

2 Review of Literature

2.1 Previous Studies Involving Silicate Mineral Fertilisers

Of the nutrients that may be supplied by silicate rock powders, K has been the most widely studied to determine whether it can become available in soils at rates significant for crop use. Potential sources of K investigated include feldspar in Columbia (Sanz Scovino and Rowell, 1988), a lava in Germany (Fragstein et al., 1988), granite, diabase, basalt and volcanic ash in Austria (Blum et al., 1989a), gneiss, syenite and amphibolite in Norway (Baerug, 1991b), granites, gneisses, charnokites, dolerite and pegmatitic mica in Sri Lanka (Weerasuriya et al., 1993) and granite and diorite in Western Australia (Bolland and Baker, 2000; Coroneos et al., 1996; Hinsinger et al., 1996).

Other nutrients studied have included Mg from olivine, serpentine and dunite in New Zealand (Chittenden et al., 1964; 1967; MacIntire et al., 1949; McNaught and Gdanitz, 1952), Fe from basalt and tuff (Barak et al., 1983), Ca, Mg and Fe from basalt, diabase, phonolite and a lava (Fragstein et al., 1988), Ca, Mg and P from granite, diabase, basalt and volcanic ash (Blum et al., 1989a) and Mg from gneiss, syenite and amphibolite (Baerug, 1991b). The availability of micronutrients and trace elements has also been investigated by Fragstein et al. (1988) and Blum et al. (1989a).

Encouraging plant responses were obtained during glasshouse pot experiments when applications equivalent to less than 20 ton ha⁻¹ of silicate rock powder were used (Baerug, 1991a; Baerug, 1991b; Coroneos et al., 1996; Hinsinger et al., 1996; Leonardos et al., 1987). Field experiments by Sanz Scovino and Rowell (1988) using ground feldspar at a rate of 1.1 ton ha⁻¹ on laterite soils in Columbia did not, however, produce significant plant response in the year of application, although a longer term response was predicted. Blum et al. (1989a) questions the effectiveness of ground silicate rock as a fertiliser for plant growth due to the low solubility of minerals, the slow release rate of nutrients, and the high content of non-nutrient elements. Indeed, the work by Coroneos et al. (1996) indicates that water soluble KCl is much more effective for immediate plant growth, but stress that the non-exchangeable fraction of K from granite may be beneficial for plant growth in leaching environments. Subsequent work by Bolland and Baker (2000) on the

same material concluded that there was little fertilizer value of granite dust in either glasshouse or field experiments.

As well as low fertility, highly weathered soils are characterised by low pH, minimal ion-exchange capacities, Al and Mn toxicities, P-fixation and Cu-deficiency (Chesworth et al., 1989; Leonardos et al., 1987). The application of silicate rock powders has been shown to raise soil pH (Coroneos et al., 1996; Gillman, 1980; Gillman et al., 2001; Hinsinger et al., 1996; Mersi et al., 1992) and improve ion exchange capacity (Gillman, 1980; Gillman et al., 2001). Hildebrand and Schack-Kirchner (2000) also suggests that silicate rock powders may be of benefit in European forest soils where lime addition risks mobilization of dissolved organic carbon and excessive nitrification.

Kahnt et al. (1986) showed that the physical properties of soils can be influenced by addition of rock dust. The field capacity of sandy soils increased with rock dust and an 11% increase in coarse pore volume was observed for clayey soils when 10% (weight/weight) rock dust was added. In addition, leachate and nutrient removal was also reduced when 10% (weight/weight) rock dust was added to sandy soils, although this was dependent on plant type and rock type. Blum et al. (1989b) cautiously conclude that the potential of ground silicate rock is mostly for its ameliorative capacity, predicting that yearly applications of 1 ton ha⁻¹ will improve the cation exchange capacity and acid neutralising capacity of extremely poor soils.

2.2 Distribution of Nutrients Within Silicate Minerals

To understand the potential effectiveness of silicate minerals and rocks as fertilisers requires knowledge of the distribution of nutrient elements, their bonding characteristics and dissolution mechanisms. Silicate minerals are diverse in their structure and compositions and consequently exhibit diverse dissolution and weathering characteristics. Apart from exchangeable interlayer cations in micas, vermiculites and other layer silicates, nutrient elements contained in silicate minerals are either nonexchangeable interlayer (ionically bound within the negatively charged interlayer of micas, vermiculites and intergrade layer silicates; Martin and Sparks (1985)) or structural (bound within a three dimensional mineral lattice structure by combined ionic and covalent bonding; Klein and Hurlbut (1993)). K dominates the nonexchangeable interlayer pool (Badraoui

et al., 1992; Binet et al., 1985; Martin and Sparks, 1985; Mengel and Rahmatullah, 1994; Moberg and Dissing Nielsen, 1983; Niebes et al., 1993; Schmitz and Pratt, 1953; Sparks and Huang, 1985), although some release of nonexchangeable Mg has been reported in plant growth experiments (Christenson and Doll, 1973; Kaila and Kettunen, 1973; Kidson et al., 1975; Rice and Kamprath, 1968; Salmon and Arnold, 1963). Structural elements in non-interlayer sites are generally considered unavailable for plant growth (Moberg and Dissing Nielsen, 1983) as complex dissolution/recrystallisation weathering reactions are required to break all the bonds between the ions of the crystal, a process which is influenced by bond strength, chemical activity of the dissolution agent and the crystal structure (Eggleton, 1986).

The silicate minerals can be divided into four major groups that are described below.

2.2.1 Quartz

Although quartz (α -SiO₂) is highly resistant to weathering, silica is slightly soluble at pH values of soil environments. Dissolution is congruent ($\text{SiO}_2(\text{s}) + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4$), and is enhanced by organic acids in soils (Barker et al., 1997). Precipitation of silica can occur at earth-surface conditions, with various forms of amorphous silica precipitating in soils including quartz of biological origin (Drees et al., 1989). Most quartz contains extremely low concentrations of plant nutrient elements other than Si.

2.2.2 Feldspars

Although feldspars are the most abundant minerals in the earth's crust, and the alkali feldspars are the largest store of K in many soils (Huang, 1989), the role of feldspars in plant nutrition is generally ignored due to this K being structural rather than exchangeable or interlayer non-exchangeable. Feldspars are a three dimensional framework silicate with linked SiO₄ and AlO₄ tetrahedra. K (with Na or Ca) occurs within this framework to maintain electroneutrality (Huang, 1989) and is coordinated to between 7 (Ca) and 9 (K, Na) oxygen ions (Smith and Brown, 1988). Feldspars are persistent during weathering and microcline is the most persistent of the K-feldspars. Feldspars commonly weather to kaolinite, with mica sometimes being the intermediate weathering phases of K feldspars (Huang, 1989). Weathering is commonly slow and the absence of epitactic and topotactic formation of secondary minerals is due to the feldspar

structure which requires complete dissolution to release K, Na and Ca (Eggleton, 1986). Use of K-feldspar as a mineral fertiliser has met with minimal success because of these limitations (Bakken et al., 1997; Bakken et al., 2000; Gautneb and Bakken, 1995; Sanz Scovino and Rowell, 1988; Weerasuriya et al., 1993).

Other minerals similar to feldspars include feldspathoids such as nepheline and sodalite which have a lower SiO₂ and higher alkalis content than feldspars, and zeolites which have large interconnecting spaces or channels (Klein and Hurlbut, 1993).

2.2.3 Micas

Mica-group minerals are of special interest for plant nutrition as they may be a major source of K, Mg, Zn and Mn (Gilkes et al., 1972; Huang, 1989). Micas have a platy morphology with a perfect basal cleavage due to their layer structure with K occurring between the layers (Deer et al., 1992). Muscovite is a dioctahedral mica that occurs in a wide variety of rocks and can be an important source of boron. Fe and Mg are present in the octahedral sites in the trioctahedral micas phlogopite (Mg:Fe>2:1) and biotite (Mg:Fe<2:1). Biotite is a common constituent of granitic rocks where it may contain most of the Mg and Fe, together with appreciable amounts of several trace elements (Mn, Zn, Cu). Chlorites resemble micas and principally occur in low-grade regionally metamorphosed rocks, as products of hydrothermal alteration in igneous rocks and in argillaceous sediments (Deer et al., 1992).

Micas may dissolve congruently, may be completely replaced by kaolinite which inherits some structural units (Singh and Gilkes, 1991) or interlayer K may be exchanged by cations from soil solution, leaving the layer structure unchanged (Fanning et al., 1989) forming vermiculite. Newman (1969) pointed out that K-fertility of soils does not correlate well with soil mica content. Similarly, Leonard and Weed (1970) identified large differences in weathering rate between the different micas and indicated that there was no simple relationship between K-ion release rates and mica properties, although K is generally more easily replaced from trioctahedral micas (Wilson, 1975).

Mica stability is partly dependent on repulsion between superposed cations in the interlayer, tetrahedral and octahedral sheets, including H⁺ and OH⁻ (Nagy, 1995). Dioctahedral micas (eg muscovite) have a lower repulsion with the octahedral hydroxyl

being inclined away from the interlayer K-ion, providing a more stable environment. Trioctahedral micas (eg biotite, phlogopite) exhibit greater repulsion and thus weather more easily. This repulsion can be reduced by the oxidation of octahedral Fe(II), with the associated tilting of OH dipoles creating a more stable environment for interlayer K (Gilkes et al., 1972; Gilkes et al., 1973a; Gilkes et al., 1973b). The presence of F-ions replacing OH-ions may also influence the stability of micas (Leonard and Weed, 1970).

2.2.4 Ferromagnesian (Mafic) Minerals

Mafic minerals of the pyroxene, amphibole and olivine structural groups have a crystal structure that allows substitution of a wide and diverse range of elements. These minerals are also quite susceptible to weathering (Eggleton, 1986; Huang, 1989), making them important potential sources of Fe, Mg, and trace elements in rock powder fertilisers. Although Ca can occur in the mineral structure of pyroxenes and amphiboles, there are no reported plant growth experiments involving the uptake of Ca from ferromagnesian minerals. Pyroxenes and amphiboles are common in metamorphic and igneous rocks and their structure allows great flexibility of ionic replacement and consequently exhibit an extremely wide range of chemical compositions. Pyroxenes are structurally composed of single chain SiO₄ tetrahedra. Amphiboles are structurally composed of double chain SiO₄ tetrahedra, linked by O atoms and the tetrahedral sharing alternately two and three O atoms. These chains are then linked by cations. Smaller cations such as Mg and Fe octahedrally coordinate two facing chains, and the resultant bond with O is relatively weaker than that between O and Si, providing a preferred cleavage plane making amphiboles quite susceptible to weathering and an important source of Mg (and Fe) for natural waters and soils (Brantley and Chen, 1995; Huang, 1989). Calcium occupies sites in amphiboles formed by opposing tetrahedral bases, and release of Ca during weathering involves mineral dissolution (Brantley and Chen, 1995). Clay minerals may inherit the octahedral sheet from some mafic minerals (Eggleton, 1986), such that the amphiboles initially weather to chlorite, then to a chlorite-vermiculite mixed layer mineral and eventually to vermiculite (Huang, 1989).

2.3 Mineral Dissolution and Weathering Reactions

Most igneous and metamorphic rocks form under reducing conditions, at lower water contents, and at higher pressures and temperatures than occur in soil environments, and are thus unstable or metastable in surface environments. As the metastable minerals in these rocks come in contact with the atmosphere and particularly water, weathering occurs and nutrients begin their journey from the mineral to the plant. Along the way, the nutrients can be involved in numerous reactions involving minerals, soil solution and atmosphere. The central process that underscores these reactions involves nutrients being released into the soil solution as simple or complex ions or as colloids. These mineral weathering processes that contribute to pedogenesis are likely to also control the release of nutrients from powdered rock fertilisers.

Geochemical explanations of the dissolution of minerals under surface conditions have often relied on the assumption of equilibrium being attained between the solid-phase (mineral), the liquid-phase (soil solution) and the gaseous-phase (soil atmosphere). The reactions of minerals in soil essentially deal with the solubility of minerals in soil solution. Uncertainties arise due to inadequate information being available on the free energy of formation/dissolution of aluminosilicate minerals, and the nature of many solid and dissolved phases in the complex soil system. In addition many aluminosilicates are metastable and their free energy and solubility change with crystal size and structure (Stumm and Morgan, 1981).

Reactions between minerals and soil solution include dissolution, oxidation, complexing reactions, hydrolysis (the reaction of minerals with soil solution which produces new hydrous solid phases), and simple hydration (minerals increase their water content). Dissolution can be either congruent (simple dissolution of the entire solid) or incongruent (partial dissolution or complete dissolution with immediate re-precipitation of some components to form secondary, and commonly hydrous minerals), sometimes with secondary minerals inheriting structural and chemical constituents of the primary mineral (Gilkes et al., 1986).

As a starting point, it can be assumed that the soil solution prior to any interaction with the mineral will be slightly acid due to the presence of CO₂. Rainwater in equilibrium with atmospheric CO₂ will have a pH of approximately 5.7. The resultant carbonic acid

is a relatively weak organic acid capable of interaction with silicate mineral surfaces (Barker et al., 1997). It is the pH of soil solution that is often the primary determinant of weathering rate and direction. Reactions between minerals and an initially acid soil solution will change the concentrations of both H-ions and dissolved species in soil solution.

As aluminosilicates are the most common primary minerals in the soil environment, most equilibrium models have dealt with the dissolution of these minerals. Dissolution of aluminosilicates is accompanied by a release of cations and silicic acid together with the precipitation of an aluminosilicate as summarised by Stumm and Morgan (1981) in the following equation:



Aluminium released during dissolution in soils above pH 5 is generally precipitated as secondary aluminosilicates, or as oxides and hydroxides (Lindsay, 1979). Although the Al-ion is the dominant form of Al in solution below pH 5 (Lindsay and Walthall, 1989), organic complexation of Al has been observed between pH 3.8 and 5.0, and was the dominant form of soluble Al in the organic horizon of spodosols treated with tephra from the Mount St. Helens eruption of 1980 (Dahlgren and Ugolini, 1989). Aluminium toxicity from the dissolution of silicate rock powders is not expected to be of concern as this only occurs at very low soil pH (Slattery et al., 1999).

2.3.1 Mechanisms of Mineral Dissolution

Release of nutrients from the mineral structure to the soil solution have direct implications to nutrient supply and plant growth. Diverse mechanisms of silicate dissolution have been strongly debated over the last 30 years, but some consistent views have emerged during the past decade. Blum and Stillings (1995), Brantley and Chen (1995), Nagy (1995) and Nahon, 1991) have published reviews of the extensive literature dealing with dissolution studies.

The dissolution of minerals involves two opposing forces: ions strongly binding to the mineral which compete against hydration processes (Banfield and Hamers, 1997). The initial step is a rapid-exchange reaction between surface modifier cations and H-ions,

H₃O-ions or water molecules (Casey and Bunker, 1990). For further dissolution to occur, structural elements are released by destruction of metal-oxygen or metal-hydroxide bonds. This can involve base cations (Holdren and Speyer, 1985a) or the detachment of an activated complex from the mineral surface (Casey and Ludwig, 1995; Sverdrup, 1990). The activated complex can be either a specific surface species or a surface complex involving a metal exposed at the surface of the solid and a ligand from solution. The exposed surface species may also be a protonated surface OH group associated with a specific metal, a deprotonated surface OH group, or a metal-ligand complex at the surface of the mineral (Drever, 1994).

The products of dissolution can undergo precipitation to form amorphous compounds, clay minerals and sesquioxides (Berner and Schott, 1982), although this process is poorly understood. Secondary minerals may either precipitate from solution or crystallise from intermediate, non-crystalline aluminosilicates (Banfield and Eggleton, 1990; Singh and Gilkes, 1993). Secondary minerals often do not appear to adhere strongly to mineral grains (Berner and Holdren, 1977; Petrovic et al., 1976), occurring as discrete clusters of particles (Singh and Gilkes, 1993). Porous clay mineral aggregates may isovolumetrically replace feldspar crystals (Gilkes et al., 1986) and Hochella and Banfield (1995) have shown weathering products growing at internal surfaces within feldspars crystals.

The nature of the surface reaction will determine the surface features of reacting grains and long-term dissolution mechanics. Deprotonation may lead to incongruent dissolution leaving a leached, sometimes protective, hydrous aluminosilicate layer covering the mineral surface (Huang and Keller, 1970; Huang and Kiang, 1972; Luce et al., 1972; Wollast, 1967; Wollast and Chou, 1985). The incongruent release of cations appears to be parabolic over time, with the rate decreasing as the leached layer thickness increases, possibly due to slow diffusion through the leached layer reducing the dissolution rate, although this curve shape is also consistent with the reaction ceasing once a solubility product limitation is reached. Examination of the surface of weathered ferromagnesian minerals using hydrogen depth profiling (HDP) (Petit et al., 1987) and auger electron spectroscopy (AES) (Mogk and Locke, 1988) indicated the relative depletion of Mg and Ca towards the surface, while Fe, Si and Al show a relative enrichment towards the

surface. These observations are consistent with the formation of a protective and dissolution-rate-limiting leached layer.

Corrosion features have, however, been observed on mineral surfaces together with porous coatings of weathering products rather than a uniform continuous leached or protective layer (Berner and Holdren, 1977; Berner and Holdren, 1979; Berner and Schott, 1982; Berner et al., 1980; Fung and Sanipelli, 1982; Holdren and Berner, 1979; Schott et al., 1981). Early dissolution features are characterised by simple etch pits, which enlarge and coalesce with increasing dissolution. These features may become more marked as dissolution continues, until the relic mineral resembles a honeycomb. Dissolution is believed to begin at sites of surface defects, cleavages, twin planes, cracks and inclusions (Banfield and Eggleton, 1990). The nature of the etch feature is controlled more by crystallography than by the etchant (Berner et al., 1980).

2.3.2 Factors Influencing Mineral Dissolution

Regardless of the mechanisms of dissolution, observations of the processes and products of mineral dissolution within the soil environment indicate that most reactions are dependent on pH, redox (for Fe, Mn minerals), soil solution composition and temperature.

Dissolution reactions are pH dependent. Reactions occur rapidly when the metal-oxygen bond is extensively coordinated with H- or OH-ions. The release of network-forming cations is rapid in strong acids and bases, and minimal in near neutral conditions (Casey and Bunker, 1990) and is typical of the pH dependent dissolution reported for feldspars (Blum and Stillings, 1995), ferromagnesian minerals (Brantley and Chen, 1995) and sheet silicates (Nagy, 1995). As agricultural soils are rarely highly alkaline, and the dissolution of minerals is minimal at near-neutral pH (i.e. the ideal condition for agricultural soils), application of silicate rocks as fertilisers will be best suited to acid soils. Reductions in soil pH due to local chemical or biological processes such as occur in the rhizosphere could also be important in determining dissolution rate. Wollast and Chou (1985), using feldspar in a continuous flow-through fluidised bed reactor, observed rapid increases in dissolved silica, aluminium, and alkali when they imposed a sudden reduction in pH after achieving a stable dissolution rate at the previous higher pH. Such results are of

considerable interest when we consider that plants may rapidly reduce the pH of the rhizosphere solution by 2 or more units (Marschner, 1995).

Oxidation reactions are important where crystals containing Fe(II) or Mn(II) are oxidised via solid state or surface oxidation which alters the local charge balance and consequently disrupts crystal structure (Hering and Stumm, 1990). These effects may enhance or retard mineral-soil solution and mineral-soil atmosphere reactions. For example Gilkes et al., 1973a; 1973b) showed that biotite becomes more stable after oxidation, whereas oxidation of Fe in olivine increases weathering rate (Nahon, 1991). The solubility of Fe-bearing minerals and the subsequent concentration of Fe in solution is low under aerobic conditions. Localised reduction processes such as root respiration, release of reducing compounds (Hinsinger, 1998) and microorganism metabolism (Barker et al., 1997) can increase available Fe in soil solution.

The composition of the weathering solution may also be important in influencing mineral dissolution. For labradorite dissolution at pH 4, Muir and Nesbitt (1991) proposed that Al-, Mg- and Ca-ions inhibited the supply of H-ions to the mineral surface after finding that a solution containing cations produced a thinner alteration layer than solutions containing H-ions alone. Stillings and Brantley (1995) found that the dissolution of several feldspars at pH 3 decreased with increasing concentration of Na-ions which competed with the H-ions for available surface exchange sites. Plagioclase minerals generally weather preferentially with respect to K-feldspars under soil conditions (Goldich, 1938). Blum and Stillings, 1995) proposed that soil porewaters generally have a composition closer to saturation with respect to K-feldspars than for plagioclase which may reduce dissolution of the K-feldspar relative to plagioclase. Stefánsson and Arnósson (2000) calculated that surface- and non-thermal groundwaters are usually undersaturated with respect to feldspars, regardless of their composition and Al-Si ordering. The composition of soil porewater may be altered by the removal of cations from solution by plants (discussed below) which may have implications for the weathering of silicate rock powders in vegetated soils.

Minerals tend to dissolve faster as temperature increases due to activation energy considerations. This has been observed during laboratory work (Lasaga et al., 1994) and field studies (Velbel et al., 1990), and is consistent with the high rates of weathering and

soil formation that occur in tropical climates (Berner and Berner, 1987). By measuring rates of silicate weathering in granitic catchments, White and Blum (1995) showed that weathering of Ca- and Mg-silicates increased with increased temperature at constant precipitation. Warmer climate zones may also have increased precipitation, thereby increasing silicate dissolution (Berner, 1995). The application of rock powder fertilisers would thus appear to be more effective in warm, humid environments where dissolution rates, and thus nutrient availability, would be greatly enhanced. Mature soils from such environments are commonly dominated by kaolin and sesquioxides and are deficient in nutrients. Mature sandy soils in wet environments experience high rates of leaching of soluble fertilisers, making the use of ground rock powder particularly appropriate.

A factor of great importance in determining the dissolution rate of primary minerals within soil environments is grain size as it relates to the exposed reactive specific surface of minerals that increases with decreasing grain size. Holdren and Speyer (1985a) showed that the dissolution of alkali feldspars became more rapid and more congruent as grain sizes decreased, due to the greater reactivity of the fine-grained material. Similarly, the release of cations from micas mostly increases as grain size decreases (Arshad et al., 1972). However, specific surface area is not the sole crystal determinant of dissolution behaviour as the density of structural defects exposed at the surface of the crystal is also important. Grains that are large with respect to the distance between adjacent defects may have reaction rates that increase linearly with the specific surface area, and as the grain size approaches the distance between the defects, this relation flattens out, possibly increasing again as the grains become submicron in size (Holdren and Speyer, 1985b). Imperfections may be crucial for, and even dominate, the overall reactivity of a mineral surface (Banfield and Hamers, 1997) although White and Peterson (1990) suggest that dislocation densities may not directly control surface reactions except for the most deformed of rocks. Lee and Parsons (1995) also describe the crystallographic and microtextural controls influencing mineral dissolution. Examining fresh, unweathered alkali feldspars with perthitic intergrowth of low albite and tweed orthoclase with some microcline, they suggested that grains with a large proportion of their surface area parallel to (001) or (010) may have a greater density of exposed reactive sites than grains with the largest surfaces parallel to (-601) owing to the irregular fracture of this plane.

The crystallographic orientation and the size distribution of exsolution lamellae thus influence mineral dissolution.

Nutrient release from ground rock fertiliser is likely to be dependent on the grain size and the density of surface defects of the material applied to the soil. Although mineral grain size and reactive surface areas are probably important in mineral dissolution, the effect of grain size on the effectiveness of rock dust applications has generally been ignored. Where reported, a range of grain sizes have been used including <100µm (Coroneos et al., 1996; Hinsinger et al., 1996; Sanz Scovino and Rowell, 1988), <2mm (Blum et al., 1989a; Hinsinger et al., 1996), and <4 mm (Baerug, 1991a; Baerug, 1991b). Several researchers used different grain size fractions; Niwas et al. (1987) used crushed rocks in the grain size classes of 250-350µm, 60-140 µm and <60µm and Wang et al. (2000) used three size fractions of gneiss (<10mm, 2-5mm and 1-2mm) and Coventry et al. (2001) used two grain size fractions of basalt (<250µm and <40µm).

Differences in grain size and grain size distribution, or an absence of grain size information, make comparison of published results difficult in relation to assessing the effectiveness of rock dust applications. Niwas et al. (1987) reported the release of K was initially higher for rocks ground to <60µm than for rocks with grain sizes ranging between 60-140 µm and 250-350 µm, becoming similar for all grain sizes after 6 weeks. Blum et al. (1989a) compared the dissolution of basalt at different grain sizes (<200 µm and <2000 µm with 70% being between 200 and 2000 µm) in 1% citric acid and found that nutrient release was greatest for the <2000 µm fraction. This result shows that a smaller grain size may not necessarily lead to greater dissolution. Ugolini et al. (1996) also showed that some >2mm clasts found in soils are a nutrient reservoir, and are not chemically inert as is generally believed. Wang et al. (2000) however showed that K uptake by ryegrass, maize and pak-choi was greater when grown on the 1-2mm fraction of gneiss compared with the 2-5mm fraction. .

2.3.3 Biologically Induced Mineral Dissolution

Although many geochemical studies of weathering are based on an equilibrium concept, the soil environment is diverse and dynamic so that no uniform equilibrium soil solution condition exists. Biological activity due to plants and microorganisms strongly influences

the chemical and physical conditions of the soil. That part of the soil that is most strongly influenced by biological process is the rhizosphere and conditions in the rhizosphere can differ greatly from those in the bulk soil (Marschner, 1995). Spatial and temporal changes in elemental concentrations, pH, temperature, moisture levels, and gaseous CO₂ and O₂ concentrations that occur in the rhizosphere, alter the rate and quasi-equilibrium of reactions between a solid phase and soil solution. Thus it is important that powdered rock fertilisers are thoroughly mixed through that part of the soil that experience the most rhizosphere activity.

For example K and P are present at very low concentrations in soil solution in the rhizosphere as they are absorbed by the root surface at a greater rate than they can be delivered to the root by mass flow, creating a diffusion gradient which brings additional nutrients to the root (Clarkson and Hanson, 1980; Darrah, 1993; Marschner, 1995). It is this capacity of roots to reduce the concentration of ions in soil solution to very low levels that may accelerate the weathering of mineral powders and greatly increases their capacity to provide nutrients to plants. Significant amounts of non-exchangeable K can be mobilised by plant roots as K concentrations in soil solution are reduced (Hinsinger, 1998). As discussed above, K-feldspar is fairly resistant in weathering, possibly due to saturation of porewater with respect to the mineral. A consequence of K uptake occurring in the rhizosphere may be to shift the concentration of K in soil solution into disequilibrium with the K-feldspar, resulting in a release of structural K.

Hinsinger and Jaillard (1993) showed that ryegrass depleted soil solution K concentration in the rhizosphere to approximately 3 mg L⁻¹, releasing interlayer K from phlogopite. Vermiculite developed within 0.5 mm of the root surface after 3 days, extending to within 2 mm of the root after 8 days. Due to reduced K concentration in soil solution in the vicinity of the roots, interlayer K in phlogopite was replaced by cations of high hydration energy (eg Ca) to form vermiculite. Kodama et al. (1994) attributed a concentration of interstratified clay minerals in the rhizosphere with respect to the bulk soil to similar mineralogical transformations. Changes in ionic concentrations and the subsequent shift in adsorption-desorption or dissolution-precipitation equilibria (Hinsinger, 1998) may influence the release of nutrients from silicate minerals applied as ground rock. Coroneos et al. (1996) showed that non-exchangeable K originating from granite was taken up by

clover and ryegrass, but the experiment did not establish whether rhizospheric depletion was responsible. It remains unclear whether rhizosphere weathering and nutrient release from silicate rock powder will substantially influence plant nutrition, and further research is required.

Dissolution of minerals may be enhanced by pH changes in the rhizosphere due to the release of H⁺-ions (reduced pH), or HCO₃⁻-ions and OH⁻-ions (increased pH) (Marschner, 1995). This release occurs to maintain electroneutrality at the soil-root interface during cation or anion uptake (Haynes, 1990). Differences in pH between the bulk soil and rhizosphere soil may be up to two pH units (Darrah, 1993; Marschner, 1995). A single plant root can both increase and decrease the pH of the rhizosphere so as to increase dissolution of compounds that are appreciably more soluble at high or low pH (Clarkson and Hanson, 1980). Lowering of the rhizosphere pH will increase the concentration of the micronutrients Mn, Fe, Zn and Cu in soil solution (Marschner, 1995).

Changes in rhizosphere pH may have important implications for mineral dissolution. The presence of H⁺-ions increases protonation at the mineral surface and a weakening of the metal-oxygen bonds of the mineral structure. A decrease in pH would be expected to increase the rate of mineral dissolution of ground silicate rocks. Such reactions have been observed for phosphate minerals. Hinsinger and Gilkes (1995) examined the influence of lupin roots on dissolution of apatite and found that rhizosphere pH was lowered by 2 units by excretion of H⁺-ions, inducing the substantial dissolution of apatite and release of P to the plants. The amount of mineral P available to rape seedlings was estimated by Grinsted et al. (1982) to increase at least 10-fold when the pH of the rhizospheric soil changed from 6.5 to 4.1. Similar releases of other nutrients may be anticipated from silicate minerals in powdered rock fertilisers in the rhizosphere. Hinsinger et al. (1993) examined dissolution of phlogopite in the rhizosphere of rape and found that pH was lowered by more than 3 units in approximately 16 days, accompanied by a significant release of interlayer K and structural Mg.

In addition to the simple release of H⁺-ions by roots, organic acids secreted by roots and rhizosphere microflora may increase the dissolution of minerals (Grinsted et al., 1982). Organic acids have been shown to dissolve feldspars (Huang and Kiang, 1972; Lundström and Öhman, 1990; Welch and Ullman, 1993; Welch and Ullman, 1996),

micas (Arshad et al., 1972; Berthelin and Belgy, 1979; Boyle et al., 1967; Huang and Keller, 1970; Kodama and Schnitzer, 1973; Schnitzer and Kodama, 1976) and olivine (Grandstaff, 1986). Mafic minerals are more susceptible to dissolution in the presence of organic solutes than felsic minerals such as feldspars (Raulund-Rasmussen et al., 1998; Schnitzer and Kodama, 1976; Sverdrup and Warfvinge, 1995). Organic acids differ in their dissolution effectiveness with bidentate ligands (e.g. oxalate) being more effective than monodentate ligands (e.g. acetate) (Barker et al., 1997).

Dissolution of minerals is generally greater in organic acids than in inorganic acids at comparable concentrations (Arshad et al., 1972; Grandstaff, 1986; Huang and Keller, 1970; Kodama and Schnitzer, 1973; Welch and Ullman, 1993) indicating that some different reactions may occur with organic acids than with inorganic acids. The complexing properties of organic acids enable the weakening of metal-oxygen bonds at the mineral surface and reduced ion concentrations in solution (Barker et al., 1997; Lundström et al., 1995; Welch and Ullman, 1993). As a result, organic acids are able to dissolve silicate minerals at near-neutral pH where simple proton-promoted dissolution is limited (Welch and Ullman, 1993; 1996). Other reactions include Ca being precipitated as oxalate or citrate salts, thereby reducing the concentrations of Ca in soil solution (Griffiths et al., 1994; Robert and Berthelin, 1986). In addition and in contrast to dissolution in mineral acids, Al dissolves equally or preferentially to Si in strongly complexing organic acids (Huang and Keller, 1970; Huang and Kiang, 1972; Welch and Ullman, 1993), and normally immobile Al and Fe(III) are transported as complexes in solution (Antweiler and Drever, 1983).

Rhizosphere microorganisms increase nutrient availability by either directly solubilizing soil minerals or by increasing the mobility of trace elements through formation of complexes and chelates (Clarkson and Hanson, 1980). Berthelin and Belgy (1979) identified altered zones on biotite due to exposure to microorganisms for 22 weeks with reductions in concentrations of Si and K characteristic of the conversion of biotite to vermiculite. Microorganisms absorb elements for their mineral nutrition, thereby providing an ion sink and accelerating weathering reactions through the mass action effect (Barker et al., 1997). An increased concentration of carbonic acid in soils due to microbial respiration is also expected to increase mineral weathering rates (Barker et al.,

1997). A similar response is expected from root respiration, another important source of carbonic acid in soils (Marschner, 1995).

The application of ground rock powders may increase microbial activity. Mersi et al. (1992) showed that microbial activity increased when a mixture of ground basalt, diabase and bentonite was used to improve soil quality under forest vegetation. Microbial activity increased in two areas, but not in a third area that had an extremely low initial soil pH of 2.8.

Mycorrhizal fungi are recognised as increasing the volume of soil explored by plant roots (Clarkson and Hanson, 1980), thereby increasing absorption and translocation of phosphorus, nitrogen, zinc, copper and sulfur (Paul and Clark, 1989). Mycorrhizal fungi are most effective in increasing plant uptake of nutrients where soil solution concentrations of the nutrients are very low, which is likely to accelerate weathering of minerals in the rhizosphere. For forest soils from the Coast Range of Oregon, there were significantly higher concentrations of nutrients in solutions collected from soils containing ectomycorrhizal mats than in soil solutions collected where mats were absent (Griffiths et al., 1994), possibly indicating that these fungi had enhanced dissolution of soil minerals, with similar effects expected for rock dust fertilisers. Leyval and Berthelin (1989) showed that ectomycorrhizal fungi were able to solubilize K, Fe, Mg and Al from phlogopite within the rhizosphere of beech. The exploration of mycorrhizal hyphae into pores in crystals of alkali and calcium feldspars, and associated release of organic exudates, was shown by Jongmans et al. (1997) to increase weathering of the minerals in European podsoles. The dissolved products were believed to be transported by the mycorrhizal hyphae directly to the host plants. Furthermore, silicate weathering is enhanced by the production of organic acids by ectomycorrhizal fungi (Landeweert et al., 2001; Olsen and Wallander, 1998; Wallander and Wickman, 1999). The potential for dissolution of silicate rock powders would be enhanced through the removal of nutrients and the addition of acids by mycorrhiza.

2.4 Attrition Milling

Fertiliser effectiveness of silicate rocks would be expected to increase with decreasing particle size (Blum et al., 1989a), yet no systematic study has been undertaken to

determine the influence of grinding on the properties and agronomic effectiveness of silicate amendments. For grinding to produce an effective silicate fertiliser, reduction in grain size by grinding may be coupled with production of a poorly crystalline to amorphous material and a reduction in bond strength of minerals. An understanding of these mechanisms may help in the development of preparative treatments for silicate rock powders to allow for greater dissolution and nutrient availability.

Attrition milling is particularly effective in reducing particle size and may increase the solubility of silicate minerals used as fertilisers. Attrition milling is used by pharmaceutical, cosmetic, ceramic and fine chemical industries (Varinot et al., 1997) to produce ultra-fine particles and for mechanical activation (Juhász and Opoczky, 1990). Attrition milling involves powders being placed in a sealed container with milling media such as hardened steel balls and violently agitated. The powder particles are subjected to severe mechanical deformation from collisions with the milling tools leading to plastic deformation at high stress rates (Fecht, 1996). The resulting material has reduced particle size, altered particle shape, and increased reactive surface area (Kerr and Reed, 1992), factors that affect the dissolution of silicate minerals (Anbeek, 1992a; Anbeek, 1992b; Blum et al., 1990). Blum et al. (1990) proposes that the presence of dislocations at a mineral surface influences dissolution by (i) changing the overall thermodynamic properties and (ii) changing the kinetic mechanism by which material is removed from the surface. The high frequency of collisions between ball-powder-ball and ball-powder-container generally involves three modes of fragmentation acting simultaneously; abrasion, cleavage and fracture (Varinot et al., 1997). The nature, intensity and rate of application of stresses and the material(s) involved determine the resultant product.

Use of attrition milling is restricted to relatively hard, brittle materials which fracture, deform and cold weld during milling (Fecht, 1996) and is thus potentially useful for silicate mineral fertilisers (Juhász and Opoczky, 1990) where mineral reactivity is enhanced by the irreversible rupturing of Si-O bonds (Boldyrev, 1987). The influence of grinding on the properties of silicate minerals has generally been investigated for economic minerals such as talc and pyrophyllite (Aglietti, 1994; Perez-Rodriguez et al., 1988; Sanchez Soto et al., 1997; Sugiyama et al., 1994; Uhlik et al., 2000; Wiewiora et al., 1993), kaolin (Gonzalez Garcia et al., 1991; Kodama et al., 1989; La Iglesia and

Aznar, 1996; Sugiyama et al., 1994; Suraj et al., 1997), spodumene (Gasalla et al., 1987) and serpentine minerals (Drief and Nieto, 1999; Papirer and Roland, 1981). Most work has involved dry grinding which produces quicker degeneration of mineral crystal structure, and also leads to aggregation of particles after approximately 30 minutes of grinding due to welding of particles or to the formation of an amorphous silicate phase which acts as a cement (Aglietti, 1994; Perez-Roderiguez et al., 1988; Sanchez Soto et al., 1997). Aggregation is likely to reduce dissolution and thus the agronomic effectiveness of silicate fertilisers. Agglomeration can be avoided by addition of a lubricant (Papirer and Roland, 1981).