral weathering has been studied extensively in the last several decades since acidification of natural waters is a major environmental problem and chemical weathering of minerals can neutralize this environmental acidity (see Eqns. 1 and 2). As shown in Fig. 1, silicate mineral dissolution in inorganic solutions is not a simple function of pH (Chou and Wollast, 1985; Blum and Lasaga, 1988; Welch and Ullman, 1993; 1996; Brady and Walther, 1989; Carroll and Walther, 1990; Wogelius and Walther, 1992; Hellmann, 1994; Tole et al., 1986; Oxburgh et al., 1994). The form of the PMD dissolution curve suggests that the reaction rate can be described by:

$$R_{PMD} = k_{PMD}\ [H^+]^n \qquad (8)$$

where R_{PMD} is the surface area-normalized PMD rate, k_{PMD} is a kinetic rate constant, $[H^+]$ is proton activity, and n is a factor related to proton adsorption on the mineral surface (Blum and Lasaga, 1988). Both k_{PMD} and n increase with increasing Al content of the feldspar mineral (Welch and Ullman, 1996). k_{PMD} increases by four orders of magnitude and n varies from approximately 0.2 to 1 with increasing An content along the plagioclase series in the absence of ligands (Brady and Walther, 1989; Oxburgh et al., 1994; Welch and Ullman, 1996), indicating that in acidic solutions, proton adsorption to Al sites at or near the feldspar surface is catalyzing the dissolution reaction. Welch and Ullman (1996) found that the pH dependence of n at low temperature was the same in oxalate solutions as in inorganic control experiments from An_3 to An_{49}, but was somewhat lower for $An_{77.}$ This difference in An_{77} behavior, however, may be an experimental artifact resulting from transport limitation of the dissolution rate of this reactive member of the feldspar series at high dissolution rates. These observations suggest that the effect of ligands on dissolution rates in highly acidic solution is to increase the rates of the PMD reaction, by perhaps buffering the reactive solution at acidic pH, rather than to control a completely independent dissolution pathway, as suggested by Eqn. 5. This is consistent with the observations that dissolution rates are independent of $H_2Ox°$ in solution (Welch and Ullman, 1992; Stillings et al., 1998).

In basic solutions above pH ≈ 8 to 9, mineral dissolution rates follow a rate law of the form:

$$R_{HMD} = k_{HMD}\ [OH^-]^m \qquad (9)$$

where R_{PMD} is the surface area-normalized HMD rate, k_{HMD} is a kinetic rate constant, $[OH^-]$ is hydroxyl activity, and m is a factor related to the adsorption of hydroxyl ions at aluminum (Blum and Lasaga, 1991) or Si sites (Brady and Walther, 1989). Surprisingly, Brady and Walther (1989) have found that m is relatively insensitive to mineral composition and has a value close to 0.3 for many silicate and alumino-silicate minerals. There are insufficient experimental determinations of LMD rates in basic solution to determine whether ligands affect the overall pH dependence of feldspar dissolution at basic pH. In one experimental study, Knauss and Copenhaver (1995) found no significant effect of malonate on alkali feldspar dissolution compared to the HMD rate in slightly alkaline solutions, in spite of a relatively large effect of malonate over the PMD rate in mildly acidic solutions. This may be the result of the inhibition of anionic ligand adsorption onto the negatively charged feldspar surface at basic pH (Fig. 2). The direct impact of ligands on dissolution rates may be negligible under basic conditions. However, ligands may still enhance dissolution rates indirectly at high pH by complexing with reaction products in solution and lowering the solution saturation state with respect to the dissolving mineral, as they do at lower pH (see discussion further on).

Equations 8 and 9 are often combined with a rate constant, k_{HD}, describing the slow rate of hydrolysis in neutral solutions, R_{HD}, to give a general empirical expression for the dissolution of feldspars in inorganic solutions, R_{inorg}:

$$R_{inorg} = R_{PPD} + R_{HD} + R_{HPD} = k_{HPD}\ [H^+]^n + k_{HD} + k_{HPD}\ [OH^-]^m \qquad (10)$$

(Wollast and Chou, 1988; Drever and Vance, 1994). This is the function plotted in Fig. 1 describing the pH dependence of feldspar dissolution rates in ligand-free solutions.

5.2.2. Other ions

There is good evidence that other ions in solution can directly affect the PMD rates of feldspar (Stillings and Brantley, 1995; Brantley and Stillings, 1996; Blake and Walter, 1999). In the case of the PMD rates, the effect of other cations in solution is to substitute for protons at the mineral surface, thus reducing the specific surface activity of the proton

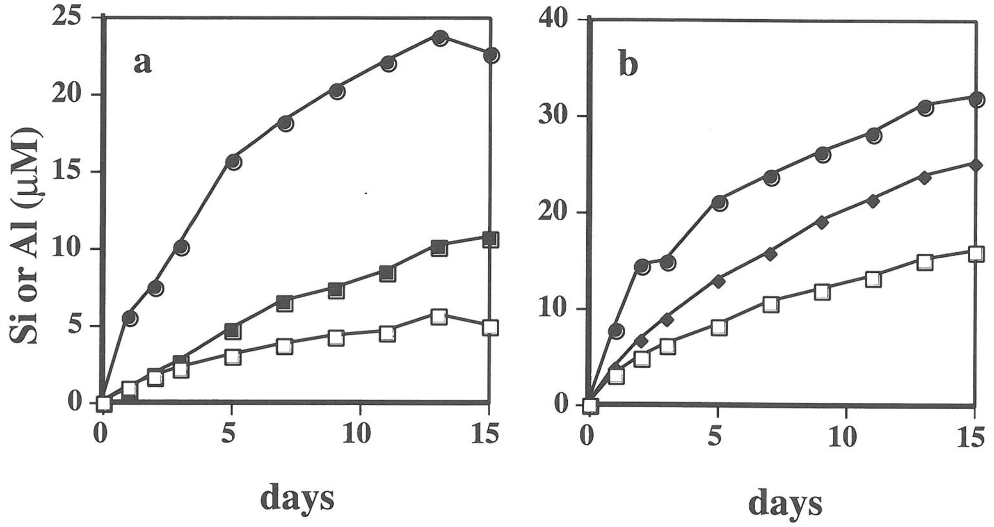

Fig. 5. The release of Si and Al to solution as a result of PMD and LMD reactions in a batch reactor at (a) 20 °C and (b) 5 °C (pH = 6-6.5; LMD Si = ■, ◆; LMD Al = ●; PMD Si control = □; no dissolved Al detected in the control; data taken from Welch and Ullman, 2000). Both initial rates and subsequent, more steady rates of Si release are higher than the controls. The initially high release rates of both Si and Al from the surface at high chemical affinities is consistent with the LMD mechanism involving surface complexation at Al sites on the mineral surface.

and therefore the PMD rate (Stillings and Brantley, 1995) This process has been described as an example of competitive cation adsorption for a finite number of reactive surface sites. In one LMD study, Blake and Walter (1999) observed that the oxalate-mediated enhancement of plagioclase dissolution could be offset by the addition of NaCl. This effect could be due to competition between Na$^+$ and protons for adsorption sites at or near the mineral surface as in the case of PMD, or alternatively, to the reduction of oxalate activity by the formation of Na-Ox complexes. However, Na-Ox complexes are fairly weak ($\log K_1(\mathrm{NaOx}^-) \approx 1$; Smith and Martell, 1998), and therefore the former competitive adsorption mechanism, analogous to the proton/Na$^+$ mechanism, but involving cation/anion competition, appears to be the most reasonable. However, other ions that form stronger complexes with ligands, including for example some of the products of feldspar weathering, Ca^{2+} and Al^{3+}, may be able to inhibit the rates of LMD by the solution complexation mechanism. Inhibition of dissolution by Al^{3+} has been proposed as a dominant rate-controlling process in feldspar dissolution (Oelkers et al., 1994). These authors propose that the effect is due to Al^{3+} adsorption and the poisoning of reactive sites. However, this effect may equally well be related to the formation of solution complexes and the reduction of free ligand activity (see below).

The indirect impact of solution processes on ligand activity may be a dominant process in some field settings. Any ion that can form stable complexes with ligands in solution will reduce the ligand activity, and therefore reduce the adsorption of ligands to dissolving mineral surfaces. This effect of ligand speciation and activity on LMD rates has been demonstrated by Welch and Ullman (1992) and Stillings et al. (1998). This effect may also be responsible, in part, for the rapid decrease in dissolution rates with time observed in batch experiments where the ligand activity may be significantly reduced as a result of the initial Al^{3+} and Ca^{2+} release to solution from the dissolving mineral (Gestsdóttir and Manning, 1992; Manning et al., 1992). The release of Ca^{2+} from feldspars during dissolution may also lead to the formation of stable mineral phases such as whewellite in experiments involving oxalate (Stillings et al., 1998).

5.2.3. Effect of chemical affinity

The overall dissolution rate of a mineral may be affected by the saturation state with respect to dissolving phase. When solutions are significantly undersaturated with respect to the dissolving phase, reaction rates are essentially independent of saturation state (Nagy and Lasaga, 1992; Nagy et al., 1991; Burch et al., 1993; Taylor et al., 2000). However, as the solution approaches saturation, the net dissolution

Table 2. A summary of experimental observations concerning ligand-mediated dissolution of feldspars.

Study	Organic Ligand(s)	Mineral(s) [Reactor Type]	pH [T°C]	Log(Rate) (mol/m^2/sec)	Notes
Amrhein and Suarez (1988)	Oxalate (also Fluoride)	Anorthite (An$_{93}$) [Batch]	5 to 6.5 [25]	−11.2 to −10.6	Rates dependent on adsorbed ligand concentration; oxalate and fluoride have similar effects
Barker et al. (1998)	Microbial cultures	Bytownite (Also Biotite) [Batch]	3.5 to neutral [22]	No Rate Data	Microbial metabolism enhances dissolution by a factor of 10 to 100 by a combination of PMD and LMD. SEM evidence of extensive feldspar dissolution.
Barman et al. (1992)	Oxalate, Citrate, Glycine, Salicylate	Microcline (Other minerals) [Batch]	0.5 to 5.6 [Room]	No Rate Data	Al released preferentially compared to Si in 0.5 M oxalic acid, citric acid, and glycine, and in 10 mM salicylic acid.
Bennett et al. (1988)	Citrate, Oxalate, Salicylate, Acetate	Quartz [Batch]	3 to 7 [25]	−10.1 to −8.5	Dissolution enhancement was: Citrate > Oxalate > Salicylate > Acetate = Water. Rates in citrate solution increase with concentration.
Bennett (1991)	Citrate, Oxalate	Quartz [Batch]	Neutral [25–70]	−12.7 to −9.9	Strong evidence is presented that organic-Si complexes form and play a role in mineral dissolution. Ligands significantly lower the apparent activation energy of dissolution.
Bennett et al. (1991)		[Field Study]	4.6 –7.7	No Rate Data	The weathering of silicates in a peat bog is controlled by silica-organic associations.
Bennett et al. (1996)		Microcline, Anorthoclase, Albite, Oligoclase (and other silicates) [Field Study]		No Rate Data	Silicate surfaces are colonized by bacteria in an anoxic, contaminated aquifer setting. Etching of silicates is correlated with bacterial settlement.
Bevan and Savage (1989)	Oxalate	K-feldspar (Or$_{83}$, Perthitic) [Batch and Flow-through]	1, 4, 9 [70 and 95]	−12 to −9.1	At pH 1, oxalate inhibits dissolution Under other conditions oxalate enhanced rates by a factor of 1.5 to 4. Temperature dependence of dissolution (E_a) is from 14.4 to 57.7 kJ/mol.
Blake and Walter (1996)	Oxalate, Citrate	Orthoclase (Or$_{70}$) (also Quartz) [Batch]	6 [80]	No Rate Data	Ligands enhance Si release by a factor of 3 compared to buffered controls. Al release is not detected in controls, but is approximately stoichiometric with ligands.
Blake and Walter (1999)	Oxalate, Citrate	Albite (An$_1$), Orthoclase (Or$_{69}$), (also Quartz), Labradorite (An$_{69}$), [Batch]	6 [70-80]	−12.0 to −8.8	Dissolution rates increase monotonically but not linearly with ligand concentration. Enhancement increases with An content. The addition of Na$^+$ to solution inhibits LMD.

Brady and Carroll (1994)	Acetate	Labradorite (An_{60}) [Flow-through]	4 [21, 35, 60]	No Rate Data	Determined E_a of labradorite dissolution of 48 kJ/mol at two different levels of pCO_2
Franklin et al. (1994)	Acetate, Oxalate (and combinations)	Albite (An_2), also Quartz [Flow-through column, 345 bars]	2.5 to 7 [100]	−10.8 to −8.9	Mixtures of acetate and oxalate enhance rates over acetate alone. Adsorption isotherm model gives good prediction of rates.
Gestsdóttir and Manning (1992)	Acetate, Oxalate	Albite [Batch, 500 bars]	6.75 – 8 [150]	No Rates per Surface Area	The results indicate that acetate increases the rate of dissolution but not overall albite solubility. Both the solubility and dissolution rate increase with increasing oxalate concentration.
Hajash et al. (1992)	Acetate, (and mixtures with Oxalate)	Albite (An_3) [Batch, 345 bars]	2.8 – 7 [100]	−11.0 to −9.0	Acetate increases dissolution rates. Mixtures of oxalate with acetate increase dissolution rates relative to acetate alone above pH = 3. Dissolution rates proportional to total oxalate concentration.
Hajash et al. (1998)	Acetate, Citrate (and in combination)	Albite [Flow–through Column, 1 and 345 bars]	4.4 – 5.7 [100, 160]	−10.9 to −9.0	Rates in organic solution are approximately 2 – 10x that of inorganic controls. Rate uncertainties due to surface area uncertainty.
Heyes and Moore (1992)	Leaf and Peat Extracts	Microcline (and other minerals) [Batch]	5.5-7.4 [25]	No Rate Data	Leaf leachates containing 50 and 300 mg/L DOC were more effective weathering agents than peat extract, HCl, or water.
Huang and Keller (1970)	Acetate, Salicylate, Tartrate, Aspartate	Microcline, Labradorite (other minerals) [Batch]	Mildly acidic	No Rate Data	Organic ligands leach Al from minerals preferentially to Si.
Huang and Kiang (1972)	Acetate, Salicylate, Aspartate, Citrate	K-spar, Albite, Oligoclase, Labradorite, Bytownite, Anorthite [Batch]	Mildly acidic	No Rate Data	The net release of feldspar into solutions of organic acids is proportional to An content. Al was preferentially leached compared to Si in strongly complexing organic solutions, Citrate > Salicylate > Aspartate > Acetate.
Huang and Longo (1992)	Catechol, Acetate, Oxalate, and EDTA (and in combination)	Anorthite (An_{98}) K-spar (Or_{73}), Oligoclase (An_{28}) [Batch]	2.9 to 8.5 [95, 100]	−11.6 (pH = 6) to −10.7 (pH = 3.5, K–spar) to −10.4 (for An_{98})	Catechol and EDTA enhance dissolution to a larger extent than oxalate. Mixtures of ligands show some inhibition.
Jorgensen (1976)	Catechol	Microcline Oligoclase (also Quartz and other Minerals) [Batch]	9.4 – 9.7 [25]	No Rate Data	Minerals dissolve incongruently in catechol solutions, leaving a residual surface enriched in Al. Five times more quartz dissolution in catechol compared to inorganic controls. No inorganic controls for feldspars.

Knauss and Copenhaver (1995)	Malonate	Albite (An$_1$), Microcline (Or$_{95}$) (and Quartz) [Flow-through]	4 – 10 [70]	–11.1 to –10.9	Feldspar dissolution rates increase monotonically by a factor of 2 – 10 in malonate solutions. The predominant impact is at mildly acidic to neutral pH.
Lundström and Öhman (1990)	Citrate, (also Streamwater and Organic Extracts from forest soils and peat)	K-spar (Or$_{64}$), Oligoclase (An$_{19}$) [Batch]	5.1 [20]	–12 to –11.5	Citrate, streamwater and extracts increase rates by a factor of 1.7 to 2.7. Microbial inoculation of extracts decreased dissolution rates to that of controls, suggesting that dissolution enhancing compounds are easily metabolizable.
MacGowan and Surdam (1988)	Acetate Oxalate Malonate	Andesine [Batch]	5.8 – 8.6 [100]	No Rate Data	Dissolution experiments with formation waters and organic acids showed extensive dissolution of mineral fragments by SEM correlated with increase of Al in solution.
Manley and Evans (1986)	Citrate, Oxalate, (and Aromatic Acids, see notes)	Labradorite (An$_{69}$), Albite (An$_6$), Microcline (Or$_{67}$) [Batch]	No Data	No Rate Data	The relative effectiveness of organic acids in dissolution enhancement was Oxalic ≈ citric > salicylic > protocatechuic ≈ gallic > p-hydroxybenzoic > vanillic ≈ caffeic. Labradorite dissolves more readily than microcline, which dissolves faster than albite.
Manning et al. (1992)	Acetate, Oxalate, Citrate	Albite [Batch 500 bars]	3 – 9 [150]	No Rates per Surface Area	Dissolution rates increase with increasing acetate concentration, not due to increases in overall mineral solubility. Oxalate and citrate increase dissolution rate and overall solubility. However, the effect may be related to PMD rather than LMD.
Mast and Drever (1987)	Oxalate	Oligoclase (An$_{13}$) (Also Tremolite) [Flow-through]	4 – 9 [Room]	–11.7	Neither pH nor oxalate concentration had any effect on Si release rates.
Panov et al. (1983)	Citrate, Tartrate	Oligoclase (An$_{13}$) Microcline (Or$_{85}$) [Batch]	Acidic [65]	No Rate Data	Trace elements are leached from feldspars by ligands.
Petersen et al. (1992)	Salicylate, Tartarate, Citrate, Pyrocatechol-Violet	Feldspar-rich Pegmatite Sand [Batch and Flow-through]	4.5 – 6	Initially: –11.4 to –8.6 Long–term: –12 to –10.5	Dissolution is approximately stoichiometric at pH 4.5 and 6 with ligands. The organic ligands increased Si release by at most a factor of 2.5. (See also Schenck et al., 1989). Pyrocatechol violet both increased and inhibited under differing conditions.

Reed and Hajash (1992)	Acetate (Acetate + Oxalate)	Granitic Sand (63% Feldspar) [Batch, 345 bars]	4.2 – 4.5 [100]	No Rate Data	Organic ligands increased release of feldspar dissolution products. Oxalate + acetate was more effective than acetate alone.
Schenk et al. (1989)	Salicylate, Tartarate, Citrate, Pyrocatechol-Violet	Feldspar-rich Pegmatite sands [Batch and Flow-through]	pH 4.5 to 6	−11.4 to −8.6	Dissolution is approximately stoichiometric at pH 4.5 and 6 with ligands, Al is undetectable in DI. Organic ligands increased Si release by at most a factor of 2.5. Pyrocatechol-violet inhibited feldspar dissolution by irreversibly adsorbing to the surface. (see also Petersen et al., 1992)
Schweda (1989)	Citrate (Also Cations)	Microcline, (Also Sanidine) [Flow-through]	4, 5.7 [25]	−13 to −10.5	At pH 4, citrate (0.1 to 1 mM) had no effect on sanidine dissolution rates. At pH 5.7 in citrate, sanidine and microcline rates approximately double. Al release in citrate solutions is approximately stoichiometric.
Shotyk and Nesbitt (1992)	Oxalate, Fluoride	Labradorite, Anorthite [Flow-through]	4.0 – 4.1 [not specified]	No Rate Data	Based on SIMS profiling labradorite dissolved incongruently and anorthite dissolved congruently. LMD produced thicker leached layers than PMD. Ligands accelerate dissolution rates.
Song and Huang (1988)	Oxalate Citrate	Microcline, Orthoclase [Batch]	Neutral and Acidic	No Rate Data	K release from minerals enhanced by citrate and oxalate. Al released preferentially to Si in acidic oxalate solution.
Stillings et al. (1996)	Oxalate	Microcline (Or$_{78}$), Albite (An$_{2}$), Oligoclase (An$_{22}$), Andesine (An$_{43}$), Bytownite (An$_{76}$) [Flow through]	3 – 7 [Room]	−11.7 to −9.4	Experiments to look at effect of mineral composition and, for one mineral, effect of oxalate concentration over a range of pH. Ligand dependence of dissolution rates best described in terms of ionic activities of ligand and adsorption model.
Stoessel and Pittman (1990)	Acetate, Propionate, Oxalate, Malonate	Microcline [Batch, 300 bars]	1.5 – 8.3 [100]	No Rate Data No Rate Data	Acetate and propionate had limited effect on dissolution rates. Oxalate and malonate enhanced dissolution. Cannot distinguish between PMD and LMD effects.
Surdam et al. (1984)	Acetate Oxalate	Microcline, Albite, Andesine, Labradorite [Batch]	2.9-3.4 [100]	No Rate Data	Acetate in formation water can increase Al solubility by an order of magnitude, Oxalate can increase Al solubility by 3 orders of magnitude.

Surdam and MacGowan (1987)	Acetate, Malonate, Salicylate	Andesine [Batch]	5-5.2 [100]	No Rate Data	Organic ligands enhance Al release and solubility.
Tan (1980)	Humic and Fulvic Acid Extracts	Microcline	2.5 – 7 [24 ± 2]	No Rate Data	At pH=7, humic acids released 2–10 times greater concentrations of Si and Al than fulvic acids. Al preferentially released to Si. At pH=2.5, fluvic acids released 25% more Si and Al than inorganic control.
Vandevivere et al. (1994)	Live Bacteria and Gluconate	Bytownite (An_{77}) and labradorite [Batch and flow through]	3 to neutral [25]	–11.6 (abiotic) to –9.2 (bacteria); –11.1 to –10.8 (from 0 to 2 mM gluconate)	Microorganisms increase Si release from feldspars at neutral pH by producing organic acid. Not clear whether LMD or PMD is more important. Dissolution rate linearly proportional to gluconate concentration.
Varadachari et al. (1994)	Oxalate, Citrate, Glycine, Salicylate	Microcline (and other minerals) [Batch]	not specified [27]	No Rate Data	SEM and XRD characterization of reacted minerals.
Welch, Barker, and Banfield (1999)	Poly-saccharides	Bytownite An_{76} [Batch]	3 – 7 [25]	–11.1 (pH=6, polymer) to –10.9 (pH=6 control) to –9.5 (pH=3, polymer)	The same polysaccharides that increased Si release in acidic solutions by a factor of 10 to 100 (compared to a control) inhibited dissolution by a factor of 2 in neutral solutions.
Welch and Ullman (1992)	Oxalate	An_3, An_{49}, An_{74}, An_{77}, and Quartz) [Flow-through]	3 – 10 [Room]	–11.0 (Quartz) to –8.3 (An_{77})	Dissolution rates dependent on Al content of feldspar. Linear dependence of dissolution rates on oxalate concentration varies with pH. LMD increases overall dissolution by a factor of 10 at neutral pH.
Welch and Ullman (1993)	Acetate, Propionate, Oxalate, Citrate, Pyruvate, Succinate, α-Ketoglutarate	Bytownite (An_{77}), Labradorite (An_{49}) [Flow-through]	3 – 10 [Room]	–11.0 to –8.2 (An_{77}) –11.2 to –9.5 (An_{49})	Polyfunctional organic ligands have a greater impact on dissolution that monofunctional ligands.
Welch and Ullman (1996)	Oxalate, Catechol	An_3, An_{49}, An_{77}, and Quartz) [Flow-through]	3, 6 [Room]	–11.3 (An_3) to –8.6 (An_{77})	PMD rate increases with Al content of mineral from quartz to An_{77}. LMD rate has pH dependence.
Welch and Ullman (1999)	Gluconate producing bacteria	Bytownite (An_{75}) [Batch]	5.7 – 7 [5 – 35]	No Rate Data	Glucose metabolism produces gluconic acid. In the presence of gluconate, dissolution rates increase by either PMD or LMD, or both. The temperature dependence of metabolism leads to higher rates of dissolution at lower temperatures.

Welch and Ullman (2000)	Acetate, Oxalate, Gluconate	Bytownite (An_{75}) [Batch]	5.7 – 7 [5-35]	–11.9 to –11.0	KNO_3 and acetate solutions have the same apparent activation energy as distilled water (≈ 43 kJ/mol). Gluconate and oxalate have lower activation energy (≈ 29 kJ/mol)
Welch and Vandevivere (1994)	Gluconate, Various Polysaccharides	Bytownite (An_{76}) and labradorite (An_{50}) [Batch]	Neutral [25]	No Rate Data	Si release from feldspar inhibited by acidic polysaccharides. Bacterial exopolymers enhanced dissolution compared to control but inhibited dissolution in gluconate solutions.

rate approaches zero. This dependence can be described by the function (Lasaga, 1995, 1998):

$$\left(1 - \frac{r_-}{r_+}\right) = 1 - \exp(-A/\sigma RT) \qquad (11)$$

where (r_- / r_+) is the ratio of the rate of the reverse (precipitation) reaction over the forward (dissolution) reaction involving the primary phase, R is the universal gas constant, T is the absolute temperature, σ is a term describing the reaction stoichiometry (e.g. Aagaard and Helgeson, 1982), and A is the chemical affinity of the overall reaction given by:

$$A = RT \ln\left(\frac{K}{Q}\right) \qquad (12)$$

where K and Q are the equilibrium constant and activity product of the overall dissolution reaction.

In the experiments of Lasaga and coworkers (Nagy and Lasaga, 1992; Nagy et al., 1991; Burch et al., 1993; Taylor et al., 2000) it is clear that at chemical affinities above some critical value, there is a plateau where dissolution rates are, as expected, independent of saturation state. For plagioclases this critical value of A is approximately 40 kJ/mol (Burch et al., 1993; Taylor et al., 2000). Both the dissolution rate and mechanism may depend on chemical affinity (Lasaga and Blum, 1986). Although, the direct inhibitory effect of chemical affinity has not been demonstrated experimentally for LMD because most experiments are conducted above this critical value, it is undoubtedly an important effect closer to saturation. Typically, undersaturation in LMD experiments is aided, in part, by the formation of ligand complexes that reduce the activity of reaction products, and therefore, future studies will require some additional certainty concerning the nature and stability of ligand complexes in solution in order to determine the effect of chemical affinity on LMD. While the complexation of ligands by reaction products may increase the chemical affinity and therefore tend to increase dissolution rates, the concomitant reduction of ligand activity may also reduce dissolution rates if free ligand activity and ligand adsorption are responsible for the LMD enhancement mechanism (Stillings et al., 1998). The experimental separation of such competing processes may be extremely difficult.

Ligand-mediated enhancement of dissolution, however, cannot be due to the solution complexation mechanism alone. If this were so, there would be no dissolution enhancement at high chemical affinities, in contrast to the observations cited above. This is clearly at odds with the experimental evidence of LMD enhancement and the concentration dependence of LMD rates under such conditions.

It is clear in some LMD experiments that there is still an apparent rate dependence on chemical affinity above the critical value (Stillings et al., 1998). Oelkers et al. (1994) also observed that the PMD rate of albite had a dependence on chemical affinity well above the critical value measured by Burch et al. (1993). Oelkers et al. (1994) and others (Chou and Wollast, 1985; Stillings et al., 1998) attribute this inhibitory effect to another process, Al^{3+} adsorption and stabilization of the dissolving surface. However, this mechanism does not appear to be important for LMD. If the release of Al^{3+} to solution and subsequent adsorption is the mechanism inhibiting the rates of dissolution in the inorganic controls, the initial rates of both LMD and analogous PMD control experiments should initially be the same, with a subsequent decline in the PMD rates with time. In batch experiments, however, ligands enhance both the initial rates of dissolution compared to inorganic controls, as well as the subsequent steady state rates (Fig. 5; Welch and Ullman, 2000). Al^{3+} adsorption is likely to have a lesser impact on LMD because the formation of Al-L complexes will limit the activity of free Al^{3+} in solution and available for adsorption (see below). Further experiments will be needed to determine the relative importance of these two co-varying mechanisms on LMD.

5.3. Effect of Feldspar Composition

Several experimental studies have shown that the PMD rate of feldspar is dependent on mineral composition (Brady and Walther, 1989; Casey, et al., 1991; Welch and Ullman, 1992; 1993; Oxburgh et al., 1994). The pH dependence of dissolution rates also increases with increasing Al content from albite to anorthite along the plagioclase series. Similarly, since organic ligands are interacting primarily with Al sites, ligands tend to have a far more pronounced effect on more Ca, Al-rich plagioclases (e.g., Manley and Evans, 1986; Welch and Ullman, 1992, 1993, 1996; Oxburgh et al., 1994; Blake and Walter 1999). Welch and Ullman (1996) found that LMD rates have a similar first- or higher-order dependence on the An content of plagioclase feldspar at pH = 3 and 6. They argue that this dependence further supports the idea that the reactivity of surface Al sites toward oxalate controls the overall feldspar dissolution rate.

There are no direct determinations of the effect of feldspar heterogeneities (intergrowths and zonation) on LMD rates. Heterogeneous dissolution and the formation of periodic dissolution textures have been observed for PMD by transmission electron microscopy (Inskeep et al., 1991). Similar evidence that differences in mineral chemistry can lead to the development of periodic textures on feldspar surfaces has been observed by scanning electron microscopy for LMD (Welch, 1991). At elevated chemical affinities, the overall dissolution of heterogeneous feldspars should be predictable on the basis of the relative amounts of the chemically distinct intergrowths and their An (or Al) content. Ordering of the Al and Si tetrahedra could also be a factor in LMD and PMD, as Al-sites linked to other Al sites in a more disordered feldspar are more susceptible to attack (Oxburgh et al., 1994). The effects of chemical zonation and structural ordering on overall feldspar dissolution rates have not been experimentally demonstrated.

5.4. Effect of Temperature

The rates of feldspar dissolution increase with increasing temperature. The temperature dependence for feldspar dissolution can be described using the Arrhenius relationship:

$$k = A_o e^{\frac{-E_a}{RT}} \tag{13}$$

where k is the rate constant, A_o is the preexponential factor, and E_a is the activation energy of the dissolution reaction. This form of the temperature dependence of a reaction is most appropriately applied to a single elementary step in a reaction mechanism. However, for a large number of complex geochemical reactions that proceed through a number of elementary steps, but where a single process controls the overall dissolution rate (such as feldspar dissolution), it is a useful approximation for describing the overall dependence of reaction rate on temperature (Lasaga, 1998). Under these conditions, E_a is more appropriately called the apparent activation energy. The magnitude of E_a, however, will depend on the kinetic expression used. In most cases where the temperature dependence of feldspar dissolution rate has been measured, all parameters except temperature are held constant and therefore, the temperature dependence of the overall reaction rate will be the same as that for the measured rate constant:

$$R_{total} = A_0^* e^{\frac{-E_a}{RT}} \tag{14}$$

The apparent activation energy for PMD has been estimated previously in a number of laboratory and field studies (Lasaga et al., 1994, and references therein; Velbel, 1990,1993; Brady, 1991; Casey and Sposito, 1992; Hellmann, 1994; Brady and Carroll, 1994; Dorn and Brady, 1995). Knauss and Wolery (1986) calculated an E_a of 54 kJ/mole for albite dissolved in a flow-through reactor at neutral pH over a temperature range of 25 to 70 °C. Bevan and Savage (1989) found E_a values for both PMD and LMD at pH=1 to be similar, 59 and 50 kJ/mole, respectively, and for LMD at pH = 3, E_a was 59 kJ/mole. However, in the absence of oxalate, the apparent activation energy of PMD at pH =3 was significantly lower (15 kJ/mole). Hellmann (1994) determined an apparent activation energy for HD of 69 kJ/mole for albite at neutral pH and temperatures between 100 and 300 °C, although E_a for albite dissolution was higher by approximately 17 to 20 kJ/mole under basic and acidic conditions, respectively, due to the enthalpy of adsorption of hydroxyls and protons to the feldspar surface (Casey and Sposito, 1992). Brady and Carroll (1994) calculated an E_a of 48 kJ/mole for PMD from labradorite feldspar in a flow-through reactor in slightly acidic solutions (pH 4) from 21- 60 °C. A tabulation of additional estimates of E_a for feldspar dissolution is given by Blum and Stillings (1995). In general, the E_a for silicate minerals dissolved at low temperatures over a range of experimental conditions varies from 40-80 kJ/mole (Lasaga et al., 1994; Blum and Stillings, 1995).

Welch and Ullman (2000) found that the apparent activation energy for bytownite (An_{75}) dissolution at near-neutral pH at low temperature and in the absence of complexing ligands was 43.0±1.2 kJ/mole. The addition of acetate had no impact on the apparent activation energy, consistent with the predictions of Kubicki et al. (1997). However, the addition of oxalate or gluconate, both ions that form strong and stable complexes with Al^{3+} in solution, and presumably at the mineral surface as well, reduced E_a by about 14 kJ/mole. Whether this decrease in E_a to 28.7 ± 1.2 kJ/mole reflects a change in reaction mechanism or the catalysis of PMD and/or HD by the organic acids cannot be determined on the basis of these experiments alone. This decrease in E_a for feldspars dissolving in organic acid solutions is consistent with a field study on biological weathering; Brady et al. (1999) estimated $E_a = 55.6$ kJ/mole for lichen-mediated weathering, compared to 96.7 kJ/mole for bare rock surfaces.

Several researchers have noted an increase in Al-organic stability constants in solution with increasing temperature (Fein and Hestrin, 1994; Tait et al., 1992; Thyne et al., 1992). In apparent contrast, Welch and Ullman (2000) report that organic ligands have a relatively greater impact on feldspar dissolution rates at lower temperatures. Although the factors controlling this apparent discrepancy are not certain, it may reflect the change in organic adsorption characteristics with temperature. Since surface adsorption is an exothermic reaction, adsorption coefficients should decrease with increasing temperature (Thyne et al., 1992; Tait et al., 1992; Piatt et al., 1996). If ligand adsorption to a mineral surface is an important contribution to the LMD mechanism, the decrease in adsorption with temperature may decrease the relative importance of LMD dissolution compared to other dissolution mechanisms at higher temperature. Alternatively, the effect of stronger ligand complexing in solution may be sufficient to reduce free ligand activity and therefore the amount of ligand available for adsorption (Thyne et al., 1992; Fein and Hestrin, 1994). Further experiments will be needed to confirm these observations and determine the mechanism of this relative change in rates.

5.5. Dissolution Stoichiometry

Feldspar dissolution in inorganic solution is often non-stoichiometric; the charge-balancing cations, Na, K, and Ca are generally released in preference to the structural cations, Al and Si. In addition, there may be preferential release of either Si or Al from the feldspar framework depending on experimental conditions. Non-stoichiometric dissolution results from the formation of leached layers during the initial stages of dissolution (Chou and Wollast, 1984; Pačes, 1973), precipitation of secondary mineral phases (Holdren and Adams, 1982), and preferential dissolution of exsolved phases (Gardner, 1983; Shotyk and Nesbitt, 1992; Inskeep et al., 1991).

At near-neutral conditions, low temperature, and in the absence of ligands, Si is usually preferentially released to solution, leaving a thin residual surface enriched in Al (10 – 20 nm, Chou and Wollast, 1995); often Al is not detectable in solution (Fig. 3; Welch and Ullman, 1993, 1996; Blake and Walter, 1996, 1999). As pH decreases, Al release increases with respect to Si release (Welch and Ullman, 1993). In mildly acidic solutions ($pH \approx 4$) the release of the feldspar mineral framework ions, Si and Al, is approximately stoichiometric (Fig. 3). In more acidic solutions ($pH < 4$) Al is preferentially leached, leaving a surface enriched in Si. At higher temperatures (≥ 100 °C) Al is preferentially released with respect to Si under acidic, near-neutral, and extremely basic conditions; under mildly basic conditions, dissolution is congruent or slightly favors Si (Hellmann, 1995). The feldspar dissolution stoichiometry is often much closer to that of the primary mineral phase for longer experiments and at both low and high temperature (Stillings and Brantley, 1995; Hellmann, 1995). In many dissolution experiments, however, non-stoichiometric release persists up to thousands of hours. The non-stoichiometric dissolution of feldspars is consistent with the observations of Casey and Bunker (1990) who suggest that the dissolution of mixed oxide minerals is a multipathway process, with each component of the mixed oxide being leached from the mineral surface by different mechanisms, at different rates, and having differing controlling factors. Because feldspar dissolution is often non-stoichiometric, care must be taken in the extrapolation of the release rates of individual ions into solution to the overall mineral dissolution rate. Nonetheless, a comparison of release rates under different experimental conditions can still yield useful information concerning the factors controlling mineral weathering in nature.

Dissolution is similarly non-stoichiometric in many solutions containing organic ligands. However, structural ions are either released stoichiometrically from neutral to acidic pH or, in some cases, Al is released preferentially to Si (Fig. 3). Al release to solution is often greater in solutions containing complexing ligands than in inorganic solutions, particularly at near-neutral pH (Huang and Kiang, 1972; Manley and Evans, 1986; Mast and Drever, 1987; Huang and Longo, 1992; Welch and Ullman, 1993; Blake and Walter, 1996, 1999), consistent with the implication that the LMD mechanism is acting primarily at Al sites at the feldspar surface.

6. MODELS OF LIGAND-MEDIATED DISSOLUTION AND RATE PREDICTION

One of the principal reasons for laboratory studies of feldspar dissolution is to estimate the rates of chemical weathering in field situations. In order to accomplish this, the above results, integrating the effects of PMD, HD, HMD, and LMD, need to be included in models of dissolution and rates need to be scaled to the field. A number of different models and approaches have been used to integrate experimental results, and these are discussed below. The question of scaling laboratory measurements of dissolution rates to field conditions and settings has not been resolved and remains an important research direction. Some of the work in this area is briefly reviewed.

6.1. Empirical Models

The simplest empirical models of feldspar dissolution that incorporate LMD are based on the linear relationship between LMD rates and ligand concentration that have been observed by a number of investigators (Fig. 4; Welch and Ullman, 1992; Vandevivere et al., 1994):

$$R_{LMD} = k_{LMD}\,[L] \tag{15}$$

This model appears to be most useful at low ligand concentrations. By analogy to the PMD and HMD reactions, as well as to experimental evidence that indicates that the dependence on ligand concentration may not be linear over the whole range of concentrations (Knauss and Copenhaver, 1995; Stillings et al., 1996; Blake and Walter, 1999), a non-linear form is often preferred:

$$R_{LMD} = k_{LMD}\,[L]^{\,p} \tag{16}$$

This form is appropriate for a single ligand and can be expanded to include a number of similar terms for each reactive ligand:

$$\Sigma\, R_{LMD} = \Sigma k^{i}_{LMD}\,[L_i]^{\,p_i} \tag{17}$$

The equation above can be added to that for R_{inorg} (Eqn. 4) to give:

$$\begin{aligned} R_{total} &= R_{inorg} + \Sigma\, R_{LMD} = R_{PMD} + \\ &\quad R_{HD} + R_{HMD} + \Sigma\, R_{LMD} \\ &= k_{PMD}\,[H^+]^{\,n} + k_{HD} + \\ &\quad k_{HMD}\,[OH^-]^{\,m} + \Sigma k^{i}_{LMD}\,[L_i]^{\,p_i} \end{aligned} \tag{18}$$

For single ligands, this empirical equation does a good job of reproducing several experimental observations. It reproduces the observation that the pH dependence of overall dissolution reaction with ligands is the same as PMD alone (Welch and Ullman, 1996). This model also reproduces the observation that the major impact of ligands on dissolution is largely focused in the near-neutral pH range. The observed effect of feldspar composition on dissolution rates can be largely incorporated into the k_{PMD} and k_{LMD} terms; the impact of composition on k_{HD} and k_{HMD} has not been investigated. Empirical equations for k_{PMD} and n are given in Welch and Ullman (1996). This empirical model (Eqn. 18), however, fails to fully reproduce the observation that the dependence of oxalate-mediated dissolution is also a function of pH (Welch and Ullman, 1992).

A number of other empirical forms have been suggested for incorporating the pH-dependence of R_{total}. These have involved incorporating an additional, pH-dependent term into Eqn. 16 (Welch and Ullman, 1992), or by adding a ligand-dependent term into Eqn. 8 (Welch and Ullman, 1996).

However, none of the empirical models take into account the apparent inhibition of dissolution that has been observed for mixtures of ligands and the possibility that competition between ligands, protons, and other ions for adsorption sites at the dissolving feldspar surface controls overall dissolution rates (see above and Table 2). A more mechanistic model of the dissolution process is needed to incorporate and model these observations.

6.2. Adsorption Models

The success of the empirical LMD model (Eqn. 16) may result from the fact that the form of the empirical equation may be derived from a consideration of ligand adsorption to the dissolving feldspar surface (Stillings et al., 1998). Stillings et al. (1998) proposed two adsorption models for LMD reactions based on the assumption (similar to that previously proposed for PMD and HMD; Blum and Lasaga, 1988, 1991; Brady and Walter, 1989; Brantley and Stillings, 1996) that the rate of LMD is controlled by the adsorption of ligands to sites on the mineral surface. These models specifically incorporate the speciation of oxalate in solution and the adsorption coefficients for both oxalate anions, HOx^- and Ox^{2-}, into a dissolution model that treats adsorption as the rate-controlling step in the feldspar dissolution process. The dissolution rate can then be expressed as a sum of linear kinetic terms dependent on the concentrations of adsorbed protons ($[H^+]_{ads}$), HOx^- ($[HOx^-]_{ads}$) and Ox^{2-} ($[Ox^{2-}]_{ads}$) on the andesine surface:

$$\begin{aligned} R_{total} &= R_{PMD} + R_{LMD} = k_{H^+}\,[H^+]_{ads} + \\ &\quad k_{HOx}\,[HOx^-]_{ads} + k_{Ox}\,[Ox^{2-}]_{ads} \end{aligned} \tag{19}$$

This adsorption model does an excellent job of reproducing the observed oxalate-mediated dissolution of andesine (An_{47}) up to 8 mM total oxalate from pH = 3 to 4.

The two adsorption models proposed by Stillings et al. (1998) differ in the type of adsorption isotherm used. In the proposed Langmuir model, the total number of adsorption sites is held constant and the number of protonated sites is determined by the difference between the total number of adsorption sites (determined by curve fitting) and the number occupied by HOx^- and Ox^{2-}. These model parameters were determined by the best fit to adsorption experiments. The total number of adsorption sites determined by the best fit procedure is greater than the expected number of Al-sites on the andesine surface, but falls within the range of adsorption sites determined by proton adsorption. This observation would suggest that more than one ligand or proton may adsorb at a single Al site at the mineral surface, or that there are other sites, perhaps bridging Al - O - Si sites near the mineral surface, that adsorb protons and ligands. This latter observation is consistent with the predictions of *ab initio* calculations (Xiao and Lasaga, 1994; Kubicki et al., 1997).

This competitive Langmuir adsorption model has been used to describe other aspects of mineral dissolution and has the potential for incorporating the observations of both enhancement and inhibition of dissolution by ligands. Stillings and Brantley (1995) and Brantley and Stillings (1996) successfully used this model to describe the effect of other cations in solution on PMD. Although best suited for examining cation-cation competition, it also appears to adequately describe anionic ligand-cation interactions (Stillings et al., 1998; Ullman and Welch, 1998).

The alternative formulation given by Stillings et al (1998) uses the Freundlich isotherm to estimate $[HOx^-]_{ads}$ and $[Ox^{2-}]_{ads}$. This model does not limit the total amount of ligand adsorption to the mineral surface to any fixed number and reproduces the experimental trends for andesine dissolution somewhat better than the Langmuir model at high total oxalate concentrations. An intriguing aspect of these models is that the rate constants, k_{H+}, k_{HOx}, and k_{Ox} given in Eqn. 19, are essentially identical and appear to be largely independent of the adsorption model used. Since these models are based only on the number of adsorption sites (Langmuir model) and the amount of adsorption (both models), and not the specific characteristics of the sites, these rate coefficients developed for andesine may be useful to model dissolution over the whole feldspar series. These results may also make it possible to generalize this model to a wide range of different adsorbed ions on the feldspar surface to determine the overall impact of a complex mixture of ligands on feldspar dissolution, given some knowledge of the adsorption characteristics of the individual ligands. However, further tests of this model will be needed to verify that the various adsorption coefficients (protons and ligands) and reaction coefficients for each type of adsorption site are constant over the range of possible conditions.

6.3. Transition-State Models

In recent years, there has been a great deal of interest in applying Transition-State Theory (TST) to the dissolution of minerals (Nagy et al., 1991; Nagy and Lasaga, 1992; Burch et al., 1993; Gérard et al., 1998; Lasaga, 1998). The application of this theory implies that the rate of dissolution has a first-order dependence on the concentration of a transition-state (or activated) complex that is formed at the mineral surface in the course of the dissolution reaction. A term incorporating the chemical affinity of the overall reaction may be included to account for the possibility of the reverse (precipitation) reaction at low chemical affinities. Although there has been some discussion concerning the nature of the transition-state complex that is responsible for feldspar dissolution (and there may be more than one dissolution pathway and therefore more than one such complex), the approach has been very useful for describing the rates of PMD for a number of aluminum silicates.

Both Oelkers and Schott (1998) and Stillings et al. (1998) have applied this theory to ligand-mediated dissolution of feldspar. The transition-state model appears to reproduce some of the features of LMD behavior. However, the model as proposed does not include any direct dependence on ligand concentration or activity in solution that the experimental evidence requires. In contrast to a great deal of experimental evidence (see section 6.4 below), Oelkers and Schott (1998) conclude on the basis of this observation that the only impact of ligands on feldspar dissolution is on the reduction of aluminum activity in solution due to complex formation, and that there is no direct impact of ligand adsorption on the reaction with the mineral surface.

Oelkers and Schott (1998) suggest by analogy to quartz dissolution, the transition-state complex is an aluminum-depleted feldspar surface created by the elementary reaction involving the exchange of protons for Al at the surface:

$$f\,(>Al) + 3f\,H^+ \rightarrow [P^*] + f\,Al^{3+} \qquad (20)$$

where $[P^*]$ represents the activated complex for silica release, $(>Al)$ represents a surface aluminum site, and f is a stoichiometric coefficient. Let us, as an alternative, propose another stoichiometry that leads to the formation of this same activated complex, but that includes an additional monovalent ligand, L^-, as a reactant:

$$f(>Al) + 3fH^+ + fL^- \rightarrow [P^*] + fAlL^{2+} \tag{21}$$

In Eqn. 21, both ligands and protons participate in the elementary reaction involving the removal of Al from the surface. Under these conditions, the rate of reaction at high chemical affinities and when

$$K^\circ\left(\frac{a^3_{H^+}\, a_{L^-}}{a_{AlL^{2+}}}\right)^f \gg 1$$

(where K^o is the equilibrium constant for the elementary reaction represented by Eqn. 21), instead of being dependent on

$$\left(\frac{a^3_{H^+}}{a_{Al^{3+}}}\right)^f$$

(Oelkers and Schott, 1998), is dependent on

$$\left(\frac{a^3_{H^+}\, a_{L^-}}{a_{AlL^{2+}}}\right)^f$$

(where a_i refers to the activity of ion i in solution):

$$R^* = k^*\left(\frac{a^3_{H^+}\, a_{L^-}}{a_{AlL^{2+}}}\right)^f \tag{22}$$

However, the activity of the aluminum-ligand complex in solution, $a_{AlL^{2+}}$, is dependent on its formation constant, $K_{AlL^{2+}}$, and the activities of Al^{3+} and L^- in solution:

$$K_{AlL^{2+}} = \frac{a_{AlL^{2+}}}{a_{Al^{3+}}\, a_{L^-}} \tag{23}$$

Substituting this form into Eqn. 22 gives exactly the same functional dependence on

$$\left(\frac{a^3_{H^+}}{a_{Al^{3+}}}\right)^f$$

that Oelkers and Schott (1998) used to conclude that ligands do not participate in the formation of the transition state complex for feldspar dissolution:

$$R^* = k^{**}\left(\frac{a^3_{H^+}}{a_{Al^{3+}}}\right)^f \tag{24}$$

where k^{**} incorporates the formation constant $K_{AlL^{2+}}$. The fact that the same form of the transition-state model applies equally well to PMD and LMD is therefore not an indication that ligands do not adsorb and react with the mineral surface as part of the LMD process. Also, some of the variation in f observed by Oelkers and Schott (1998) and Stillings et al. (1998) may be related to slightly different, but reasonable, alternative stoichiometries for Eqn. 21. The identical forms of the transition state expressions, with and without ligands, provide a very useful tool for incorporating LMD into reactive-transport models without having to determine adsorption constants for each ligand species. Only the nature and stability of aqueous complexes will be relevant to this model, although some independent knowledge of reaction stoichiometry f will be required.

For the moment, all that can be concluded is that a number of models can predict equally well LMD dissolution rates as measured in experiments. Some of these models have mechanistic components whereas others are purely empirical. No best model, however, can be identified because of the covariance of the many chemical and thermodynamic parameters that occur in these models (Stillings et al., 1998). The choice of model, therefore, will depend on the conditions to be modeled and the availability of data to apply the chosen model.

6.4. Adsorption vs. Solution Control of Feldspar Dissolution

It is apparent from the previous discussions of the dissolution models that there is considerable debate whether complexation of Al in solution or at the mineral surface is the primary factor influencing the rates of LMD. Oelkers, Schott, and coworkers (Oelkers et al., 1994) demonstrate that Al^{3+} added to solution inhibits feldspar dissolution by adsorbing to mineral surfaces and inhibiting the formation of the activated complex for silica release (P^* in Eqns. 20 and/or 21). From this they conclude that the major impact of organic ligands on dissolution is to decrease the activity of Al^{3+} in solution by the formation Al-organic complexes (Oelkers and Schott, 1998). In contrast to this, Burch et al. (1993) and Taylor et al. (2000) have demonstrated that for feldspar dissolution in the absence of complexing ligands and at high chemical affinities, the rate is independent of solution composition, including the Al^{3+} released from the feldspar. Therefore, formation of Al-organic complexes in solution should have negligible effects on LMD. The model of Chen and Brantley (1997) suggests that the discrepancy between the low-temperature experiments of Burch et al. (1993) and Taylor et al. (2000) and the high-temperature experiments of Oelkers et al. (1994) may be due to an increase in Al^{3+} adsorption with increasing temperature.

Some degree of organic complexation at Al-sites on mineral surfaces does occur (Furrer and Stumm, 1986; Fein and Brady, 1995; Kubicki et al., 1999), but it is not known how important this effect is for mineral dissolution kinetics. There are a number of lines of experimental evidence showing that Al complexing at the mineral surface and removal of Al from the feldspar plays an important role in LMD. It is possible that Al release from the feldspar surface, leading to the formation of the activated complex for silica release (P^* in Eqns. 20 and 21), involves the initial formation of an Al-ligand activated complex for Al release. This is consistent with Casey and Bunker's (1990) view of feldspar dissolution as a multipathway leaching process.

There is clear experimental evidence that LMD dissolution rates are directly proportional to total ligand concentrations under a wide range of conditions (see Fig. 4 and Section 5.1), including at neutral pH where free Al^{3+} is undetectable in the presence or absence of complexing ligands. Also, there is clear evidence of the compositional dependence of feldspar dissolution with the more Ca, Al-rich members of the plagioclase series dissolving significantly more rapidly than the Na, Si-rich members, under comparable conditions. If dissolution was inhibited by Al^{3+} in solution, the more aluminous feldspars, which release more Al to solution, should have lower overall dissolution rates in contrast to the experimental observations (Casey et al., 1991; Welch and Ullman, 1996).

The adsorption of organics is greater at lower temperatures (see Section 5.4 above) and this leads to a larger relative enhancement of dissolution rates due to LMD at lower temperatures compared to inorganic controls. This also leads to a lower apparent activation energy for LMD compared to PMD alone (Welch and Ullman, 2000). At higher temperatures, where more total aluminum is available in solution, the relative impact of ligands on feldspar dissolution is less.

In batch reactors where Al^{3+} should and does increase with time, the initial rates of dissolution at high chemical affinities are higher in ligand-containing solutions than in non-complexing media, and remain higher throughout most experiments (Fig. 5; Welch and Ullman, 1996, 2000; Blake and Walter, 1996, 1999). Under conditions of initially high chemical affinity, the initial rates should be identical only if Al inhibition is important.

It is likely that both solution and surface complexation affect reaction rates (Stillings et al., 1998). Surface complexation should be more important at: (1) lower temperatures where ligand adsorption is stronger; (2) under conditions of high chemical affinity; (3) at neutral pH. Solution complexation is likely to be more important at: (1) low chemical affinity; (2) at higher temperatures (as the stability of aqueous Al-ligand complexes in solution increase, ligand adsorption to surfaces decreases and Al^{3+} adsorption increases); (3) for ligands (such as polymers) that cannot adsorb to the reacting surface due to steric hindrances.

6.5. *Laboratory vs. Field Measurements*

It is well documented that apparent dissolution rates in field settings are significantly lower than rates measured in the laboratory (Velbel, 1990, 1993; Brantley, 1992). There are several reasons for this discrepancy. Laboratory experiments are often performed in acidic solutions (pH < 3), where mineral dissolution rates are elevated due to PMD. However, even mineral dissolution experiments in neutral solutions yield dissolution rates greater than rates estimated from field studies (Velbel, 1986, 1990, 1993; Swoboda-Colberg and Drever, 1992). Most laboratory experiments are run at temperatures that are warmer than conditions in soils and groundwater and would therefore result in higher mineral dissolution rates (Velbel, 1990). Furthermore, minerals used commonly in laboratory experiments have fresh, clean, and very reactive surfaces which should weather faster than natural surfaces. Natural mineral surfaces have already had the more reactive components of their surfaces removed, have developed leached layers, and have been covered by secondary precipitates or other adsorbed compounds that inhibit dissolution. Laboratory experiments with naturally weathered mineral samples can better reproduce natural dissolution rates (Suarez and Wood, 1996).

This latter issue plays an important role in the potential use of laboratory estimates of LMD rates in field settings. Because feldspars used in the laboratory are so reactive, very high concentrations of ligands must be used to demonstrate a significant LMD effect over the PMD and HD effects. It is not likely that millimolar concentrations of any single dissolution-enhancing ligand are going to be found in bulk groundwater or soil solutions. However, there may be micro-environments isolated from the bulk solution, where higher ligand concentrations can be created and sustained. Recent field evidence of microbial-mediated dissolution suggests that such concentrations do occur and that LMD may be an important process in a range of field settings (Bennett and Siegel, 1987; Bennett et al., 1988, 1996; Thorseth et al., 1992; Staudigel et al., 1995; Barker and Banfield, 1996, 1998). For the moment, the LMD process can only be inferred from field observations and rates cannot be directly measured. However, experimental and observational advances may make it possible to do both simultaneously, or almost simultaneously, in the future.

Feldspar dissolution rates in field settings are also likely to be depressed by the elevated saturation state of solutions relative to the dissolving phase. In contrast to most laboratory experiments, natural waters are often closer to equilibrium saturation with respect to the dissolving phases (low chemical affinities), resulting in a net decrease in dissolution rates according to Eqn. 11. Mineral dissolution rates are also a function of the physical rate of exchange of the solution in contact with the mineral surfaces, which may impact the chemical affinity near the reacting surface (Berner, 1978). Even in flowing, open hydrological systems, there may be isolated microenvironments where solutions exchange only slowly with the bulk flow and therefore flow has minimal impact. Laboratory experiments do not adequately reproduce the limited interaction of the mineral surface with the bulk solution in soils and aquifers due to transport limitations. Although laboratory experiments are not very effective for predicting the absolute rates of mineral weathering in nature, they are nonetheless useful for determining the differences in mineral weathering rates under different experimental conditions and for determining which factors may play an important role in mineral weathering in nature. Furthermore, laboratory dissolution experiments are useful for determining mineral dissolution reaction mechanisms.

7. SUMMARY

Organic ligands participate in the overall feldspar dissolution process. They may enhance or inhibit dissolution and the release of reaction products to solution by forming complexes in solution or at mineral surfaces. The indirect effects of the formation of metal-ligand complexes in solution may inhibit dissolution by reducing the activity of free reactive ligands and therefore the adsorption of ligands to the sites (primarily Al-sites) on the mineral surface. However, when solutions are nearly saturated with respect to the dissolving mineral, the formation of ligand-metal complexes with reaction products may enhance the overall dissolution rate by increasing the chemical affinity of the overall reaction.

Experiments show that a wide range of organic ligands enhance feldspar dissolution rates. Polyfunctional aliphatic anions which form stable and soluble bidentate complexes with the ionic components of the mineral, principally Al, appear to enhance dissolution rates to a larger extent than mono-functional anions, although it is not clear to what extent this is due to the formation of stable complexes in solution or at the mineral surface. Polyfunctional aromatic ligands may also enhance dissolution rates, but not to the same extent as polyfunctional aliphatic ions. Organic polymers may either enhance or inhibit dissolution depending on their affinity for adsorption to mineral surfaces. The inhibitory or enhancement effect of ligands and polymers is a strong function of pH in acid solution, and this dependence needs to be incorporated into models of the dissolution process.

Ligands affect not only the rate of the dissolution reaction but may affect the mechanism and stoichiometry of the reaction. In solutions containing complexing organic ligands, the concentrations of Al and the Al/Si ratio released to solution are commonly greater than in the absence of complex-forming ligands. This effect is most pronounced at near-neutral pH where the solubilities of Al-containing secondary products are at their minimum. Since the major effect of organic ligands is interaction with Al at the mineral surface and in solution, the effects of ligand-mediated dissolution are most pronounced for the more aluminous members of the feldspar group.

The inhibition of ligand-mediated dissolution by mixtures of organic ligands and by other cations in solution suggests that there is competition between these solutes and organic ligands for adsorption on surface sites at mineral surfaces. There is also competition between cations (some of which may be products of the dissolution reaction) for the formation of cation-ligand complexes in solution. Models of the dissolution process are only beginning to take these competitive reactions into account.

Empirical, adsorption, and transition-state models are all useful for predicting rates of dissolution in the laboratory. However, none of these models is applicable to all experimental conditions. These models do not appear to be useful, at present, for estimating the rates of feldspar dissolution in field settings. The scaling of laboratory models to field conditions is an important future direction for feldspar weathering studies.

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