

## Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview

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### Abstract

Rock-forming minerals of igneous and metamorphic rocks contain most of the nutrients required by higher plants for growth and development. Ground rock fertilisers may provide a source of nutrients to depleted topsoils where bulk soil solutions are not in equilibrium with fresh primary minerals. Slow dissolution rates of silicate minerals may inhibit the use of rock powders in agriculture unless suitable soils are identified and optimum rock powder properties developed. This review identifies previous research where the agronomic effectiveness of ground rock fertilisers has been evaluated. There are many contradictory findings that need to be evaluated by reference to basic geochemical knowledge. Geochemical studies of mineral dissolution indicate the general reaction pathways by which nutrients are released, assuming that equilibrium between the soil solution and primary mineral is achieved. In soils, mineral dissolution is enhanced by disequilibrium between soil solution and mineral surfaces through the removal of ions by processes such as leaching and nutrient uptake. Rhizosphere processes and other biological activity may further enhance mineral dissolution through the release of H<sup>+</sup>-ions and complexing organic compounds which react with mineral surfaces. Geochemical principles can be used to predict some of the reactions that occur when ground silicate minerals are added to soils as mineral fertilisers. A range of weathering rates for minerals have been identified in the laboratory and the field and are dependent on physical, mineralogical and biogeochemical factors. The rate limiting steps may be those that involve reactions between the soil solution and mineral surface. Dissolution primarily occurs at defects at the mineral surfaces and an understanding of these surface reactions may lead to preparative procedures to enhance nutrient release from the mineral surface. Normalising the release rates of nutrients to a unit surface area basis can aid in predicting nutrient release during dissolution from various ground rock materials. Identifying the relationships between release rates of minerals and plant uptake is vital to developing an understanding the effectiveness of rock dust applied to vegetated soils.

### Introduction

Welch (1995) identifies 17 elements required by higher plants. Nine macronutrients are normally present in plant tissues at concentrations greater than 0.1% dry weight (C, H, O, N, K, Ca, Mg, P, S) and eight micronutrients at concentrations of less than 100  $\mu\text{g g}^{-1}$  dry weight (B, Cl, Cu, Fe, Mn, Mo, Ni, Zn). Some additional nutrients are required for some plants or under particular environmental conditions (Co, Na, Si). Nutrients essential to plant life occur at various concentrations in the aluminosilicate, fer-

romagnesian silicate and accessory minerals of rocks. The aluminosilicates and ferromagnesian silicates are major rock-forming minerals that vary in structure and composition, and may be a primary source of many nutrients required for plant growth.

Ground rock has been proposed as a slow release fertiliser for highly weathered soils and leaching environments where soluble fertilisers may be easily removed (Gillman, 1980; Leonardos et al., 1987; Sanz Scovino and Rowell, 1988; Chesworth et al., 1989; Weerasuriya et al., 1993; Coroneos et al., 1996; Hinsinger et al., 1996). Nutrients from ground rock

released under leaching conditions may be released at a rate that allows them to remain in the top soil to be utilised by plants (Coroneos et al., 1996). Ground rock may also be used in organic agriculture as an alternative source of nutrients to chemical fertilisers (Bockman et al., 1990), and in developing countries where the cost of importing fertilisers may be prohibitive (Sans Scovino and Rowell, 1988; Chesworth et al., 1989). There is also interest in finding a use for the waste product of quarrying (Barak et al., 1983; Chesworth et al., 1989; Coroneos et al., 1996; Hinsinger et al., 1996).

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 (Sans Scovino and Rowell, 1988), a lava in Germany (von Fragstein et al., 1988), granite, diabase, basalt and volcanic ash in Germany (Blum et al., 1989a), gneiss, syenite and amphibolite in Norway (Baerug, 1991a), granites, gneisses, charnokites, dolerite and pegmatitic mica in Sri Lanka (Niwas et al., 1987; Weerasuryia et al., 1993) and granite and diorite in Western Australia (Coroneos et al., 1996; Hinsinger et al., 1996). Other nutrients studied have included Ca, Mg and Fe in basalt, diabase, phonolite and a lava (von 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 von 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<sup>-1</sup> of silicate rock powder were used (Leonardos et al., 1987; Baerug, 1991a, b; Coroneos et al., 1996; Hinsinger et al., 1996). Field experiments by Sans Scovino and Rowell (1987) using ground feldspar at a rate of 1.1 ton ha<sup>-1</sup> 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 they stress that the non-exchangeable fraction of K from granite may be beneficial for plant

growth in leaching environments. The effectiveness of silicate rock powder may increase when initial nutrient levels in soils are low (Sans Scovino and Rowell, 1988; Hinsinger et al., 1996).

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 (Leonardos et al., 1987, Chesworth et al., 1989). The application of silicate rock powders have been shown to raise pH (Gillman, 1980; von Mersi et al., 1992; Coroneos et al., 1996; Hinsinger et al., 1996) and improve ion exchange capacity (Gillman, 1980). 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<sup>-1</sup> will improve the cation exchange capacity and acid neutralising capacity of extremely poor soils.

The limited evidence in the literature indicates that there is potential for silicate rock powder as fertilisers and/or soil conditioners. There is however concern about the true effectiveness of this material with the low solubility of silicate rock powders potentially being the limiting factor. The pathways and rate limiting reactions that control the flow of nutrients from the rock to the root are poorly understood by most soil scientists and agronomists, but the controlling mineralogical and geochemical processes have been well researched by earth scientists. Nutrient elements (K, Ca, Mg, P, S, B, Cl, Cu, Fe, Mn, Mo, Ni, Zn, Co, Na and Si) have diverse associations with minerals and are released by a variety of weathering reactions. This paper identifies some of the reactions that are likely to control the release to plants of nutrients from rock powders applied to soils to better define this potential agricultural resource.

### **Distribution of nutrients within rocks and rock forming minerals**

Many plant nutrient elements occur predominantly in rocks in minor or trace amounts of accessory minerals (e.g. S in sulphides, P in apatite) as well as these elements sometimes occurring as substituents within the structures of rock-forming silicate minerals. In order to restrict the size of this review, discussion is mostly limited to the rock-forming silicate minerals, but a complete knowledge of the sources and release mechanisms of nutrients from rocks to plants will also require knowledge of the behaviour of accessory

minerals. Indeed much is known of the weathering behaviour of apatite (Bolland et al., 1986) and sulphides (Doner and Lynn, 1989) in soils, but this is not the case for all nutrient-containing accessory minerals (e.g. tourmaline, a highly resistant B mineral).

The occurrence of rock-forming minerals within igneous and metamorphic rocks is given in Tables 1 and 2. Note that the term 'rock-forming mineral' refers to the major and essential minerals associated with each rock type. The major rock-forming minerals of almost all igneous and metamorphic rocks are silicates. Similarly, the dominant rock-forming minerals in sediments are usually silicates. Data relating to the distribution of many nutrient elements in commonly occurring igneous rocks are presented in Figure 1. Data for metamorphic minerals are more limited, but the occurrence of nutrient elements within rock-forming and common accessory minerals in Table 1 and 2 is given in Table 3 and is discussed in the following text.

For brevity, this paper does not discuss the mineralogy of sedimentary rocks where many nutrients are associated with the layer silicate clay minerals together with sesquioxides, carbonates, sulphides and organic compounds. However, the principles described in this paper apply equally to sedimentary rocks. Furthermore, for simplicity, this paper will consider that all igneous and metamorphic rocks consist of mixtures of the four major rock-forming mineral groups; quartz, feldspars, micas and ferromagnesian minerals. The relative distribution of minerals within rocks is shown in Figure 2.

### *Quartz*

Although quartz ( $\alpha$ -SiO<sub>2</sub>) 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 (Wilding et al., 1977). Most quartz contains extremely low concentrations of plant nutrient elements other than Si.

### *Feldspars*

Feldspars are alkali aluminosilicates and are, by far, the most abundant igneous rock forming minerals, and in terms of plant nutrition, are important sources of K, Ca and Na. Feldspars can be divided into alkali feldspars based on the solid-state sequence between

orthoclase (KAlSi<sub>3</sub>O<sub>8</sub>) and albite (NaAlSi<sub>3</sub>O<sub>8</sub>), and plagioclase feldspars based on the solid-state sequence between albite and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). Feldspars are observed to weather in the field at different rates with anorthite weathering faster than albite, and orthoclase being the most resistant (Goldich, 1938). As feldspars belong to a solid-state sequence where demixing is common, there can be differences in composition within the mineral due to intergrowths and twinning which may lead to preferential weathering of a particular mineral (Blum and Stillings, 1995; Lee et al., 1998). Other minerals similar to feldspars include feldspathoids such as nepheline and sodalite which have a lower SiO<sub>2</sub> and higher alkali content than feldspars, and zeolites which have large interconnecting spaces or channels (Klein and Hurlbut, 1993).

Plagioclase and orthoclase are important sources of Ca and K in soils, and in some cases orthoclase may be the largest reservoir of K (Huang, 1989). Rapid formation of secondary minerals from feldspars is restricted by their resistant framework structure. The lack of octahedrally coordinated cations for replacement, and the requirement for complete disruption of the tetrahedral framework during weathering, prevents secondary clay minerals from inheriting any structural elements from feldspars thus reducing the rate of weathering (Eggleton, 1986). Consequently, feldspars persist in soils where many other primary minerals have been altered to secondary minerals (Allen and Hajek, 1989). Feldspar in rock powders may provide a slow release source of Ca and K together with any included minor elements.

### *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 (Deer et al., 1963c), due to their layer structure with K occurring between the layers. 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 trioctahedral micas phlogopite (Mg:Fe > 2:1) and biotite (Mg:Fe < 2:1). Chlorites resemble micas and principally occur as products of hydrothermal alteration in igneous rocks and in regionally metamorphosed basic igneous rocks and pelitic sediments (Deer et al., 1963c). Biotite is a common constituent of granitic rocks where it may contain

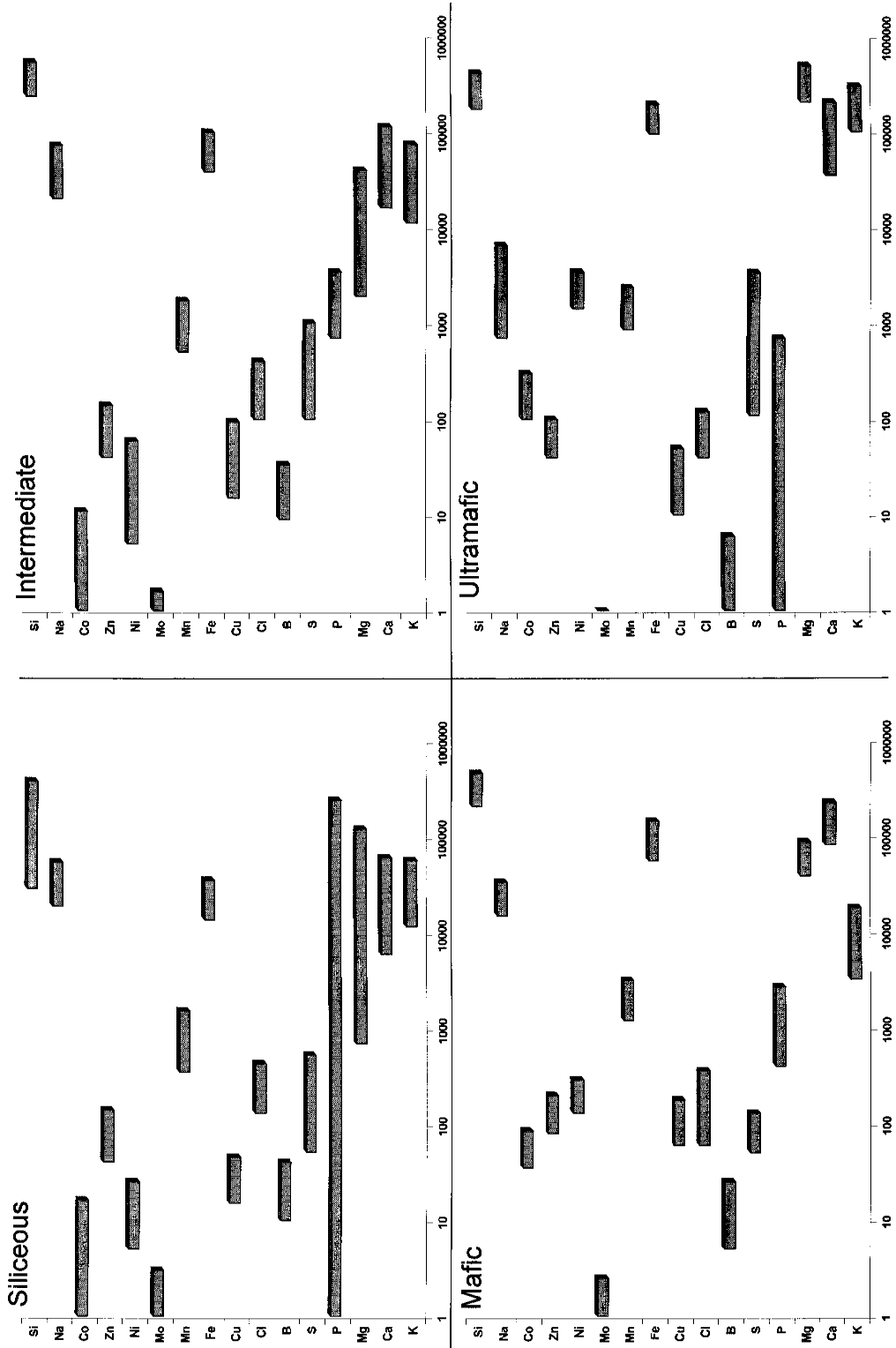


Figure 1. Concentration of plant nutrient elements in several igneous rocks. Concentrations in mg kg<sup>-1</sup>. Sources: Wedepohl (1978), Kabata-Pendias and Pendias (1992).

Table 1. Common igneous rock types and their constituent minerals. Sources: Thorpe and Brown (1985), Le Maitre (1989)

	SILICEOUS ROCKS			INTERMEDIATE ROCKS				MAFIC ROCKS	ALKAIC ROCKS		ULTRA-MAFIC ROCKS
	Rhyolite	Dacite	Obsidian, Pitchstone, Perlite, Pumice	Trachyte	Latite	Andesite	Phonolite				
Glassy Fine Grain (<1mm)							Tachyite Basalt				
Medium (1-5mm) & Coarse Grain (>5mm)	Granite	Granodiorite	Tonalite	Syenite	Monzonite	Monzodiorite	Gabbro	Nepheline-syenite	ijolite	Peridotite Dunite Pyroxenite Hornblendite	
SiO <sub>2</sub> Content	>65%				52-65%		45-52%	<45%		<45%	
Ferro-magnesian Content	<20%				20-40%		>40%	<30%	>30%	>40%	
Quartz	>20%				0-20%		0%	0%		0%	
Feldspar	K-feldspar > Plagioclase	K-feldspar < Plagioclase	Na-Plagioclase	K-feldspar > Plagioclase	K-feldspar = Plagioclase	K-feldspar < Plagioclase	Ca-Plagioclase	Feldspathoids		Absent	
Other Minerals	Muscovite Biotite Hornblende	Biotite Hornblende Pyroxene	Biotite Hornblende Pyroxene	K-feldspar > Plagioclase	Biotite Hornblende Pyroxene	Na-Plagioclase	Biotite Hornblende Pyroxene	K-feldspar Biotite Amphibole Pyroxene	Alkaline-pyroxene	Biotite Hornblende Pyroxene Olivine Chromite	
Common Accessory Minerals	Amphibole Magnetite Sphene Apatite Tourmaline		Magnetite Ilmenite Sphene Apatite				Olivine Magnetite Ilmenite Chromite Apatite	Sphene Sodalite	Olivine Magnetite Ilmenite		

Table 2. Common metamorphic rock types and their constituent minerals. Source: Huang (1962), Fry (1984)

Metamorphism type	Rock type	Major minerals	Common accessory minerals
Contact	Hornfels	Mica, Garnet, Pyroxenes, Andalusite, Cordierite	Quartz, Feldspars, Carbonates
	Skarn	Garnet, Epidote, Diopside, Fe-, Mg-, and Ca-silicates	Quartz, Feldspars, Carbonates
Contact or Regional	Marble	Calcite, Dolomite	Tremolite, Diopside, Olivine, Ca- and Mg-silicates
	Quartzite	Quartz	Garnet, Mica, Sillimanite
	Serpentinite	Serpentine	Quartz, Talc, Magnesite
Regional	Slate	Quartz, Micas, Chlorite	—
	Phyllite	Quartz, Micas, Chlorite	Sericite
	Mica-schist	Micas, Chlorite, Quartz	Feldspar, Tourmaline, Epidote, Calcite
	Calc-schist	Calcite, Micas, Quartz	Graphite, Calcium, Mg-silicates
	Greenschist	Chlorite, Actinolite, Epidote	Feldspar, Carbonates, Magnetite
	Talc-schist	Talc	Carbonates, Magnetite
	Glaucophane-schist	Glaucophane	Lawsonite, Garnet, Rutile, Micas, Quartz, Calcite
	Hornblende-schist	Hornblende, Feldspar	Garnet, Quartz, Biotite, Magnetite
	Garnet-schist	Garnet, Micas, Chlorite	Feldspars, Hornblende, Quartz
	Staurolite-schist	Staurolite, Micas	Kyanite, Garnet, Quartz
	Sillimanite-schist	Sillimanite, Micas	Quartz, Micas, Garnet
	Graphite-schist	Graphite, Micas, Quartz	Feldspar, Chlorite
	Gneiss	Quartz, Feldspar	Mica, Hornblende, Garnet, Tourmaline
	Amphibolite	Hornblende, Feldspar	Garnet, Micas, Epidote
	Granulite	Quartz, Feldspar OR Pyroxene, Feldspar	Garnet, Kyanite, Pyroxene, Tourmaline
Charnokite	Hypersthene, Quartz, Feldspar	Diopside, Hornblende, Garnet	
Eclogite	Omphacite, Garnet	Kyanite, Rutile	
Migmatite	Quartz, Feldspar	Biotite, Hornblende	

Table 3. Distribution of plant nutrients in igneous and metamorphic minerals. Source: Deer et al. (1963a, b, c, d), Wedepohl (1978), Klein and Hurlbut (1993)

	K	Ca	Mg	P	S	B	Cl	Cu	Fe	Mn	Mo	Ni	Zn	Co	Na	Si
Quartz				T	T		T	T	T				T	T		X
Feldspar Group																
K-feldspar	X			T	T		T	T	T	T			T	T		X
Plagioclase		X		T	T	T		T	T	T			T	T	X	X
Feldspathoids																
Nepheline	X	T	T						T						X	X
Sodalite	T				T		X								X	X
Mica group																
Muscovite/Sericite	X			T		C		T		T			T	T	T	X
Phlogopite (Mg:Fe>2:1)	X		X				T		X				T+			X
Biotite (Mg:Fe<2:1)	X		X	T	T	T	T	T	X	T+	C		T	T		X
Other Sheet Silicates																
Chlorite	T	T	X						X	T+					T	X
Talc			X						T	T						X
Serpentine		T	X			C			T	T						X
Amphibole Group																
Hornblende	T	X	X		T		T		X	T+				T	X	X
Actinolite	T	X	X						X	T					T	X
Glaucophane	T	T	X						X						X	X
Tremolite		X	X													X
Pyroxene group																
Epidote		X		T					X	X						X
Diopside		X	X						T	T					T	X
Hypersthene	T	T	X						X	T					T	X
Omphacite		X	X						X						X	X
Ortho- and Ring Silicates																
Olivine Group			X	T	T		T	T	X	T+		T	T	T		X
Garnet Group		X	X	T+	T		T	T	X	X		T	T+	T		X
Sphene		X			T								T			X
Lawsonite		X														X
Sillimanite/Andalusite/Kyanite									T							X
Staurolite			X					T	X	T		T	T	T+		X
Cordierite	T	T	X						X	T					T	X
Tourmaline	T	X	X		T	X			X						X	X

Table 3. Continued.

	K	Ca	Mg	P	S	B	Cl	Cu	Fe	Mn	Mo	Ni	Zn	Co	Na	Si
Carbonates																
Calcite		X								T						
Dolomite		X	X						T							
Magnesite		T	X							T						
Phosphates																
Apatite		X		X	T		T									
Oxides																
Chromite								T		T+						
Ilmenite							T	X	C	T						
Magnetite								T		T+	T		T			
Rutile									T							T

X = Main structural element in mineral.  
 T = Trace element in mineral often as an inclusion of a "foreign" ion or mineral.  
 T+ = Localised high occurrence of trace element.  
 C = Important carrier mineral of trace element.

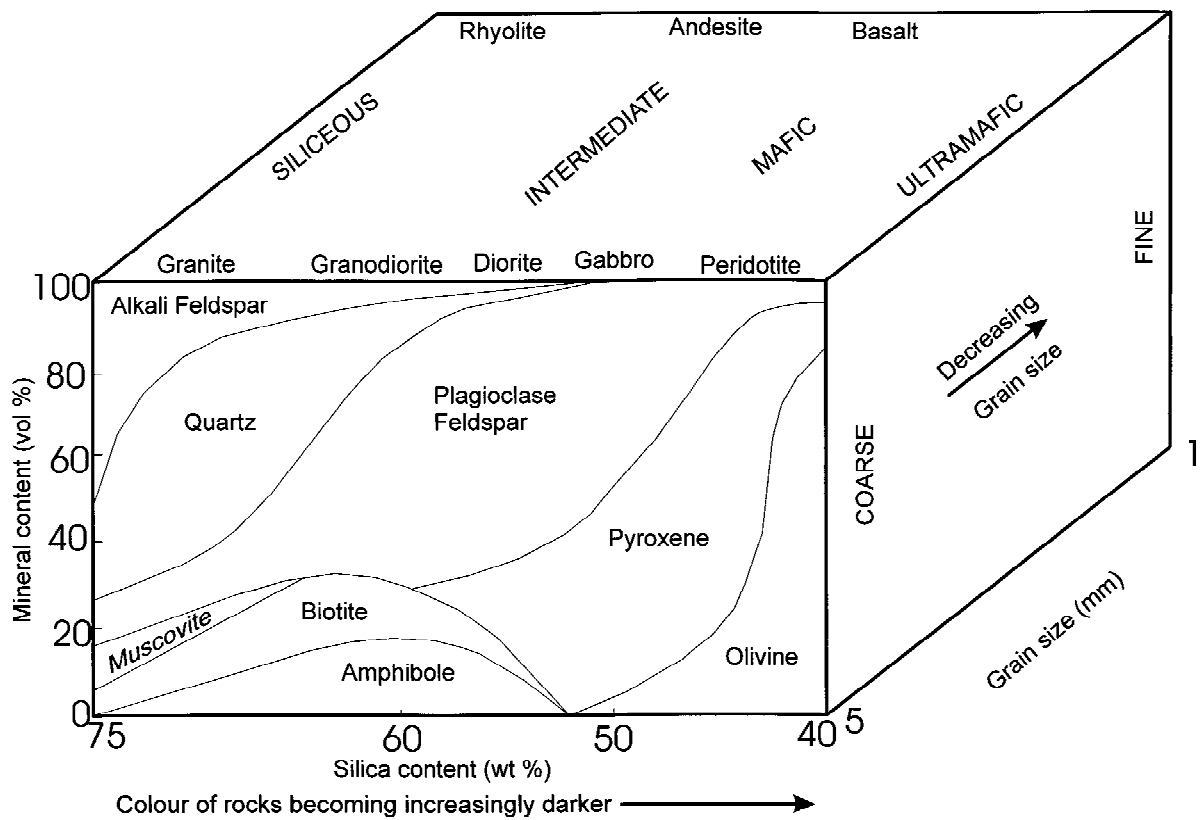


Figure 2. The proportions of minerals in common igneous rocks. Sources: Thorpe and Browne (1989), Le Maitre (1989).



most of the Mg and Fe, together with appreciable amounts of several trace elements (Mn, Zn, Cu).

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 (Nagy, 1995). Dioctahedral micas (e.g. muscovite) have a lower repulsion with the octahedral hydroxyl being inclined away from the interlayer K-ion, providing a more stable environment. Trioctahedral micas (e.g. 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, b). The presence of F-ions replacing OH-ions may also influence the stability of micas (Leonard and Weed, 1970).

#### *Ferromagnesian minerals*

As the silica content of igneous rocks decreases and the colour of the rocks become darker, Fe and Mg concentrations increase as these elements become incorporated into silicate minerals of the pyroxene, amphibole and olivine structural groups. The crystal structure of these minerals allows substitution of a wide and diverse range of elements. These minerals are also quite susceptible to weathering (Eggleton, 1986; Allen and Hajek, 1989), making them important sources of Fe, Mg, and trace elements in rock powder fertilisers. The amphibole structure admits great flexibility of ionic replacement and minerals of this group exhibit an extremely wide range of chemical compositions. Olivine is characteristic of mafic and ultramafic igneous rocks, commonly containing minor substitutions of several metallic elements.

Ferromagnesian minerals commonly dissolve congruently and/or alter to Mg-rich trioctahedral expansive clay minerals or chlorite (Wilson, 1975; Anand

and Gilkes, 1984). Redox reactions are important in the weathering reactions of these minerals due to the presence of Fe(II) and Mn(II) in octahedral coordination. Dissolution of Fe-containing amphiboles and pyroxenes can be either enhanced or retarded by Fe(II) oxidation (Brantley and Chen, 1995).

#### **Mineral dissolution and weathering reactions**

Igneous and metamorphic rocks form under reducing conditions, at lower water content, 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 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.

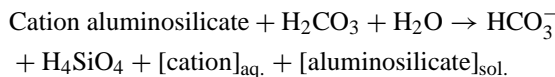
Geochemical explanations of the dissolution of minerals under surface conditions have often relied on the assumption of equilibrium being attained between the solid-phase (mineral), the liquid-phase (soil solution) and the gaseous-phase (soil atmosphere). The reactions of minerals in soil essentially deal with the solubility of minerals in soil solution. Uncertainties arise due to inadequate information being available on the free energy of formation 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). Despite these limitations, an equilibrium model can be used to evaluate the numerous chemical reactions occurring simultaneously in the soil and to predict final equilibrium weathering products.

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 reprecipitation 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 CO<sub>2</sub>. Rainwater in equilibrium with atmospheric CO<sub>2</sub> will have a pH of approximately 5.7. The resultant carbonic acid is a relatively weak ionic species 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<sup>+</sup>-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<sup>3+</sup>-ion is dominant 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.

#### *Mechanisms of mineral dissolution*

Release of nutrients from the mineral structure to the soil solution has 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. Nahon (1991), Blum and Stillings (1995), Brantley and Chen (1995) and Nagy (1995) 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<sup>+</sup>-ions, H<sub>3</sub>O<sup>+</sup>-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 and Warfvinge, 1995). 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). Casey and Ludwig (1995) and Sverdrup and Warfvinge (1995) describe such ligand-exchange kinetics in detail, and the reader is referred to these publications for further information on this topic. Structural elements such as Ca, K, Na, Mg, Fe, and Si can either be removed from the reaction site via soil solution or be incorporated into alteration products (Banfield and Eggleton, 1990).

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 do not appear to adhere strongly to feldspar grains (Petrovic et al., 1976; Berner and Holdren, 1977), 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 (Wollast, 1967; Huang and Keller, 1970; Huang and Kiang, 1972; Luce et al., 1972; 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 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, 1979; Holdren and Berner, 1979; Berner et al., 1980; Schott et al., 1981; Berner and Schott, 1982; Fung and Sanipelli, 1982). 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).

#### *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). This trend in dissolution rate is shown in Figure 3, 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), applica-

tion of silicate rocks as fertilisers will be best suited for acid soils. Sudden decreases 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 for a sudden reduction in pH after achieving a stable dissolution rate at the previous higher pH (Figure 4). 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, b) 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 aqueous cations produced a thinner alteration layer than 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 plagioclase which may reduce dissolution of the K-feldspar relative to plagioclase. The composition of soil porewater and the removal of cations from solution by plants (discussed below) may have implications for the weathering of silicate rock powders in vegetated soils.

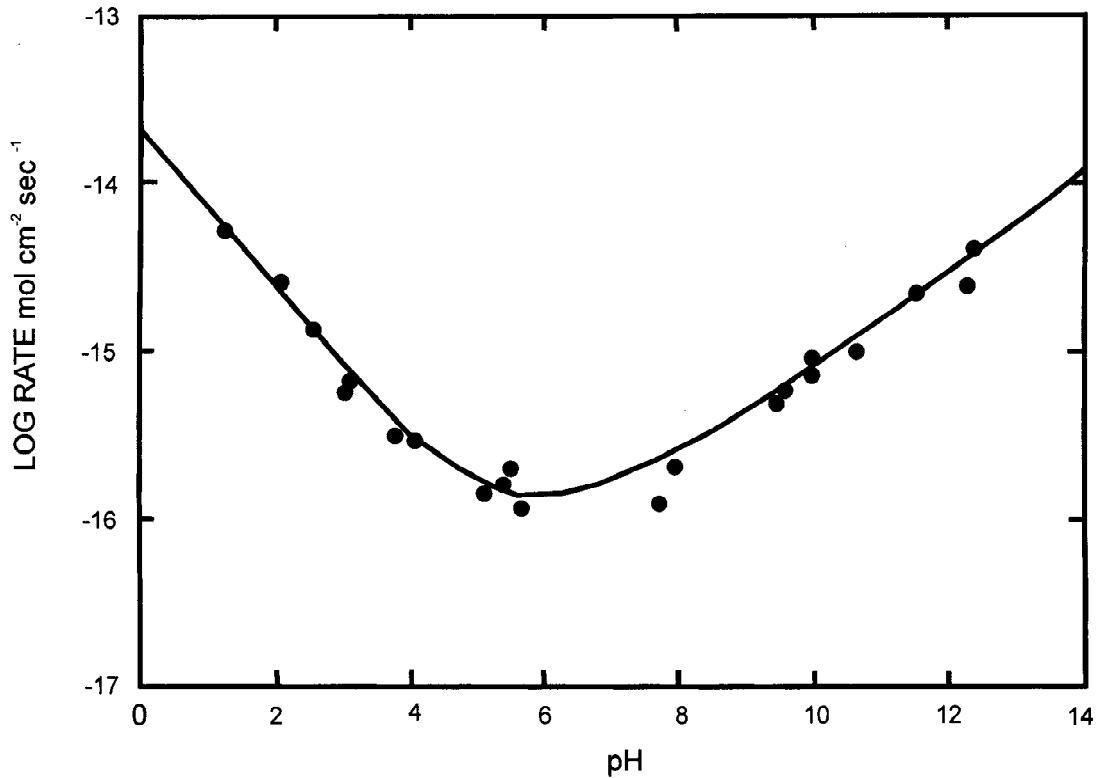


Figure 3. Influence of pH on albite dissolution rate (modified from Wollast and Chou (1985) with kind permission from Kluwer Academic Publishers).

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, as pointed out earlier, 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 surface of minerals and which increases inversely 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 will have reaction rates that vary linearly with the specific surface area. As the grain size approaches the distance between the defects, then this relation flattens out, but may increase 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

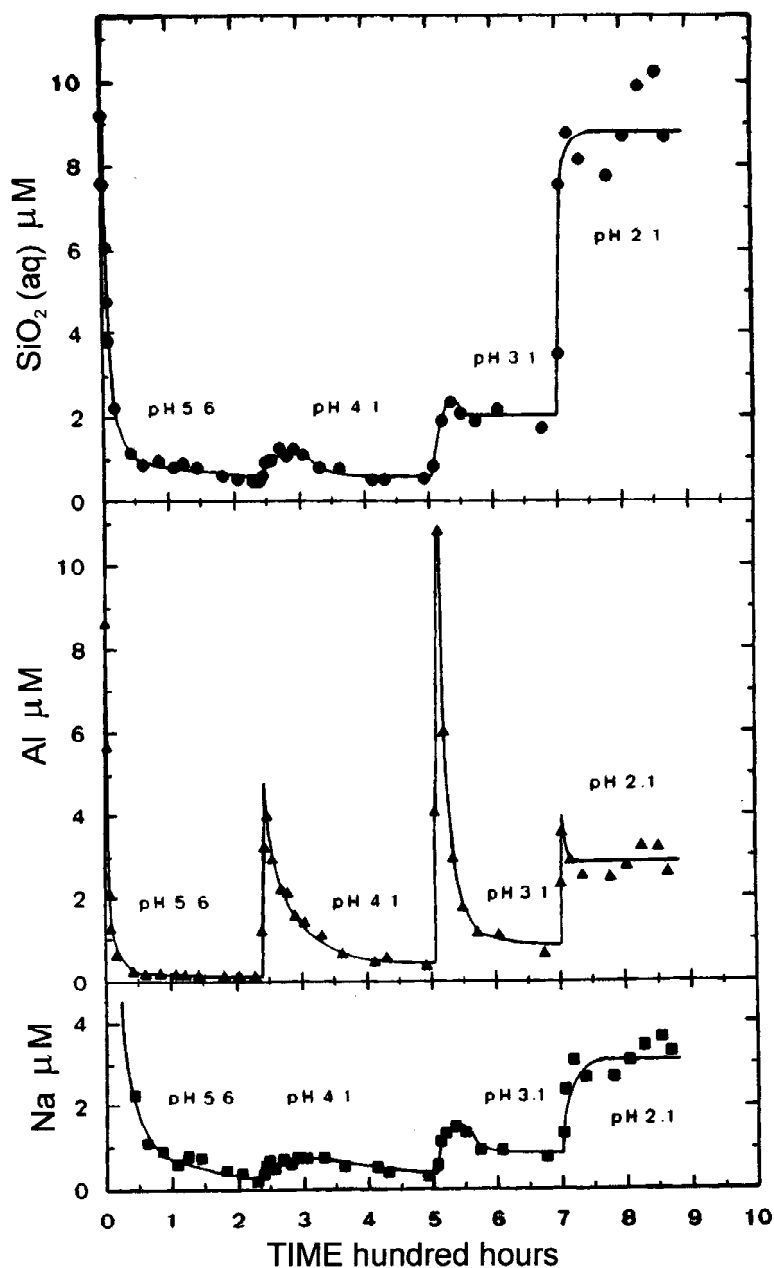


Figure 4. Concentrations of dissolved Si, Al and Na from feldspar as affected by sudden reductions in pH (modified from Wollast and Chou (1985), with kind permission from Kluwer Academic Publishers).

mineral surface (Banfield and Hamers, 1997). Nutrient release from ground rock fertiliser will thus be dependent on the grain size and the density of surface defects of the material applied to the soil. 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.

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  $<100 \mu\text{m}$  (Niwas et al., 1987; Sans Scovino and

Rowell, 1988; Hinsinger et al., 1996; Coroneos et al., 1996), < 2 mm (Niwas et al., 1987; Blum et al., 1989a; Hinsinger et al., 1996), and < 4 mm (Baerug, 1991a, b). Differences in grain size and grain size distribution, or an absence of grain size information, make comparison of published results difficult in assessing the effectiveness of rock dust applications. Niwas et al. (1987) prepared rocks to three different grain sizes for dissolution with deionized water. The release of K was initially higher in rocks ground to < 60  $\mu\text{m}$  than for rocks with grain sizes ranging between 60–140  $\mu\text{m}$  and 250–350  $\mu\text{m}$ , becoming similar for all grain sizes after 6 weeks. Blum et al. (1991a) compared the dissolution of basalt at different grain sizes (< 200  $\mu\text{m}$  and < 2000  $\mu\text{m}$  with 70% being between 200 and 2000  $\mu\text{m}$ ) in 1% citric acid and found that nutrient release was greatest for the < 2000  $\mu\text{m}$  fraction. This result shows that a smaller grain size may not necessarily lead to greater dissolution. Ugolini et al. (1996) also showed that > 2 mm clasts found in soils are a nutrient reservoir, and are not chemically inert as is generally believed.

Further work is required to better understand the influence that grain size and reactive surfaces have on dissolution of rock powders. A technique that may be borrowed from the earth scientists involves estimating the exposed surface area of the mineral grain. Determining dissolution rates (discussed below) is dependent on normalising the reacted mineral mass to a unit area basis (White, 1995). This estimation is however difficult and needs to take into account surface roughness and internal porosity, and possibly even the complex weathering fronts within mineral grains (Hochella and Banfield, 1995). Normalising the reactive surface area allows the quantitative assessments of the influence of grain surface properties on nutrient release.

#### *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 (root environment), and the 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  $\text{CO}_2$  and  $\text{O}_2$

concentrations such as 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 experiences 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 rock forming minerals applied as 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 noted to be fairly resistant in weathering environments, possibly due to saturation of porewater with respect to the mineral. An implication 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 K concentration soil solution in the rhizosphere to approximately  $3 \text{ mg l}^{-1}$ , 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 (Figure 5). 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 (e.g. 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.

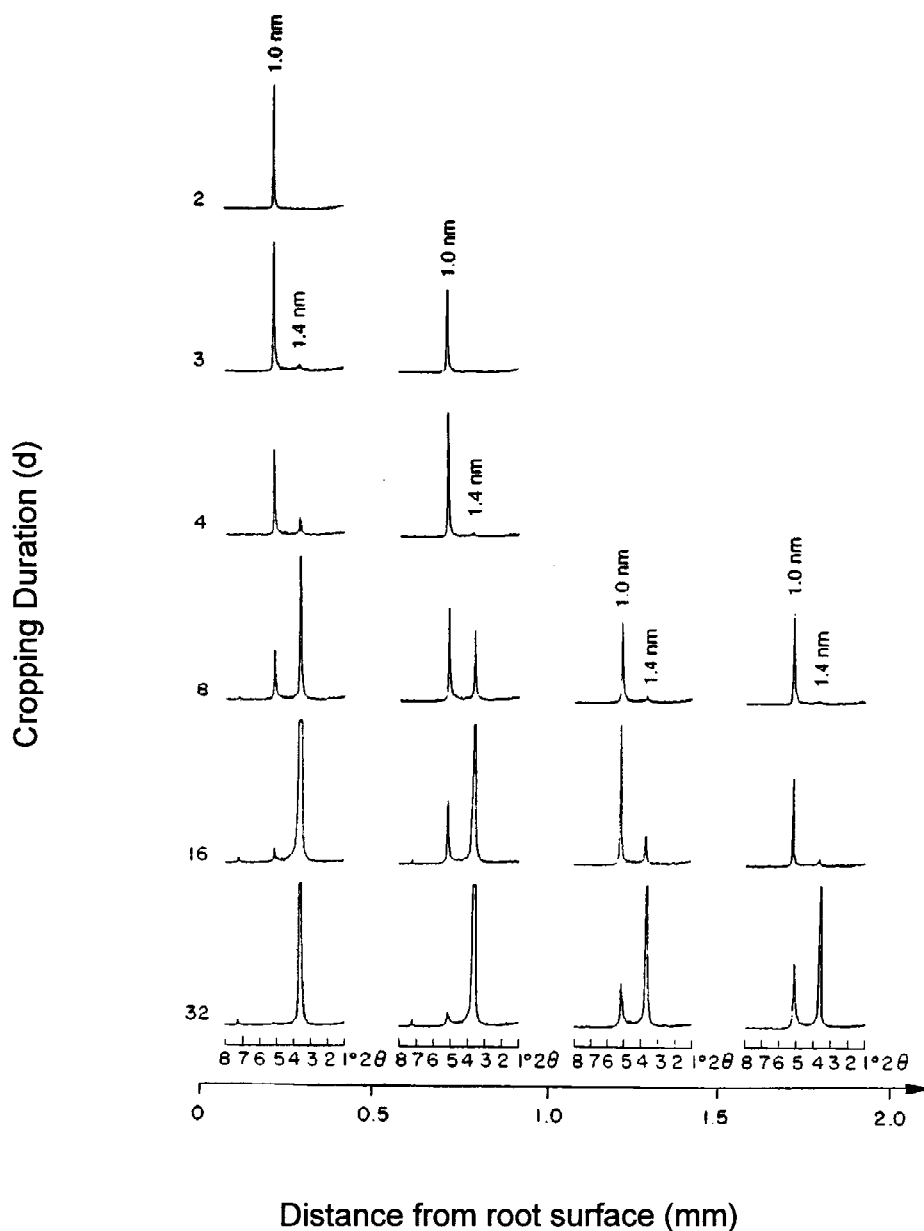


Figure 5. XRD pattern of phlogopite recovered from the rhizosphere of ryegrass as a function of the cropping duration and distance to the root. Vermiculite (1.4 nm) has formed by K removal from phlogopite (1.0 nm) (modified from Hinsinger and Jaillard, (1993), with kind permission from Blackwell Science Ltd.)

Dissolution of minerals may be enhanced by pH changes in the rhizosphere due to the release of H-ions (reduced pH), or  $\text{HCO}_3^-$ -ions or 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

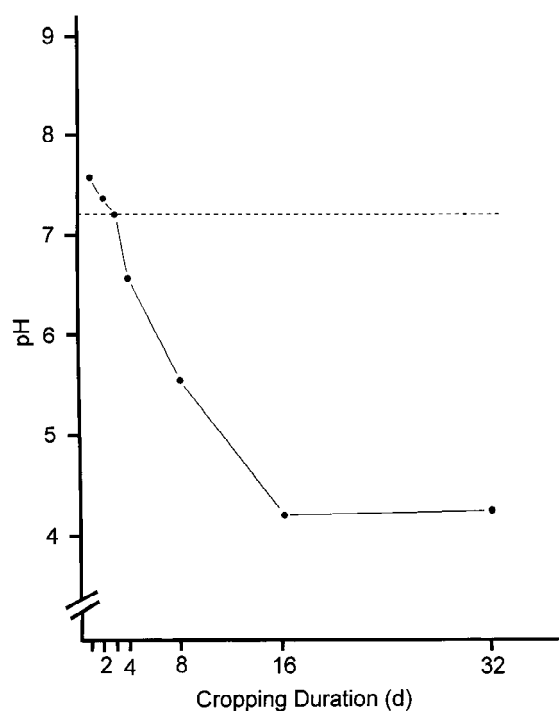


Figure 6. Changes in the pH of the rhizosphere of rape grown on phlogopite-agar substrate. Dotted line corresponds to initial pH value of control treatment (modified from Hinsinger et al., (1993), with kind permission from Blackwell Science Ltd.)

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 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 rock phosphate. Hinsinger and Gilkes (1995), examined the influence of lupin roots on dissolution of the calcium phosphate mineral apatite and found that rhizosphere pH was lowered by 2 points 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 (Figure 6), accompanied by a significant release of interlayer K and structural Mg.

In addition to the 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 Öman, 1993; Welch and Ullman, 1993, 1996), micas (Boyle et al., 1967; Huang and Keller, 1970; Arshad et al., 1972; Boyle and Voigt, 1973; Kodama and Schnitzer, 1973; Schnitzer and Kodama, 1976; Berthelin and Belgy, 1979) and olivine (Grandstaff, 1986). Mafic minerals are more susceptible to dissolution in the presence of organic solutes than felsic minerals such as feldspars (Schnitzer and Kodama, 1976; Sverdrup and Warfvinge, 1995; Raulund-Rasmaussen et al., 1998). Organic acids differ in their dissolution effectiveness with bidentate ligands (eg 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 (Huang and Keller, 1970; Arshad et al., 1972; Kodama and Schnitzer, 1973; Grandstaff, 1986; Welch and Ullman, 1993) indicating that some different reactions may occur with organic acids than with inorganic acids. The complexing properties of organic acids allow for the weakening of metal-oxygen bonds at the mineral surface and reduced ion concentrations in solution (Welch and Ullman, 1993; Lundström et al., 1995; Barker et al., 1997). 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 concentration of Ca in soil solution (Robert and Berthelin, 1986; Griffiths et al., 1994). 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 able to be 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 microorgan-



isms 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). The application of ground rock powders may increase microbial activity. Von Mersi et al. (1991) 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. There were significantly higher concentrations of nutrients in solutions collected from soils containing ectomycorrhizal mats than in soil solutions collected where mats were absent for forest soils from the Coast Range of Oregon (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 solubilise 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 subsequent release of organic exudates, was shown by Jongmans et al. (1997) to increase weathering of the minerals in European podsols. The dissolved products were believed to be transported by the mycorrhizal hyphae directly to the host plants. The potential for dissolution of silicate rock powders is enhanced through the removal of nutrients and the addition of acids by mycorrhiza.

### *Weathering Reactions*

The composition of soil solution has been shown to be important in determining both the nature and rate of weathering reactions of the silicate minerals, and thus the provision of nutrients to soil solution for plant

uptake. A consideration of the composition of soil solution in relation to weathering processes and the external nutrient requirements of plants is likely to provide an insight into these complex interactions, and aid in studying the role of powdered rock fertilisers.

As mentioned earlier, feldspars are abundant in many rocks and soils and have simple chemical and structural properties. Consequently, they have been extensively studied with respect to weathering and dissolution (Blum and Stillings, 1995). Stability diagrams for the feldspar-clay mineral system have been commonly used to determine mineralogical controls on soil solution composition (White, 1995) and may provide a useful tool for determining the soil solution controls on rock dust dissolution.

The stability relationships of phases in the albite-clay mineral system  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  are shown in Figure 7 as an example. The stability of albite is a function of the relative activities of Na-ions, H-ions and  $\text{H}_4\text{SiO}_4$ . Assuming a closed system containing only albite and an initial dilute soil solution, undersaturated with respect to Na-ions, H-ions and  $\text{H}_4\text{SiO}_4$ , the composition of the soil solution will fall within the stability field of gibbsite (marked as an X on Figure 7). In an open system with leaching and diffusion removing dissolution products this state may persist and gibbsite will be the major weathering product. However, in this example we are considering that exports by leaching and diffusion are ineffective so that the soil approximates to a closed system. Consequently, as concentrations of Na-ions and  $\text{H}_4\text{SiO}_4$  increase in the closed system, the soil solution composition moves towards the kaolinite-gibbsite stability boundary, at which point kaolinite begins to precipitate, and silica being released from the dissolution of albite would react with the existing gibbsite to form kaolinite. Once all the gibbsite has been converted to kaolinite, the concentration of silicon in solution will increase. The solution will still be undersaturated with respect to the primary mineral albite. Dissolution continues until the soil solution has a composition that corresponds to the kaolinite-smectite boundary, where smectite would be precipitated as the secondary mineral. Dissolved silicon and alkali cations would then convert kaolinite to smectite, albeit that these transformations might occur at very slow rates. At this stage, the newly released silicon and cations from feldspar will form smectite directly and not via gibbsite and/or kaolinite. Once the transformation of early weathering products to smectite is complete, the concentration of alkali cations and silicon will again

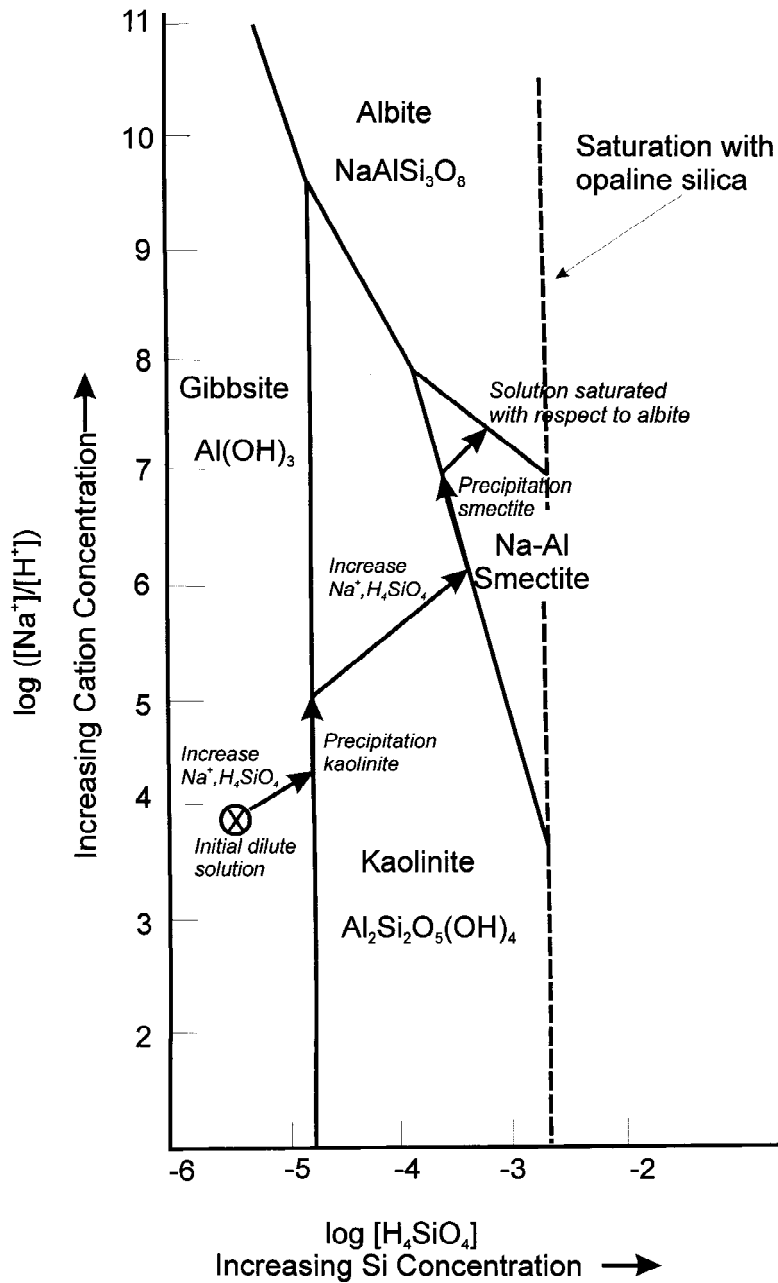


Figure 7. Mineral stability diagram for the system Gibbsite-Albite-Kaolinite-Na smectite. A typical weathering reaction path is shown by the arrows (modified from Berner and Berner, 'The Global Water Cycle' (©1987). Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.)

increase in the soil solution until the soil solution is saturated with respect to albite, at which point dissolution stops. The primary mineral albite then buffers the composition of the soil solution.

In practice, soil solution does not exist as a closed system and it changes in composition depending on the dynamics of water and inorganic and organic processes affecting the concentration of dissolved ions. Flushing of the soil profile due to climatic or topo-

graphic effects has been shown to have an important influence on the weathering rate of primary minerals, where an increase in flushing increases the rate of dissolution (Berner, 1978). During periods of high flushing, ions will be removed from the system by a combination of flow and diffusion. The stable secondary mineral under these conditions would be either kaolinite (moderate flushing removing alkali cations but not all silicon) or gibbsite (higher flushing where both alkali cations and silicon are removed). Such predictions are consistent with field observations. Gibbsite commonly occurs in soils of good internal drainage on hilltops and steep valley sides, and is absent in relatively poorly drained areas of catchments where dissolved ions accumulate (Cleaves et al., 1970). Thus authigenic smectite may be present in the lower slopes or sumps in the landscape where drainage water accumulates due to limited external drainage (Velde, 1992), and smectite is characteristic of such sites in semi-arid regions (Berner and Berner, 1987) where ions in soil solution are concentrated due to drainage, high evaporation, and evapotranspiration. Use of irrigation and the tendency towards either leaching or waterlogging within irrigated soils, may also play important roles in controlling the release of nutrients from minerals.

As discussed above, the principles of stability diagrams can be applied to predicting the dissolution of silicate rock powders in agricultural soils. Soil solutions, either bulk or rhizospheric, that plot outside the stability fields of the minerals applied to soils will indicate those minerals that will dissolve and the potential secondary products that will be produced. White (1995) has plotted the composition of many samples of soil solution on activity diagrams for  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ ,  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  systems (Figure 8). Soil solution concentrations fall predominantly within the kaolinite stability field which is consistent with evidence from mineralogical studies of weathered granitic rocks where kaolinite is the most common weathering product (Velde, 1992; White, 1995). The locations of minerals in these stability diagrams support the argument made by proponents of the use of ground silicate rock fertilisers for highly weathered soils (Leonardos et al., 1987; Sanz Scovino and Rowell, 1988; Chesworth et al., 1989; Weerasuriya et al., 1993). Soils with high contents of gibbsite and kaolinite will have bulk soil solutions in equilibrium with these minerals, and thus outside the stability range of primary minerals, which would therefore be predicted to undergo

dissolution reactions. Stability diagrams can thus be used as predictive tools to ascertain the potential of dissolution of silicate rock powders in particular soils.

Stability diagrams may also be used to relate the weathering trend of minerals to the nutrient requirements of plants. Asher (1978) has estimated that the minimum soil solution concentrations for the adequate growth of many plant species range between 10 and 1000  $\mu\text{M}$  K, and 0.5 to 1000  $\mu\text{M}$  Ca. These ranges of external nutrient requirements are shown on the  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  stability diagrams (Figure 8), assuming a bulk soil solution with pH 5. A large proportion of soil solution values occur within the external plant requirement range that indicates that soil solution concentrations required for adequate plant growth are undersaturated with respect to the primary minerals, leading to dissolution. This indicates that mineral dissolution is likely to occur in the presence of plants. The depletion of K and Ca from the rhizosphere soil solution will shift its composition towards the stability field of kaolinite or gibbsite, resulting in the further dissolution of primary minerals. Rhizosphere soil solutions are likely to have nutrient concentrations lower than the bulk soil solutions, with, for example, a K concentration of 2–3  $\mu\text{M}$  at the root surface of maize reported by Classen and Jungk (1982). This concentration would plot below the area of sufficient external K supply shown on Figure 8, indicating that dissolution will be more rapid in rhizospheric soil solution than in bulk soil solutions.

### Weathering rates

Equilibrium concentrations of soil solution provide an indication of the instantaneous nutrient supply status and final equilibrium states but provide no information of the rate of replenishment of nutrients. It is the rate of supply of nutrients during plant growth that will determine sufficiency or deficiency and the rate of uptake of nutrients changes greatly during the phases of plant growth (Marschner, 1995). The rate of chemical weathering of minerals which will supply nutrients is dependent on the composition of soil solution, the nature of reactions at mineral surfaces, the diverse mixture of primary minerals and secondary phases together with the rhizosphere processes discussed earlier (Colman and Dethier, 1986). In this section we compare rates of demand for nutrients by plants and rates of supply of nutrients from mineral dissolution.

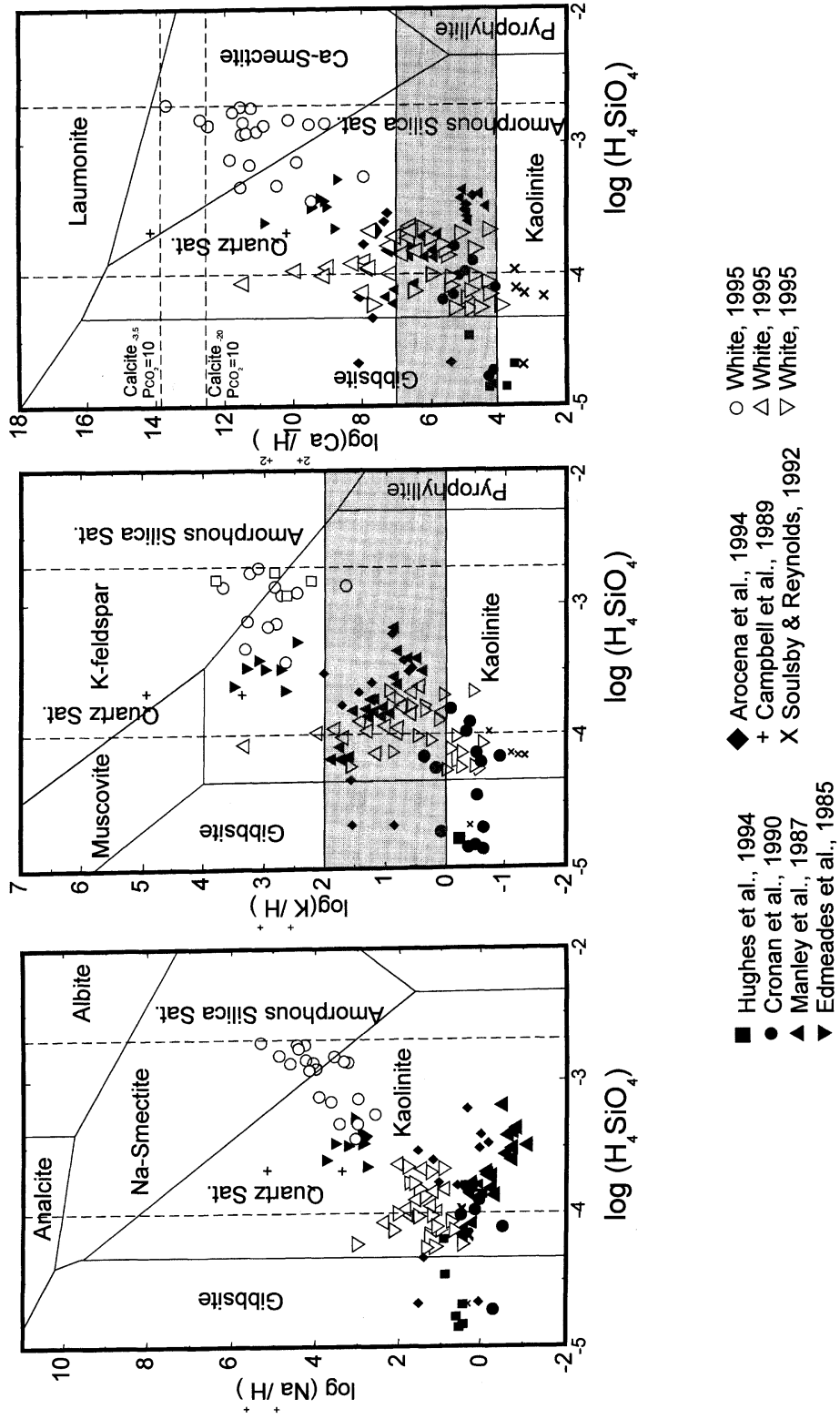


Figure 8. Soil solution concentrations (molar basis) plotted on mineral stability fields for the systems  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ ,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{K}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ . The range of minimum external requirements for K and Ca for a wide range of plant species are plotted for pH 5 as the horizontal shaded band (modified from White (1995) with kind permission from the Mineralogical Society of America).

The extent of chemical weathering ( $M_j$ ) of a primary mineral  $j$ , in a soil in time  $\Delta t$  has been defined by White (1995) as:

$$M_j = k_j S \Delta t$$

where  $M_j$  is the mass loss (usually in moles),  $k_j$  is the rate constant (usually in moles  $\text{cm}^{-2} \text{s}^{-1}$ ),  $S$  is the surface area (usually in  $\text{cm}^2$ ). It is of interest to the agronomist studying the dissolution of ground silicate rocks to identify if the rate constant ( $k_j$ ) is consistent with the rate of demand for nutrients by plants.

A range of methods including laboratory simulations, field weathering studies, hydrochemical balances for catchments, solute fluxes, and mineral etching (Colman and Dethier, 1986) have been used to determine weathering rates of rocks and minerals. White (1995) has summarised and assessed published data on natural and experimental dissolution rates for several minerals (Table 4). Weathering rate constants ( $k_j$ ) for silicate minerals range between  $10^{-20.5}$  to  $10^{-15.2} \text{ mol cm}^{-2} \text{ s}^{-1}$ . It is notable that weathering rates based on natural systems are of 1 to 3 orders of magnitude less than those estimated in laboratory experiments (Paces, 1983; Velbel, 1986, Sverdrup, 1990).

Such differences may be due to the complex interactions occurring within the biogeochemical zone. Factors such as diffusion of ions being affected by diffusion distance, tortuosity, soil water content, changes in reactive surface with time due to etch pit formation and coatings, and differential access of reactive fluids to soil surfaces (Sverdrup and Warfvinge, 1988; Velbel, 1989; Hochella and Banfield, 1995, White et al., 1996) may provide rate-limiting conditions in the field. In contrast, laboratory experiments involve continuously stirred or flushed systems where surface reactions and not diffusion are likely to be the rate limiting steps. Hochella and Banfield (1995) describe a continuum of weathering rates that extend from laboratory conditions at the upper end to natural weathering environments with complete structural replacement of minerals at the lower end. All conditions are believed to exist within the many diverse natural environments provided by the soil.

Differences in methods of sample preparation and estimation of exposed surface affect determinations of dissolution rate (Sverdrup, 1990). White et al. (1996) found that dissolution rates based on geometric surface area are 2 to 3 orders of magnitude greater than those that incorporate variable surface roughness, showing the importance of correctly identifying surface area.

Vegetation has been shown to increase the rate of mineral weathering through the diverse rhizosphere and nutrient source/sink processes discussed earlier. Drever and Zobrist (1992) have shown that weathering rates on the same rock type are 25 times greater at lower elevations where rainfall, temperature and vegetation are greater than they are higher elevations. A comparison of the release of cations between forested areas, bare ground, talus slopes and permanent snowfield in the Rocky Mountains, found that the cationic denudation rate per unit area of the whole watershed was three times higher than the rate for bare ground (Arthur and Fahey, 1993). Mass balance calculations for catchments in North America (Taylor and Velbel, 1991) and South America (Benedetti et al., 1994) have shown that when nutrient uptake by vegetation is taken into consideration, weathering rates are up to 4 to 5 times faster than without vegetation. Drever (1994), however, suggests that the direct chemical effects of land plants on weathering may be over-rated, and the rate is probably no more than a factor of 2 greater under vegetation than for unvegetated areas, with the possibility of it being higher by a factor of 10 in highly localised weathering environments (e.g. the rhizosphere).

Plants are a sink of nutrients and the effects of removal of products need to be considered for agricultural and forest soils where removal of the nutrients from the system will presumably increase weathering of silicate rock powders. Biogeochemical models such as PROFILE and SAFE which have included biotic influences such as uptake of Ca, Mg and K are believed to indicate full consistency between field and laboratory weathering rates (Sverdrup and Warfvinge, 1995). As these models can be used at the scale of the soil profile, they may provide useful numerical tools for quantifying weathering rates of silicate minerals applied as fertilisers.

### Concluding remarks

Dissolution of rock powder in soil is likely to be influenced by the composition of soil solution and the action of plants with many factors including climate, temperature, pH, bulk soil solution composition, changes in rhizosphere pH and redox, and chelation by organic acids being involved. Processes within the rhizosphere may greatly enhance the weathering rates of silicate minerals, and hence the rate of release of nutrients for plant uptake. Localised weathering within

Table 4. Comparison of dissolution rate constants ( $k_j$ ) of selected silicate minerals. Rate constants for natural environments (soil, soil solution, catchment and aquifer) are less than values determined under experimental conditions. Source: White (1995)

Mineral	$k_j$ $\text{mol cm}^{-2} \text{ s}^{-1}$	pH	Environment	Calculation method
<i>Plagioclase</i>				
Oligoclase	$10^{-19.9}$	4.5–7.0	Soil	Mineralogy
Oligoclase	$10^{-19.5}$	4.5–7.0	Soil	Solute flux
Andesine	$10^{-18.7}$	5	Catchment	Watershed balance
Oligoclase	$10^{-18.5}$	5.8	Catchment	Watershed balance
Labradorite	$10^{-17.7}$	6.0–7.5	Aquifer	Groundwater
Oligoclase	$10^{-17.4}$	4.5–7.0	Soil	Mineralogy
Oligoclase	$10^{-17.3}$	2.0–4.5	Soil Solution	Solute flux
Oligoclase	$10^{-17.1}$	5.6–6.1	Soil	PROFILE model
Oligoclase	$10^{-16.5}$	6.8	Catchment	Watershed balance
Oligoclase	$10^{-16.1}$	5	Catchment	Watershed balance
Albite	$10^{-16.1}$	5	Experiment	Dissolution
Oligoclase	$10^{-16.0}$	5	Experiment	Dissolution
Albite	$10^{-15.9}$	5.6	Experiment	Dissolution
<i>K-feldspars</i>				
Orthoclase	$10^{-20.5}$	4.5–7.0	Soil	Mineralogy
Orthoclase	$10^{-19.7}$	4.5–7.0	Soil	Solute flux
K-feldspar	$10^{-18.1}$		Soil	Etch pitting
Orthoclase	$10^{-17.8}$	4.5–7.0	Soil	Mineralogy
K-feldspar	$10^{-17.3}$	5.6–6.1	Soil	PROFILE model
K-feldspar	$10^{-17.3}$	2.0–4.5	Soil Solution	Solute flux
Microcline	$10^{-16.8}$	5.6	Experiment	Dissolution
<i>Hornblende</i>				
Hornblende	$10^{-20.1}$	4.5–7.0	Soil	Mineralogy
Hornblende	$10^{-18.5}$	2.0–4.5	Soil Solution	Solute flux
Hornblende	$10^{-18.1}$		Soil	Etch pitting
Hornblende	$10^{-17.6}$	5.6–6.1	Soil	PROFILE model
Hornblende	$10^{-17.5}$	4.5–7.0	Soil	Mineralogy
Hornblende	$10^{-15.2}$	4	Experiment	Dissolution
Hornblende	$10^{-14.7}$	5	Experiment	Dissolution

the rhizosphere zone can be much greater than is estimated purely on the basis of bulk geochemical studies. The assumption of reactions between the minerals and soil solution operating in closed systems is not appropriate. Powdered rock fertilisers are likely to be most effective in soils dominated by minerals that are the products of extreme weathering (i.e. gibbsite, kaolinite) and where the soil and its plant/microbiological communities can provide an adequate source of acidity for dissolution and to be a sink for dissolved ions. There is evidence that biological and/or pedoturbation processes in the solum may prevent the formation of

the protective coatings that persist in deep undisturbed regolith so that dissolution rates of rock dust fertilisers (i.e. nutrient supply rates) may approach those obtained under laboratory conditions.

For ground silicate rock powder to be an effective fertiliser involves the release of nutrient cations at a rate that will support adequate plant growth. Encouraging but inconclusive results have been obtained in some studies of the application of silicate rock as a fertiliser, but it is clear that although the underlying geochemical processes are not well understood so

that materials and conditions can be manipulated to achieve maximum agronomic effectiveness.

A basic requirement is that weathering solutions are at disequilibrium with respect to the minerals applied to the soil. It is therefore necessary to maintain the soil solution at disequilibrium with respect to the nutrients within the mineral. The role of biota in achieving this is critical in cropping systems. Nutrient uptake and rhizosphere processes such as increasing H-ion concentration and exudation of complexing organic compounds play important roles in mineral dissolution. A knowledge of bulk soil or rhizosphere soil solution chemistry can be related to mineral stability diagrams to predict how applied minerals will react in these solutions. Nutrient requirements of specific plants can also be incorporated into stability diagrams to aid prediction.

A second important consideration in the dissolution process is the mineral surface itself. Kinetic studies involving the release of nutrients from minerals and rocks of various grain sizes and surface reactivities will provide guidance towards mineral preparation techniques that will enhance mineral dissolution. Knowledge of rates of release of nutrients from a unit surface area of a mineral under various soil conditions will help predict application rates and grain size requirements for differing plant and soil systems. A fruitful area of research is likely to be the creation of defects at the crystal surface to enhance surface reactivity and nutrient release.

Incorporating minerals into various soil types to determine dissolution kinetics and plant uptake of nutrients makes recovery and observations of mineral surfaces difficult. *In situ* techniques as developed by Hatton et al. (1987) and Ranger et al. (1991) may prove useful for the study of rock powders. In these studies, minerals in permeable bags were placed in various soil horizons to determine active geochemical processes. The bags are removed and the minerals are available for analysis free of contamination. The same principles can be used for the study of the effects on the dissolution of silicate rock powders of various cropping systems, soil mineralogies, grain size and surface features.

The development of an understanding of the geochemical processes of rock dust dissolution in soils will provide mechanistic explanations and quantitative predictions of optimum practices for agricultural applications. Determination of nutrient release rates, including the influence of grain size and rock prepara-

tion will enable the more effective use of this material on agricultural and forested lands.

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