THE EFFECTS OF HIGH ENERGY MILLING ON THE PERFORMANCE OF SILICATE ROCK FERTILIZERS

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ABSTRACT

Many researchers have proposed the use of silicate rock fertilizers (SRFs) as alternatives to chemical fertilizers. However, the application of SRFs in modern agricultural practices is limited due mainly to the slow release of plant-nutrient elements from SRFs and consequently many tonnes/ha of SRFs may need to be applied. Simple and inexpensive methods of modifying the physicochemical properties of SRFs are needed to improve the agronomic effectiveness of SRFs. This thesis is focused on the evaluation of high-energy milling to produce superfine particles to improve the effectiveness of mafic (basalt and dolerite) and felsic (gneiss and K-feldspar) rocks for use as fertilizers. The ground mafic rocks are for use as Ca and Mg fertilizers and the ground felsic rocks as K fertilizers.

Laboratory and glasshouse experiments were conducted with several potential SRFs. In laboratory experiments, initially milled rocks (Ø < 250 μm for basalt, dolerite, and gneiss; Ø < 150 μm for K-feldspar) were further milled with a ball mill (Spex-8000) for 10, 30, 60, 90, and 120 min under dry and wet (rock/water ratio = 1/3) conditions. To investigate possible reaction between constituents, other subsamples of initially milled basalt, dolerite, and gneiss were added to reagent grade NaCl or KCl (4.5 g rock + 0.5 g NaCl or KCl) and milled for 120 min under dry and wet conditions. Basalt and dolerite were also mixed with K-feldspar at a ratio of 1 : 1 and milled for 120 min under dry and wet conditions. For use in the glasshouse experiment, the initially milled rocks were further milled with a vertical stirred ball mill for 1 h in a dry condition. The elemental and mineralogical compositions of the SRFs were determined using XRF and XRD. Effects of milling on major physicochemical properties of milled rocks were determined, including particle size (Malvern Mastersizer), surface area (BET-N_2), quantities of amorphous constituents (XRD, oxalic acid-oxalate extraction, TEM), extractable cations (1*M* CH_3COONH_4 pH 7), pH_{H2O}, and electric conductivity. Dissolution kinetics in 0.01*M* acetic-citric acids (for 56 days) and soil (for 10 months) were determined. Based on the results of these laboratory experiments, a glasshouse experiment was carried out for 12 months to evaluate the effects of SRF application on growth and nutrient uptake of ryegrass grown on several soils.

Milling reduced particle size, enhanced amorphism, and increased the release of structural cations from the rocks, with the effects due to dry milling being greater than for wet milling. The optimum milling times which produced maximum amounts of exchangeable cations (Na, K, Ca, and Mg) were 30 - 90 min, depending on rock type. The use of NaCl and KCl as milling additives did not enhance the properties of the SRF.

These effects of milling on properties of SRF enhanced the extent of dissolution of SRFs in 0.01*M* acetic-citric acid and in the soil. More amorphous and/or structurally disordered materials than crystalline materials were dissolved in both dissolution media. The proportion of rapidly dissolved elements, which may be considered to be plant-available, was increased by milling, i.e., from about 2 % (for initially milled rocks) to 70 % (for 120 min dry-milled rocks) of total content, with this proportion for monovalent cations (Na and K) mostly being 2 – 3 fold higher than for divalent cations (Ca and Mg). Incubation of SRFs in soils provided a significant liming effect with a minor salinity effect. The extent of dissolution of SRF in the soil could be accurately predicted by the SRF dissolved in acetic-citric acid in 1 h. Neither SRF nor soil properties were highly predictive of dissolution of basic cations from SRFs in soils, although equations including % sand, % clay, and exchange acidity of the soils are quite predictive of dissolution.

The application of Ca in basalt and dolerite SRFs at the rates of 333 – 1332 mg of total Ca/kg soil (≈ 4 – 16 t SRF/ha) greatly increased plant yield and Ca uptake of ryegrass grown on highly acidic and/or Ca deficient soils, but did not do so for plants grown on less acidic and/or relatively Ca-rich soils. The large effects on plants were due mainly to the increase in soil pH rather than Ca supply from the SRFs. Thus application of these SRFs at much lower rates (≈ 0.2 – 1 t SRF/ha) as Mg fertilizers had only minor effects on pH and consequently on plant growth and nutrient uptake. The applications of milled gneiss at rates of 225 – 1332 mg of total K/kg soil (≈ 25 – 100 t SRF/ha) and K-feldspar (5 – 20 t/ha) greatly increased plant growth and K uptake on soils deficient in K. Milled gneiss was nearly as effective as K_2SO_4 for use as a K fertilizer based on total content of K in dry tops of plants, but K-feldspar was not effective. However, much of the K_2SO_4 had been consumed by plants and also these high application rates of K-SRF caused a large confounding effect due to the increase in soil pH which affected the internal efficiency of K in

producing increased yield. It is apparent that milling greatly improves the effectiveness of silicate rocks for use as fertilizers, thus high-energy milling may be used for manufacturing effective SRF.

Results of this research were mostly consistent with pioneering findings by other researchers which found that SRFs may be effective soil ameliorants. SRFs are multinutrient fertilizers (including Si) and SRFs are effective liming materials. The multiple beneficial effects of SRFs were greatly improved by high intensity milling of the SRFs. However, further research is needed to identify optimum and inexpensive milling methods for use at an industrial scale. The effectiveness of milled-silicate rocks as multinutrient fertilizers under field conditions for various soils and plants, liming materials, and salt neutralizers, should also be determined.

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CONTENTS

Chapter 1. INTRODUCTION

Chapter 2. EFFECTS OF MILLING TIME, CONDITIONS, AND REACTIVE ADDITIVES ON THE CHARACTERISTICS OF SILICATE ROCKS

Chapter 3. DISSOLUTION OF MILLED-SILICATE ROCKS IN ORGANIC ACID

Chapter 4. DISSOLUTION OF MILLED-SILICATE ROCKS IN THE SOIL

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

Chapter 1

INTRODUCTION

1.1. General Background

The possibility of using silicate rocks as fertilizers has received significant attention from agronomists and soil scientists during the last two decades. Although some advantages over chemical fertilizers may be proposed (Leonardos *et al*. 1987 and 2000; Coroneos *et al*. 1996; Hinsinger *et al*. 1996; Bolland and Baker 2000; Coventry *et al*. 2001), the present day use of silicate rock fertilizers (SRFs) in agricultural practices is very limited mostly due to uncertainty about the true effectiveness of SRFs. Despite conflicting experimental agronomic results, the generally very small and slow release of nutrients from SRFs into soil solution is the main limiting factor (Hinsinger *et al*. 1996). Efforts should, therefore, be made to identify appropriate methods for accelerating the release of nutrients, as well as to identify those factors determining the suitability of particular soils and plants for fertilization with SRFs.

Silicate rocks may contain several elements essential for plants, and so may be used as multinutrient fertilizers as suggested by Leonardos *et al*. (1987, 2000) and Coventry *et al*. (2001). Global resources of some conventional sources of fertilizer feedstocks (e.g., KCl) are limited so that identification of alternative sources will enable optimum use of resources. For many developing countries that spend scarce dollars to import chemical fertilizers, locally produced SRF may be an appropriate material for their farming systems. From an environmental point of view, applying SRF is non-polluting due to the slow release of nutrients to soil solution such that water pollution resulting from leaching or erosion of SRF from agricultural land will be minimal. Furthermore, some SRFs do not contain elevated levels of contaminants such as Cd, F, and U that occur in some chemical fertilizers and thus provide a more sustainable source of plant nutrients. The use of SRFs in broad scale agriculture has been proposed for the utilization of quarry by-products in Western Australia (Coroneos *et al*. 1996; Hinsinger *et al*. 1996; Bolland and Baker 2000), Queensland (Coventry *et al*. 2001), and Brazil (Leonardos *et al*. 1987), and the utilization of mine tailing (Bakken *et al*. 1997, 2001). These materials have been evaluated in plant growth experiments.

Evaluations of the effectiveness of SRFs have produced conflicting results. Applications of silicate rocks, including basalt (de Villiers 1961; Gillman 1980; Barak *et al*. 1983; Priyono 1991; Gillman *et al*. 2001, 2002; Coventry *et al*. 2001) and gneiss (Wang *et al*. 2000a, 2000b), granite (Coroneos *et al*. 1996, Hinsinger *et al*. 1996), fly ask (Pathan *et al*. 2003) or silicate minerals such as felspars (Sanz Scovino and Rowell 1988), hornblende, microcline, and biotite (Harley 2002) or micas (Weerasuriya *et al*. 1993) positively affected soil properties and stimulated plant growth. On the other hand, granite quarry dust provided minor amount of soluble K and reduced wheat yield by up to 65 % (Bolland and Baker 2000) relative to standard fertilizers. These different results may be due to the large diversity of rocks, grinding methods, plant species, and soils used in these experiments. Most authors agree that the major limiting factor for the use of SRFs in agriculture is the very slow release of nutrients from the SRFs so that consequently very large rates of SRFs should be applied (Hinsinger *et al*. 1996).

Mafic rocks which are dominated by ferromagnesian minerals contain higher concentrations of several essential plant nutrients (e.g., Fe, Mg, Ca, and Mn) than do felsic rocks (Krauskopt 1972; Aubert and Pinta 1977; Harley and Gilkes 2000), and consequently mafic rocks may be more suitable fertilizers than are felsic rocks. However, the selection of rock type will depend on the specific nutrient deficiencies of the soil (Coroneos *et al*. 1996; Hinsinger *et al*. 1996; Bolland and Baker 2000). Ground feldspar (Sanz Scovino and Rowell 1988), mica (Weerasuriya *et al*. 1993), and gneiss (Wang *et al*. 2000a) may be much more suitable sources of K than are mafic rocks that contain little K. Soil properties, including texture (Priyono 1991), pH (Holdren and Berner 1979), water content and organic matter content (Oliva *et al*. 1999), may also determine the effectiveness of SRFs. Similarly the different external nutrient requirement of different plant species is likely to affect the agronomic effectiveness of SRFs.

In comparison to the little amount of literature dealing with the potential use of silicate rocks in agriculture, there is an extensive literature on the dissolution of silicate minerals, although not so much the dissolution of silicate rocks. The extent and rate of dissolution of solids is commonly highly dependent on particle size

(Feigenbaum *et al.* 1981; Strömberg and Banwart 1999). Particle size was shown to greatly determine the effects of basalt dust on soil properties (Gillman *et al.* 2001, 2002). Milling methods that produce superfine particles of minerals with enhanced chemical reactivity have been evaluated for industrial uses by several workers, including Garcia *et al.* (1991), Sugiyama *et al.* (1994), and Suraj *et al.* (1997). These milling methods also have been employed to improve the fertilizer effectiveness of several silicate minerals (Harley 2002) and phosphate minerals (Lim *et al.* 2003). Further evaluation of high-energy milling as a method for manufacturing SRFs, including the use of reactive additives to enhance fertilizer effectiveness, is proposed and has been evaluated in this thesis. In addition, soil properties that affect the dissolution of SRFs in the soil were identified. These properties may be appropriate indicators for soil testing to evaluate the potential for use of SRFs for specific soils and plant species.

1.2. The Objectives of Research

The main hypotheses of this research are that (1) high-energy milling affects several physicochemical properties of silicate rocks and increases the release of plant nutrient elements from SRFs and (2) soil properties affect the dissolution of SRF in the soil. To evaluate these hypotheses, several experiments were carried out with the following main objectives.

1. To identify the effects of the condition and duration of high-energy milling of silicate rocks variously combined with reactive additives on the physicochemical properties of mafic (basalt and dolerite) and K-rich felsic (gneiss and K-feldspar) rocks.
2. To identify the dissolution characteristics of the milled rocks in a dilute organic acid to provide a simple method for predicting dissolution of the milled rocks in soils.
3. To identify soil properties that influence the dissolution of SRFs in soils.
4. To measure the agronomic effectiveness of ground mafic (basalt and dolerite) and felsic (gneiss and K-feldspar) rocks for plants grown on several soils.

1.3. Organisation of the Thesis

Following the above objectives, the main content of this thesis is divided into 6 chapters including this chapter. Chapter 2 describes the milling methods used in this research and the physicochemical characteristics of the milled rocks. Dissolution of the milled rocks in a dilute organic acid is described in Chapter 3, and dissolution in soil is discussed in Chapter 4. Chapter 5 describes a glasshouse experiment that measured the agronomic effectiveness of milled mafic and felsic rocks as fertilizers. A summary of research findings, their limitations and recommendations for future research are provided in Chapter 6, followed by the lists of references and appendices. Tables and figures are placed within the corresponding text.

Chapter 2

EFFECTS OF MILLING TIME, CONDITIONS, AND REACTIVE ADDITIVES ON THE CHARACTERISTICS OF SILICATE ROCKS

2.1. Introduction

An effective method to accelerate the release of nutrients from SRFs to soil solution is high-energy milling that produces superfine reactive particles. Many workers (Gasalla *et al.* 1987; Kühnel and Van der Gaast, 1989; Garcia *et al.* 1991; Sugiyama *et al.* 1994; Aglietti 1994; Suraj *et al.* 1997; Uhlík *et al.* 2000) have reported that high-energy milling has major effects on several physicochemical properties of minerals and rocks. High-energy milling may destroy the structural order of minerals and increase the effective surface area, both effects will increase the reactivity of minerals. For example, Aglietti (1994) showed that dry milling of talc increased CEC and the amount of Mg dissolved in water. High-energy milling accelerated nutrient release from several silicate minerals (Harley 2002) and rock phosphates (Lim *et al.* 2003) in the soil. Too intensive milling, however, may cause agglomeration or sintering of fine particles resulting in a decrease of the effective surface area. Agglomeration is due to a number of processes including exposed hydrogen ion bonding of surface hydroxyl groups on the fine particles, agglomeration may be avoided by immersing the material in a polar liquid during milling (Veale 1972), e.g., wet milling in H_2O (Reay 1981; Harley 2002) or in hydrocarbons including alcohol (Papirer and Roland 1981). The addition of potentially reactive additives, such as NaCl and KCl, to eliminate agglomeration and to supply additional plant nutrients may be beneficial has not been investigated for silicate rocks. This chapter describes the results of investigations of the effects of milling methods including milling time and condition and the use of NaCl and KCl additives on several physicochemical characteristics of mafic (basalt and dolerite) and felsic (gneiss and K-feldspar) rocks.

The specific objectives of the research described in this chapter are to identify (1) the effects of milling time and condition (wet and dry) and (2) the effects of adding NaCl, KCl, and K-feldspar during the milling process on several physicochemical characteristics of the silicate rocks.

2.2. Materials and Methods

2.2.1. Samples of Silicate Rock

The silicate rocks used in this research were (meta) basalt, (meta) dolerite, gneiss, and K-feldspar, respectively from Bunbury, Jarrahdale, Northam, and Port Hedland, Western Australia. The bulk samples of the first three rocks were washed with deionized water, air dried, and broken with a hammer to about 1-cm diameter, ground with a steel Tema ring mill for 3 min at 760 rpm, and sieved to pass a 250µm sieve. K-feldspar (Ø < 150 µm) was supplied by Commercial Mineral Ltd. Perth, Western Australia, which material commercially used in ceramic bodies and glazes, and as an abrasive powder, consisting of microcline (65.6 %), albite (31.2 %), anorthite (0.6 %), kaolinite (< 1.0 %) and free quartz (< 1.0 %) (Commercial Minreral Ltd., 1997). These materials are designated as initially milled rock (T0).

2.2.2 Milling Procedures

The initially milled rocks (5 g) were further milled with a ball mill (Spex-8000) using a 80cm^3 steel vial and 50 g of ∅ 5mm steel balls for 10, 30, 60, 90, and 120 min. In the following discussion, milling times will be denoted as T0, T10, T30, T60, T90, and T120. For wet milling, 15 mL H_2O was added to the samples prior to milling. Other subsamples of initially milled basalt, dolerite, and gneiss, respectively were added to reagent grade NaCl or KCl (4.5 g rock + 0.5 g NaCl or KCl) and milled for 120 min under dry and wet conditions. Basalt and dolerite T0 were also mixed with K-feldspar at a ratio of 1 : 1 and milled for 120 min under dry and wet conditions. The adhered rock powders on the mill vial were scratched with a stainless steel spatula, and for those on mill balls were removed by hand shaking the balls using stainless steel screen. All of these powders were transferred to plastic containers for storage. The wet-milled samples were removed from the mill vial and ball surfaces using a DI-spray bottle, and were transferred to plastic bottles through plastic panels equipped with a stainless steel screen. The suspensions of the wet-milled rocks were centrifuged for 10 min at 11,000 rpm using Eppendorf 5810 Centrifuge (maximum capacity of 4 x 1.1 kg and speed 12,000 rpm), the supernatant was discharged and the powders were oven dried at 60^o C for 48 h and placed in plastic containers for storage.

2.2.3 Analytical Methods

Identification for physicochemical properties of the milled rocks was carried out in their original condition (without any pre-treatment) as that might be used in practices. However, an exception was made for the measurement of particle size by using Malvern Mastersizer that the rock powders were ultrasonically dispersed prior to measurement. This treatment was applied due to concern to the possibility of scratching on the detection lens of the instrument by coarse (agglomerated) particles being measured. Care should be taken, therefore, in interpreting the results of this measurement as such pre-treatment to the samples may result underestimate values of particle size relative to those for the untreated SRFs.

The concentrations of major elements in the initially milled (T0) and milled (T10 – T120) silicate rocks were determined by XRF (Philips PW 1400) after fusing the samples with lithium metaborate (Karathanasis and Hajek 1996). The determination of Fe was done in spite of the potential risk for sample contamination due to the use of Fe-steel ball mill, and hence of overestimation of the actual dissolution rate.

An extracting solution of 1*M* ammonium acetate (CH_3COONH_4) buffered at pH 7.0 was used to measure the quantities of exchangeable basic cations (Ca, Mg, K, and Na) in the milled rocks. A subsample (250 mg) of rock powder each was added to 20 mL extracting solution in a 30mL plastic container, and then shaken for 1 h on an end-over end shaker. This step was repeated three times for the same sample and the filtrates from each extraction were combined. The concentrations of Ca and Mg in the filtrates were measured using Atomic Absorbance Spectrophotometry (AAS), K and Na were measured using flame emission. The lanthanum solution ($LaCl_3$) was added to suppress interferences for Ca determination, and Cs solution was added to overcome ionization interference for K determination. The quantity of each exchangeable cation was calculated in units of centimole charge per kg rock dust ($cmol_c$/kg) and % of total in rock (i.e., the amount of each exchangeable element relative to the total content of the element in rock powder for each milling time and condition).

The quantity of amorphous constituents was determined as (Fe + Al + Si) soluble in 0.2*M* ammonium oxalate-oxalic acid buffered at pH 3.0 using the procedure described by Rayment and Higginson (1992). The concentrations of Fe and Al in the filtrate were measured using AAS and Si was determined using the molybdate blue method (Strickland and Parsons 1968). In addition, the concentrations of Mg and K in the filtrates for milled basalt, dolerite, and gneiss, and K and Na in the filtrate for milled K-feldspar were measured using AAS (for Mg) and flame emission (for Na and K). The concentration of Ca in the filtrate was not measured due to the present of white precipitate in the filtrate when lanthanum solution was added as a suppressing agent for measurement of Ca with AAS. Further identification of the precipitate was not carried out. It was presumed that the precipitate might be La-oxalate complex as such precipitate only present when La solution was added to oxalate filtrates, but there was no precipitate caused by adding La to the other filtrates (e.g., filtrates of ammonium acetate, acetic-citric acids, and CH_3COONH_4 extractions). The pH_{H2O} (1 : 5) and electric conductivity (1 : 5) of water extracts of the milled rocks were measured with pH (Cyberscan 2000) and EC (Cyberscan 2000) meters.

The particle size distribution of rock powders was measured in duplicate by using a Malvern Mastersizer (the lowest detection limit is Ø 0.02 µm). The sample was ultrasonically dispersed in water for 5 min prior to measurement and stirred continuously during measurement. Specific surface area of duplicate samples (without dispersion) was measured by the BET-N_2 method (Brunauer *et al.* 1938) using a Micromeritics Gemini III 2385 Surface Area Analyser. Before measurement of specific surface area, subsamples of the rocks that had been dry-milled with NaCl and KCl were washed with deionized water twice to dissolve free NaCl and KCl that may have remained in the rock powders. Mineralogical characteristics of rock powders were derived through analysis of XRD patterns by applying a X-ray Powder Diffraction Analysis Software (XPAS) V.3.0 described by Singh and Gilkes (1992). The XRD patterns were collected with a Philips PW-3020 diffractometer using monochromatised Cu Kα radiation, generated at 50 kV and 20 mA. The diffraction intensity was recorded between 5 and 70° 2θ at a scanning rate of 0.02° per second.

2.3. Results and Discussion

2.3.1. General Characteristics of Silicate Rocks

The total elemental and mineral compositions of the silicate rocks (T0) are presented in Table 2.1. The total content of elements for each rock milled for different time and condition is presented in Appendix A1, which values are used as the basis for calculating the proportion of extractable or dissolved elements (i.e., % of total in rock) throughout the thesis.

Table 2.1. Total elemental and mineral compositions of the silicate rocks at their initial condition (T0)

Rock	Element[a] (oxides) %											
	SiO_2	Al_2O_3	Fe_2O_3[b]	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	P_2O_3	SO_3	Total[c]
Basalt	47.95	19.15	11.25	11.11	6.08	0.18	2.10	1.76	0.16	0.19	0.05	100
Dolerite	49.92	13.94	15.22	11.37	6.32	0.37	1.21	1.89	0.21	0.13	0.12	100
Gneiss	74.01	15.02	2.64	2.01	0.74	1.09	4.06	0.31	0.02	0.08	0.01	100
K-feldspar	61.53	19.05	0.02	0.05	0.01	11.56	2.51	0.05	0.01	0.22	0.01	100

	Mineral Composition[d]
Basalt	: Mg-Hornblende (5 - 6), Pargasite (5 - 6), Augite (5 - 6), Albite (6 - 6.5), Anorthite (6 - 6.5), Biotite (2.5 - 3), Phlogopite (2 - 2.5)
Dolerite	: Mg-Hornblende, Pargasite, Augite, Albite, Anorthite, Biotite, Diopside (5.5 – 6.5)
Gneiss	: Quartz (7), Albite, Biotite, Chlorite (2 – 3)
K-feldspar	: Microcline (6 – 6.5), Albite, Anorthite

[a] Average values of 4 replicates.

[b] Total iron is expressed as Fe_2O_3, much Fe is present as Fe^{+2}.

[c] Normalized to total of 100 % to exclude structural H_2O.

[d] Duplicate measurements, and minerals listed in order of decreasing abundance, followed by relative hardness numbers (Deer *et al.* 1992).

As shown in Table 2.1, mafic (basalt and dolerite) and felsic (gneiss and K-feldspar) rocks have quite different elemental and mineral compositions and contain minerals of various relative hardness values. These differences may relate to their suitability for use as fertilizers and their responses to milling treatments.

The mafic rocks have similar elemental and mineral compositions, which are dominated by ferromagnesian silicates (hornblende, pargasite, and augite) of the amphibole group. The total contents of silica are 47 - 50 % SiO_2 and alumina are 14 – 20 % Al_2O_3, with several macronutrient elements present in relatively large amounts Ca (11 % CaO) and Mg (6 % MgO). The hardness of most minerals present in the mafic rocks is 5 – 6.

The felsic rocks have different elemental and mineralogical compositions to the mafic rocks. Gneiss is dominated by quartz with some feldspars and micas, whereas the K-feldspar is reported by Commercial Minerals Ltd. (1997) to consist of microcline (65.6 %), albite (31.2 %), and anorthite (0.6 %) with minor kaolinite and free quartz. Both felsic rocks contain high concentrations of silica (61 - 75 % SiO_2) and alumina (15 – 19 % Al_2O_3), the major plant nutrients are K and Na. The concentration of K in K-feldspar (11.5 % K_2O) is much larger than that for gneiss (1 % K_2O), conversely the concentration of Na in K-feldspar (2.5 % Na_2O) is lower than that in gneiss (4 % Na_2O). Appreciable amount of Ca and Mg occur in minor mafic minerals in gneiss. The relative hardness of most minerals composing these felsic rocks is 6 – 6.5.

Based on their major plant nutrient contents, the mafic rocks could be potential sources of Ca and Mg, and the felsic rocks potential sources of K providing that these elements are released to soil solution. An evaluation of these milled SRFs is needed to identify the solubility of nutrient elements in soils.

2.3.2. Effects of Milling Time and Condition

2.3.2.1. Physical and Mineralogical Properties

Particle Size and Surface Area

Plots of volume median particle size (D_{50}) and surface area versus milling time are presented in Figure 2.1. Although each type of rock exhibits different responses to milling treatments as indicated by the changes in particle size and surface area, some general trends may be summarized as follows:

1. Milling clearly reduced particle size for all silicate rock dusts used in this study. The most significant effect of milling occurred for 10 min of milling which reduced particle size to 2 – 3 μm for dry milling and 5 – 10 μm for wet milling.
2. The changes in surface area due to milling did not always systematically follow the changes of particle size measured with the Malvern Mastersizer, especially for dry-milled basalt. This condition was due partly to difference in sample pre-treatment (i.e., the samples of rock powders for particle size measurement were

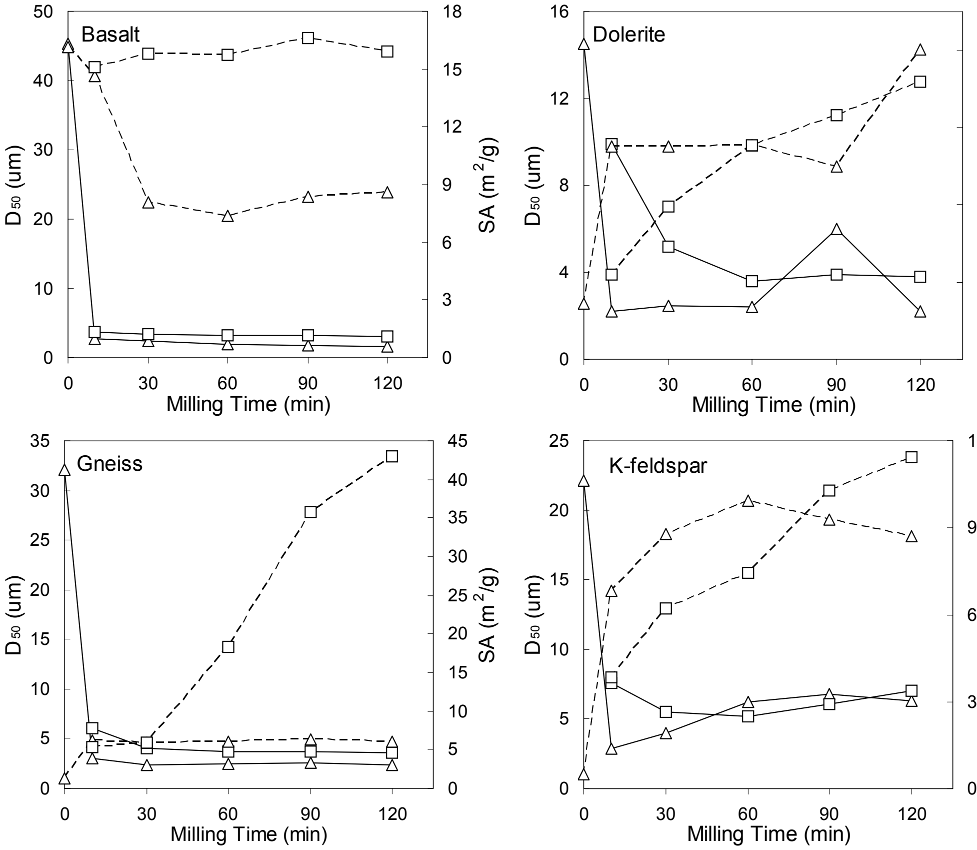


Figure 2.1. Median particle size ($D_{50,}$ full lines) and specific surface area (SA, broken lines) for dry- (∆) and wet- (□) milled rocks as a function of milling time.

dispersed, but those for surface area measurement were not). Moreover, the BET-N_2 method may measure the area of both external and internal (porosity) surfaces of rock particles (Hodson 1999).

Dry milling for 10 min caused the powder to adhere strongly to the grinding vial with this effect increasing with increasing milling time. In this condition, only a small proportion of rock particles were impacted by the steel balls so that dry milling for more than 10 min was ineffective in further reducing particle size. Moreover, the process may also promote agglomeration in the form of larger particles as was observed with the Malvern Mastersizer. For wet milling, on the other hand, only a minor proportion of the powder adhered to the grinding vial, so that agglomeration was unlikely to have occurred in this condition and the powder was easily removed from the vial.

As shown in Figure 2.1, basalt powder has a high surface area (16.2 m^2/g) in its initial state (T0), indicating that this basalt is a microporous material. Basalt was sampled from the exposure of rock blocks of Ø 0.25 – 0.50 m on which weathering may have occurred for centuries. Thus, this microporosity of basalt, at least partly, is as a consequence of natural alteration and it is possible also gas vesicles in the glass component of basalt. Regardless the characteristics of this microporosity for basalt, the reduction in surface area of dry-milled basalt might not be solely due to agglomeration, but also to the collapse of initial pores as extensive agglomeration was unlikely to occur during wet milling of basalt. The overall result of these opposing mechanisms was the relatively constant surface area of wet-milled basalt.

For dolerite dust, dry milling for 10 min decreased particle size about 7 fold (i.e., from 14.5 to 2.2 μm) and increased surface area about 4 fold (i.e., from 1.4 to 5.5 m^2/g). However, further milling increased particle size to about 6 μm (for T90), indicating that agglomeration occurred for dolerite powder when it was dry milled for 10 – 90 min which caused a slight decrease of surface area, then increase to about 8 m^2/g for T120. Wet milling for 10 min reduced particle size about 3 fold and it remained constant for further milling although surface area continuously increased about 3 fold, i.e., from 2 (T0) to 7 (T120) m^2/g.

For gneiss dust, dry and wet milling for 10 min decreased particle size about 10 fold, i.e., from 35 to 3 μm (dry milling) and to 4 μm (wet milling), and increased surface area by about 5 fold, i.e., from 1.3 to 6.2 m^2/g. Further milling under the dry condition had no effect on the surface area of gneiss dust, while further milling under the wet condition increased the surface area of gneiss dust to 43 m^2/g (T120) although there was no corresponding reduction in particle size.

Dry milling increased the surface area of K-feldspar dust by about 23 fold over its initial state, i.e., from 0.5 m^2/g (T0) to 11.8 m^2/g (T120). Wet milling for 10 min increased surface area about 14 fold (from 0.5 to 6.8 m^2/g). Further milling for 120 min increased surface area to about 9 m^2/g. The particle size of wet milled K-feldspar was reduced to about 5.5 μm for 60 and 120 min of milling while the particle size of dry milled K-feldspar dust showed a complex behaviour that may reflect agglomeration of particles for the longest milling time.

Agglomeration of dry-milled silicate minerals has been reported for α-spodumene (Gasalla *et al.* 1987), kaolins (Juhász 1980; Garcia *et al.* 1991), talc (Aglietti 1994), and antigorite (Drief and Neito 1999). These authors reported that different grinding times were necessary for the occurrence of agglomeration depending on milling procedure and mineral species, and that agglomeration either decreased surface area (Garcia *et al.* 1991; Sánchez-Soto *et al.* 1997) or increased surface area (Gasalla *et al.* 1987). These conflicting results may be due to differences in the minerals, grinding methods, and procedures for measuring surface area but the same apparently conflicting trends were observed in the present work using standard procedures for grinding and measurement.

The absence of agglomeration for several silicate minerals wet milled in H_2O was reported by Reay (1981) and Harley (2002), and for milling in hydrocarbons by Papirer and Roland (1981). According to Veale (1972), immersing particles in a polar liquid during milling reduces sintering as water and other polar organic liquids surround and neutralise positive and negative charges on the newly exposed surfaces of particles, thereby limiting direct interactions between particles.

Characteristics of XRD Reflections

The XRD patterns of the SRFs are presented in Figures 2.2 – 2.5, results of measurement for relative peak area (RPA) and width at half peak height (WHPH) are presented in Figure 2.6.

The silicate rocks consist of mixtures of several minerals (Table 2.1), consequently their XRD patterns are more complex than for K-feldspar. Many of the XRD reflections of the minerals present in basalt, dolerite, and gneiss coincide, consequently, only the limited number of XRD reflections that did not coincide were available for measurements of RPA and WHPH (Figure 2.6) as indices of crystal properties using an interactive program of XPAS (Singh and Gilkes 1992).

Peak area is an indicator of the abundance of a mineral and the width of a reflection is an inverse measure of crystal size or more specifically the size of the coherently scattering zone (Klug and Alexander 1974). As shown in Figure 2.6, milling increased WHPH and decreased RPA. These trends indicate that milling reduced crystal size and also induced structural disorder in the minerals which decreased total diffracted intensity (i.e., area under peak) as amorphous material does not diffract coherently but contributes to background scattering. The increased broadening of XRD reflections indicates a reduction in the crystal size of the remaining crystalline mineral (Klug and Alexander 1974). Most of the effects of milling on the XRD patterns of rock dusts (see Figures 2.2 – 2.5) occurred during 60 min of milling with the effects for dry milling being greater than for wet milling.

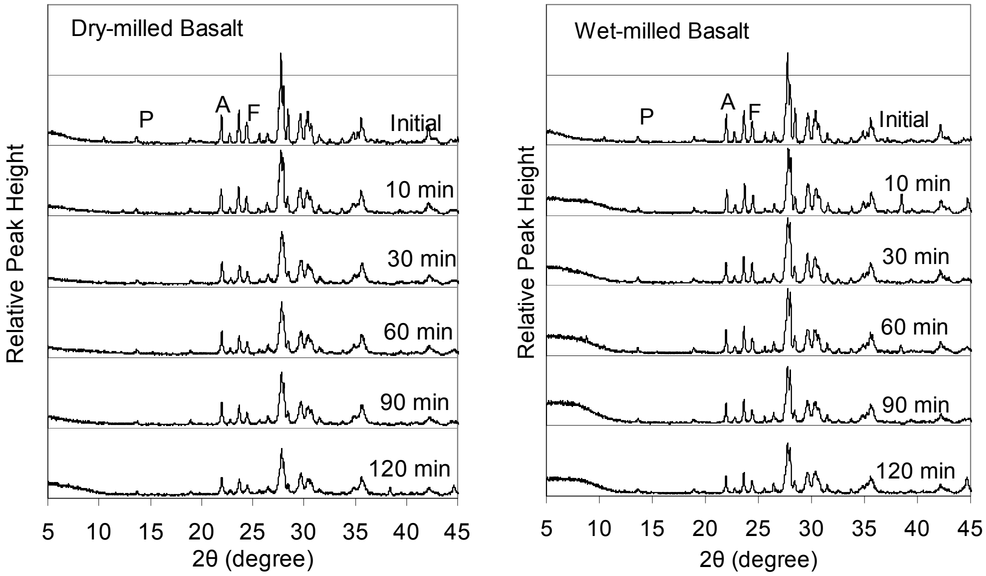


Figure 2.2. XRD patterns of basalt milled for several milling times under dry and wet conditions. P = pyroxene 110 (d = 6.45 Å), A = amphibole 131 (d = 3.89 Å), and F = feldspar 114 (d = 3.47 Å).

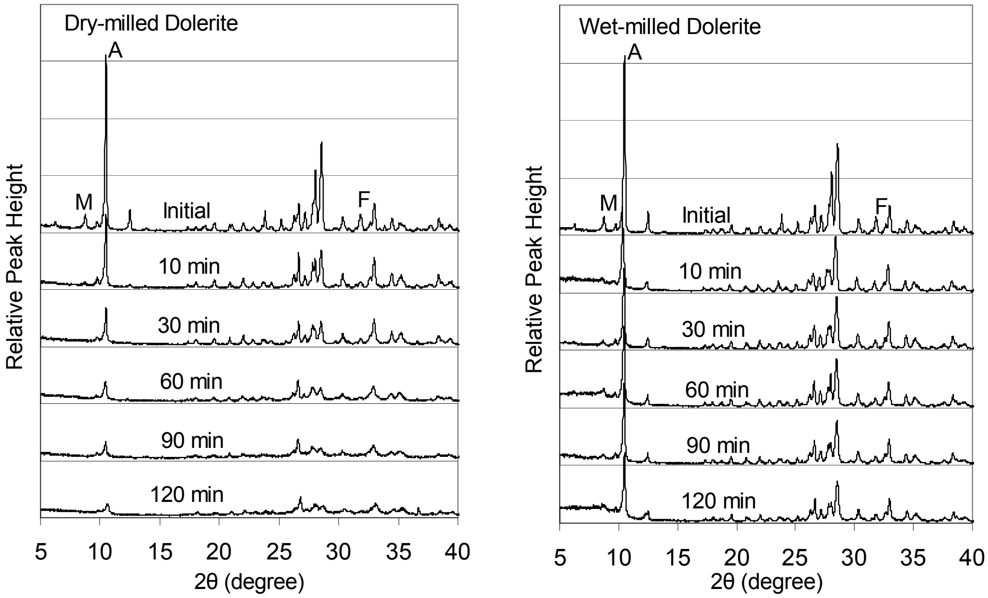


Figure 2.3. XRD patterns of dolerite milled for several milling times under dry and wet conditions. M = mica 002 (d = 10.06 Å), A = amphibole 110 (d = 8.4 Å), and F = feldspar 113 (d = 2.83 Å).

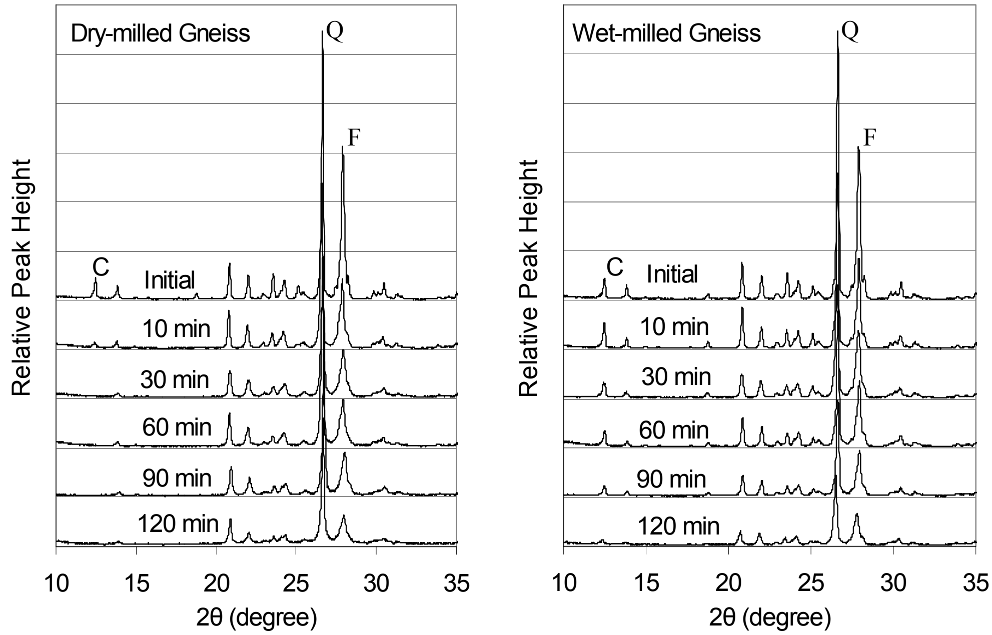


Figure 2.4. XRD patterns of gneiss milled for several milling times under dry and wet conditions. C = chlorite 004 (d = 7.0 Å), Q = quartz 101 (d = 3.43 Å), and F = feldspar (albite) 220 (d = 3.17 Å).

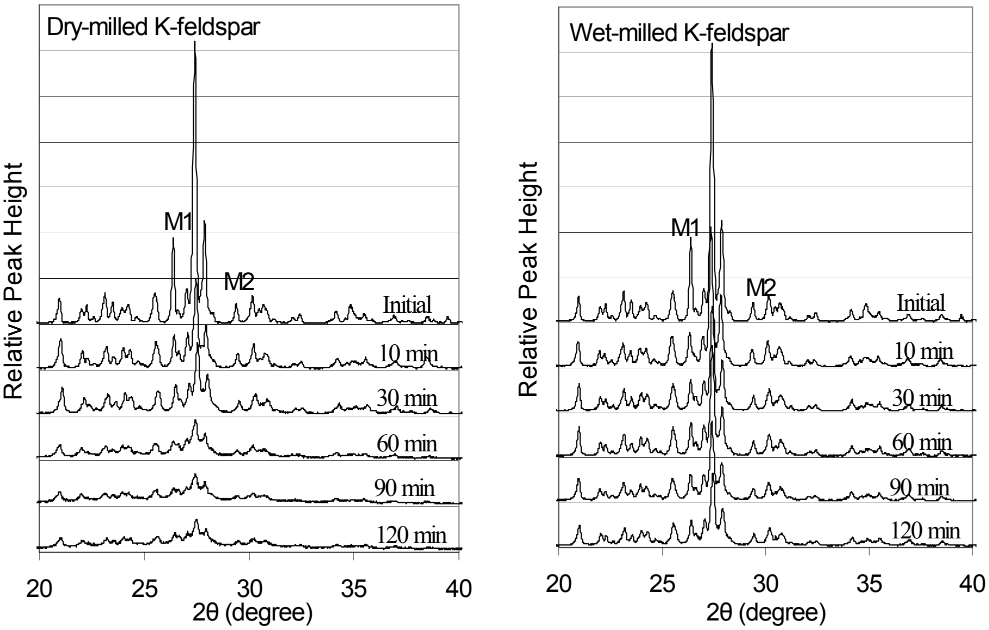


Figure 2.5. XRD patterns of K-feldspar milled for several milling times under dry and wet conditions. M1 = microcline 112 (d = 3.49 Å) and M2= microcline 131 (d = 3.03 Å).

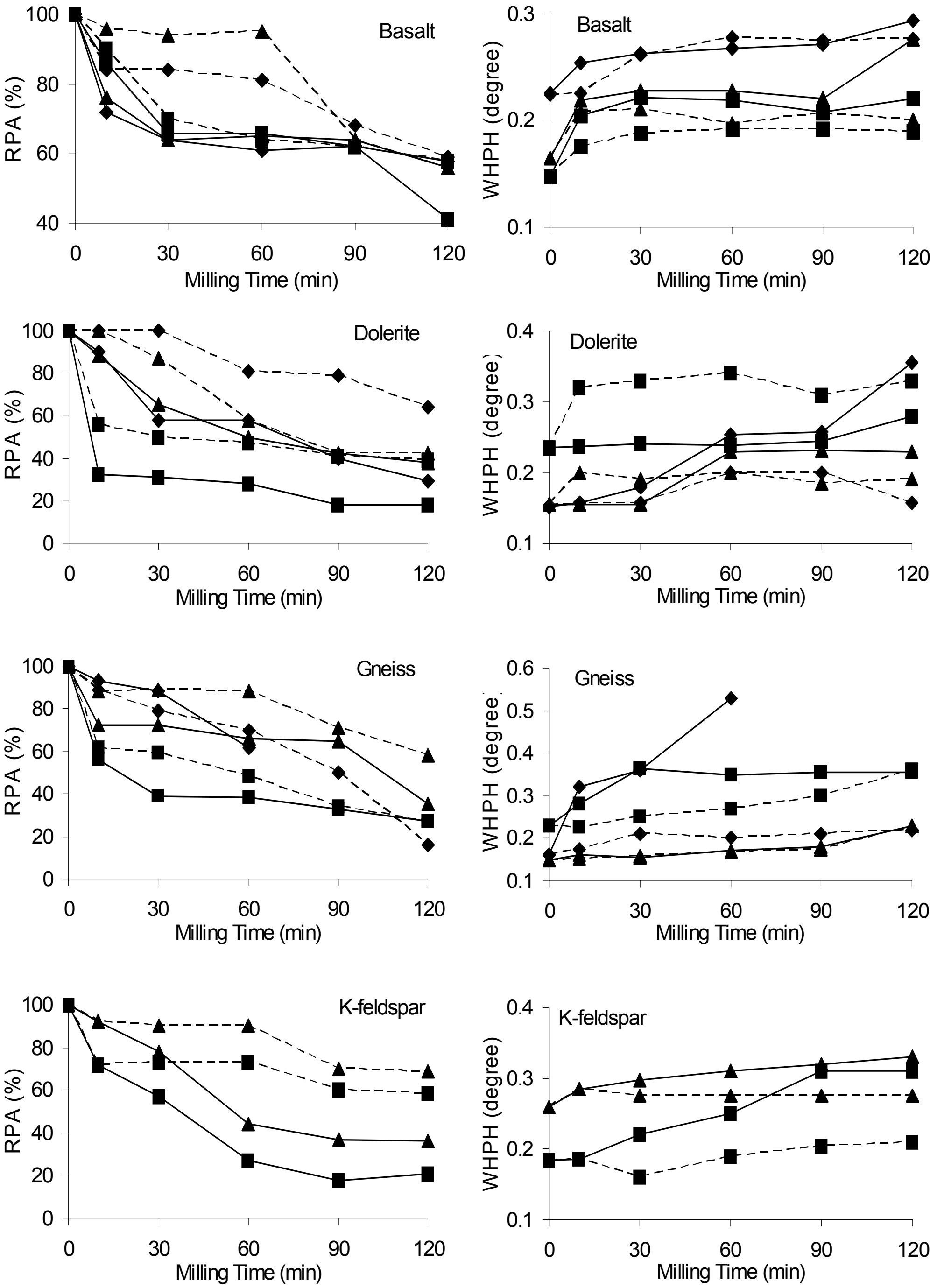


Figure 2.6. Relative peak area (RPA) and width at half peak height (WHPH) versus milling time for several diagnostic reflections (hkl) of several minerals in basalt, dolerite, gneiss, and K-feldspar dusts. Full and broken lines are respectively for dry- and wet-milled rocks. The analysed peaks are referred to in the XRD patterns presented in Figures 2.2 – 2.5.

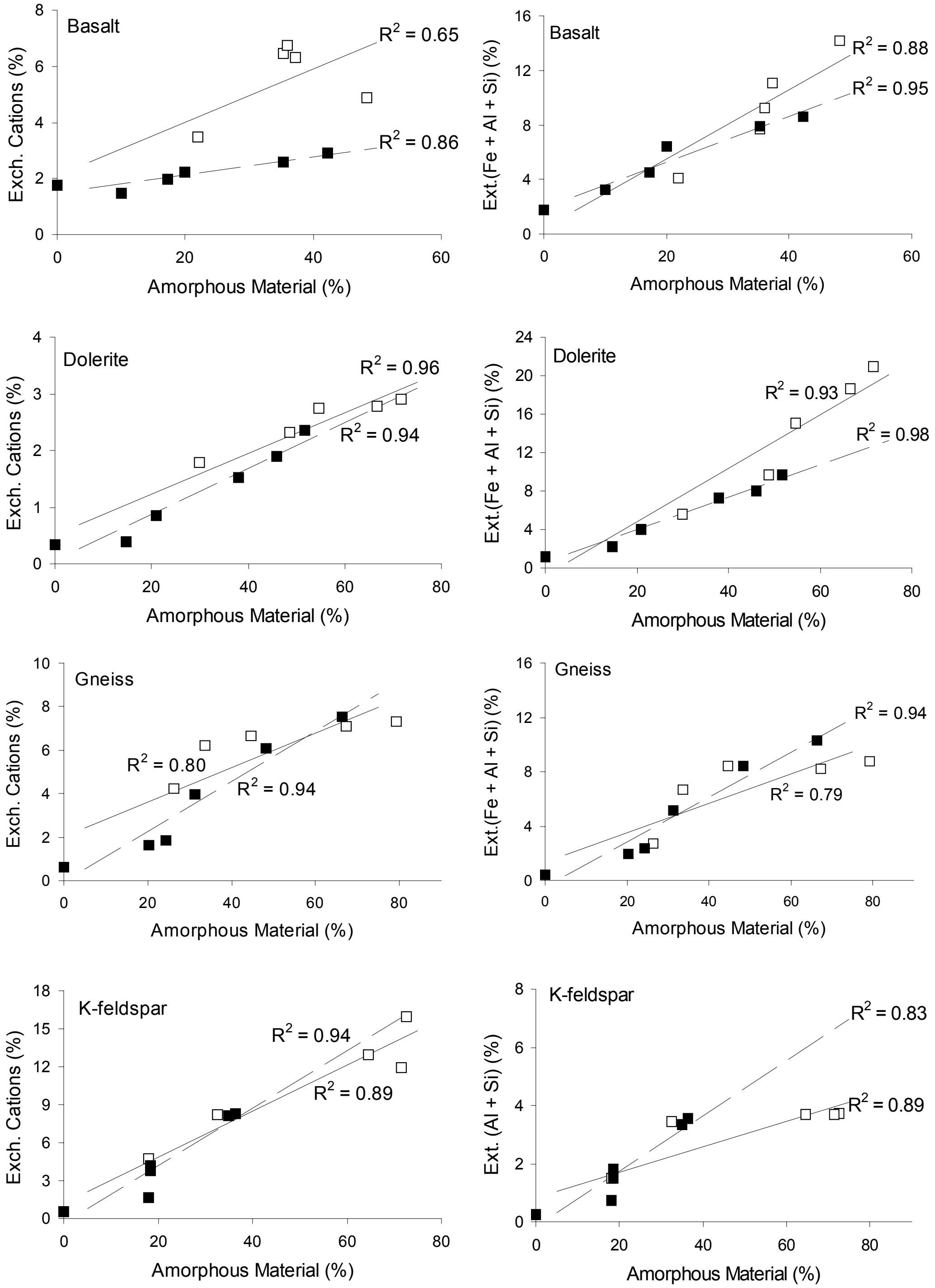


Figure 2.7. The relationships between percentages of exchangeable basic cations (Ca + Mg + K + Na) and oxalate-extractable (Fe + Al + Si) versus the percentage of amorphous materials (calculated as averaged [100% - RPA] for several XRD peaks of several minerals) for dry- (□ full lines) and wet- (■ broken lines) milled rocks.

Assuming that the XRD peak area after 120 min of milling is a measure of the abundance of crystalline minerals remaining in the rocks (Klug and Alexander 1974), it appears that non crystalline (amorphous) forms of minerals in the rock dusts increased from an initial value of zero to about 40 (wet) – 60 % (dry) for basalt, 30 – 80 % for dolerite, 45 – 85 % for gneiss, and 30– 80 % for K-feldspar dusts. These major changes in crystal size and structural order (e.g., amorphization) due to milling are likely to have a major impact on the solubility of ground rocks in soil solution and thus the effectiveness of ground SRFs. Figure 2.7 indicates that the quantity of amorphous materials is closely related to the percentages of CH_3COONH_4-exchangeable basic cations (Ca + Mg + K + Na) and acid oxalate-extractable (Fe + Al + Si) in the milled rocks.

2.3.2.2. Chemical Properties

Contamination by Iron

The concentration of total iron expressed as Fe_2O_3 in the milled rocks increased with increasing milling time due to contamination by metallic Fe from mill vial and balls, with wet milling producing greater contamination than dry milling (Figure 2.8). For milled basalt, dolerite, and K-feldspar, the maximum percentage contamination was < 2 % Fe_2O_3 and this is unlikely to be a serious problem in relation to the use of the milled rocks as fertilizers or for wear of the milling equipment. Contamination of milled gneiss was much higher (7 – 10 % Fe_2O_3) which may be a consequence of the presence of the abrasive mineral quartz (hardness = 7, Table 2.1) in this rock type and indicates an unacceptable rate of wear of the milling equipment.

pH and EC

The effects of milling time and milling condition on pH and EC of 1 : 5 rock dust : water extracts are presented in Figure 2.9. Milling increased the pH of most rock dusts with dry milling having the greater effect. The increase of pH due to milling for 120 min was in ranges of 1.0 - 1.5 and 0.3 - 1.0 units respectively for dry and wet milling. Milling also increased the EC of 1 : 5 rock dust : water extracts, except for basalt dust. The increases of EC due to milling for 120 min were about 120 and 100 μS/cm (for dry- and wet-milled dolerite, respectively), 250 and 170 μS/cm (for dry- and wet-milled gneiss respectively), 300 and 100 µS/cm (for dry- and wet-milled K-feldspar respectively).

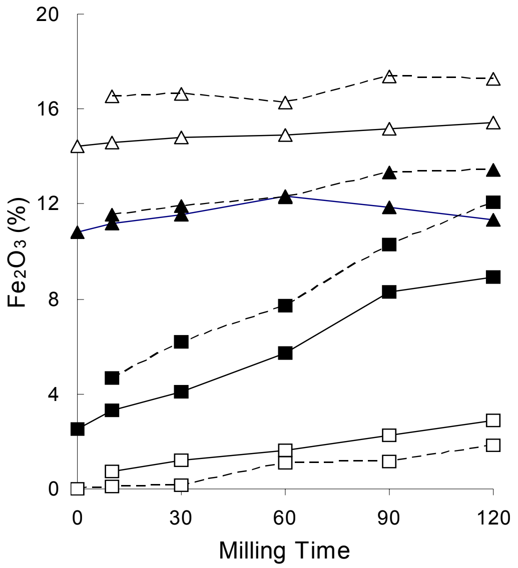


Figure 2.8. Concentration of iron (expressed as % Fe_2O_3) versus milling time of basalt (▲), dolerite (Δ), gneiss (■) and K-feldspar (□) milled under dry (full lines) and wet (broken lines) conditions.

The increased surface area of minerals exposes more basic cations to exchange by H^+ in extracting solution and amorphization may reduce bond strengths thereby increasing surface ion exchanges which will increase dissolution and the pH and EC of extracts of the milled rocks. For the same milling times, the pH and EC values for dry-milled rocks were higher than for wet-milled rocks, presumably because this exchange process occurred during wet milling and the solution containing dissolved basic cations was discarded. Consequently, values of pH and EC for wet-milled rocks tended to be lower than for dry milled and in some instances unmilled rocks (T0).

Solubility of Basic Cations

It is evident that the amounts of exchangeable and extractable elements in the milled rocks are closely related to the amounts of amorphous silicate present (Figure 2.7) which generally increase with milling time. The plots of quantities of exchangeable basic cations (Ca, Mg, K, and Na) versus milling time are presented in Figures 2.10 and 2.11. The quantities of exchangeable Mg and K (for basalt,

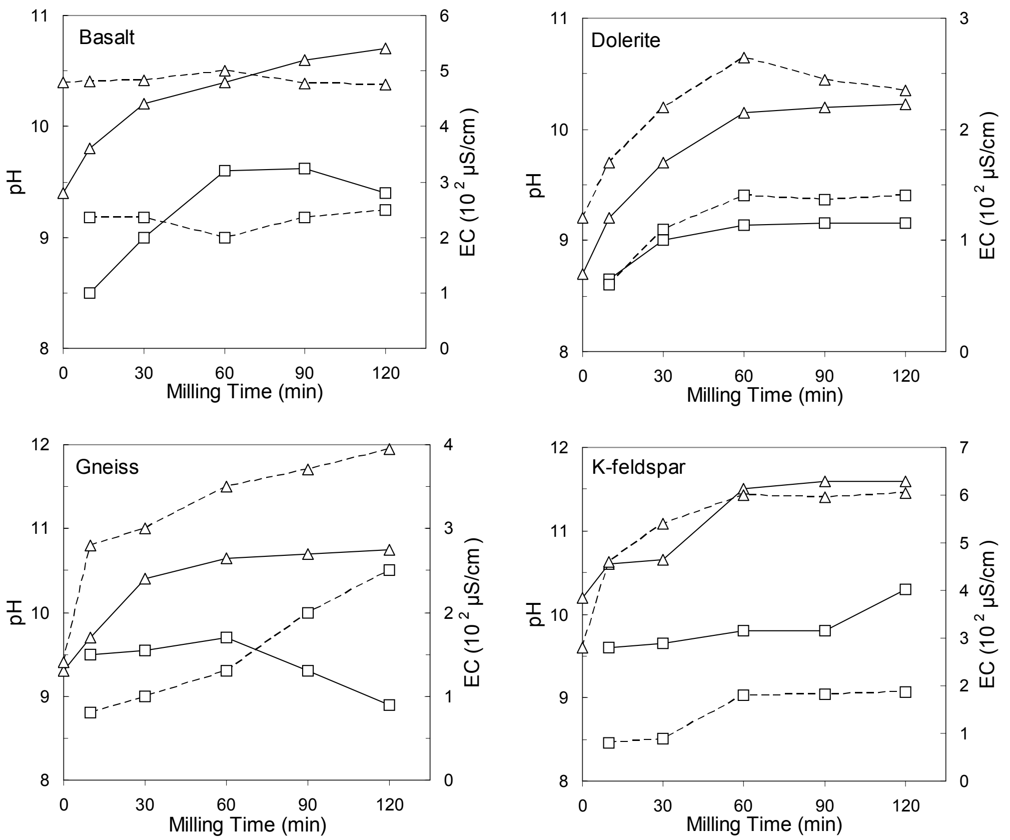


Figure 2.9. The pH$_{H_2O}$ 1 : 5 (full lines) and EC 1 : 5 (broken lines) of suspensions of dry- (Δ) and wet- (□) milled rocks as a function of milling time.

dolerite, and gneiss dusts), K and Na (for K-feldspar dust) were also compared to the quantities of these cations extracted with 0.2*M* ammonium oxalate-oxalic acid (Figure 2.12) to identify the effect of amorphization during the milling process on quantity of exchangeable divalent- (represented by Mg) and monovalent- (represented by K) basic cations in 1*M* CH_3COONH_4 pH 7.

These figures show three general trends: (1) milling increases exchangeable basic cations with the increase due to dry milling being larger than for wet milling, (2) the plots of exchangeable basic cations versus milling time for dry milling are approximately parabolic, while those for wet milling are linear (Figures 2.10 and 2.11), and (3) milling greatly increases the amount of soluble amorphous cations and the difference between % oxalate-extractable cations (soluble amorphous cations) and % exchangeable cations becomes larger with increasing milling time, especially for dry-milled rocks, indicating the strong retention of basic cations by the amorphous materials.

For dry-milled rocks, the maximum values of extractable basic cations were reached for various milling periods (10 – 90 min). The maximum values of exchangeable Ca for dry-milled basalt and dolerite were similar, i.e., about 3 % of total Ca, but exchangeable Mg for milled basalt was larger (about 8 % of total)

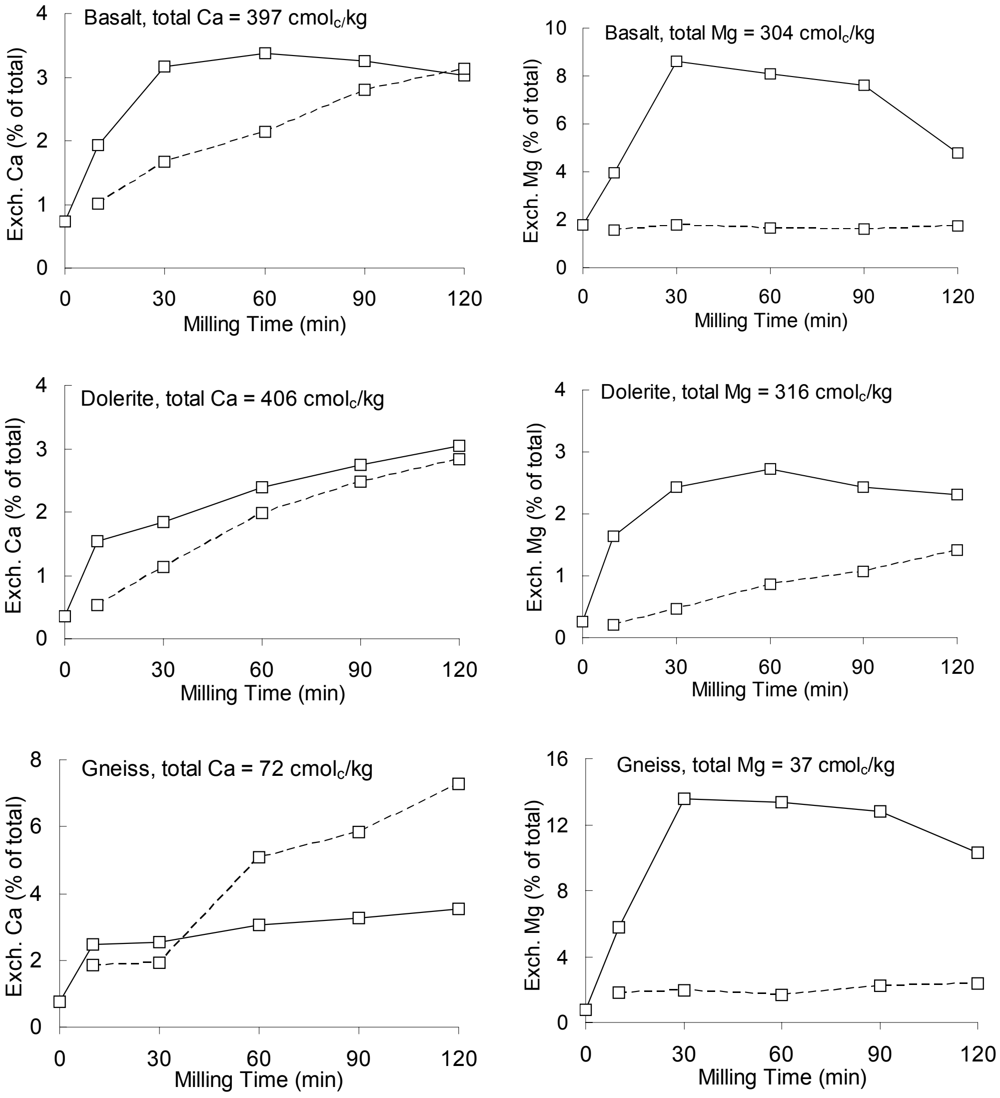


Figure 2.10. The percentages of CH_3COONH_4-exchangeable Ca and Mg for basalt, dolerite, and gneiss milled under dry (full lines) and wet (broken lines) conditions as a function of milling time. The % exchangeable cation is calculated relative to total of this cation in rock for each milling time and condition (Appendix A1). Total element presented in each graph is for initially milled rock (T0).

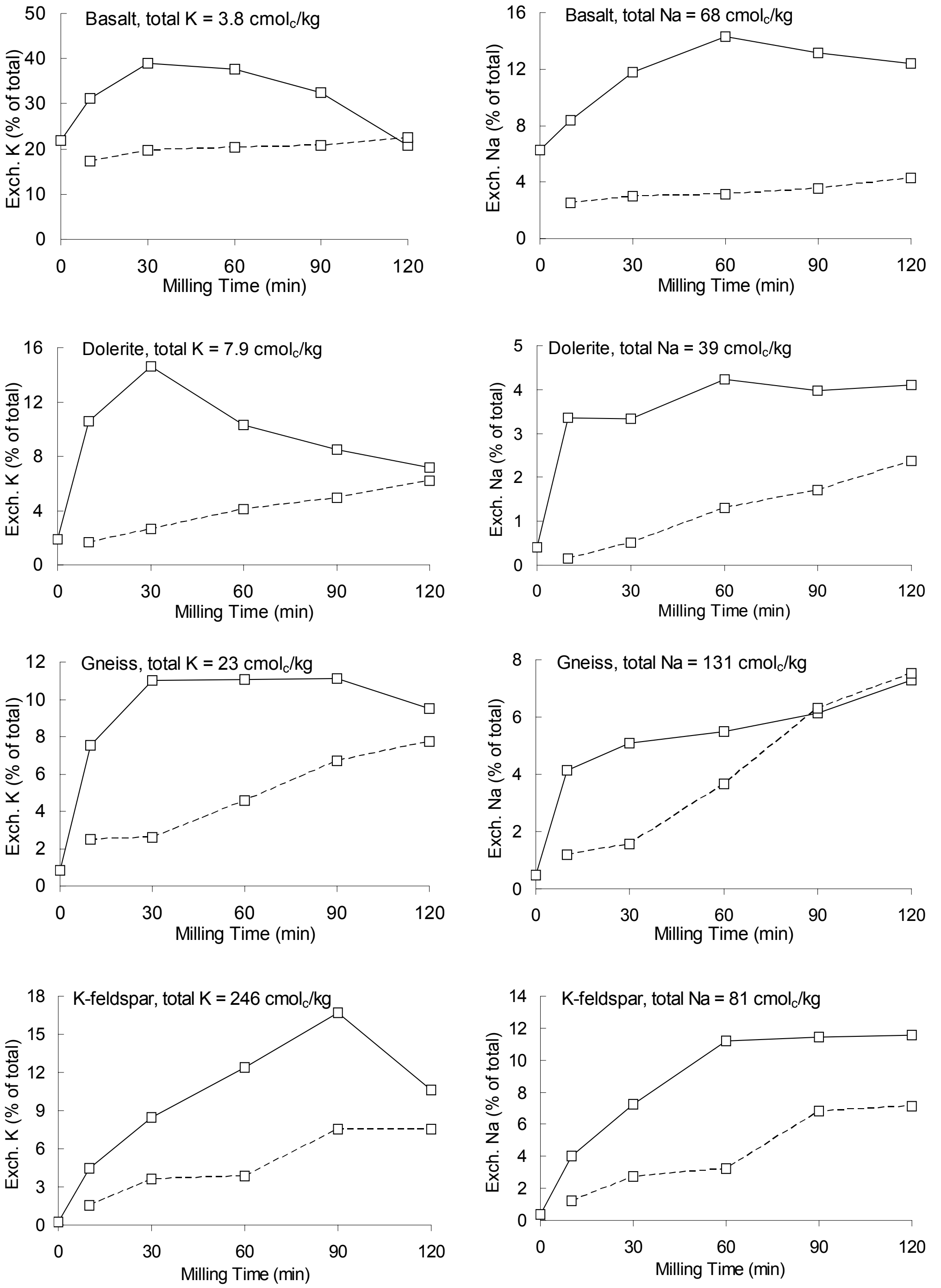


Figure 2.11. The percentages of CH$_3$COONH$_4$-exchangeable K and Na for basalt, dolerite, and gneiss, and K-feldspar milled under dry (full lines) and wet (broken lines) conditions as a function of milling time. The % exchangeable cation is calculated relative to total of this cation in rock powder for each milling time and condition (Appendix A1). Total element presented in each graph is for initially milled rock (T0).

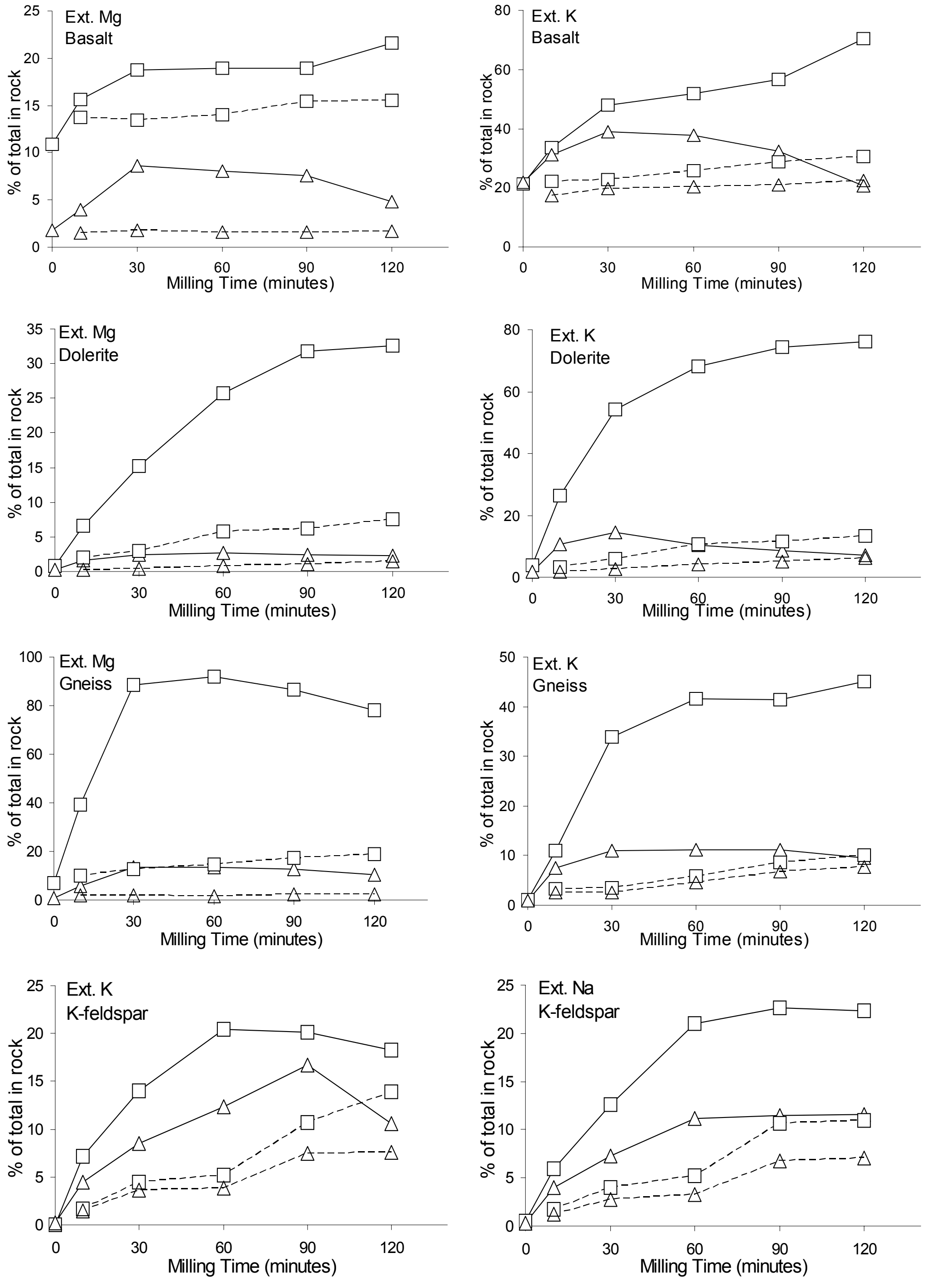


Figure 2.12. The percentage of Mg and K (for basalt, dolerite, and gneiss dusts), K and Na (for K-feldspar dust) extracted in 0.2*M* ammonium oxalate-oxalic acid (□) and 1*M* CH_3COONH_4 pH 7 (Δ) (i.e., exchangeable cations) as a function of milling time. Full and broken lines are respectively for dry- and wet-milled rocks. The % extractable element (y axes) is calculated relative to total of this element in rock powder for each milling time and condition (Appendix A1).

than for dolerite dust (about 3 % of total). The maximum values of exchangeable Ca and Mg for gneiss dust were about 4 and 15 % respectively. The highest values of exchangeable basic cations for wet-milled rocks (at T120) were about half those for dry-milled rocks. An exception was for gneiss milled for more than 30 min for which exchangeable Ca for wet milling was 2 to 3 fold higher than for dry milling.

Amounts of oxalate-extractable cations consistently increased with increasing milling time up to 120 min, while the amounts of exchangeable cations decreased for milling times longer than 30 min. These different trends may indicate that some exchangeable divalent and monovalent cations are trapped in the amorphous materials by sintering, and are thus not exposed to exchange in CH_3COONH_4. It is impossible to identify specific contributions of minerals in the rocks (basalt, dolerite, and gneiss) of those extractable cations that occur in two or more minerals in a single rock. Monovalent cations (K, Na) are mainly present in feldspars (microcline, albite, and anorthite) with some K in biotite. Divalent cations (Ca, Mg) are in hornblende, Ca is also present in feldspar and Mg in chlorite and biotite. Two major feldspar species (microcline, albite) were present in the K-feldspar.

Amorphous Constituents

The acid oxalate reagent extraction procedure was developed to remove Fe, Al, and Si present in amorphous materials in soil (Rayment and Higginson 1992) and may be indicative of poorly ordered or amorphous silicates in general and in milled-silicate rocks in particular. A reservation to this interpretation is that crystalline minerals also exhibit a finite solubility in this extractant as indicated by data for T0 samples in Figure 2.13. Milling increased oxalate-extractable (Fe +Al + Si) to about 3 to 20 % of those elements in the rock dusts, with dry milling generally producing a larger increase in solubility. This result indicates that milling induced amorphization with the process being more severe for dry than for wet milling. The increase in amorphous material determined on this basis was in the sequence dolerite > basalt > gneiss > K-feldspar for dry milling and dolerite = basalt = gneiss > K-feldspar for wet milling.

As shown in Figure 2.13, the relationships between the soluble amorphous materials in dry-milled rocks and milling time are quadratic, whereas those for wet-

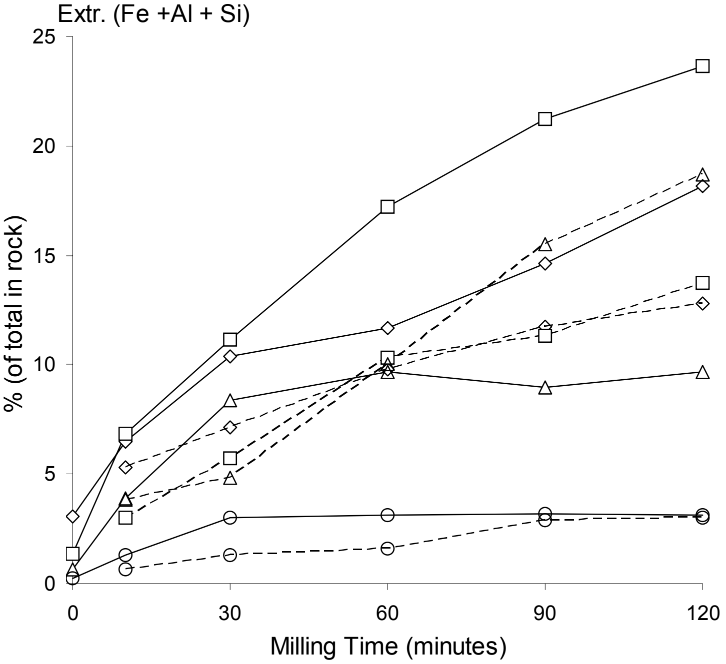


Figure 2.13. The percentage of extractable (Fe + Al + Si) in 0.2*M* ammonium oxalate-oxalic acid for basalt (◊), dolerite (□), gneiss (Δ), and K-feldspar (○) milled under dry (full lines) and wet (broken lines) conditions as a function of milling time. The values for y axes was not corrected with Fe contaminant from steel vial and ball mill, thus these values will be slightly overestimate, especially for milled gneiss, if most of the metallic Fe contaminants are extractable in this extractant.

milled rocks are nearly linear. These relationships for dry-milled rocks indicate the lesser effect of longer milling times under dry condition on amorphization. The increases (values for T120 minus for T0) of amorphous materials were about 14 and 20 fold respectively for dry-milled basalt and dolerite. For wet milling, the increase in amorphous material for both rocks was similar at about 10 fold. For dry-milled felsic rocks (gneiss and K-feldspar), amorphous materials increased up to 7 and 3 fold respectively at T30, then the values remained almost constant for further milling. For wet-milled felsic rocks, the content of amorphous materials increased linearly to reach the same values as for dry-milled felsic rocks at T120. In summary, acid oxalate extraction indicates that milling produced more amorphous material for basalt and dolerite than for gneiss and K-feldspar and that more amorphous material was produced by dry milling than by wet milling.

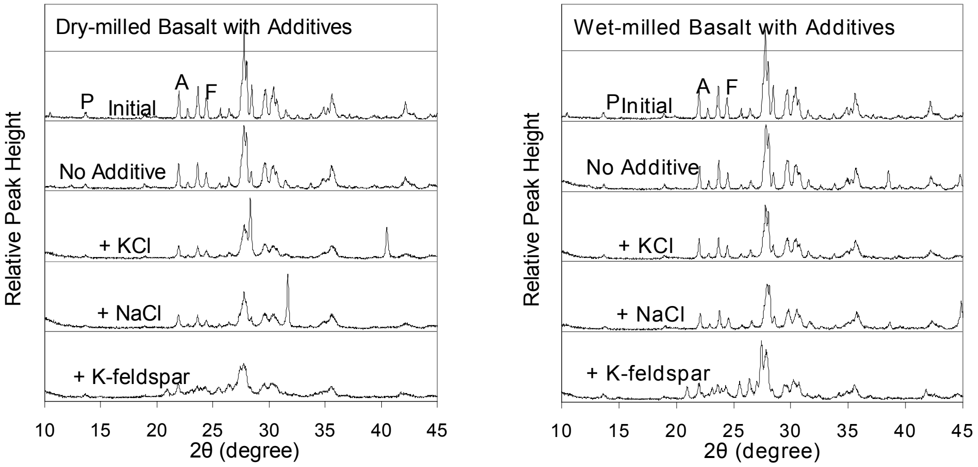
There are mostly very clear linear relationships between the amount of amorphous material estimated from XRD peak intensities and both the amounts of exchangeable cations and oxalate-extractable (Fe + Al + Si) (see Figure 2.7). This observation is consistent with a major effect of milling being the production of amorphous silicates which have more exchangeable basic cations and are much more soluble in acid oxalate extractant than are the initially milled-silicate rocks. The increase in solubility is not solely due to the increase of specific surface area as the extent of dissolution is not simply proportional to surface area. Whether this greatly increased solubility in reagents will also apply to the solubility of SRFs in soil solution under practical agricultural conditions remains to be evaluated.

2.3.3. Effects of Reactive Additives

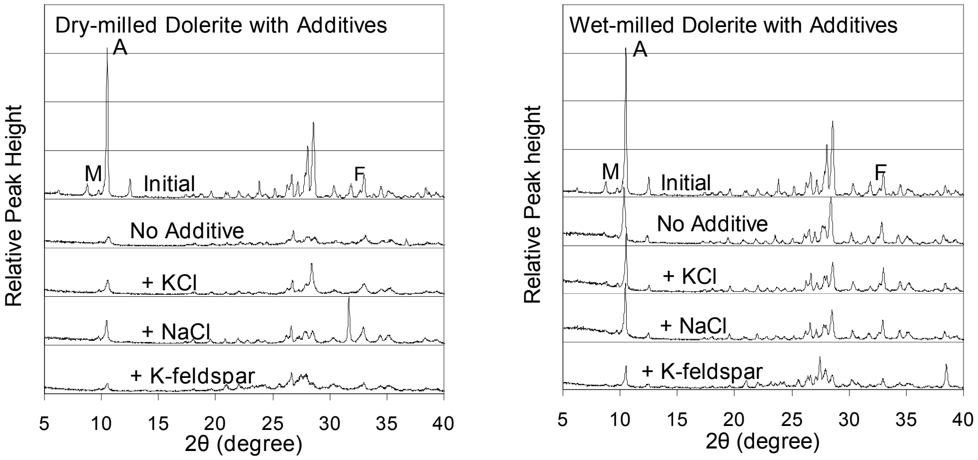
The particle size data indicate that agglomeration decreased the capacity of milling to reduce particle size and increase effective surface area, thus potentially reducing the rate and extent of dissolution in extractants. The use of a reactive additive (NaCl, KCl) as a flux or lubricant during the milling process was intended to reduce agglomeration so that milling produced free fine particles with high surface area and reactivity. Addition of a flux is a common procedure in milling technology where it is a standard practice to mill materials in a supporting medium (Juhász and Opoczky 1990), and in some instances electrolyte solutions at low concentration (up to 0.25 %) are most effective. In this experiment, addition of NaCl and KCl to the silicate was expected to neutralize the unbalanced charges on mineral particles that are responsible for agglomeration of these particles (Veale 1972). Adding other K and Na-rich materials (e.g., K,Na-feldspar) to basalt and dolerite might be expected to have a similar effect to adding NaCl and KCl in that agglomeration (bonding or sintering) of different mineral species may not be as favourable as bonding of particles of a single mineral species.

The XRD patterns of rocks milled with the additives for 120 min are compared to those for initially milled rock (T0) and for milled rock T120 without additives in Figure 2.14. The effects of adding the reactants on particle size, surface area, percentages of exchangeable cations (Ca + Mg) and amorphous constituents (% oxalate-extractable Fe + Al + Si) are presented in Figures 2.15 and 2.16.

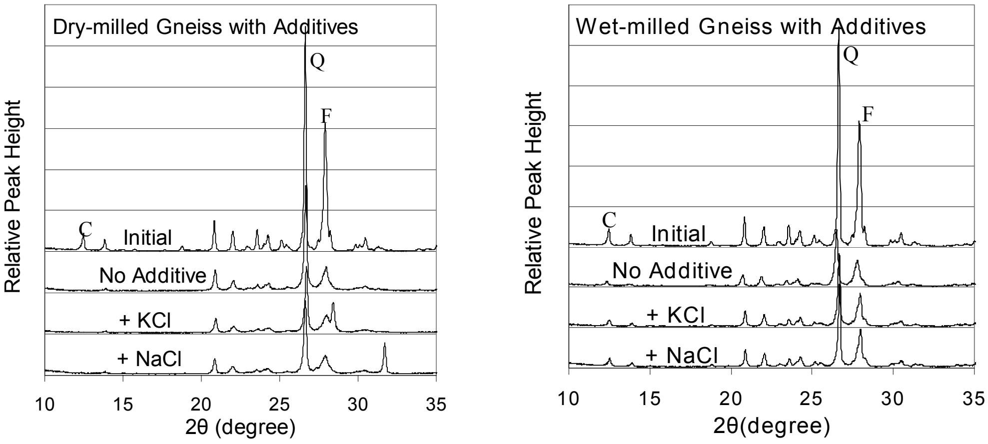
Results indicate that there were no systematic effects of additives on the above mentioned physicochemical properties of milled rocks, and that each rock exhibited different responses to additives, as follows.



P = pyroxene 110; A = amphibole 131; F = feldspar 114



M = mica 002; A = amphibole 110; F = feldspar 113



C = chlorite 004; Q = quartz 101; F = feldspar (albite) 220

Figure 2.14. XRD patterns of silicate rocks milled for 120 min with and without additives. The XRD patterns of initially milled rocks are presented for comparison.

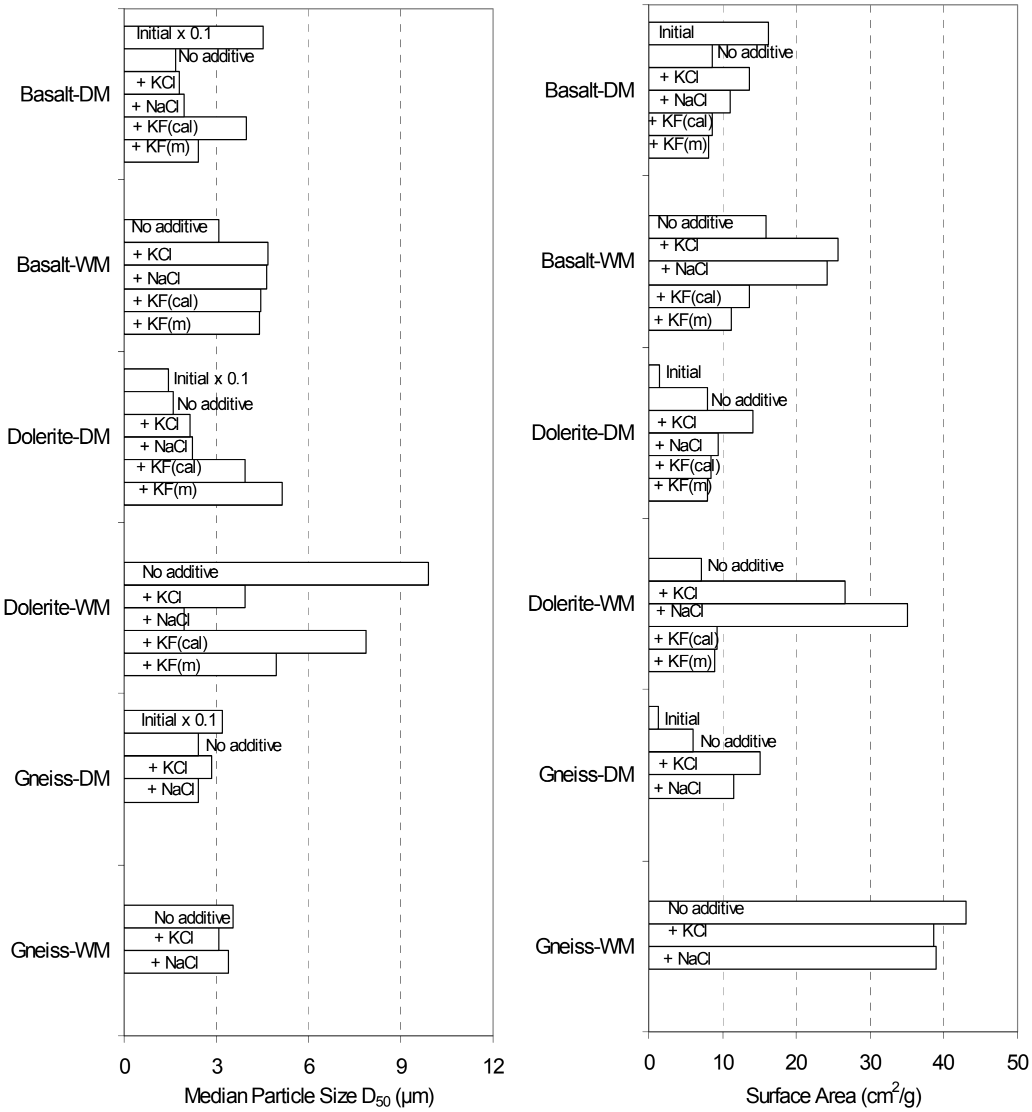


Figure 2.15. Median particle size (D_{50}) and surface area of basalt, dolerite, and gneiss milled with additives (NaCl, KCl, or K-feldspar) for 120 min under dry (DM) and wet (WM) conditions. The values for initial and no additive (T120) rocks are presented for comparison. KF(m) and KF(cal) respectively are measured and the calculated values for mixed silicates (i.e., the average values for basalt or dolerite and K-feldspar milled separately for 120 min as presented in Figure 2.1 and are combined on a *pro rota* basis).

1. For dry-milled basalt, adding NaCl or KCl had a minor effect on particle size but increased surface area (about 30 – 50 %), reduced amorphous constituents (about 25 %) and produced a large increase of exchangeable Ca and Mg (80 – 100 %) relative to basalt with no additive. For wet-milled basalt, adding NaCl or KCl tended to increase both particle size and surface area but had no effect on the

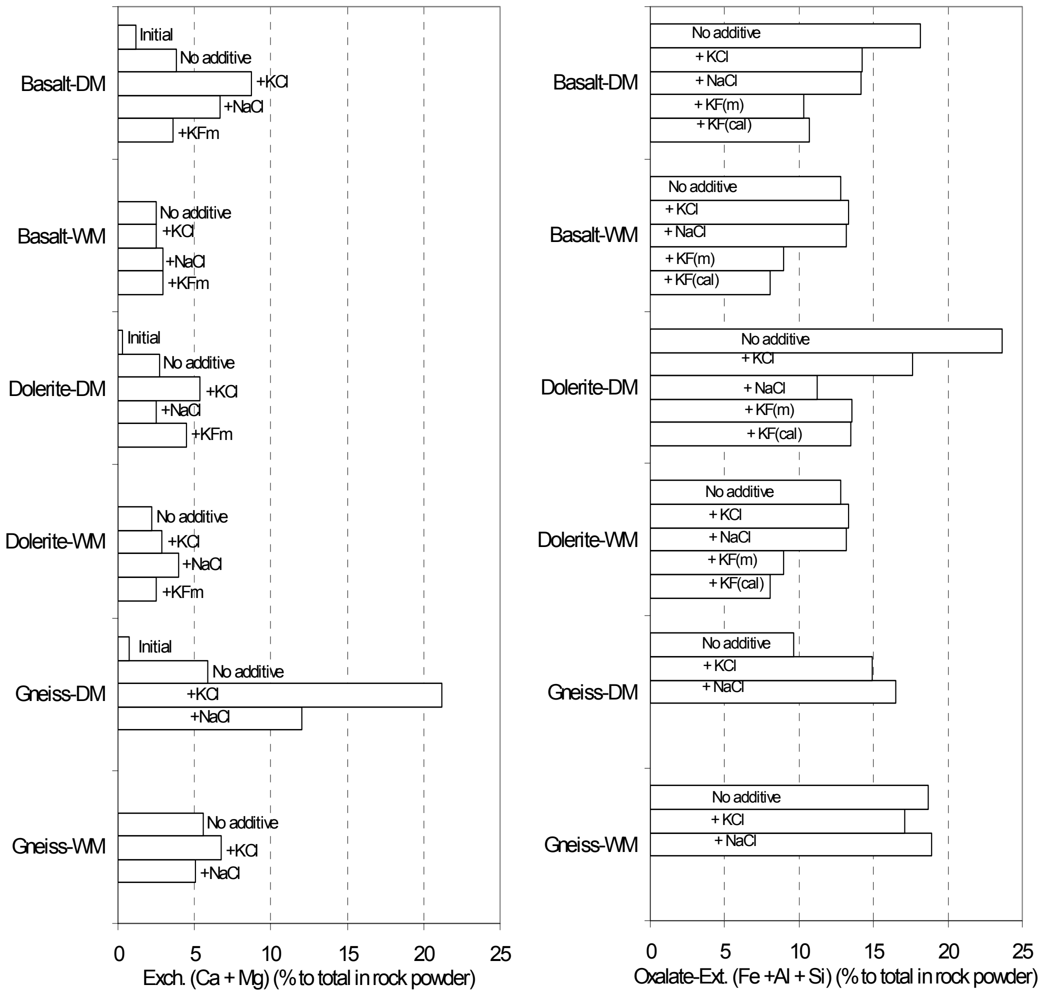


Figure 2.16. Percentages exchangeable (Ca + Mg) and oxalate-extractable (Fe + Al + Si) of basalt, dolerite, and gneiss milled with additives (NaCl, KCl, or K-feldspar) for 120 min under dry (DM) and wet (WM) conditions. The values for initial and no additive (T120) rocks are presented for comparison. KF(m) are measured values of basalt + K-feldspar powder and dolerite + K-feldspar powder. KF(cal) is average values for basalt or dolerite and K-feldspar milled separately for 120 min and are combined on a *pro rota*. KF(cal) of exchangeable (Ca + Mg) values are calculated as half of exchangeable (Ca + Mg) for basalt or dolerite (see Figure 2.10), because the quantity of exchangeable (Ca + Mg) for K-feldspar are under detection limit. KF(cal) of oxalate-extractable (Fe + Al + Si) are calculated from the values presented in Figure 2.13, i.e., average of those for basalt or dolerite and K-feldspar.

percentages of amorphous constituents and exchangeable cations. Mixing basalt with K-feldspar for both dry and wet milling did not affect the average value of these properties relative to rocks milled separately.

2. Adding NaCl or KCl for dry milling of dolerite tended to increase particle size (about 25 %) and surface area (40 – 80 %), reduced amorphous constituents (about 30 %) and greatly increased exchangeable Ca and Mg (about 200 %) relative to those of dolerite T120 with no additive. For wet-milled dolerite, these additives greatly reduced particle size (by 50 – 75%), increased surface area and exchangeable Ca and Mg (40 – 100 %) relative to dolerite T120 with no additive. Mixing dolerite with K-feldspar prior to dry and wet millings did not affect average values ($KF_{(m)}$) of these properties relative to when both rocks were milled separately ($KF_{(cal)}$).
3. Adding NaCl or KCl for dry milling of gneiss greatly increased surface area (2 – 3 fold) and increased exchangeable Ca and Mg. However, these treatments did not affect these properties for wet milled gneiss.

In short, adding reactants had no systematic effects on particle size and surface area of milled rocks, but clearly increased the amount of exchangeable cations for dry and wet-milled basalt and dolerite, and dry milled gneiss. As discussed in an earlier section, the amount of exchangeable basic cations for rocks milled under dry condition decreased which may be due to trapping of some cations in compound particles by sintering. Thus increases in exchangeable basic cations for dry-milled basalt and dolerite with additives may be associated with the decrease of amorphous constituents due to the present of additives, thereby reducing the amounts of trapped cations in the milled materials. For gneiss, however, the increase of exchangeable cations may be related to the enhanced effect of milling in reducing particle size and increasing surface area.

2.4. Conclusions

The main focus of this study was to identify an appropriate milling time for manufacturing SRF and to evaluate if additives and wet milling further improved the potential of milled silicate rocks as fertilizers. Effects of milling on physicochemical properties of silicate rocks shown in this study were consistent with the results found by previous researchers who used different minerals or rocks and milling methods (Gasalla *et al.* 1987; Kühnel and Van der Gaast 1989; Garcia *et al.* 1991; Sugiyama *et al.* 1994; Aglietti 1994; Suraj *et al.* 1997; Harley 2002; Lim *et al.* 2003). Milling clearly reduced particle size, enhanced amorphism, and increased the release of structural cations from the rocks, but in some cases the effects of milling were minor. Dry milling appears to be more effective than wet milling. Although agglomeration occurred for some dry-milled rocks, it did not reduce surface area, except for basalt, or exchangeable basic cations (Ca, Mg, K and Na). There was also slightly less contamination with Fe for dry-milled basalt, dolerite, and gneiss indicating that less wear of the milling equipment had occurred.

Based on the total exchangeable basic cation data, it is not necessary to mill for a long period to produce an effective fertilizer and a milling time as short as 10 min or less may be optimum. However, further evaluation of the solubility and agronomic effectiveness of nutrient elements in SRFs is necessary before SRF products produced by milling at an industrial scale can be recommended to the agricultural industry. Adding NaCl and KCl as milling lubricants which was proposed to reduce agglomeration had minor effects on the physicochemical properties of SRFs, consequently the use of reactive additives will not provide a significant benefit in manufacturing SRFs.

Chapter 3

DISSOLUTION OF MILLED-SILICATE ROCK FERTILIZERS IN ORGANIC ACID

3.1. Introduction

The extent to which plant nutrient elements in silicate minerals dissolve in the soil will greatly affect the agronomic effectiveness of silicate rocks. The dissolution of plant nutrient elements from rocks and minerals has been studied for decades through dissolution experiments under laboratory conditions. In many dissolution experiments, the ground solid materials are pre-treated prior to investigation in order to eliminate very fine particles produced by grinding. The pre-treatments include successive washing with deionized water (Huang and Keller 1970; Barman *et al.* 1992; Harley 2002), acid washing (Bloom and Erich 1987), ultrasonic cleaning (Zhang and Bloom 1999), and wet sieving (Lundström and Öhman 1990). These treatments were related to the purposes of the researches which were mostly to identify steady dissolution rate, mechanisms, pathways and processes of primary minerals in solutions, requiring very fine- and amorphous-free solid materials.

Various organic acids are known to occur and involve in numerous reaction processes in the rhizosphere, including dissolution of nutrient elements from silicate minerals and rocks into soil solution (Jones 1988). For this reason, organic acids have been used in many dissolution studies. The acids are responsible for a substantial complexion of metal cations, especially for the polyvalent cations such as Si and Al, originating from dissolution of aluminosilicates (Huang and Keller 1970; Huang and Kiang 1972; Song and Huang 1988; Eick *et al.* 1996) or soil fractions (Rasmussen *et al.* 1998) and these acids may produce higher dissolution rates than for dilute inorganic acids or water (Welch and Ullman 1992, 1996; Blake and Walter 1999; Zhang and Bloom 1999; Oelkers and Gislason, 2001).

Most of above authors and Shotyk and Nesbitt (1992) proposed that the higher dissolution rate of minerals in organic acids is associated to the presence of ligand-assisted mechanism and the mechanism was affected by pH (Ludwig *et al.* 1996). The dissolution rate through this mechanism increase linearly with the decrease of pH (Amrhein and Suarez 1988). Enhanced dissolution by Al-organic complexion, surface coordination of organic acids, or acid-catalysed hydrolysis was proposed mechanisms in acidic condition (pH < 5) (Stumm and Furrer 1987), whereas aluminum complexion does not seem to greatly enhance silicate dissolution at near neutral pH (Ludwig *et al*. 1996) since aluminum mobility and silicate solubility are nearly minimum and organic-complexes are relatively unstable (Driscoll *et al.* 1985). Other authors (Stumm and Furrer 1987; Wieland *et al.* 1988) also suggested that coordination of organic ligands onto silicate surfaces may strongly influence dissolution of silicates. Bennett (1991) proposed that the interaction of mechanism may consist of inner-sphere coordination of an organic ligand, weakening crystal framework of minerals due to charge transfer or other inductive effects.

Organic acids in soils may be released by decomposition of organic matter, microbial metabolism, and rhizosphere activities or root exudation (Stevenson 1967; Stevenson and Arkadani 1972). The concentration of organic acids in soils varies spatially from plant root, and for different soil types, cultivation methods, and land uses, ranging from nearly nil to several thousands micromole/L soil solution (Jones, 1988). Among organic acids commonly present in soils, oxalic, citric, and acetic acids at concentrations varied from 0.001 to 0.01*M* were mostly used as solvents for studying the dissolution of silicate minerals and rocks under laboratory conditions (Huang and Kiang 1972; Song and Huang 1988; Lundström and Öhman 1990; Barman *et al.* 1992; Stillings *et al.* 1996; Eick *et al.* 1996; Blake and Walter 1996, 1999; Zhang and Bloom 1999; Hamer *et al.* 2003). Huang and Kiang (1972) found that acetic and citric acids (0.01*M*) are the weakest and strongest respectively among the organic acids they evaluated for dissolving metallic elements from silicate minerals.

As described in Chapter 2, high energy milling greatly increased the amount of exchangeable and soluble cations. However, whether this improvement in the solubility of plant nutrient elements from the silicate fertilizers in extractants will occur in soil solution, remains to be evaluated. To provide some insight into this topic, dissolution of milled silicate rocks in dilute organic acids that are commonly present in soils (i.e., acetic and citric acids) was utilized to measure the amount of plant nutrient elements that may dissolve in soils. In this experiment, cleaning of the rock powders to eliminate fines as mentioned above was avoided as such treatments may cause loss of the readily soluble nutrients from the materials and furthermore such fractionation will be not applicable to commercially manufactured fertilizers. In stead of using individual acid as the solvent, mixture of the acids is simple and presumed will be more representative for various combination of main organic acids in soils.

The central objective of this experiment was to identify the effects of high-energy milling on the dissolution kinetics of several silicate rocks in a mixture of 0.01*M* acetic and citric acids. The results of this experiment were subsequently used to provide an indication of the appropriate application rates of SRFs for laboratory, glasshouse, and field experiments.

3.2. Materials and Methods

The silicate rocks investigated in this experiment were basalt, dolerite, gneiss, and K-feldspar milled for 0, 10, 60, and 120 min as described in Chapter 2. A mixture of 0.01*M* acetic acid + 0.01*M* citric acid at a ratio of 1:1 was used as the solvent. Four hundred milligrams of each rock powder and 400 mL of solvent were transferred into a 500mL plastic container, tightly capped, then continuously agitated on a rotary shaker at 130 rpm and an ambient temperature of 25^o C. Subsamples of suspension were taken periodically from 1 hour up to 56 days by removing the containers from the shaker, the suspension was homogenised by hand-shaking for 5 seconds, and immediately 20 mL of suspension was taken by pipette. The samples of suspension were centrifuged at 4000 rpm for 20 min using an Eppendorf 5810 Centrifuge (maximum capacity 6 x 125 g and speed 4000 rpm), and about 17 mL of clear solution was transferred by a pipette into a plastic tube. The concentrations of Ca, Mg, and Al in the solution were measured using AAS, Na and K were determined using flame emission, and Si using a colorimetric method described by Rayment and Higginson (1992). The pH and EC of solutions were measured with pH and EC meters (Cyberscan 2000). At the end of the dissolution experiment, the remaining rock powder was centrifuged, oven-dried at 60^o C (for two weeks) and used for XRD and transmission electron microscopy (TEM) analyses to provide explanations of dissolution mechanisms.

The XRD patterns of each rock powder (before and after dissolution) were collected using the methods described in chapter 2, and the diffraction intensity was recorded between 5 and 40° 2θ. For TEM analysis, well-dispersed powder of the rocks milled under the dry condition for 120 min (samples before and after partial dissolution) were prepared on carbon coated-copper grids. Two sub samples for each rock powder were prepared in this manner. High magnification (250 – 300 k) micrographs for several (10 – 20) particles of ground rock powder and electron diffraction patterns for several (3 – 5) zones of selected particles were obtained using a JEOL 3000 FEG instrument operated at 300 kV.

3.3. Results and Discussion

3.3.1. Dissolution Kinetics of Silicate Rocks

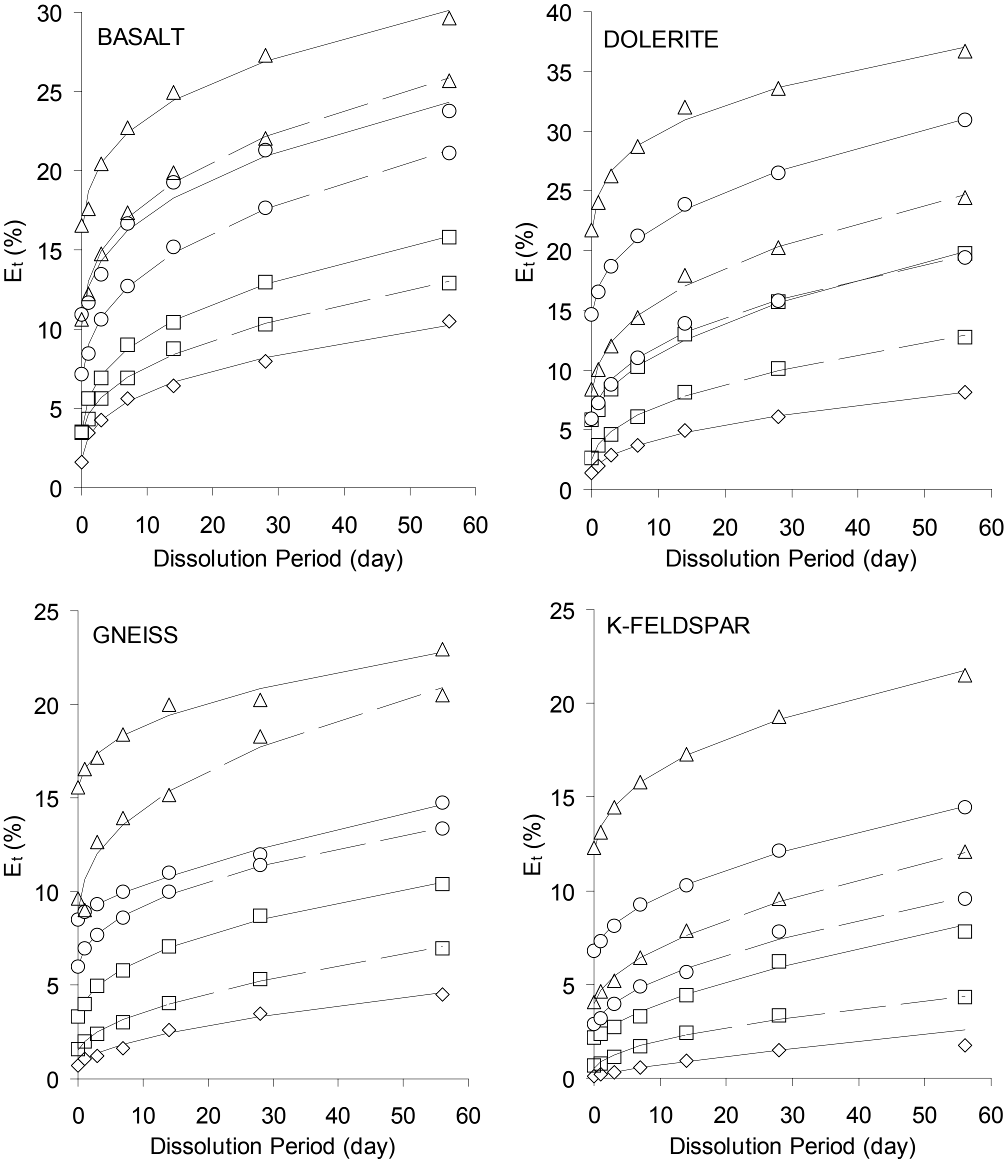
The quantity of rock dissolved in mixed organic acids was estimated from the percentage of total mole charge of major elements, i.e., mole charge of ($K^+ + Na^+ + Ca^{+2} + Mg^{+2} + Fe^{+2} + Al^{+3} + Si^{+4}$) for basalt, dolerite, and gneiss, and ($K^+ + Na^+ + Al^{+3} + Si^{+4}$) for K-feldspar, dissolved relative to the total mole charge of the corresponding elements in the rock. The relationship between the quantity of dissolved rock dust versus dissolution time was fitted to a modification of the power equation developed by Zhang and Bloom (1999). The modified equation is:

$$E_t = Eo + at^n \qquad \text{Eq. (3.1)}$$

where E_t is the quantity of rock dissolved (%) at time t (in days), Eo is the quantity of rapidly soluble rock (%) which is E_t at t equals zero (actually extrapolated to zero), a is a constant that relates to the amount of reactive sites on the surface of rock particles, and n is an experimental constant (reaction order). The dissolution rate R_t at time T is calculated from first derivative of Eq. (3.1):

$$R_t = dE_t/dt = ant^{n-1} \qquad \text{Eq. (3.2)}$$

The quantity of total dissolved elements (E_t) as function of dissolution time (t) was very well described by Eq. (3.1), as indicated by $R^2 \approx 1.00$ in most cases and the standard deviation of regression ($S_{x.y}$) was < 1 % relative to sample mean. The plots of E_t versus t and R_t versus t are presented in Figures 3.1 and 3.2, respectively. The values of Eo, a, and n are presented in Table 3.1.



Milling: ◊ initial, □ 10 min., ○ 60 min., Δ 120 min.; (—) dry and (---) wet conditions

Figure 3.1. The quantity of dissolved rock powder (E_t), estimated from the total mole charge of major elements (Ca + Mg + Na + K + Fe + Al + Si) for basalt, dolerite, and gneiss, and (Na + K + Al + Si) for K-feldspar dissolved in 0.01*M* acetic-citric acid as % of the total mole charge of corresponding elements in rock powder, as functions of dissolution time (t). The rocks were milled under dry (full lines) and wet (broken lines) conditions. The lines are statistical fits to Eq. (3.1) for the corresponding data.

This dissolution kinetic is basically consistent with results of other dissolution experiments, such as dissolution of muscovite (Lin and Clemency, 1981), yellow and black tuffs (Silber *et al.* 1999), basaltic glass (Oelkers and

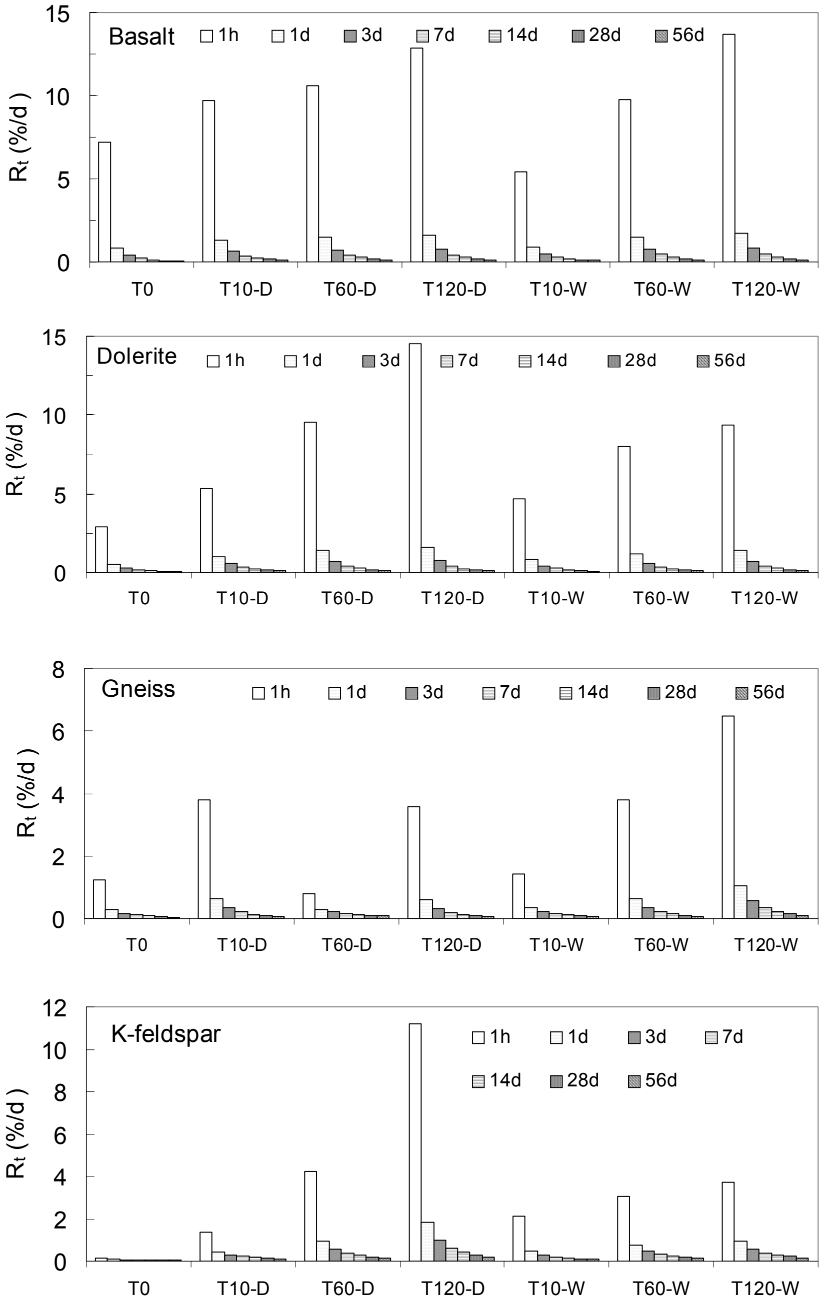


Figure 3.2. Dissolution rate of rock (R_t) at various contact times estimated from the total mole charge of major elements (Ca + Mg + Na + K + Fe + Al + Si) for basalt, dolerite, and gneiss, and (Na + K + Al + Si) for K-feldspar dissolved in 0.01*M* acetic-citric acid per day relative to the total mole charge of corresponding elements in rock. The values of R_t were calculated using Eq. (3.2) for the rocks milled for 0, 10, 60 and 120 min (T0, T10, T60, and T120) under dry (D) and wet (W) conditions.

Gislason 2001), lunar basalt (Eick *et al.* 1996), and silicate minerals (Siever and Woodford 1979; Harley 2002). Some of these authors consider that this form of kinetic curve indicates that the initial rapid release of elements attributed to preferential dissolution of superfine fine particles, because this effect is not obtained anymore if caution is taken to remove the smaller particles in order to conduct the dissolution experiments on a restricted rage of particle size (Holdren and Berner 1979), and dissolution mechanisms are ion exchange reactions in which soluble

Table 3.1. The values of Eo, *a*, n, and R^2 for Eq. (3.1) for dissolution of rocks estimated from the total mole charge of major elements (Na, K, Ca, Mg, Fe, Al, and Si) dissolved for basalt, dolerite, and gneiss, (Na, K, Al, and Si) dissolved for K-feldspar relative to the total of these elements in rock (Appendix A1).

Rock Type	Milling		Eo (%)	*a*	n	R^2
	Condition	Time (min)				
Basalt	Dry	0	1.09	2.13	0.36	0.99
		10	2.56	3.04	0.37	1.00
		60	9.16	3.46	0.37	0.98
		120	14.58	4.14	0.33	0.98
	Wet	10	2.86	1.76	0.43	1.00
		60	5.93	3.11	0.40	1.00
		120	8.92	4.07	0.35	0.99
Dolerite	Dry	0	1.12	1.04	0.47	1.00
		10	5.08	2.02	0.50	1.00
		60	13.52	3.40	0.41	1.00
		120	19.44	5.15	030	0.99
	Wet	10	2.05	1.71	0.46	1.00
		60	4.83	2.77	0.42	0.99
		120	7.17	3.31	0.41	0.99
Gneiss	Dry	0	0.56	0.45	0.55	0.99
		10	2.87	1.28	0.44	1.00
		60	8.55	0.35	0.71	1.00
		120	15.20	1.36	0.43	0.98
	Wet	10	1.44	0.56	0.57	1.00
		60	5.66	1.28	0.45	1.00
		120	8.35	2.31	0.42	0.96
K-feldspar	Dry	0	0.00	0.19	0.56	0.98
		10	1.29	0.46	0.64	0.99
		60	4.74	0.94	0.54	1.00
		120	8.31	1.57	0.47	1.00
	Wet	10	0.26	0.43	0.55	0.99
		60	1.85	0.62	0.60	0.99
		120	2.53	0.87	0.57	1.00

surface cations are exchanged equivalently by H^+ from the acidic solvent. In addition, organic acids (e.g, acetic and citric acids) are capable of extracting mainly polyvalent ions as suggested by Huang and Keller (1970), Welch and Ullman (1996), and Blake and Walter (1999). The following much slower dissolution may be attributed to ion release involving dislocation of structural bonds in the silicate structure (Oelkers and Scott 2001; Oelkers and Gislason 2001). An interpretation of the present results that is different from the above and is consistent with XRD analysis of ground silicates and their residues after partial dissolution (see section 3.3.5) is as follows. Acetic-citric acid rapidly dissolved much of the amorphous materials and the structurally disordered/microcrystalline minerals present in intensively milled rocks, followed by slower dissolution of residual crystalline materials. The large increase in solubility of the rocks due to milling is mostly associated with a large difference in the quantity of the rapidly dissolved fraction (Eo) which is considered to be mostly the amorphous and disordered/micro-crystalline silicate phases (see Figures 3.7 and 3.8).

During dissolution of the silicate rocks, the pH of solution increased with increasing milling and dissolution times (Figures 3.3 and 3.4). The initial pH of the solvent was about 2.50 and this value increased by about 0.25 units (for initially milled rocks) and between 0.50 and 0.75 units (for 120 minute-milled rocks) after dissolution for 1 hour. At the end of dissolution experiment (56 days), the pH of solution had increased by about 0.75 units (for initially milled rocks) and between 1.0 and 1.2 units (for 120 minute-milled rocks). Conversely, the EC of the initial solvent was about 1.25 mS/cm and decreased to about 0.7 mS/cm after 56 days of dissolution which may be due to precipitation of salts.

These increases in pH indicate the occurrence of surface exchange reactions as explained in Chapter 2 section 2.3.2.2, especially during the early stages of dissolution in which quite large amount of cations were released from the milled rocks. The rate of dissolution of cations was greatly enhanced by milling. At the same time, the precipitation of amorphous material from solution may have occurred or alternatively dissolved ions may have neutralised the free charges on the functional groups of the organic acids (i.e., dissolution solvent), thereby decreasing the electrical conductivity of the solution. This neutralization process maybe an indication of the occurrence of a ligand-assisted dissolution mechanism as suggested

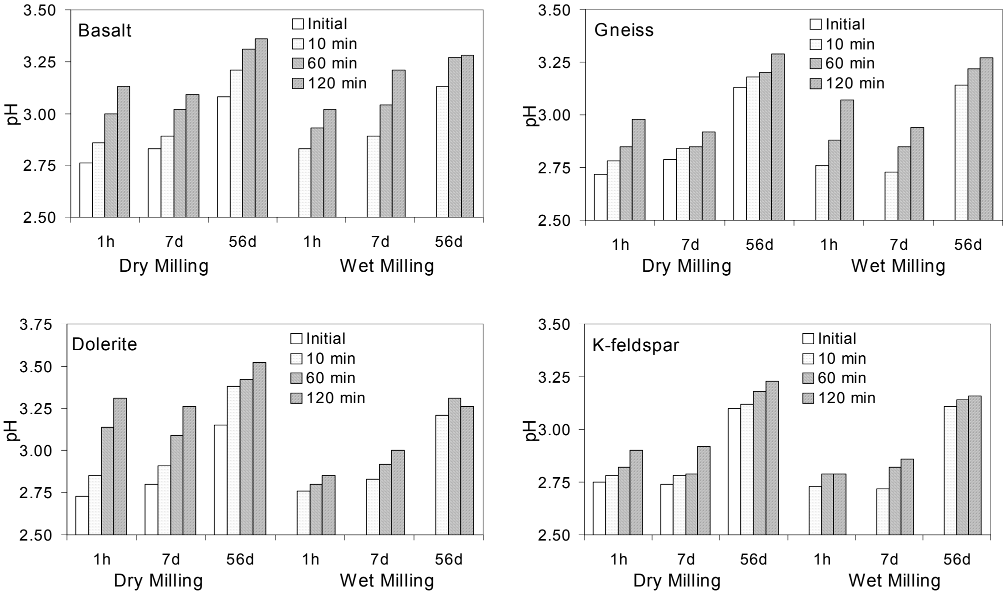


Figure 3.3. pH of solution after dissolution of silicate rock powders for 1 hour, 7, and 56 days (1h, 7d, and 56d) as affected by milling time of the rocks. The pH of solution before dissolution was 2.50.

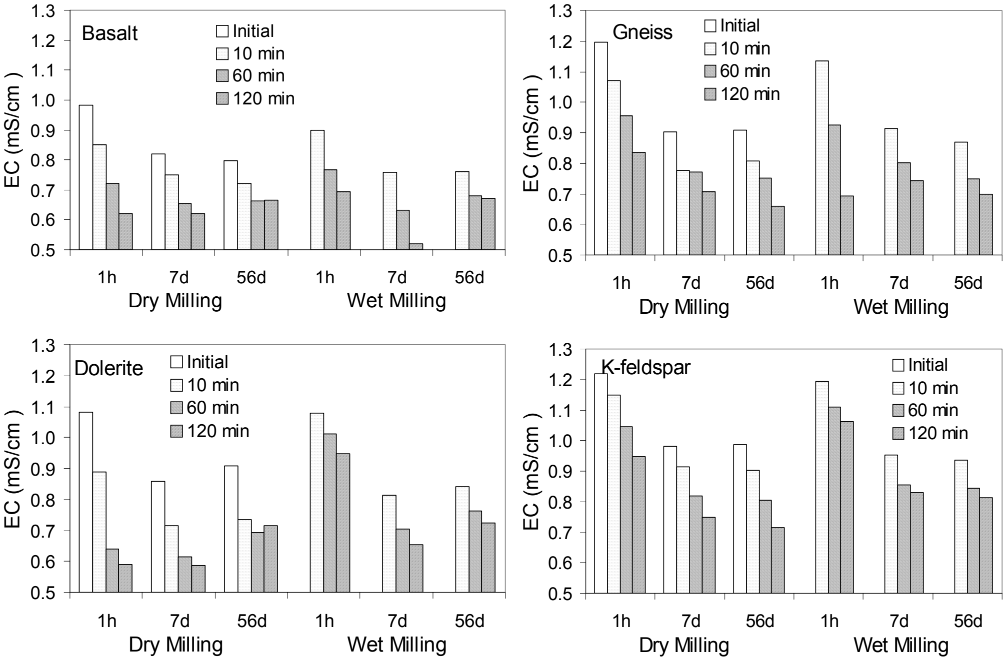


Figure 3.4. EC of solution after dissolution of silicate rock powders for 1 hour, 7, and 56 days (1h, 7d, and 56d) as affected by milling time of the rocks. The EC of solvent before dissolution was 1.3 mS/cm.

by Shotyk and Nesbitt (1992) and Welch and Ullman (1996) that the dissolved polyvalent cations (mainly Al) form metal-organic complexes thereby increase the concentration gradients of these cations within solution – rock particle interfaces, enhancing diffusion rate of these cations from the rock particles to bulk solution. In this present experiment, this dissolution mechanism occurred more intensively for dry- than wet-milled rocks.

3.3.2. Effects of Milling on Dissolution Kinetics

The effects of milling time and milling condition on the dissolution kinetics of silicate rocks may be summarized as follows, and is based on the results presented in Table 3.1, Figures 3.1 and 3.2:

1. Milling increased the proportion of rocks dissolved (E_t) with the increase produced by dry milling being greater than for wet milling.
2. Milling increased the quantity of rapidly soluble rock (Eo) and the amount of reactive sites on the surfaces of rock particles (as indicated by coefficient a), with the increases due to dry milling being higher than for wet milling (Table 3.1).
3. Milling increased the dissolution rate (R_t) (Figure 3.2).
4. There was no systematic trend of reaction order (n) with increasing milling time, apart from values for original rocks (T0) mostly being larger than for milled rocks (T10 – T120). The values for mafic rocks were mostly lower (0.30 – 0.50) than those for felsic rocks (0.41 – 0.71).

As shown in Figure 3.1, the percentage dissolution of ground basalt and dolerite (mafic rocks) was greater than for ground gneiss and K-feldspar (felsic rocks). For example the E_t values at t = 56 days for initially milled-basalt and dolerite were about 10 % and were increased to about 35 % by dry milling and 25 % by wet milling for 120 min. The E_t values at t = 56 days for initially milled-gneiss and K-feldspar were about 3 %, and were increased to about 22 % by dry milling and 12 % by wet milling for 120 min. For all rocks most of the increased dissolution produced by milling was due to the large increase in rapidly dissolved rock (Eo).

In addition to the increase in initial dissolution (Eo) milling greatly increased dissolution rate (R_t) (Figure 3.2) during the early stages of dissolution (within 1 h of dissolution) up to values of about 15 %/d for milled mafic rocks and 6 – 10 %/d for milled felsic rocks. The dissolution rates decreased greatly with the increase of dissolution time, trending towards a constant dissolution rate. This result may be interpreted as indicating that by 56 days of dissolution of only crystalline minerals was occurring for both dry- and wet-milled samples.

It is therefore concluded that the reduced particle size, the increased effective surface area, and the increased abundance of amorphous and disordered constituents due to milling resulted in an increase in exchangeable alkali and other cations. These changes also resulted in an increase in the dissolution rate (R_t), the proportion of rapidly soluble rock (Eo), and the amount of reactive sites on the surface of particles (a). The changes in dissolution due to milling were greater for dry than for wet milling.

3.3.3. Elemental Dissolution of Silicate Rocks

The above discussion of dissolution relates to the dissolution of the whole rock particles based on the sum of cations dissolved. However, dissolution may not be congruent as several mineral species may be present in a rock and may dissolve at different rates, additionally some dissolved ions may precipitate so that these laboratory data can not be used directly to predict the release of plant nutrient ions to soil solution. The main objective of this dissolution experiment was to provide an indication of the potential utility of silicate materials as Na, K, Mg or Ca and Mg fertilizers. Therefore, it is necessary to present and discuss the results of dissolution measurements on a single element (plant nutrient) basis. Clearly, the rapid release of nutrients (Table 3.2) is directly related to the rapidly soluble fraction (Eo) of the individual plant nutrient cations (i.e., Ca, Mg, K, and Na). These values of elemental Eo, calculated using Eq. (3.1) in units of cmol_c/kg and % of total in rock, may be used to estimate the quantity of nutrients made available for plant growth by the rapid dissolution of SRFs in soil.

The proportions of the rapidly soluble plant nutrients (Ca, Mg, K, and Na) (Table 3.2) were increased by milling and the increases due to dry milling were higher than for wet milling. Milled mafic rocks (basalt and dolerite) rapidly released Na (up to 42 % of total Na) and K (up to 73 %), which were higher proportions than for felsic rocks (up to 34 % Na and 54 % K). The total content of K in K-feldspar (12 % K_2O, see Table 2.1) is much higher than for the other silicate materials (4 %

Table 3.2. The quantities of rapidly dissolved major plant nutrient elements[1] (Eo) for basalt, dolerite, gneiss, and K-feldspar SRFs, calculated using Eq. (3.1.) for individual elements. The values of Eo are also presented as % of total in rock (e.g., percentage cmol$_c$ an element dissolved over total cmol$_c$ the element in the milled rock).

Milling		Ca		Mg		K		Na	
Condition	Time (min)	(cmol$_c$/kg)	(%)	(cmol$_c$/kg)	(%)	(cmol$_c$/kg)	(%)	(cmol$_c$/kg)	(%)
				Basalt SRF					
Dry	0	9.4	2.4	5.4	1.8	0.8	21.7	2.4	3.5
	10	13.7	3.5	44.0	14.7	0.2	5.0	6.0	8.9
	60	42.6	11.4	62.9	22.2	1.6	43.5	18.2	27.3
	120	61.8	16.1	75.2	26.6	1.5	42.3	27.2	42.1
Wet	10	15.6	3.9	23.4	8.0	0.5	13.2	2.7	4.0
	60	30.4	7.9	28.8	10.1	0.9	24.2	7.8	12.0
	120	40.7	10.9	31.3	10.9	1.2	32.2	9.6	14.0
				Dolerite SRF					
Dry	0	0.0	0.0	6.4	2.0	2.3	28.6	0.4	1.0
	10	13.7	3.4	27.4	8.7	3.6	46.8	2.2	5.6
	60	43.1	10.8	74.6	23.7	4.7	61.3	7.9	21.0
	120	89.3	22.8	120.9	38.6	5.4	72.6	16.0	40.4
Wet	10	5.1	1.3	9.5	3.0	2.6	35.2	0.8	1.9
	60	8.0	2.0	16.4	5.2	2.8	38.4	1.6	3.9
	120	7.6	2.0	26.8	8.7	3.3	48.2	3.2	8.2
				Gneiss SRF					
Dry	0	2.4	3.3	2.3	6.2	0.9	4.0	0.6	0.5
	10	5.2	7.2	7.0	19.0	3.2	13.6	6.5	5.0
	60	6.8	9.7	36.6	100	9.0	39.6	16.1	12.7
	120	7.9	11.5	36.6	100	12.0	53.8	41.2	33.7
Wet	10	4.7	6.6	3.0	8.1	1.2	5.4	1.2	1.0
	60	5.3	7.4	5.2	14.8	1.1	4.6	6.8	5.4
	120	7.5	11.6	6.2	16.9	3.5	16.8	11.5	10.1
				K-feldspar SRF					
Dry	0	-	-	-	-	0.9	0.4	< 0.1	0.1
	10	-	-	-	-	15.4	6.6	3.2	3.8
	60	-	-	-	-	44.9	19.5	9.2	11.7
	120	-	-	-	-	53.3	23.4	16.7	23.6
Wet	10	-	-	-	-	4.5	1.9	0.7	0.9
	60	-	-	-	-	19.7	8.6	4.2	5.5
	120	-	-	-	-	26.3	12.7	8.3	8.9

[1] It is assumed that Na is essential to (some) plants.

K_2O for gneiss and < 1 % K_2O for basalt and dolerite), so that K-feldspar is potentially an effective K fertilizer. The milled felsic rock (gneiss) rapidly released 100 % of its Mg which was a much higher proportion than for milled mafic rocks (e.g., 27 and 39 % respectively for basalt and dolerite). However, gneiss (with total content < 1 % MgO) may only supply small quantities of Mg for plant growth, whereas basalt and dolerite (with 6 % MgO) are likely to be better Mg fertilizers. The proportion of the rapidly released Ca for milled-mafic and felsic (gneiss) rocks was similar (up to about 16 %). Although this proportion of rapidly released Ca is quite low, mafic rocks are likely to be better sources of Ca than felsic rocks. It is notable that these rocks may act as multielement or compound fertilizers.

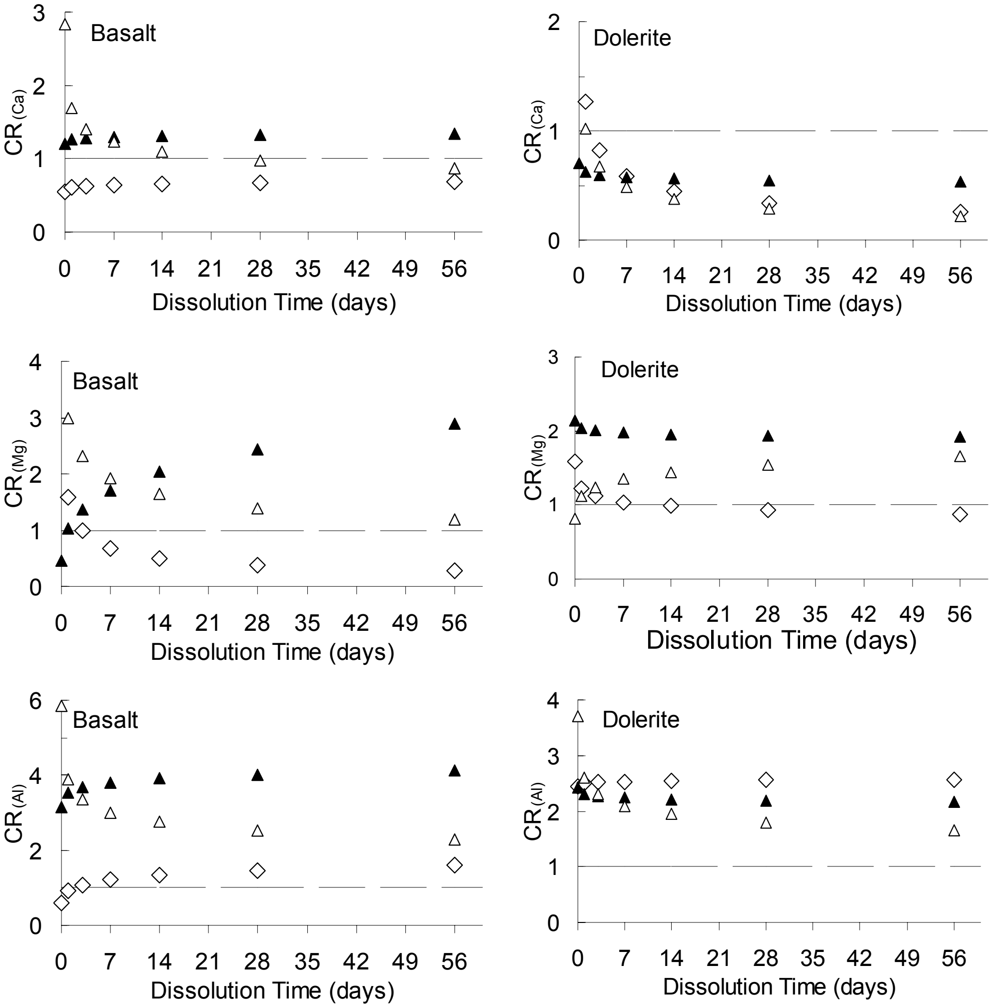
3.3.4 Dissolution Congruency

The dissolution congruency for each element ($CR_{(e)}$) may be expressed by the ratio of total dissolved mole charge of the element relative to mole charge of Si dissolved in unit time ($R_{(e)}/R_{(Si)}$) divided by the ratio of mole charges of those elements in the rock (A) (Holdren and Speyer 1986). Derived from Eq. (3.2), the equation for the congruency ratio of an element as a function of time is:

$$CR_{(e)} = (R_{(e)}/R_{(Si)})/A = [(n_e/n_{Si}).(a_e/a_{Si}).t^{(n_e - n_{Si})}]/A \qquad \text{Eq. (3.3)}$$

The value of $CR_{(e)}$ should be equal to one for congruent dissolution.

Results indicate that dissolution of the silicate rocks was commonly incongruent with basic cations being preferentially dissolved relative to Si. However, there was no simple trend in congruency ratio in relation to milling time and milling condition, as the congruency ratio for each element for each type of rock showed different trends with increasing dissolution period. Examples of the results are presented in Figures 3.5 and 3.6 for the values of $CR_{(Ca)}$, $CR_{(Mg)}$, and $CR_{(Al)}$ (basalt and dolerite), $CR_{(K)}$, $CR_{(Na)}$, and $CR_{(Al)}$ (gneiss and K-feldspar) for T0 and T120. The complete results are presented in Appendixes A6 – A9. As shown in these figures, the values of $CR_{(Al)}$ are larger than one for all of the silicate rocks whereas for the other elements CR values are either less or more than one for the various rocks.



Milling: ◊ initial, ▲dry-milled for120 min, Δ wet-milled for120 min

Figure 3.5. Congruency ratios ($CR_{(Ca)}$, $CR_{(Mg)}$, and $CR_{(Al)}$) for milled basalt and dolerite as functions of dissolution time. The values of CR were calculated using Eq. (3.3).

For basalt, dolerite, and gneiss, the occurrence of incongruent dissolution as indicated in these figures can simply mean that the various silicate minerals present in each of these rocks dissolve at different rates. For K-feldspar, this explanation is also valid as the rock consists of a mixture of minerals (the feldspar is finely demixed into K + Na feldspars). For dry milled K-feldspar much (37 %) of the K dissolved rapidly (Eo) whereas little Si dissolved rapidly so that subsequent dissolution could not be congruent. The same situation may not apply to gneiss as although much K dissolved quickly (34 %) the presence of poorly soluble quartz would have maintained $R_{(K)}/R_{(Si)}$ at a high value.

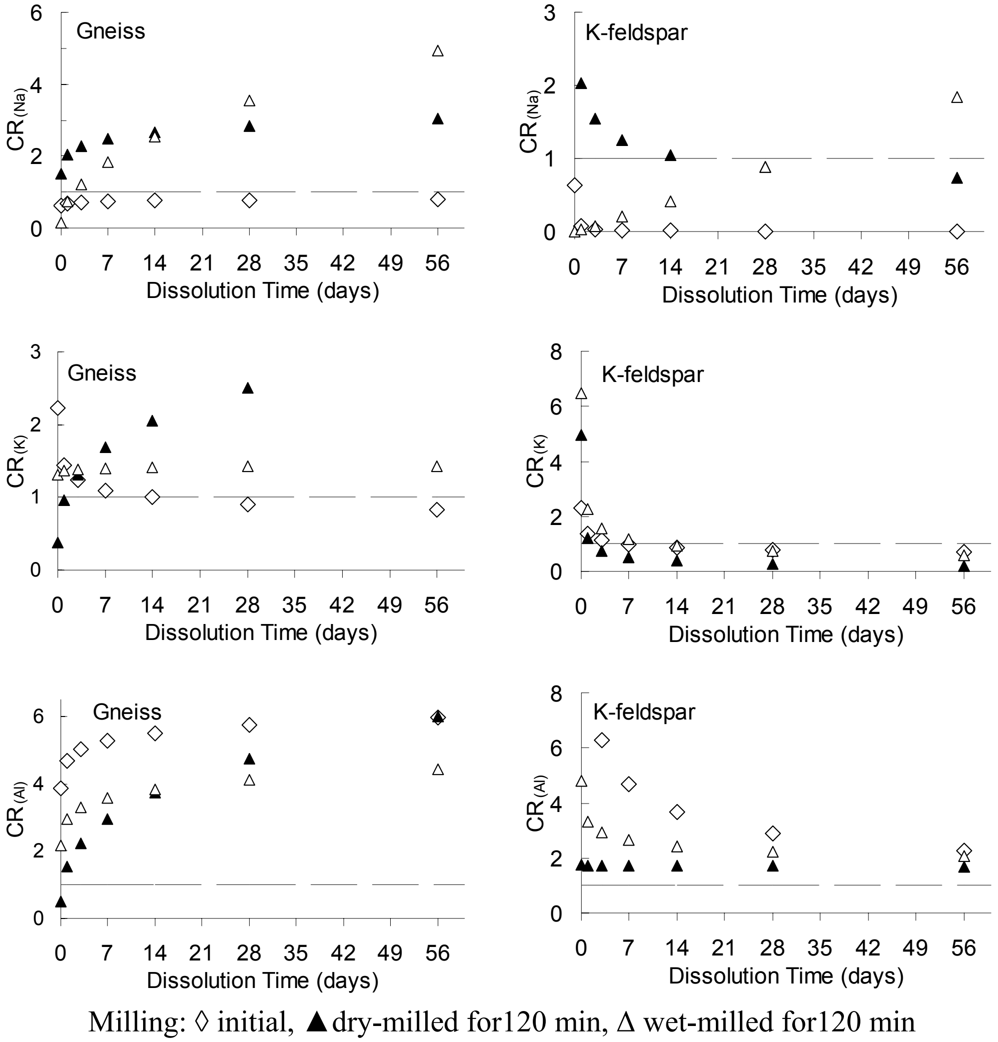


Figure 3.6. Congruency ratios ($CR_{(Na)}$, $CR_{(K)}$, and $CR_{(Al)}$) for milled gneiss and K-feldspar as functions of dissolution time. The values of CR were calculated using Eq. (3.3).

Incongruent dissolution due to higher dissolution rates for alkaline and alkaline earth cations relative to Si has been associated with the formation of cation-depleted siliceous layers on the surface of altered minerals, for instance in the dissolution of plagioclase feldspars (Chou and Wollast 1984; Holdren and Speyer 1985, 1986; Muir *et al.* 1990; Jordan *et al.* 1999; Shotyk and Nesbitt 1992). The presence and thickness of the altered layers are considered to be dependent on the Si content of dissolved minerals (Shotyk and Nesbitt 1992). These authors found that dissolution of low Si feldspar (anorthite, $Ca_{1.00}Al_{1.94}Si_{2.05}O_8$) in acidic solution was essentially congruent with formation of only a very thin siliceous altered layer, and that dissolution was incongruent for a Si-rich feldspar (labradorite, $Na_{0.35}Ca_{0.60}Al_{1.57}Si_{2.43}O_8$).

3.3.5. Characteristics of Residual Rocks after Partial Dissolution

The characteristics of residual rocks after partial dissolution were identified using XRD, TEM, and the quantity of (Fe + Al + Si) dissolved in 0.2*M* ammonium oxalate-oxalic acid buffered at pH 3 (as an estimate for the quantity of amorphous constituents). These analyses were mainly designed to investigate the dissolution mechanism which may be associated with the dissolution and/or precipitation of amorphous constituents for the milled rocks.

The XRD patterns for the rocks before and after partial dissolution in acetic-citric acid for 56 days are presented in Figures 3.7 – 3.8. The figures show that after partial dissolution, minerals in the residual rocks produced sharper and more intense XRD reflections with lower background counts than for before dissolution, indicating preferential dissolution of non-diffracting amorphous constituents by the acetic-citric acid. However, the XRD peak areas of most minerals in the milled rocks after dissolution are lower than those for minerals in unmilled rocks (T0) before dissolution, indicating that some amorphus materials remain in the residual rocks after partial acid dissolution. Whether these residual amorphous materials are the undissolved amorphous products of milling or amorphous materials produced by precipitation of salts of polyvalent cations during acid dissolution can not be identified using these data.

A comparison was made of the XRD patterns of dry-milled rocks (T120) before and after acetic-citric acid dissolution and after oxalate extraction (Figure 3.9). As shown in this figure, both acid dissolution (AD) and oxalate extraction (OE) removed much of the amorphous materials from the four dry-milled rocks (T120), as is indicated by the sharper XRD reflections of the rocks after acid dissolution or oxalate extraction relative to XRD reflections before these treatments. Comparison of XRD reflections for each rock AD versus OE indicates somewhat different trends (Figure 3.9). The XRD reflections for basalt AD residue were weaker than for basalt OE residue, indicating that a higher quantity of amorphous materials remained in the basalt AD residues than in basalt OE residues. In contrast, the XRD reflections for

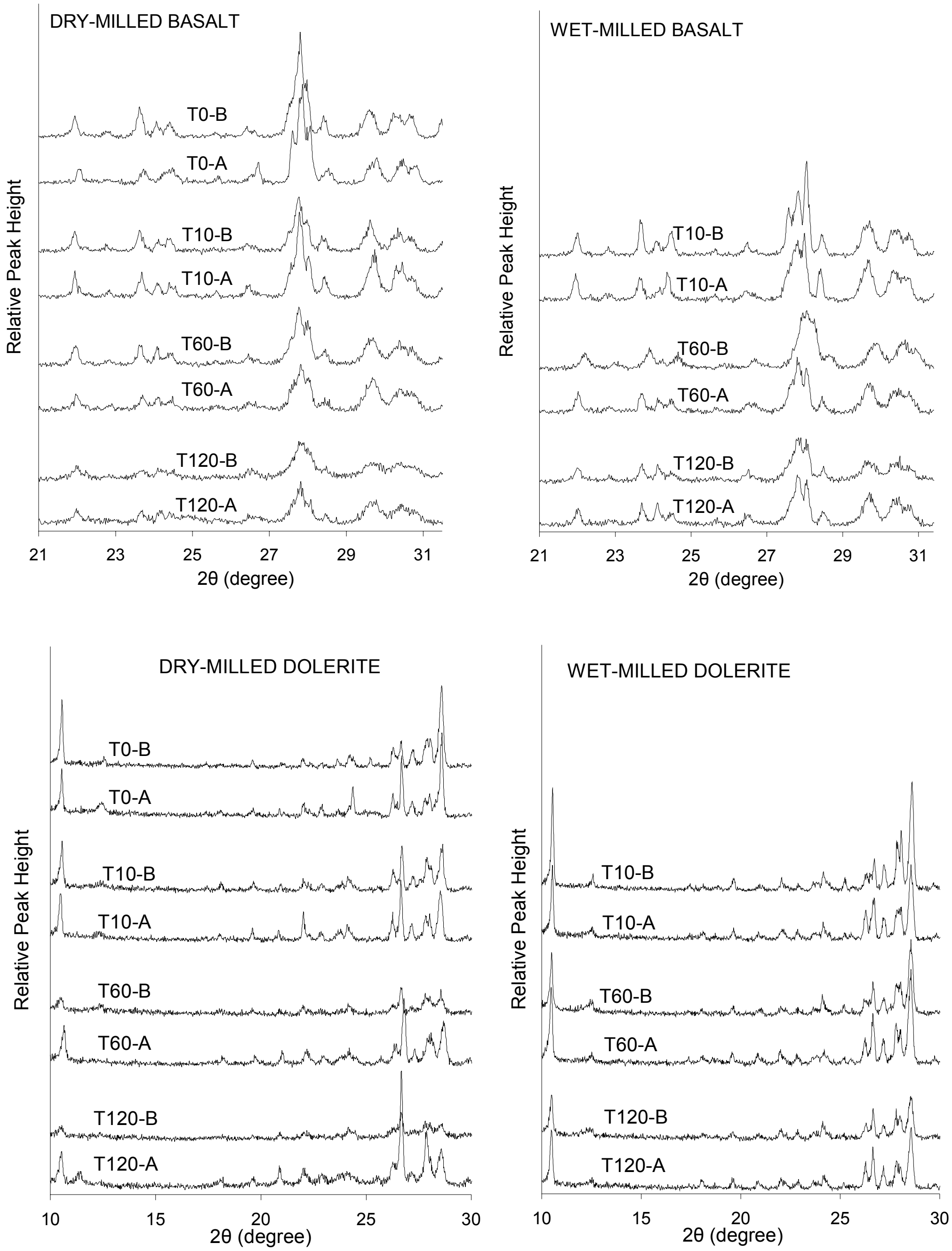


Figure 3.7. XRD patterns of basalt and dolerite milled for 0 (T0), 10 (T10), 60 (T60), and 120 (T120) min under dry and wet conditions, samples before (B) and after (A) dissolution in 0.01*M* acetic-citric acid for 56 days.

AD residue were sharper than for OE residue for the other rocks indicating a larger crystal size.

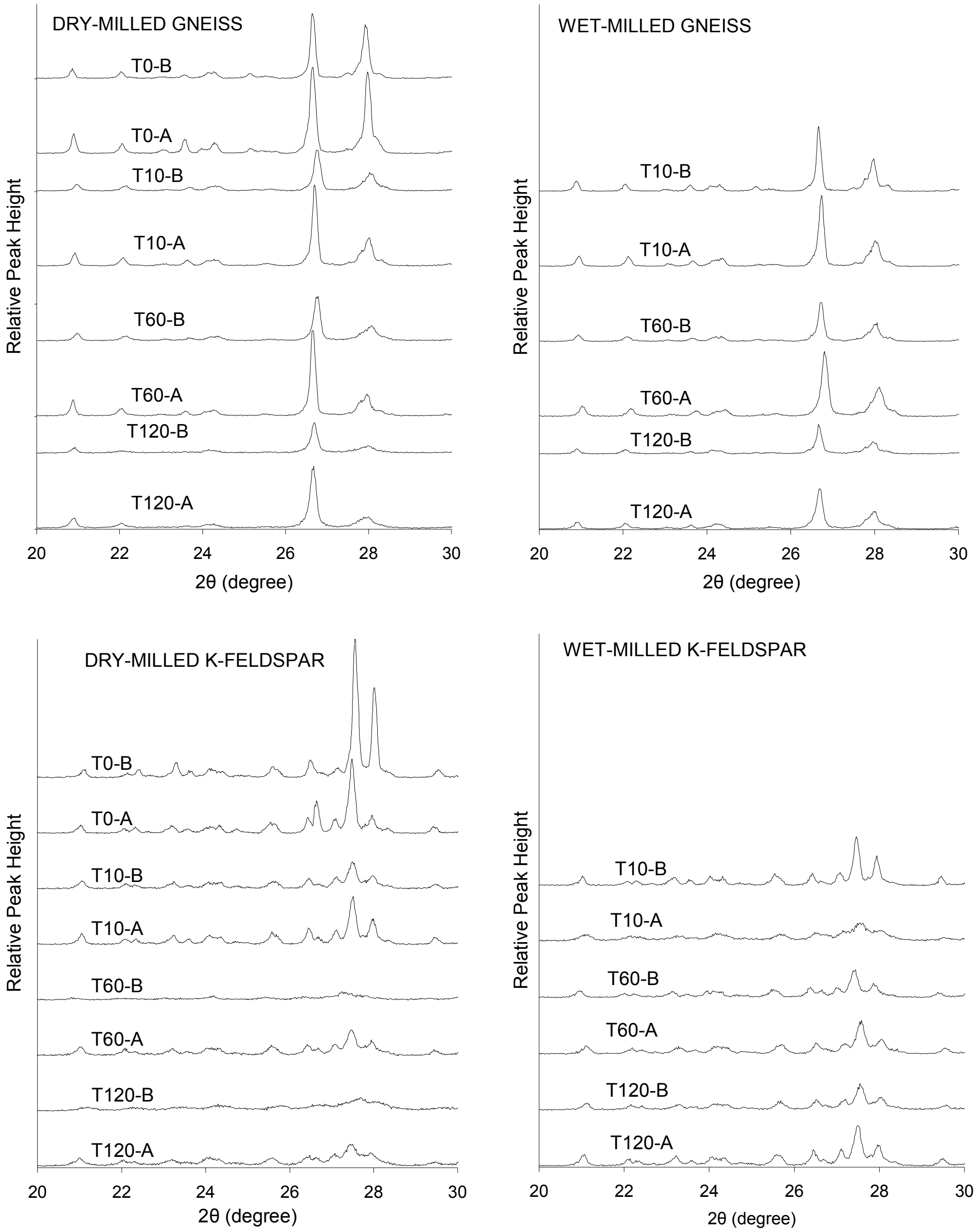
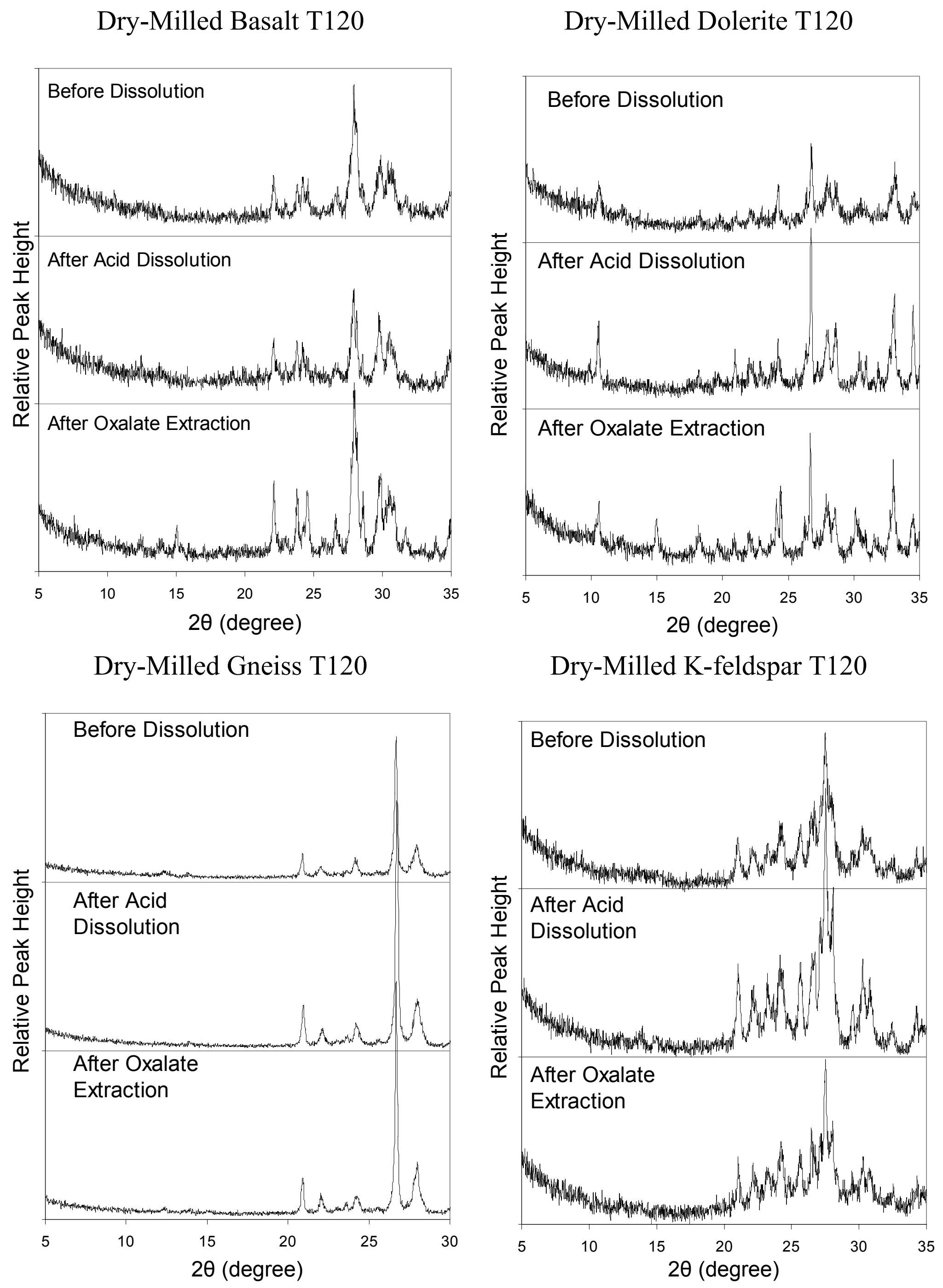


Figure 3.8. XRD patterns of gneiss and K-feldspar milled for 0 (T0), 10 (T10), 60 (T60), and 120 (T120) min under dry and wet conditions, samples before (B) and after (A) dissolution in 0.01*M* acetic-citric acid for 56 days.

Values of % (Fe + Al + Si) dissolved in acetic-citric acid (recalculated from data in Figure 3.1 excluding Ca, Mg, K, and Na) may be used as a measure of quantity of the amorphous constituents in milled rock that had dissolved, similar to the % extractable (Fe + Al + Si) calculated for oxalate extraction, and those data are


Dry-Milled Basalt T120

Dry-Milled Dolerite T120

Dry-Milled Gneiss T120

Dry-Milled K-feldspar T120

Figure 3.9. XRD patterns of dry-milled basalt, dolerite, gneiss, and K-feldspar for 120 min, samples before dissolution, after acid dissolution and after oxalate extraction.

compared in Figure 3. 10. Acetic-citric acid (after 56 days) had removed about twice the amount of (Fe + Al + Si) than did oxalate extraction. This indicates that most of the amorphous materials present in AD residues of rocks are likely to be a result of precipitation, and that more precipitation occurred for basalt than for the other rocks.

To identify which of these polyvalent cations were most likely re-precipitated after acid dissolution, the percentages of amorphous Fe, Al, and Si (e.g., extractable in oxalate acid) for rock powder samples before acetic-citric acid dissolution and those for after acetic-citric acid dissolution (AD) are compared in Figure 3.11.

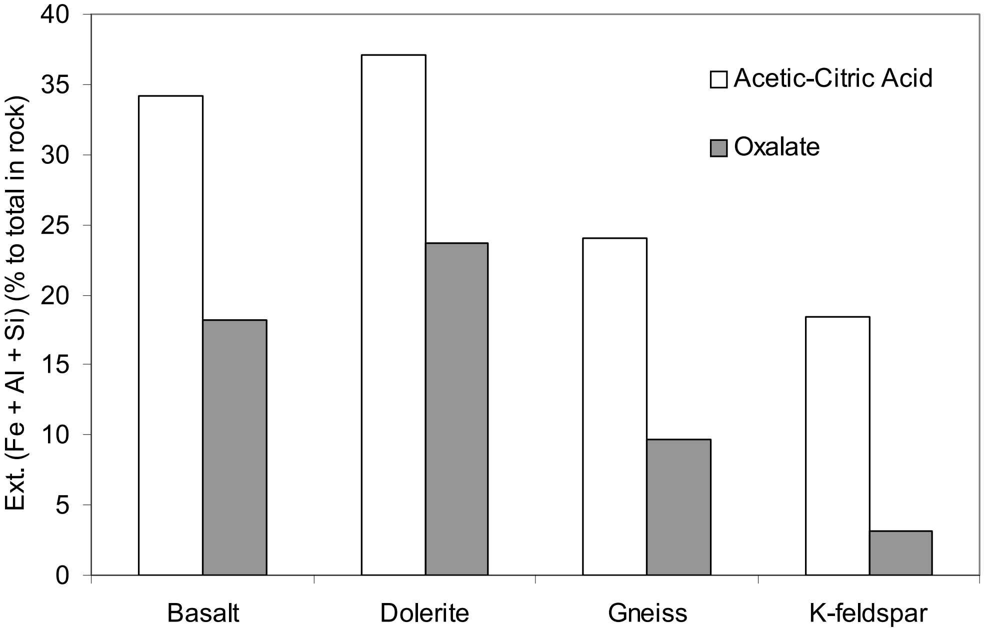


Figure 3.10. The percentages of (Fe + Al + Si) dissolved in 0.01*M* acetic-citric acid during 56d dissolution and those for in 0.2*M* oxalate acid extraction (4 h) of rocks dry milled for 120 min.

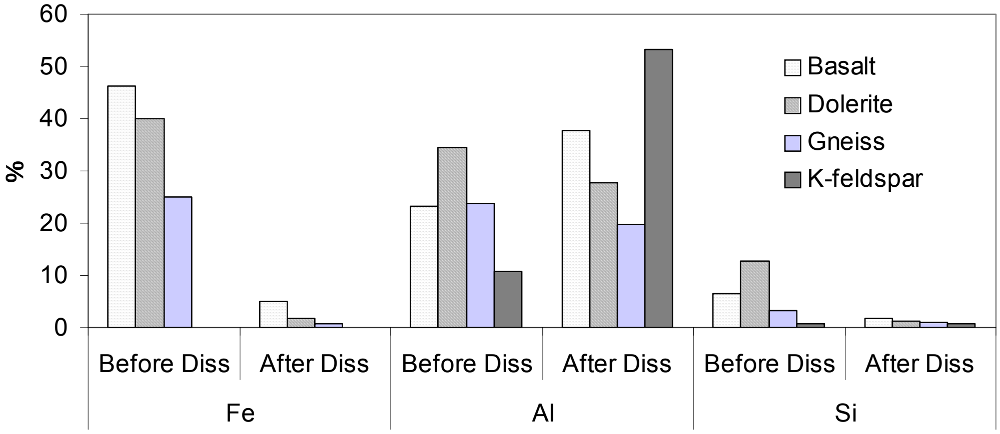


Figure 3.11. The quantities of amorphous Fe, Al, and Si (i.e., extractable in 0.2*M* ammonium oxalate buffered at pH 3) for the rock powders before dissolution and for the residual rock powders after 56d dissolution in acetic-citric acid.

As mentioned in above discussion, large amounts of Fe, Al, and Si were dissolved during 56d dissolution in acetic-citric acid (Figure 3.10). Figure 3.11 indicates that the quantities of amorphous Fe and Si after dissolution were much smaller than those for before dissolution in the acid, but the quantity of amorphous Al after partial dissolution was about the same as that for before dissolution. These trends may be interpreted as indicating that the dissolved amorphous Al and/or structural Al in acetic-citric acid was mostly re-precipitated as an amorphous material. Thus, some of the amorphous materials remaining in the AD residues were most probably precipitates of Al-organic complexes. This interpretation is consistent with the possible concurrency of a ligand-assisted dissolution mechanism as discussed in section 3.3.1 which may also be associated to the preferential dissolution of Al over Si (see Figures 3.5 and 3.6).

The TEM images for several particles of dry-milled rocks (T120) from samples before and after partial acid dissolution are presented in Figure 3.12 – 3.16 as examples. Most parts of particles of dry-milled rocks after and before partial acid dissolution were amorphous as they did not diffract electron coherently and lattice images were not detected. Observations using high magnification indicated that zones of amorphous and crystalline materials were present within the same micrometric rock particles. Interpretations based on these TEM observations should be treated with caution due to several technical limitations in using TEM to differentiate crystalline and amorphous silicate materials. The first problem was associated to the irregular forms of the particles causing difficulties in focusing the electron beam on the targeted areas within a rock particle, also producing unclear/diffuse electron diffraction patterns (Figure 3.16) and lattice images. Moreover, as discussed in the caption of the micrographs most particles observed consisted of several lamellae/agglomerates which could be mixtures of discrete crystalline and amorphous materials. Although the rock samples had been intensively dispersed in water prior to TEM, it is not possible to completely separate sintered particles. Secondly, only a few and very fine particles (Ø < 10 nm) may be observed in a single field at high magnification, thus the results are probably not quantitatively representative of the relative abundances of crystalline and amorphous materials present in the milled rocks before and after acid dissolution.

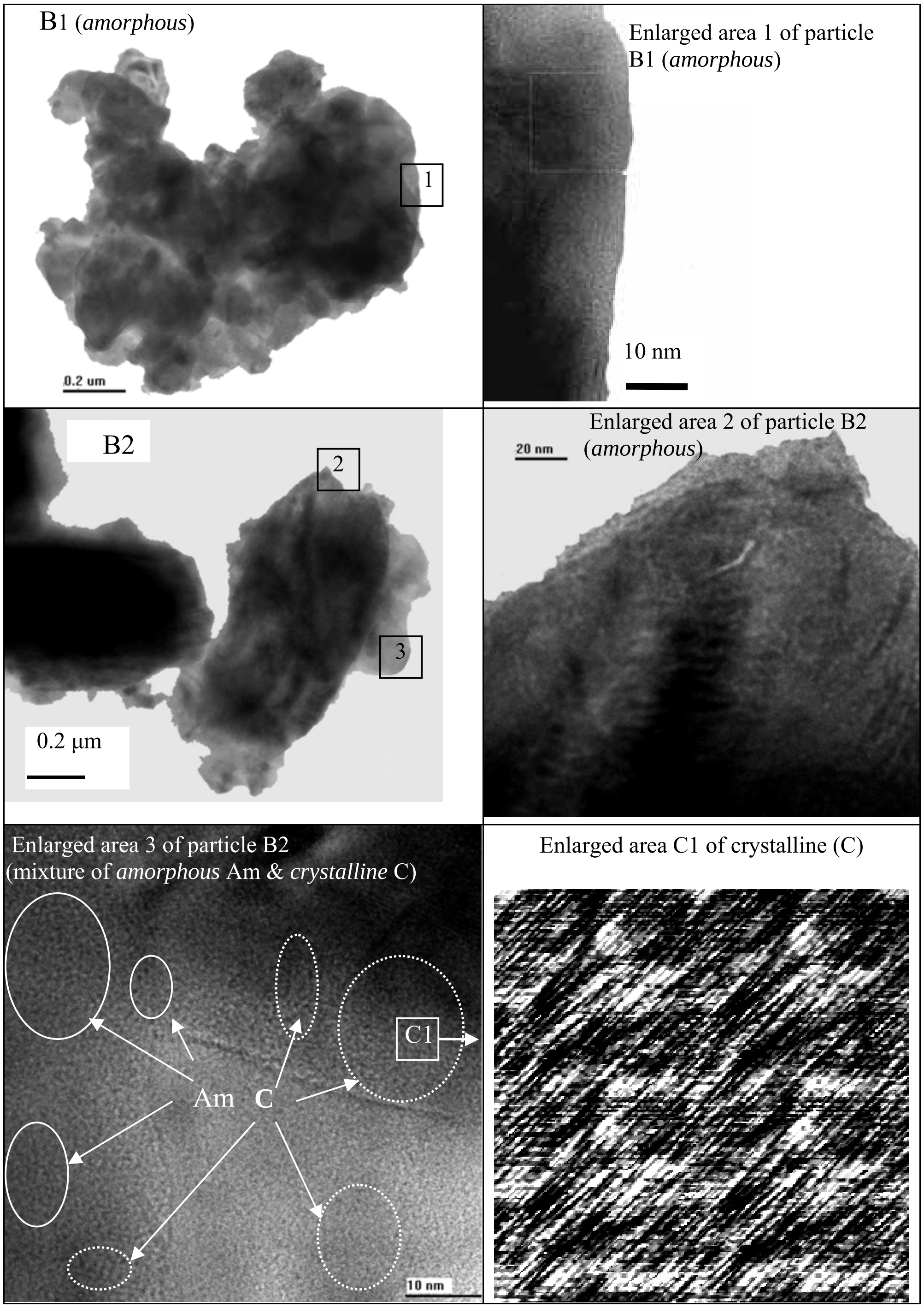


Figure 3.12. Transmission electron micrographs of particles of dry-milled basalt (T120) before partial acid dissolution (B1 and B2) showing extensive volumes of amorphous materials that do not provide lattice images together with crystalline and amorphous materials in small volumes of material.

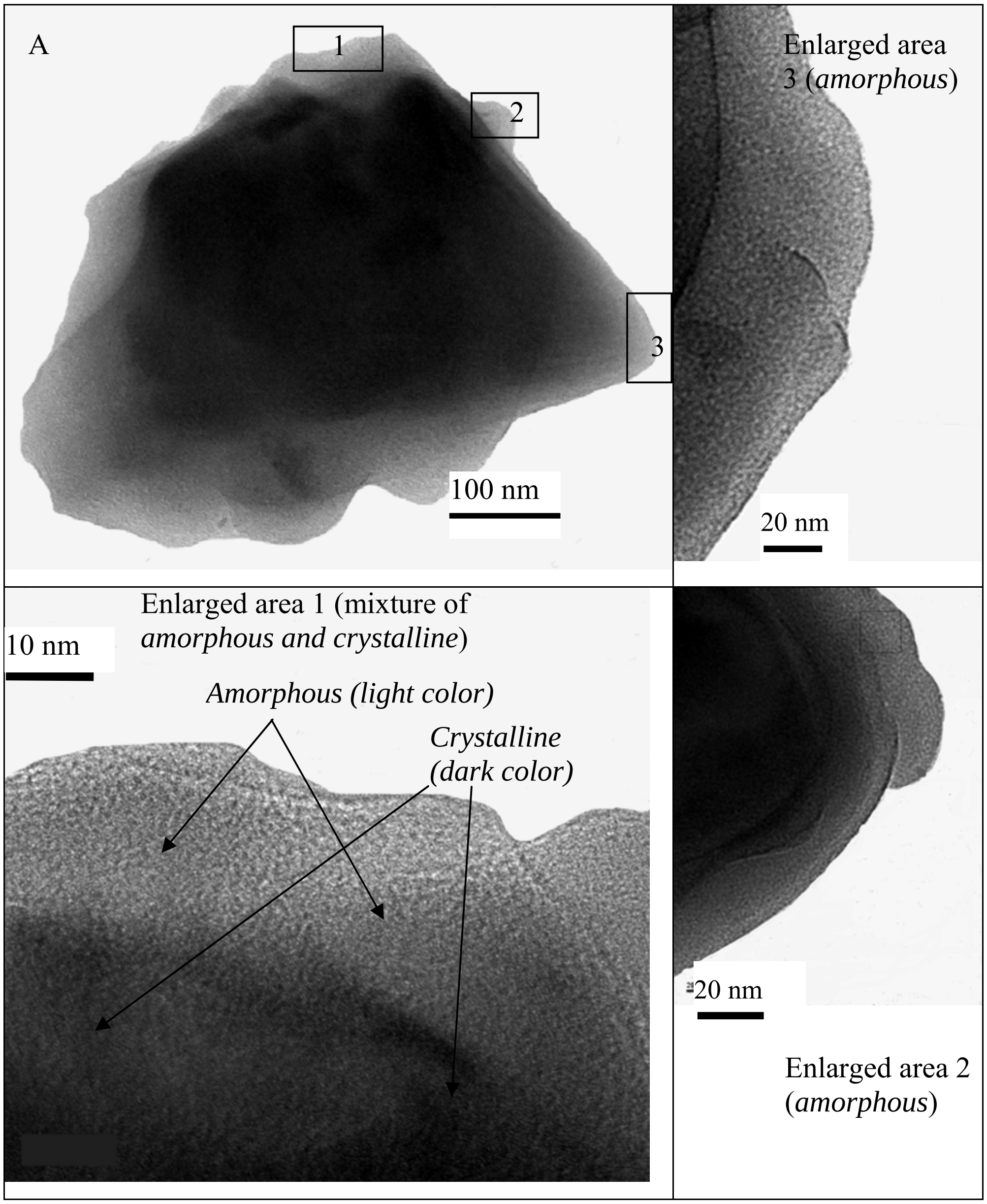


Figure 3.13.Transmission electron micrographs of a particle of dry-milled basalt (T120) after partial acid dissolution (A). Crystalline (lattice fringes resolved) and amorphous materials are present within the same particle.

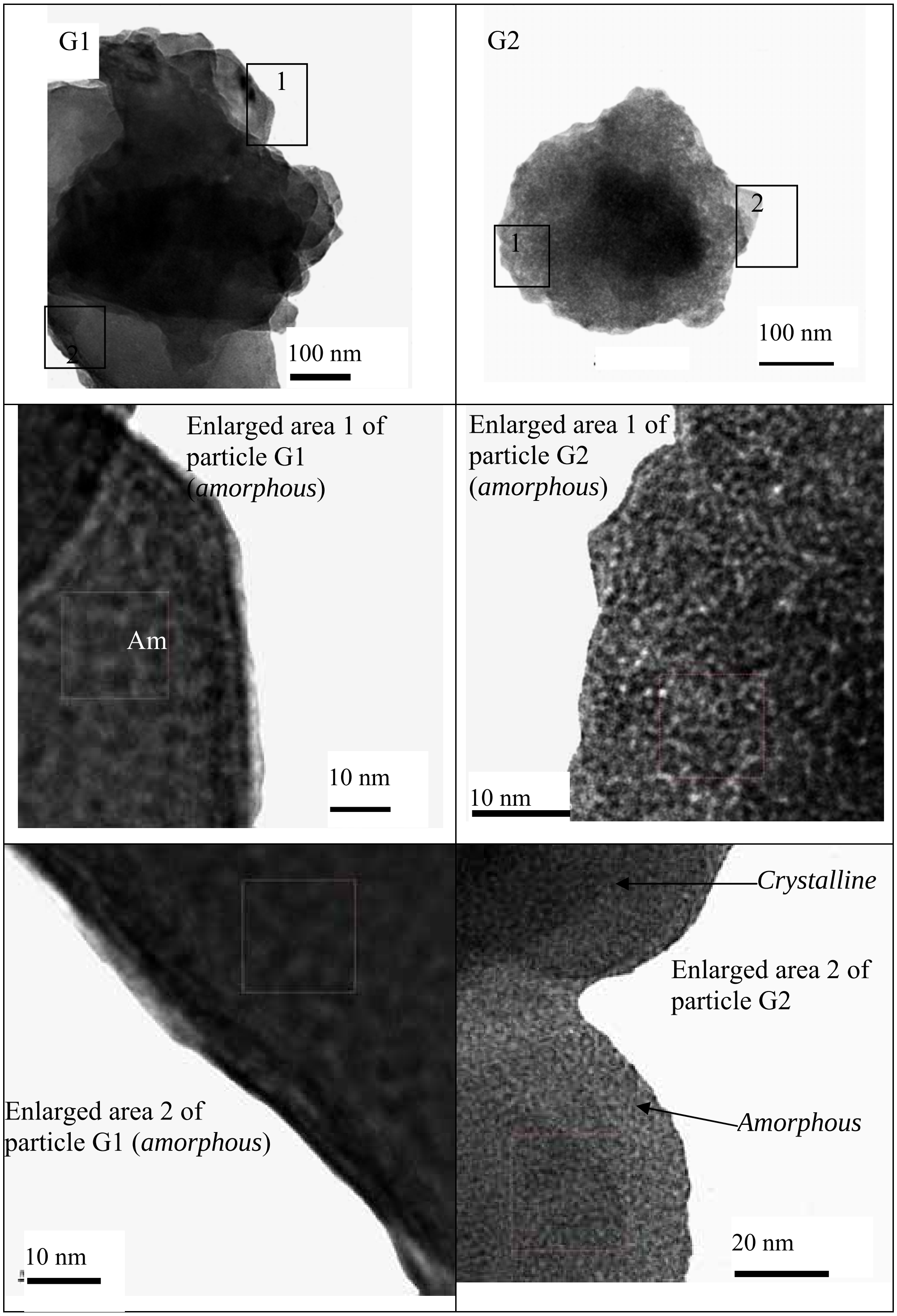


Figure 3.14. Transmission electron micrographs of particles of dry-milled gneiss T120 before partial acid dissolution (G1 and G2). Most parts of these particles are amorphous.

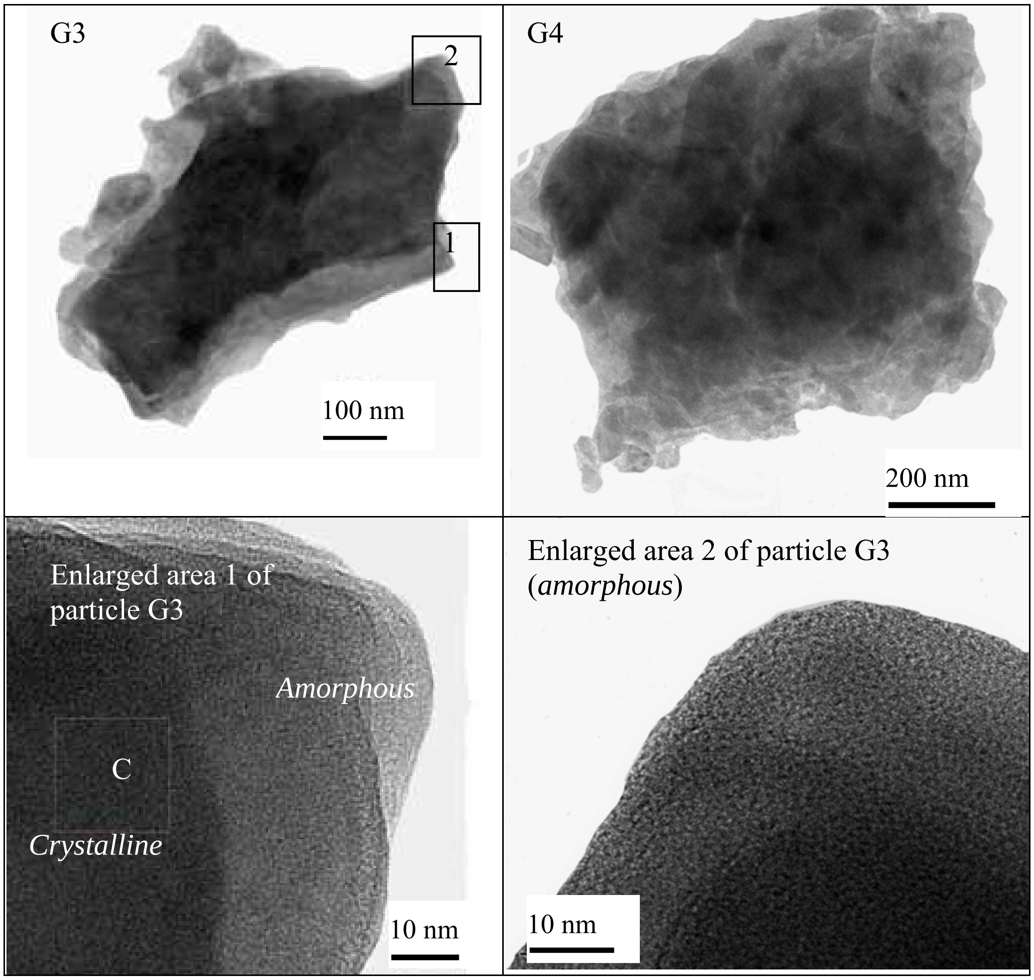


Figure 3.15. Transmission electron micrographs of several particles of dry-milled gneiss T120 after partial acid dissolution (G3 and G4). Some edges of particle G3 were amorphous, whereas the middle parts (dark colored) were crystalline (C). All parts of particle G4 were amorphous.

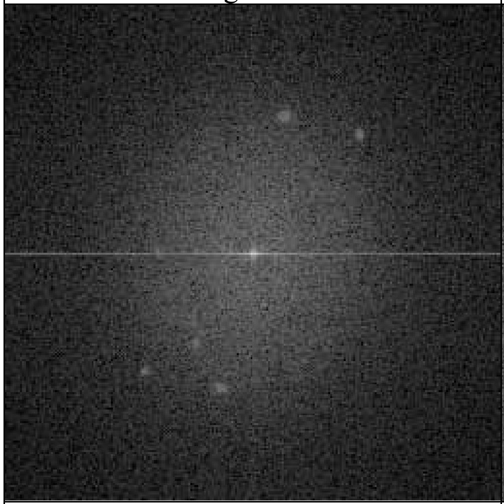
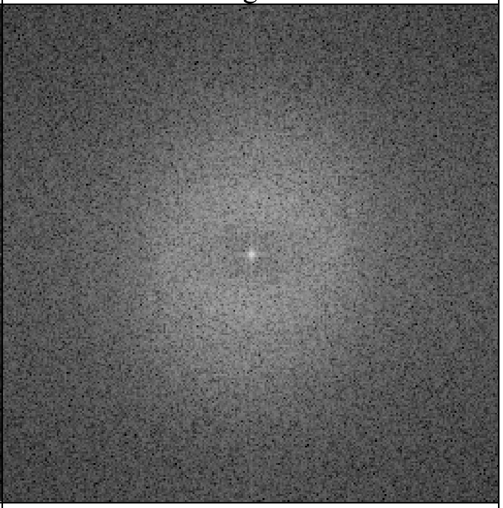
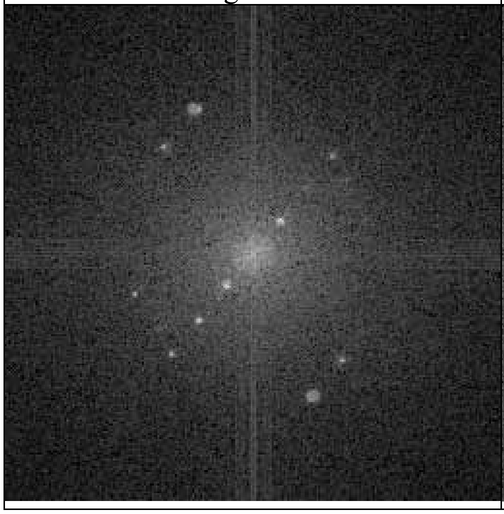
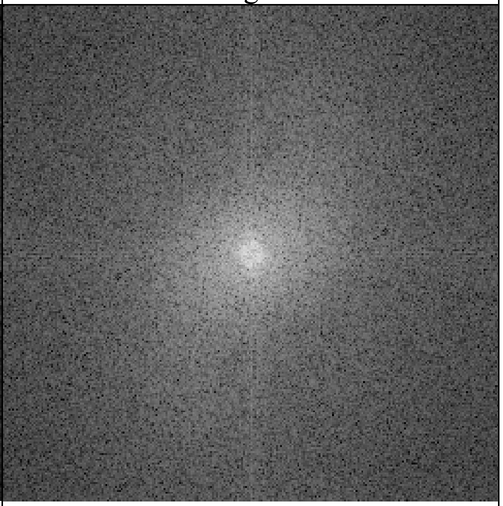
An electron diffraction image of crystalline area C of area 3, particle B2 in Figure 3.11	An electron diffraction image of amorphous area Am of area 3, particle B2 in Figure 3.11
	
An electron diffraction image of crystalline area C of area 1, particle G3 in Figure 3.14	An electron diffraction image of amorphous area Am of area 1, particle G1 in Figure 3.13
	

Figure 3.16. Examples of electron diffraction images for crystalline (left) and amorphous (right) particles of dry-milled basalt and gneiss. The crystalline materials generate weak-broad diffraction spots.

Based on observations described above, there was clear evidence that acetic-citric acid dissolved more amorphous than crystalline materials from milled silicate rocks, promoting a high dissolution rate during the early stage of the dissolution process, and at the same time some initially dissolved structural polyvalent cations, mainly Al, were re-precipitated producing (secondary) amorphus materials. This dissolution mechanism differs from mechanisms suggested by other workers (Huang and Keller 1970; Welch and Ullman 1996; Blake and Walter 1999; Oelkers and Scott 2001; Oelkers and Gislason 2001) as mentioned earlier that dissolution mechanisms are ion exchange reactions in which soluble surface cations are exchanged equivalently by H^+ from the acidic solvent and complexion polyvalent cations by organic acids, followed by slower dissolution being attributed to ion release involving dislocation of structural bonds in the silicate structure .

3.4 Conclusions

Results of this dissolution experiment were closely associated with the structural properties of the minerals in the rocks as affected by the milling treatments. The general trends of rock dissolution in this present study were consistent with those found by other researchers (Huang and Keller 1970; Welch and Ullman 1996; Blake and Walter 1999; Oelkers and Scott 2001; Oelkers and Gislason 2001; Harley 2002). However, pretreatment by removing amorphous constituents from ground rocks or minerals as applied by the above workers results in different dissolution mechanisms. In particular the high initial dissolution rate was not so important for “cleaned” materials. In this present study, the dilute organic acid mixture dissolved more amorphous than crystalline material, whereas the mechanism suggested by the cited authors involves an initial higher dissolution rate associated with the detachment of outmost structural elements from ordered structures.

The enhanced solubility of the milled rocks encourages the view that high-energy ball milled basalt and dolerite may be used as Ca and Mg fertilizers and milled K-feldspar as a K fertilizer. However, only relatively minor percentages of total plant nutrients were rapidly released from milled rocks. In marked contrast most commercial chemical Ca, Mg, and K fertilizers dissolve rapidly and to a major extent shortly after application. Dissolution of milled silicate rocks must be evaluated for the soil environment where dissolution of SRF relies partly on soil acidity. There may be substantial modifications of soil chemistry in the rhizosphere due to plant roots enhancing the availability of plant nutrients from poorly soluble sources through the evaluation of inorganic and organic solvents (Hinsinger and Gilkes 1995; Hinsinger *et al.* 2001). Furthermore plant growth experiments should be carried out to identify if the large increase in solubility of nutrient elements created by milling is accompanied by large increased in plant uptake of these elements. These topics are investigated in subsequent chapters.

Chapter 4

DISSOLUTION OF MILLED-SILICATE ROCKS IN THE SOIL

4.1. Introduction

The earlier chapters have shown that milling changed several physical and chemical properties of silicate rocks including increasing the amount of exchangeable base cations, with the effects of dry milling being greater than for wet milling. Milling also increased dissolution of SRFs in dilute mixed acetic-citric acids, and increased the dissolution of amorphous constituents more than for crystalline constituents. However, it remains unclear whether milling will produce a similar increase in dissolution of SRFs in the soil where diverse soil properties and reactions are involved. An important question relating to agricultural practice is to determine those soils for which the application of SRFs will be most advantageous. A dissolution experiment for milled SRFs in soil was, therefore, carried out to investigate this situation.

The objectives of this research were to identify (1) the effects of milling on the proportion of major elements dissolved from the SRFs in soil and (2) soil properties that influence the dissolution of ground SRFs. The experiment was carried out under laboratory conditions using 23 soils from south-western Australia.

4.2. Materials and Methods

4.2.1. Silicate Rocks and Soil Samples

Silicate rock fertilizers used in this experiment were dry-milled basalt, dolerite, gneiss, and K-feldspar that had been milled for 0 (initial), 10, 60, and 120 min, as used in acid dissolution experiment (Chapter 3). The virgin soils (under bush vegetation) were from 23 soil reference sites in south-western Australia (McArthur 1991). The top 15cm excluding the organic matter layer was sampled, air dried and sieved to pass a 2-mm sieve. Selection of the soils was based on the results of previous research by Hughes and Gilkes (1994) who found that these soils were capable of dissolving more than 40 % of added rock phosphate. It was postulated that these soils would also dissolve SRFs. Complete information on the sites used for soil sampling and soil profile data are available in McArthur (1991). Soil properties used for investigation of relationships between soil properties and dissolution rate of SRFs are presented in Table 4.1.

4.2.2. Analytical Methods

The methods used for measurement of soil properties presented in Table 4.1 and for soil-SRF mixtures from incubation experiment are as follows.

1. pH_{H2O} and pH_{CaCl2} and EC at a soil : solution (H_2O and 0.01*N* $CaCl_2$) ratio of 1 : 5 were measured with pH- and EC-meters (Cyberscan 2000).
2. $\Delta pH = pH_{CaCl2} - pH_{H2O}$.
3. Organic carbon was determined by wet oxidation with $K_2Cr_2O_7$ (Walkley and Black 1934).
4. Cation exchange capacity (CEC) was determined using 1*M* ammonium acetate (CH_3COONH_4) pH 7 as an extracting solution (Thomas 1982) with 3 extractions. The three filtrates were collected and used for measurement of exchangeable base cations, i.e., Ca and Mg (by AAS) and K and Na (by flame emission). The NH_4^+ retained by the soil was displaced using 1*N* KCl. The excess of KCl in the soil was removed using ethanol, and the remaining K^+ on the exchange sites of soil was displaced using 1*N* $CaCl_2$, and the filtrate was collected. The concentration of K^+ in the filtrate was determined by flame emission, and the quantity of K^+ was considered to represent the value of the cation exchange capacity (CEC) and is presented in units of centimole charge per kg soil ($cmol_c/kg$).
5. Effective cation exchange capacity (ECEC) was calculated as total exchange bases + total exchange acidity.
6. Base saturation (BS) was calculated as the sum of exchangeable base cations as a % of CEC.
7. Total exchange acidity was extracted with 1*N* KCl and determined by titration using 0.01*N* NaOH (Thomas 1982).
8. Percentages of sand, silt, and clay were determined by the pipette method (Gee and Bauder 1986).

Table 4.1. Major Properties of soil samples used in this experiment

No	Sample	pH H_2(	pH CaC	ΔpH	EC	C-Org.	CEC	ECEC	Exch. Basic Cations ($cmol_c/kg$)					BS	Ex.Acidity	Sand	Clay	Amphous
	Code	1 : 5	1 : 5	pH	uS/cm	(%)	$cmol_c/kg$	$cmol_c/kg$	Na	K	Ca	Mg	Total	(%)	$cmol_c/kg$	%	(%)	(%)
1	ALB-1 *	4.73	3.75	-0.98	76	4.4	26.4	6.1	0.26	1.10	2.13	1.24	4.73	18	1.416	94.0	0.8	0.10
2	ALB-5	5.62	5.00	-0.62	273	5.9	36.9	14.1	0.84	0.98	8.37	3.86	14.05	38	0.093	81.7	8.1	0.22
3	DEN-2	5.73	4.84	-0.89	99	4.0	27.2	11.3	0.25	1.76	6.28	2.92	11.20	41	0.092	77.8	16.0	0.42
4	DEN-4	5.60	4.59	-1.01	89	7.0	41.3	12.0	0.18	1.59	6.32	3.56	11.65	28	0.300	63.6	29.5	0.64
5	DEN-7	6.05	5.28	-0.77	71	3.8	26.7	9.5	0.25	2.17	4.78	2.20	9.41	35	0.068	83.8	6.6	0.68
6	KTG-2	5.95	5.70	-0.25	793	1.9	35.7	22.1	4.62	2.34	5.27	9.77	22.00	62	0.080	34.9	45.6	0.17
7	WP-6 *	4.08	3.75	-0.33	71	2.8	17.0	4.2	0.18	2.14	0.55	0.61	3.48	21	0.681	93.0	4.4	0.06
8	MR-5 *	5.60	4.25	-1.35	65.5	4.3	19.0	6.3	0.15	2.15	2.57	0.57	5.44	29	0.878	79.3	8.2	0.52
9	SCP-3	6.22	5.62	-0.60	162	5.3	27.2	13.8	0.42	2.24	7.52	3.54	13.73	51	0.033	76.2	12.4	0.27
10	SCP-4	6.43	6.11	-0.32	240	8.1	50.3	29.5	0.32	2.06	22.85	4.09	29.32	58	0.130	53.6	28.3	1.39
11	SCP-5	5.91	5.04	-0.87	52	3.5	40.1	14.3	0.16	2.77	4.97	6.29	14.19	35	0.076	53.9	32.1	0.54
12	SCP-6	6.06	5.38	-0.68	79.2	3.8	23.2	9.3	0.09	1.79	4.34	2.97	9.18	40	0.071	79.3	15.8	0.36
13	SCP-11*	6.14	4.98	-1.16	21	1.9	14.2	5.7	0.00	1.08	3.84	0.71	5.64	40	0.071	96.4	1.6	0.02
14	PTN-3	5.87	4.70	-1.17	159	4.0	19.4	5.2	0.42	1.01	2.40	1.18	5.01	26	0.206	77.1	0.8	0.57
15	PTN-4 *	5.50	4.13	-1.37	45	4.1	11.1	2.8	0.04	1.11	1.08	0.35	2.58	23	0.256	79.9	4.4	0.11
16	PTN-5 *	5.24	4.02	-1.22	66	3.2	15.1	3.6	0.10	0.66	1.57	0.65	2.98	20	0.582	84.6	3.5	0.10
17	BSN-1 *	5.70	4.79	-0.91	57.4	1.5	10.5	3.0	0.09	0.78	1.27	0.75	2.89	28	0.145	86.8	9.2	0.22
18	BSN-4 *	5.31	4.38	-0.93	53	1.8	13.7	3.3	0.18	1.30	0.75	0.52	2.75	20	0.518	70.0	16.9	0.37
19	DP-1 *	5.83	4.82	-1.01	36	3.3	13.6	5.8	0.08	1.04	3.32	1.15	5.60	41	0.157	77.1	10.7	0.34
20	DP-6 *	5.91	4.92	-0.99	42.2	2.8	15.7	4.5	0.04	0.82	2.69	0.84	4.39	28	0.091	85.0	5.5	0.17
21	BTN-2	5.98	4.86	-1.12	54	4.0	23.2	7.3	0.17	0.52	4.83	1.65	7.17	31	0.133	89.6	4.8	0.33
22	BTN-3v	5.67	4.52	-1.15	58	3.7	27.9	9.9	0.16	1.34	5.61	2.28	9.38	34	0.479	77.5	13.7	0.56
23	BTN-3	5.61	5.17	-0.44	406	4.7	41.9	16.3	2.02	1.05	5.89	6.90	15.85	38	0.468	65.3	22.6	1.41

* Soils that were incubated for 10 months

9. Fe, Al, and Si extracted with 0.2*M* ammonium oxalate $(COONH_4)_2.H_2O$ buffered to pH 3.0 were determined using the method described by Rayment and Higginson (1992). The % (Fe + Al + Si) from this measurement is used as an estimate of the quantity of amorphous constituents in rocks and soils.
10. Measurement of field capacity of the soils used for incubation experiment: 20 g soil (< 2 mm) was transferred into a beaker glass, over saturated with DI water, then transferred onto a filter paper (Whatman No 40) on a panel, covered with plastic to minimize evaporation and was allowed to drain overnight. The water content remaining in the soil (measured with gravimetric method) was defined as the water content at the field capacity of soil.
11. The quantities of CH_3COONH_4-extractable basic cations (Ca, Mg, K, and Na) for soil-SRF mixtures: triplicates of 5g soil-SRF mixture or soil without added SRF were mixed with 25mL 1*M* CH_3COONH_4 pH 7 in plastic vials, shaken on an end-over end shaker for 1h. Concentrations of the basic cations in the filtrate were measured by method described in point 4. The values of extractable Ca, Mg, K, and Na for soil-SRF mixture incubated for 0, 2, and 10 months minus those for soil without SRF (control) are designed as E_0, E_{2M}, and E_{10M} respectively. The amount of elements dissolved during the first 2 months and between 2 and 10 month incubations (ΔE_{0-2M} and ΔE_{2-10M}) respectively were calculated from ($E_{2M} - E_0$) and ($E_{10M} - E_{2M}$).

4.2.3. Incubation Experiment

Each SRF milled for each time (0, 10, 60, and 120 min) was mixed with each of the 23 soils at the rate of 1 g SRF/100 g soil (≈ 10 t SRF/ha) in sealed plastic bags, giving a total of 368 treated soils. The soil-SRF mixtures were wetted with Milli-Q water to 110 % of field capacity and 1mL toluene was added for microbial suppression. The soil-SRF mixtures were then stored in a dark-constant temperature room at 20^o C. A set of control soils (23 soils without added SRF) was prepared in the same manner. To determine the dissolution of the SRFs that occurs in the extractant alone, 25 g of each soil type was mixed with 0.25 g SRF without adding water and toluene, then immediately three subsamples were taken from these mixtures and also from control soils for analysis of CH_3COONH_4-extractable cations as described in section 4.2.2.

After incubation for 2 months, three subsamples were taken from each treated and untreated (control) soil for measurements of CH_3COONH_4-extractable Ca, Mg, K, and Na. An additional subsample was taken for measurements of soil pH and EC. The remaining samples were retained for further incubation up to 10 months. After incubation for 10 months, these measurements were made only on the 10 soils (see Table 4.1) where SRFs had dissolved extensively during incubation for 2 months.

4.3. Results and Discussion

4.3.1. Properties of the Soils

As shown in Table 4.1, the soils used in this experiment have a wide range of properties. The soil texture ranges from sand (0.8 % clay) to clay (45.6 % clay), most soils are slightly acid (pH_{H_2O} 5.0 – 6.0) and non to slightly saline (EC_{H_2O} 1:5 = 21 to 793 µS/cm). The range of oxidisable-organic C is from 1.5 to 8.1 %, CEC ranges from 10.5 to 50.6 $cmol_c$/kg. Total exchange acidity ranges from 0.3 to 1.4 $cmol_c$/kg. The quantities of individual-exchangeable base cations (Na, K, Ca, and Mg) vary widely with the total of exchangeable base cations ranging from 2.58 to 29.32 $cmol_c$/kg which represents 18 to 62 of the CEC. The relatively low base saturation is partly due to the strongly pH-dependent nature of the charge on some of the soils, thus measurement of CEC using CH_3COONH_4 buffered at pH 7.0 (1 – 3 units higher than original pH of soils) results in an overestimate of the CEC of the soils. A more realistic indicator of effective CEC is provided by the sum of exchangeable basic cations including exchange acidity. However, selection of the method for CEC measurement, in addition to the wide use of this method, was based on a presumption that adding SRFs will quickly (possibly within the first week of incubation) increase the pH of soil-SRF mixtures which maybe significantly affect dissolution rate of the SRFs. Thus the CH_3COONH_4 buffered at pH 7 was proposed to be an appropriate cation exchanger solution, especially for use in identifying the relationship between the CEC of soils and the dissolution rate of SRFs in the soils (see section 4.3.4).

4.3.2. Effects of Milling Time

4.3.2.1. Dissolution of Major Plant Nutrient Elements

The focus of discussion in the following sections will be on the dissolution of Ca and Mg for basalt and dolerite SRFs, K and Na for gneiss and K-feldspar SRFs, as those are the plant nutrient elements that are most abundantly provided by these SRFs. To evaluate the effect of milling time on the dissolution of elements, analysis of variance was employed for the values of Eo, E_{2M}, and E_{10M}, in which soil type was considered as the block. Average values of dissolution for the 10 soils plotted against milling time are shown in Figures 4.1 – 4.2 which enables comparison of dissolution values for different milling and incubation times (2 and 10 months).

The dissolved basic cations in soil-SRF mixtures presented in Figures 2.1 and 4.2 (i.e., calculated as $E_{soil+SRF} - E_{control}$) may be originated from the soil itself and the SRF added. These dissolved basic cations from the soil in soil-SRF mixture are most probably due to liming effects (e.g., increase of pH) due to SRFs added. The use of extracting solution (CH_3COONH_4) buffered to pH 7 (higher than pH of soils used in this experiment) was aimed to minimize this contribution of dissolved cations from soil itself to E values (y axes in Figures 4.1 and 4.2) thereby the E values may be appropriately defined as the quantities of dissolved basic cations from SRFs incubated in the soils.

Figures 4.1 and 4.2 show that considerable dissolution of nonincubated SRFs occurred during the extraction (i.e., E_0 values are substantial) and presumably much of this material will also dissolve in the soil. Relatively minor dissolution occurred for initially milled SRFs (T0) and milling greatly increased the percentages of elements dissolved for the SRFs for all 3 incubation periods. The dissolution plots for mafic SRFs (basalt and dolerite) followed parabolic relationships indicating that milling for longer than 60 min had not substantially increased dissolution. For felsic SRFs (gneiss and K-feldspar) dissolution increased linearly with milling time up to 120 min of milling for each period of soil-SRF incubation.

Basalt and dolerite have similar chemical and mineralogical compositions (see Table 2.1) and dissolution of Ca and Mg followed similar trends with respect to milling and incubation time for these two SRFs. The proportions of these elements

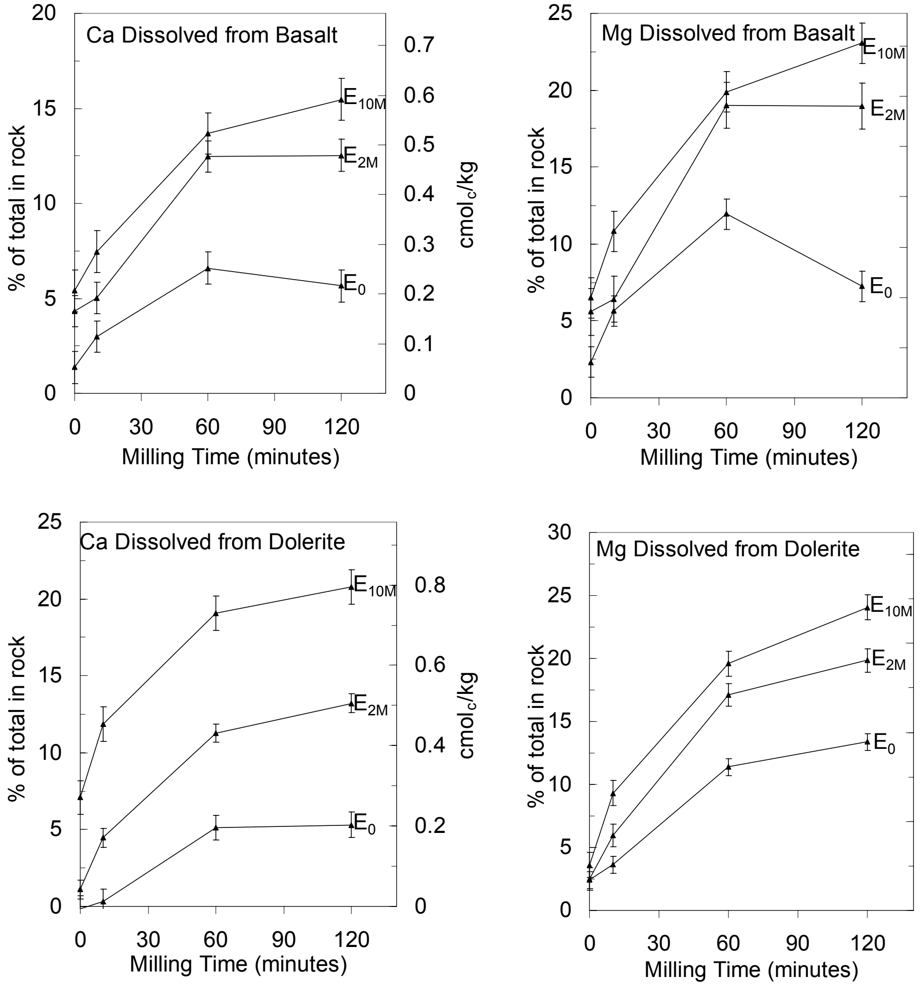


Figure 4.1. Mean quantities of Ca and Mg dissolved from 10 mixtures of soil + basalt SRF and soil + dolerite SRF minus those for untreated soil after 0, 2, and 10 month incubations (E_0, E_{2M}, and E_{10M}), as functions of milling time. The values for y axes are calculated as % of CH_3COONH_4-extractable these cations relative to total of these cations in the rock powder (see Appendix A1). The error bars are for standard deviation of mean.

that were rapidly dissolved (Eo) for basalt SRF were about 2 % Ca and 2.5 % Mg (for initial milling, T0) and were doubled for T120 (see Figures 4.1 – 4.2). After incubation for 2 months (E_{2M}) dissolution had increased by about 2 - 3 fold for all grinding times with a relative minor additional increase for incubation for 10 months ($\Delta E_{2\text{-}10M}$ = 1 – 4 % for both Ca and Mg). The values of E_{10M} were about 16 % Ca and 23 % Mg for 120 min-milled basalt SRF. For basalt SRF, milling for 120 min reduced the value of E_0 and E_{2M} which might be due to agglomeration of particles occurring between 60 and 120 min of milling but this explanation is not supported

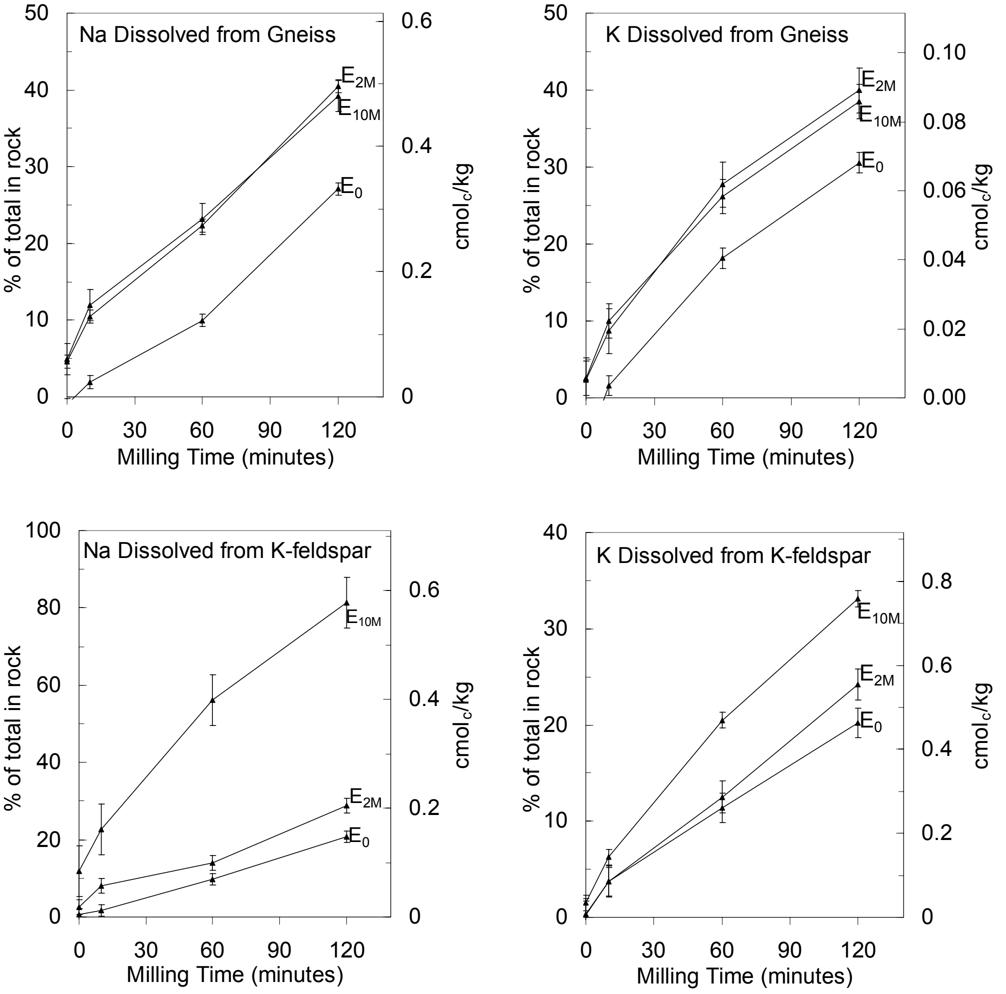


Figure 4.2. Mean quantities of K and Na dissolved from 10 mixtures of soil + gneiss SRF and soil + K-feldspar SRF minus those for untreated soil after 0, 2, and 10 month incubations (E_0, E_{2M}, and E_{10M}), as functions of milling time. The values for y axes are calculated as % of CH_3COONH_4-extractable these cations relative to total of these cations in the rock powder (see Appendix A1). The error bars are for standard deviation of mean.

by surface area or particle size data as discussed in Chapter 2. The dissolution trends of Ca and Mg for dolerite SRF were as quite similar to those for basalt SRF, although values for dolerite SRF were 2 - 5 % larger than for basalt SRF.

These results are very much in agreement with finding of Gillman *et al.* (2002) that the quantity of Ca and Mg dissolved from crushed basalt (Ø < 150 μm) in 7 lateritic soils for 3 months varied from 3 to 60 % with the extent of dissolution being dependent on soil properties, and percentage dissolution values consistently decreased with increasing application rate (1 - 50 t/ha). These authors did not separately determine rapidly dissolved elements. Gillman (1980) found that the quantity of Ca and Mg from basalt dust that dissolved in soil was affected by the particle size of the basalt, which is similar to the effect of milling time reported in the present research.

Figure 4.2 shows that the % Na and K that dissolved rapidly (E_0) for gneiss SRF was approximately 0 % (for T0) increasing to about 28 % Na and 30 % K (for T120). An additional 5 - 14 % Na and 3 - 10 % K dissolved after incubation for 2 months for all milling times, but no further dissolution occurred for incubation up to 10 months ($\Delta E_{2\text{-}10M} \approx 0$). For K-feldspar, the rapidly dissolved Na and K (E_0) was about 0 % (for T0), and was increased by milling to about 20 % for T120 for both elements. There was little extra dissolution of Na and K during the first 2 months of incubation ($\Delta E_{0\text{-}2M}$ = 0 - 5 %) for any milling time, but a considerably larger proportion of Na and K had dissolved after incubation for 10 months ($\Delta E_{2\text{-}10M}$ = 25 % Na and 20 % K), reaching values of about 80 % Na and 35 % K for E_{10M}. This great difference in dissolution behavior of Na and K presumably relates to the existence of Na and K rich feldspar species as lamellae in the material, i.e., microcline ($KAlSi_3O_8$) and albite ($(Na,K)AlSi_3O_5$) which were determined by Commercial Mineral Ltd. (1987) respectively at about 65.6 and 31.2 %.

Clearly, milling increased the proportion of basic cations dissolved (i.e., extractable in CH_3COONH_4) from the SRFs in soils. After incubation for 10 months, about 20 - 25 % of both Ca and Mg had dissolved from highly milled basalt and dolerite, about 30 % of both Na and K had dissolved from milled gneiss, and about 80 % of Na and 35 % of K had dissolved from milled K-feldspar. Between 1/3 and 2/3 of dissolved basic cations during the 10 month dissolution occurred for the initial (time zero) incubation period (= Eo). This rapid dissolution may approximate to the dissolution that occurs in soils in the first days or weeks after application of SRFs.

For the present experiment, the quantities of plant nutrient elements from the SRFs released to soil solution were small (i.e., about 0.6 and 0.8 $cmol_c/kg$ for Ca and Mg, respectively from both basalt and dolerite SRFs, 0.5 and 0.09 $cmol_c/kg$ of Na and K respectively from gneiss SRF, 0.6 and 0.8 $cmol_c/kg$ of Na and K respectively from K-feldspar SRF) in comparison to the amounts of the exchangeable of this each element already present in the soils (Table 4.1) and this small increase might not have a substantial agronomic effect. The present research may, however, underestimate dissolution under field conditions as rhizosphere dissolution of silicates is greater than in soil alone due to chemical modification of the rhizosphere by plant roots (Hinsinger and Gilkes 1995, 1997; Hinsinger *et al.* 2001) and the activities of microorganisms in rhizosphere soil (Liermann *et al.* 2000; Dong *et al.* 2000; Un Lee and Fein 2000). Furthermore, highly acid soils in the tropics and elsewhere commonly have extremely low values of base saturation and for these soils the amounts of basic cations released by dissolution of SRFs will contribute substantially to the stock of plant available basic cations.

4.3.2.2. Soil pH and EC

Adding silicate rock powders increased pH and EC of soil-SRF mixtures, and these increases were increased by prolonged milling. The increases of soil pH and EC respectively were calculated from the value for treated soil minus the value for the control soil. The mean increases of pH and EC after incubation for 2 and 10 months as functions of milling time are presented in Figures 4.3 and 4.4.

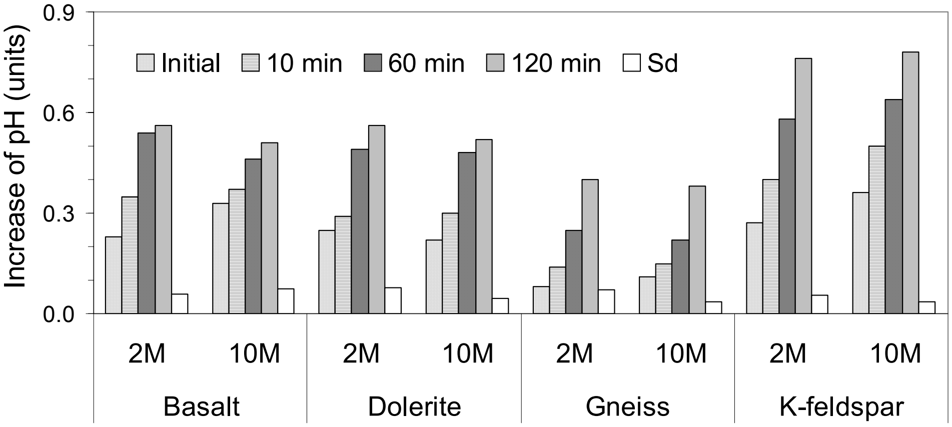


Figure 4.3. Mean increase of pH ($pH_{treated\ soil} - pH_{control\ soil}$) of 10 soils receiving SRF milled for 0 (initial), 10, 60, and 120 min and incubated for 2 and 10 months (2M and 10M). Sd is the standard deviation of mean.

The mean increases of pH (the positive liming effect) after 2 and 10 month incubations for soil-basalt SRF and soil-dolerite SRF mixtures are about 0.2 units (T0) to 0.6 units (T120), 0.2 to 0.5 units for soil-gneiss SRF, and 0.3 to 0.8 units for soil-feldspar SRF. Thus all SRFs had a positive liming effect that would be

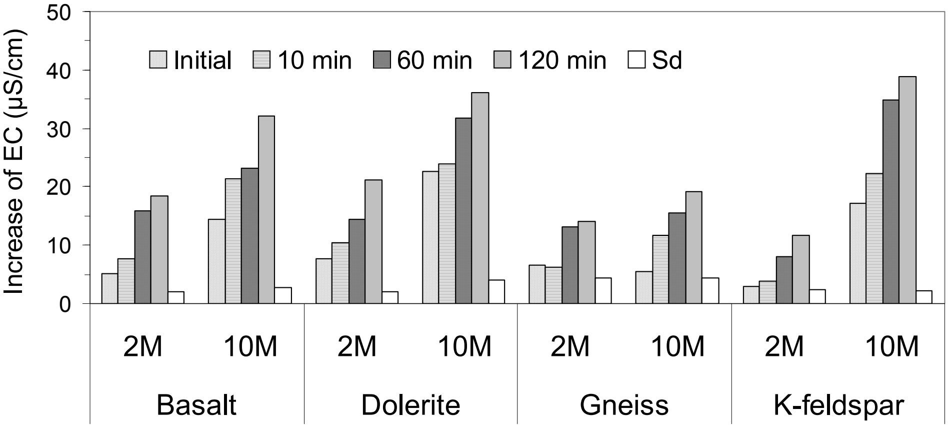


Figure 4.4. Mean increase of EC ($EC_{treated\ soil} - EC_{control\ soil}$) of 10 soils receiving SRFs milled for 0 (initial), 10, 60, and 120 min and incubated for 2 and 10 months (2M and 10M). Sd is the standard deviation of mean.

beneficial to some plants on these acid soils. Basalt and dolerite SRFs increased the EC of soil-SRF mixtures incubated for 2 months by about 5 µS/cm (for T0) to about 20 µS/cm (for T120) and these values are about doubled for soil-SRF mixtures incubated for 10 months. Gneiss SRF had a small effect on EC, i.e., increased by about 5 µS/cm (for T0) to about 15 µS/cm (for T120) for both 2- and 10-month incubations. The effect on EC of adding K-feldspar SRF was small for soil incubated for 2 months, i.e., increased by 4 - 10 µS/cm, but these values increased about 3 fold for 10 month incubations. Adding SRFs increases soil salinity but in every case these increases in EC (salinity) were negligible from an agricultural perspective (Hunt and Gilkes 1992). Thus use of SRFs at rate of about 10 t/ha (equivalent to about 1 % in top soil) may provide a significant liming benefit and will not adversely affect soil salinity. Positive liming effects (increasing pH) due to amendment of acid soils with SRFs have been reported by several workers (Coroneos *et al.* 1996; Hinsinger *et al.* 1996; Gillman 1980; Gillman *et al.* 2002; Coventry *et al.* 2001; von Wilpert and Lukes 2003) with no effect on salinity being observed for soils receiving 20 t/ha of granite dust (Hinsinger *et al.* 1996).

It is thought that the increases of pH and EC for soils with added SRFs are essentially due to consumption of hydrogen ions during dissolution of the SRFs and the concomitant release of basic cations from the powders. Consequently plots of means of the increases of pH and EC versus the increase of EAC (CH_3COONH_4-extractable basic cations) (Figure 4.5) show that close relationships exist. The relationships are quite different for each SRF as the SRFs have different capability in increasing soil pH of soil-SRF mixtures and released different amounts of each element during dissolution.

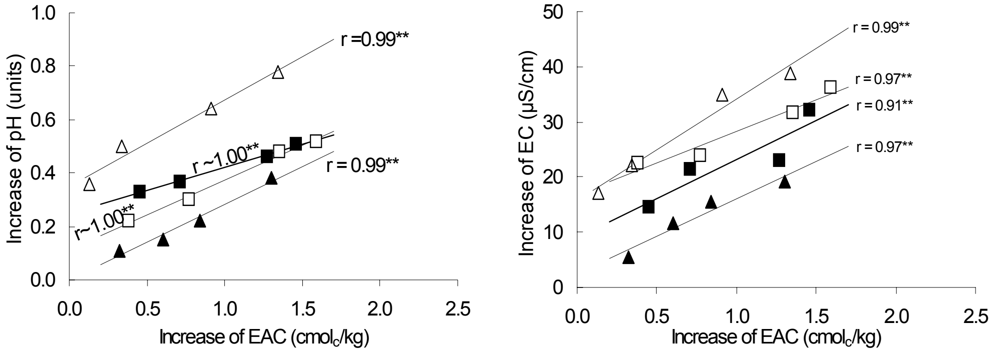


Figure 4.5. The relationships between mean values of the increases of pH and EC and the mean increase of exchangeable base cations (EAC) for 10 soils mixed with basalt (■), dolerite (□), gneiss (▲), and K-feldspar (Δ) SRFs milled for 0 (initial), 10, 60, and 120 min under dry condition.

4.3.3. Dissolution in Dilute Acetic-Citric Acid versus Dissolution in the Soil

Dissolution of the milled silicate rocks in dilute acetic-citric acid as discussed in Chapter 3 may be an indicator of fertilizer effectiveness as it provides an indication of the content of readily soluble material that will dissolve in soil. The relationships between the cumulative amount of alkali elements dissolved in dilute acetic-citric acid in 1 hour (E_{1H}), 1 day (E_{1D}), and 56 days (E_{56D}) may be related to the cumulative amount of those elements dissolved in soil in two months (E_{2M}) (Figure 4.6 based on mean values for 23 soils). An overview of statistical data for this relationship for the 23-indivual soils is given in Table 4.2. Dissolution trends for Ca and Mg, and for Na and K in both acetic-citric acid and soil are similar. For brevity, data for these similar elements are combined, i.e., (Ca + Mg) and (Na + K) in Figure 4.6 and Table 4.2.

The measures of dissolution in acetic-citric acid for different dissolution times are closely correlated with the proportion of basic cations dissolved in the soil (Figure 4.6). The extents of dissolution in the two media are different with dissolution of dolerite SRF in acid being about twice as great as in soil. For basalt, gneiss, and K-feldspar SRFs, the two measures are approximately equal for citric-acid extraction for 1 h which thus provides a fully quantitative prediction of dissolution in soil and is likely to be an effective predictor of the effectiveness of SRFs.

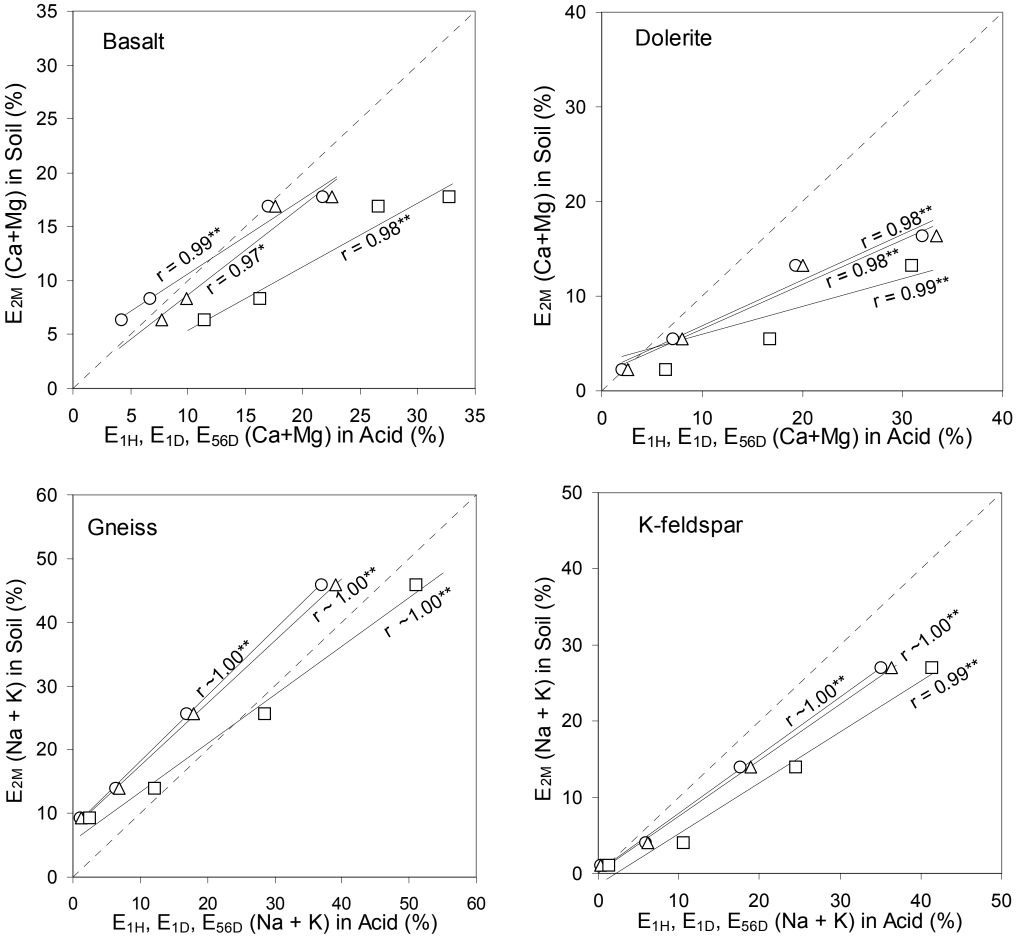


Figure 4.6. The relationships between mean quantities of basic cations from silicate rock powders dissolved in 23 soils after incubation for 2 months (E_{2M}) and quantities dissolved in 0.01*M* acetic-citric acid for 1 hour, 1 day and 56 days (E_{1H}, E_{1D}, and E_{56D}), designated respectively with r values for regression lines calculated from 4 (T0, T10, T60, T120) data points of ○, Δ and □ respectively.

The trends discussed above indicate that dissolution of SRFs in dilute acetic-citric acid can be used to predict dissolution in soil. Evaluation of this relationship for each of 23 soils (Table 4.2) shows that the correlation coefficient of this relationship for basalt SRF varies widely and is sometimes small (i.e., r = 0.45) but there is much less variation for dolerite, gneiss, and K-feldspar SRFs and values of correlation coefficient are much larger (i.e., r > 0.73). This anomalous behaviour for basalt may again reflect the tendency of basalt powder to agglomerate during prolonged milling, resulting in a reduction in surface area relative to unmilled material (Table 2.1) so that dissolution in soil may be restricted by inadequate exposure to soil solution and associated slow diffusion of dissolved ions to and from reacting surfaces.

Table 4.2. Distribution of the values of coefficient correlation (r) for the linear relationship between dissolution of basic cations from the SRFs in 0.01*M* acetic-citric acid for 1 hour, 1 day, and 56 days (E_{1H}, E_{1D}, and E_{56D}) versus the average dissolution that occurred in 23 soils for 2 months (E_{2M}).

SRF	Dissolution Variables	Distribution of r values				% soils with $r > 0.95$
		Max	Min	Mean	Sd	(significant at $p < 0.05$)
Basalt	E_{1H} v E_{2M}	1.00	0.51	0.85	0.16	35 %
	E_{1D} v E_{2M}	1.00	0.45	0.84	0.17	35 %
	E_{56H} v E_{2M}	1.00	0.48	0.84	0.15	30 %
Dolerite	E_{1H} v E_{2M}	1.00	0.74	0.95	0.06	70 %
	E_{1D} v E_{2M}	1.00	0.73	0.95	0.06	65 %
	E_{56H} v E_{2M}	1.00	0.78	0.96	0.05	78 %
Gneiss	E_{1H} v E_{2M}	1.00	0.93	0.99	0.02	87 %
	E_{1D} v E_{2M}	1.00	0.93	0.99	0.02	87 %
	E_{56H} v E_{2M}	1.00	0.93	0.98	0.02	91 %
K-feldspar	E_{1H} v E_{2M}	1.00	0.89	0.98	0.02	96 %
	E_{1D} v E_{2M}	1.00	0.89	0.98	0.03	96 %
	E_{56H} v E_{2M}	1.00	0.85	0.97	0.04	94 %

4.3.4. Dissolution of SRFs versus Soil Properties

Simple and multiple regression analyses were employed to identify relationships between the amounts of dissolved elements (Eo, E_{2M}, E_{10M}, $E_{0\text{-}2M}$, and $E_{2\text{-}10M}$ from the SRFs in soils and the soil properties listed in Table 4.1. The dissolved elements involved in the analysis are (Ca + Mg) for basalt and dolerite SRFs and (K + Na) for gneiss and K-feldspar SRFs.

Results of simple-linear regression (Table 4.3) indicate that soil properties which are significantly correlated to dissolution of SRFs in soil are commonly different for each SRF, milling time, and incubation period, with correlation coefficients (r) being mostly smaller in magnitude than 0.70. Thus single soil properties mostly indicate < 50 % of the variation in dissolution of basic cations from SRFs in the soils. No single soil property is highly predictive of dissolution in soils for any SRF, incubation time, or milling time.

Table 4.3. Soil properties with significant-linear bivariate relationships ($p < 0.05$) with dissolution of basic cations from the SRFs in 10 soils for each milling time. Dissolution is presented as % of (Ca + Mg) and (K + Na) dissolved in 10 soils relative to total content of these cations in SRF.

SRF (cations)	Dissolution (% of total)	Soil Properties (Correlation Coefficient)
Basalt (Ca + Mg)	Eo	% org. C (-0.45) only for T0
	E_{2M}	% sand (-0.48 to -0.67) and % clay (+0.44 to +0.62)
	$\Delta E_{0\text{-}2M}$	EC (+0.40 to + 0.62), CEC (+0.43 to + 0.48), % sand (-0.45 to -0.59), and % clay (+0.43 to +0.64)
	$\Delta E_{2\text{-}10M}$	% sand (-0.63) and % clay (+0.65) only for T60
Dolerite (Ca + Mg)	$\Delta E_{0\text{-}2M}$	% sand (-0.41 to – 0.53) and % clay (+0.48 to +0.52)
Gneiss (K + Na)	Eo	% sand (-0.41 to -0.53) and % clay (+0.48 to +0.52)
	E_{2M}	EC (+0.70 to +0.86), CEC (+0.45 to + 0.57), % sand (-0.52 to -0.59), and % clay (+0.43 to +0.62)
	$\Delta E_{0\text{-}2M}$	EC (+0.79 to +0.85), % sand (-0.50 to – 0.71), and % clay (+0.57 to +0.75)
K-feldspar (K + Na)	Eo	org C (+0.47 for T10 and +0.44 for T60)
	E_{2M}	pH_{H_2O} (-0.46 for T60 and -0.52 for T120), and org C (+0.43 for T0 and T10)
	E_{10M}	pH_{H_2O} (-0.62 to -0.82), EC (+0.70 to +0.83), CEC (+0.65 to +0.80), and exch. acidity (+0.69 to +0.93)
	$\Delta E_{0\text{-}2M}$	pH_{H_2O} (-0.44 only for T60)
	$\Delta E_{2\text{-}10M}$	CEC (+0.83) for T10, CEC (+0.91) and exch. acidity (+0.93) for T60.

The stepwise multiple regression method was employed to evaluate if incorporation of several variables improved the predictive relationships between dissolution of basic cations from the SRFs and soil properties. Values of dependent (E and ΔE) and independent (soil properties) variables were also incorporated as log and square root transformed values to test for non-linear relationships. Examples of results from multiple regression analysis expressed as predictive equations with coefficients of determination (R^2) > 0.50 are presented in Table 4.4.

Table 4.4. Multivariate equations relating dissolution of basic cations from SRFs to soil properties with the determination coefficient (R^2) > 0.50 for those relationships

SRF (Element)	Milling Time (min)	Equation		R^2
Basalt (Ca + Mg)	60	E_{2M} (%)	= 291 - 178[log(pH$_{H2O}$)] - 16[log(exch. Acidity, cmol$_c$/kg)] - 69[log(sand, %)]	0.55
	120	log E_0 (%)	= 3.9 - 0.67[log(exch. Na, cmol$_c$/kg)] - 2[log(sand, %)]	0.52
		E_{2M} (%)	= 158 - 76[loh(sand, %)] - 7[log(oxalate-extr. (Fe + Al + Si), %)]	0.53
		?$E_{0\text{-}2M}$ (%)	= 222-72[log(sand, %)] - 93[log(pH$_{H2O}$)]	0.71
Dolerite (Ca + Mg)	Initial	$\Delta E_{0\text{-}2M}$ (%)	= 81 − 40 [log(sand, %)] − 7 [org. C, %]	0.53
	10	$\Delta E_{0\text{-}2M}$ (%)	= 68 − 30 [log(sand, %)] − 1.3 [org. C, %]	0.52
		log[$\Delta E_{2\text{-}10M}$(%)]	= 1.1 − 0.01 [EC, μS/cm]	0.60
	Initial	$\Delta E_{0\text{-}2M}$ (%)	= 86 − 51 [log(sand, %)] + 10[log(org.C, %)]	0.61
Gneiss (K + Na)	Initial	$\Delta E_{0\text{-}2M}$ (%)	= 148 − 73 [log(sand, %)]	0.59
	10	E_{10M} (%)	= 76 − 9 [pH$_{H2O}$] − 4 [CEC, cmol$_c$/kg]	0.54
		$\Delta E_{2\text{-}10M}$ (%)	= − 0.5 + 0.5 log[CEC, cmol$_c$/kg]	0.78
	60	Eo (%)	= 50 + 26 [log(CEC, cmol$_c$/kg)] − 12 [pH$_{H2O}$]	0.52
		$\Delta E_{2\text{-}10M}$ (%)	= − 0.1 + 0.3 [exchange acidity, cmol$_c$/kg]	0.83
K-feldspar (K + Na)	120	Eo (%)	= 67 + 22 [log(CEC, cmol$_c$/kg)] − 12 [pH$_{H2O}$]	0.54
		E_{10M} (%)	= 44 + 0.3 [EC, μS/cm] - 0.8 [CEC, cmol$_c$/kg]	0.78
		$\Delta E_{2\text{-}10M}$ (%)	= 117 − 88 [ΔpH] + 21 [exchange acidity, cmol$_c$/kg]	0.82
		log$\Delta E_{2\text{-}10M}$ (%)	= 2.9 + 1.8 [ΔpH] + 0.1 [exchange acidity, cmol$_c$/kg]	0.75

In general there is no substantial improvement in the prediction of dissolution by use of relationships generated by multiple regression compared to the results for simple bivariate regression analysis, but a few quite predictive equations were generated. The variables % sand (negative) and % clay (positive) appear several times in both the bivariate and multivariate relationships. It appears that dissolution of ground silicate rocks is greater in clay rich soils. Both CEC and exchange acidity are positively related to the extent of dissolution of alkali elements from K-feldspar in soils. This outcome parallels that observed by Hughes and Gilkes (1994) who found only poorly predictive bivariate relationships between the percentage dissolution of rock phosphate in soil and single soil properties for 228 soils from south-western Australia. Multiple regression analysis indicated a combination of titratable acidity (positive) and % sand (negative) explained about 61 % of total variation in percentage dissolution of rock phosphate in soil. In the present work, exchange acidity (positive) and % sand (negative) also appear in several of the multivariate equations.

4.3.5. Percentage Dissolution versus SRF Properties

Simple bivariate regression was employed to identify relationships of properties of milled SRFs (i.e., median particle size (D_{50}), effective surface area (SA), and % amorphous constituents (AC)) with the % dissolution in soil of basic cations from the SRFs (Eo, E_{2M}, E_{10M}, $\Delta E_{0\text{-}2M}$ and $\Delta E_{2\text{-}10M}$) for each soil. As a summary of the results, the distribution of r values for relationships of the properties of milled rocks versus E_{2M} and $\Delta E_{0\text{-}2M}$ are presented in Table 4.5.

The values of the correlation coefficient for these bivariate relationships vary widely between different soils, and relationships are mostly not significant ($p > 0.05$). Thus these properties of SRFs are not sufficiently predictive of dissolution of basic cations in soil and can not provide the basis of a fertilizer testing procedure.

4.4. Conclusions

Milling increased dissolution of basic cations from SRFs in the soil, and this dissolution also increased the pH and EC of soil. The proportion of dissolved (Ca + Mg) for basalt and dolerite SRFs (T120) for a 10-month incubation in soil reached 18 %, and (K + Na) dissolution from gneiss and K-feldspar SRFs (T120) was about

Table 4.5. Distribution of values of correlation coefficient (r) for bivariate relationships between median particle size (D_{50}), effective surface area (SA) and amorphous constituents (AC) of milled rocks with dissolution (E_{2M} and $\Delta E_{0\text{-}2M}$) of basic cations (i.e., Ca + Mg for basalt and dolerite SRFs, K + Na for gneiss and K-feldspar SRFs) in each of 23 soils incubated for 2 months.

SRF		Dissolution[1]	Values of r			Soils with
Type	Properties	(% to total)	Max.	Min.	Mean[2]	r > 0.94 [3]
Basalt (Ca + Mg)	D_{50} (μm)	E_{2M}	- 0.94	- 0.33	- 0.61	None
		$\Delta E_{0\text{-}2M}$	- 0.99	- 0.02	+/- 0.42	1
	SA (m^2/g)	E_{2M}	- 0.99	- 0.52	- 0.85	8
		$\Delta E_{0\text{-}2M}$	- 0.99	- 0.07	+/- 0.54	1
	AC (%)	E_{2M}	+0.99	+0.38	+ 0.82	7
		$\Delta E_{0\text{-}2M}$	+1.00	- 0.04	+/- 0.62	4
Dolerite (Ca + Mg)	D_{50} (μm)	E_{2M}	- 0.90	- 0.53	- 0.70	None
		$\Delta E_{0\text{-}2M}$	- 0.92	+0.17	+/- 0.68	None
	SA (m^2/g)	E_{2M}	+0.94	+0.62	+ 0.84	None
		$\Delta E_{0\text{-}2M}$	+1.00	+0.14	+/- 0.68	3
	AC (%)	E_{2M}	+1.00	+0.82	+ 0.97	18
		$\Delta E_{0\text{-}2M}$	+1.00	- 0.02	+/- 0.77	7
Gneiss (K + Na)	D_{50} (μm)	E_{2M}	- 0.73	- 0.40	- 0.60	None
		$\Delta E_{0\text{-}2M}$	- 1.00	- 0.05	+/- 0.42	2
	SA (m^2/g)	E_{2M}	+0.70	+0.37	+ 0.57	None
		$\Delta E_{0\text{-}2M}$	+1.00	+0.02	+/- 0.41	2
	AC (%)	E_{2M}	+0.99	+0.72	+ 0.87	3
		$\Delta E_{0\text{-}2M}$	+0.99	+0.14	+/- 0.61	2
K-feldspar (K + Na)	D_{50} (μm)	E_{2M}	- 0.61	- 0.20	- 0.44	None
		$\Delta E_{0\text{-}2M}$	- 0.96	- 0.11	+/- 0.58	2
	SA (m^2/g)	E_{2M}	+0.80	+0.35	+ 0.66	None
		$\Delta E_{0\text{-}2M}$	- 0.98	+0.14	+/- 0.77	3
	AC (%)	E_{2M}	+0.95	+0.58	+ 0.84	2
		$\Delta E_{0\text{-}2M}$	- 0.96	+0.31	+/- 0.81	8

[1] E_{2M} and $\Delta E_{0\text{-}2M}$ respectively are amount of elements dissolved from the SRFs within 2 month incubation and that dissolved between 0 and 2 month incubations ($\Delta E_{0\text{-}2M} = E_{2M} - Eo$, where Eo is the amount of rapidly dissolved elements).

[2] Calculated from absolute values.

[3] Significant r values ($p < 0.05$).

40 %. Comparable results were obtained by Gillman *et al*. (2002) who added basalt dust (Ø < 150 μm) to lateritic soils at application rates up to 50 t/ha. This increased soil pH by about 0.2 – 1.0 units, and the dissolved base cations mostly represented less than 10 % of the added base cations. The extent of dissolution of the SRFs in soil may be quite accurately estimated by a one hour extraction in 0.01*M* acetic-citric acid. Neither SRFs nor soil properties were adequately predictive of the dissolution of alkali elements from the rocks in soil, and this is a similar conclusion

to that reached by Hughes and Gilkes (1994) for dissolution of rock phosphates in soils.

It is evident that milling can substantially increase the availability to plants of the basic cations in SRFs. This procedure may provide a basis for the manufacture of relatively low cost fertilizers. Fine-ground basalt and dolerite may be effective Ca and Mg fertilizers, and K-feldspar can be used as a K fertilizer, whereas gneiss may be less effective as a K fertilizer due to its low content of K. This work should be extended to the evaluation of SRF on diverse nutrient deficient soils and with diverse plant species that will enable the prediction of the agronomic effectiveness of SRFs for practical agricultural uses.

Chapter 5

A GLASSHOUSE EXPERIMENT

5.1. Introduction

Milling has been shown to greatly increase the release of plant nutrient elements from SRFs in chemical solutions and the soil environment. It is necessary, however, to evaluate SRFs in the soil-plant system to provide appropriate evidence of the effectiveness of SRF for agricultural purposes. Whether the SRFs act as nutrient sources and/or are general ameliorants of soil conditions remains unclear. Thus, a glasshouse experiment was conducted using several soils and SRFs, ryegrass was grown for one year as the indicator plant. Ryegrass was also used as the indicator plant for evaluation of the effectiveness of granite dust (Hinsinger *et al.* 1996) and high-energy milled silicate minerals (Harley 2002) as fertilizers assessed in a glasshouse.

The main objectives of this experiment were (1) to identify the effects of the applications of milled-SRF on the growth of ryegrass for several soils and (2) to compare the agronomic effectiveness of the SRF relative to standard fertilizers for the corresponding plant nutrients (Ca, Mg, and K)

5.2. Materials and Methods

5.2.1. Fertilizers

The initially milled basalt, dolerite, gneiss and K-feldspar as described in earlier chapters were further milled using a vertical stirred ball mill (attrition mill) for 1h under a dry condition. This milling time and conditions were based on the investigation of optimum milling procedures obtained from an earlier experiment (Chapter 2) (Figures 2.10 and 2.11), and dry milling was more effective and practical than wet milling.

The mill is constructed from stainless steel with effective volume of 7L. One kg of rock sample and 23 kg steel balls Ø 0.25″ were loaded and milled at a speed of 1500 rpm for 1 h. A salt (solid NaCl) washing (regrinding) of the milling machine was employed after each milling, and then the salt was removed by brushing and air blowing before the next rock sample was loaded.

5.2.2. Experimental Design

Four soils used in this experiment were from Walpole (WP-6), Margaret River (MR-5), Busselton (BSN-1), and Waroona (SCP-11), south-western Australia (numbers are for WA reference soil sites, McArthur 1991), and were chosen at the basis that laboratory measurements had shown that they dissolved added SRF. Soil WP-6 was presumed to be a Ca and Mg-deficient soil, MR-5 was Ca-rich soil, whereas BSN-1 and SCP-11 were K-deficient soils, based on interpretation to the values of exchangeable cations listed in Table 5.1. Three sets of experiment were prepared to provide the response curves of ryegrass to the application of Ca, Mg, and K in silicate rocks and reference fertilizers for corresponding nutrients (Ca, Mg, and K). The designs of experiments are as follows.

1. **Ca experiment**: the nutrient concerned was Ca, the SRFs were ground basalt and dolerite with a reference Ca fertilizer ($CaCl_2$), and the soils used were WP-6 and MR-5.
2. **Mg experiment**: the nutrient concerned was Mg, the SRFs were ground basalt and dolerite with a reference Mg fertilizer ($MgSO_4$), and the soils used were WP-6 and MR-5.
3. **K experiment**: the nutrient concerned was K, the SRFs were ground gneiss and K-feldspar with a reference K fertilizer (K_2SO_4), and the soils used were BSN-1 and SCP-11.

Three rates of each fertilizer and a control (zero rate) were applied in triplicates for each nutrient and soil. The maximum application rates of SRF were based on the amount of nutrient dissolved in 0.01*M* acetic-citric acid for the 60 minute-dry milled rocks as described in Chapter 3 (i.e., 12 % Ca and 25 % Mg dissolved from basalt and dolerite SRFs, 40 % K dissolved from ground gneiss, and 20 % K dissolved from ground K-feldspar). The 3 rates of application of SRFs were based on the maximum, ½ maximum, and ¼ maximum of these dissolution rates for each of the nutrients concerned. The amount of nutrients supplied in the SRFs and the rates of application of SRFs based on the above assumption are respectively presented in Tables 5.3 and 5.4. The basal fertilizer (Table 5.2, excluding treatment elements) (Harley, 2002) was applied to all pots.

For each pot, 1kg air-dried soil (< 2-mm) in a plastic bag was thoroughly mixed with the appropriate fertilizer, watered to field capacity with DI water, and

Table 5.1. Several properties of soils used for glasshouse experiment.

Soil Code	Classification [1]	pH (1 : 5)		EC	Exch. Cations (cmol$_c$/kg)			
		H_2O	$CaCl_2$	(µS/cm)	Ca	Mg	K	Na
WP-6	(Sider)aquod	4.0	3.8	71	0.55	0.61	2.14	0.18
MR-5	Rhodic Kandiudalf	5.6	4.3	65	2.57	0.57	2.15	0.15
BSN-1	Plinthic Eutrudox	5.7	4.8	57	1.27	0.75	0.78	0.09
SCP-11	Dystric Xeropsamment	6.1	5.0	21	3.84	0.71	1.08	<0.01

[1] Refers to (McArthur 1991).

Table 5.2. The rates of nutrients (mg element) added to soil (1 kg) as basal fertilizer (rates and source of nutrients were adapted from Harley 2002).

Nutrient	Luxury Level (mg/kg)	Source of Nutrient
N	23	NH_4NO_3
P	20	$Na_2HPO_4.7H_2O$
K	90	K_2SO_4
Ca	40	$CaCl_2.2H_2O$
Mg	2	$MgSO_4.7H_2O$
Cu	0.5	$CuSO_4.5H_2O$
Zn	1	$ZnSO_4.7H_2O$
Mn	2.6	$MnSO_4.H_2O$
Fe	2.6	$FeSO_4.H_2O$
Co	0.06	$CoSO_4.7H_2O$
Mo	0.08	$NaMoO_4.2H_2O$
B	0.12	H_3BO_3
S[1]	44.4 (a) 44.1 (b) 7.6 (c)	

[1] Total S was calculated from the sources of nutrient (salts) containing S: (a) was total S including all salts containing S, applied as basal fertilizer for Ca experiment, (b) was total S excluding S from $MgSO_4$, applied as basal fertilizer for Mg experiment, and (b) was total S excluding S from K_2SO_4, applied as basal fertilizer for K experiment.

placed in a nondraining plastic pot. The plastic bag was closed to prevent evaporation loss until seed sowing. After a week of equilibration, 15 seeds of ryegrass (*Lolium multiflorum* cv Richmond) were sown in each pot and 10 uniform plants were grown for 12 months (February 2002 – February 2003). During the experiment, the pots were randomized each fortnight within treatments for the same soil, and watered with DI water to maintain the soil water content at about field capacity. Nitrogen solution (NH_4NO_3) at 1/3 rate of basal N fertilizer was applied fortnightly for all pots, and complete basal fertilizer was applied after each harvest.

Table 5.3. Amounts of nutrient supplied by SRF based upon acetic-citric acid dissolution data and considered to be equivalent to a luxury nutrient supply.

SRF	Nutrient	Maximum Diss. (%)	Luxury Conc. in soil (mg/kg)	Element required for various proportions of maximum dissolution of SRF [1]		
				Max. diss. (mg/kg)	½ Max. diss. (mg/kg)	¼ Max. diss. (mg/kg)
(A)	(B)	(C)	(D)	(E)	(F)	(G)
Basalt	Ca	12	40	333	666	1332
Dolerite	Ca	12	40	333	666	1332
Basalt	Mg	25	2	8	16	32
Dolerite	Mg	25	2	8	16	32
Gneiss	K	40	90	225	450	900
K-feldspar	K	20	90	450	900	1800

[1] Total content of element (mg) in SRF to be added to 1 kg soil to reach the luxury concentration based on the proportions of maximum (Max.), a half of maximum (½ Max.), and a quarter of maximum (¼ Max.) dissolution listed. Values in column (E) = 100/(C) x (D) mg/kg; (F) = [100/(1/2 x (C))] x (D) mg/kg; (G) = [100/(1/4 x (C))] x (D) mg/kg.

Table 5.4. The amounts of SRF added to 1 kg of soil to supply the amounts of nutrients listed in Table 5.3.

SRF	Nutrient	SRF added to soil (g/kg)		
		Max. diss	½ Max. diss	¼ Max. diss
Basalt	Ca	4.44	8.88	17.76
Dolerite	Ca	4.16	8.32	16.64
Basalt	Mg	0.24	0.48	0.96
Dolerite	Mg	0.21	0.42	0.84
Gneiss	K	25	50	100
K-feldspar	K	5	10	20

The plants were harvested four times at intervals of 3 months by cutting the tops at about 1 cm above the soil surface, tops were oven-dried at 60^{o} C and weighed. Subsamples of plant tops were finely ground and analyzed for nutrient content (i.e., Ca, Mg, K, Na, Cu, Zn, Mn, Fe, Si, P, S, and Cl) using XRF (Phillips 1400) after pressing the sample into a boric acid backing at about 350 bar. After the end of experiment (12 months), a subsample of soil was taken from each pot, screened (< 2 mm) to exclude plant roots, and air dried at room temperature. Soil samples of the three replicates were combined and analyzed for pH, EC, and CH_3COONH_4-extractable elements (Ca, Mg or K) using the methods described in Chapter 4 section 4.2.2.

5.2.3. Analysis of Data

Analysis of variance was employed to evaluate the effects of application rate of SRFs and reference fertilizer on cumulative yield (oven-dried plant tops), cumulative uptake of nutrients concerned, and concentration of nutrients in dry tops for each nutrient source (fertilizer), growing period, and soil. The occurrence of deficiency and toxicity concentrations of nutrients in plant tops was identified using critical values of nutrient concentration in plant tops proposed by Pinkerton *et al*. (1997). Care should be taken in this interpretation, however, since these critical values were established based on concentrations of nutrients for various cultivars of ryegrass and for different growing conditions from those used in this research. For example, the critical levels of a nutrient may be shifted due to interactions with other elements (Munson, 1968) and may not be appropriate to the present experimental condition. It is also probable that these critical values are too high for nutrient efficient cultivar used in this experiment.

The agronomic effectiveness (AE) of SRFs relative to reference fertilizer was calculated using the values of cumulative uptake of the nutrient concerned. The value of nutrient uptake is a combined response of yield and nutrient concentration to the application of fertilizer, and thus was the preferred indicative measure of AE (Mackay *et al.* 1984). For the present experiment, moreover, total uptake of nutrient may be used to indicate the extent of release of the nutrient by dissolution of SRF in the soil. Principally, the relative agronomic effectiveness (RAE) of SRF was defined as the ratio of the effectiveness of SRF over that for the reference fertilizer. Different methods of RAE calculation were employed as were appropriate for the data provided by each experiment:

1. The RAE values for Ca and Mg experiments using soil WP-6 can not be defined due to most of the plants in these experiments dying.
2. For Ca and Mg experiments using soil MR-5, there was only minor effect of the application of Ca and Mg fertilizers on nutrient uptake so that response functions were poorly defined. The RAE (%) values were interpreted graphically based on the response curves, and are the ratio of the rate of SRF required to support 50 % of maximum cumulative uptake of the nutrient concerned (i.e., Ca for Ca experiment and Mg for Mg experiment) relative to the corresponding rate of reference fertilizer.

3. For K experiment, the RAE values were calculated based on the best fit equations describing response curves of cumulative K uptake as a function of the application rate of K fertilizers. The best fit equations for the response curves of K_2SO_4 (reference fertilizer) were linear, whereas those for SRFs were quadratic. If the rate for the $+K_2SO_4$ is extended to much higher than 90 mg K/kg, it will result a quadratic equation with the maximum K uptake achieved at a much greater rate than 90 mg K/kg. However, the maximum or half of maximum values of K uptake for the $+K_2SO_4$ treatment can not be defined based on its response curves obtained in this present research. Therefore, the RAE values for the K-SRFs were defined as the ratio of the slopes for the application rate of 90 mg K as K-SRF/kg (i.e., the highest rate of K for the $+K_2SO_4$ treatment).

The internal efficiency (IE) functions describing the effect of nutrient uptake on plant yield were obtained by plotting the value of yield (dry plant tops) versus the value of nutrient uptake for each harvest, and the IE coefficient is taken to be the slope of this relationship. The relative internal efficiency (RIE) was defined as ratio of the IE value for SRF to that for the reference fertilizer.

5.3. Results and Discussion

5.3.1. Plant Growth and Nutrient Uptake

Results of analysis of variance for effects of the application of fertilizers on cumulative plant yield (oven-dried plant tops) and cumulative uptake of nutrients concerned are presented in Appendix B1. The plots for mean values of these variables versus the application rates of Ca, Mg, and K fertilizers are presented in Figures 5.1 - 5.6.

Ca Experiment

There was a large response for plant yield and Ca uptake to the application of Ca as basalt and dolerite to soil WP-6 (Figure 5.1). Most of plants (> 95 %) grown on soil WP-6 for nil Ca (control) and $+CaCl_2$ treatments did not survive beyond early growth, so data for these treatments are not included in subsequent discussions. The response curves for the $+CaCl_2$ treatments to soil WP-6 presented in Figure 5.1 are for surviving plants (1 - 2 plants and only in one pot) for each application rate.

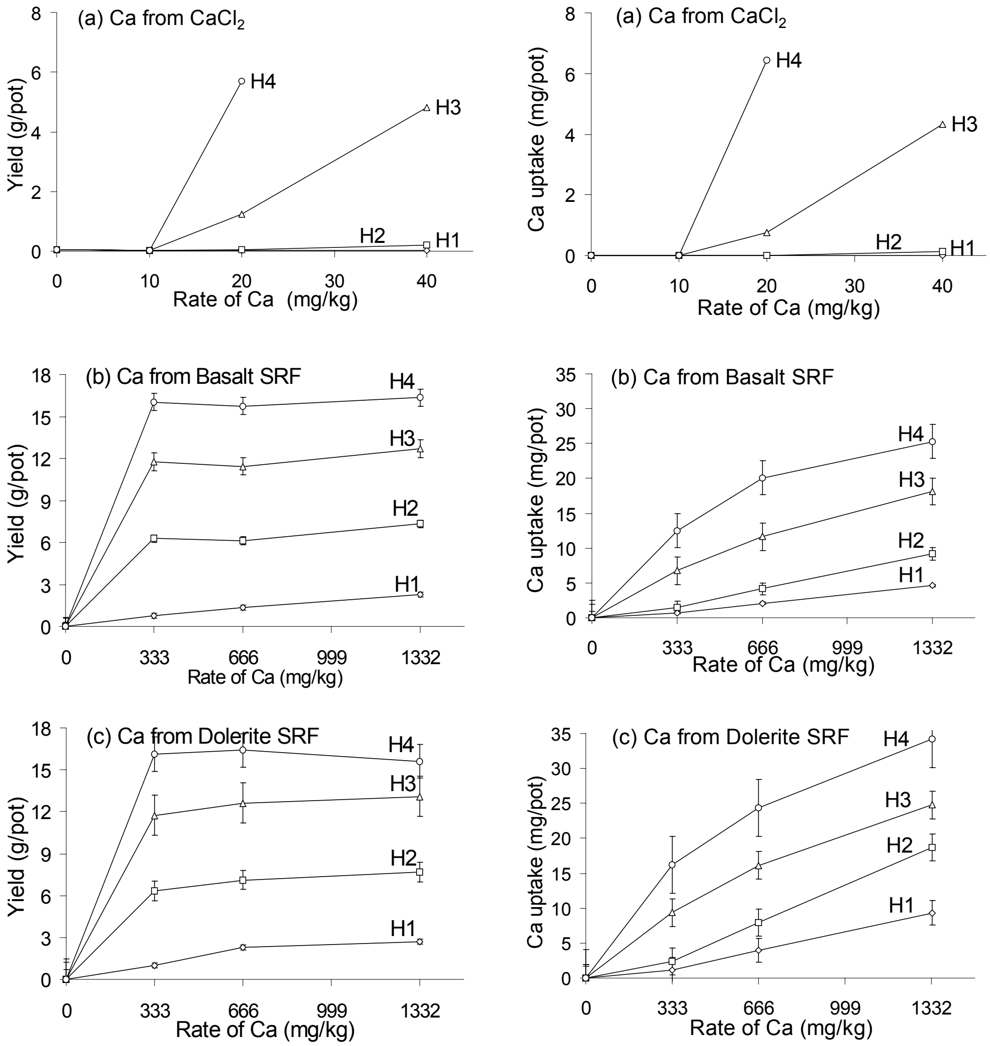


Figure 5.1. Effects of the application of Ca as $CaCl_2$, basalt SRF, and dolerite SRF on cumulative yield (oven-dried plant tops) and cumulative Ca uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) of ryegrass grown on soil WP-6. For the reference treatment (+$CaCl_2$) the amount of dry tops for H1 was too small for elemental analysis, and plants for the +40 mg Ca treatment died after H3, so that Ca uptake data for those treatments are not available. Error bars are the standard error of mean.

Plants grown on soil WP-6 were deficient in Ca with concentration of Ca in dry-plant tops for the +SRF treatments was about 0.1 - 0.2 % (see Appendix B4). However, the growth response of ryegrass for soil WP-6 may not simply reflect the response to the deficiency in Ca but instead be due to alleviation of the acidic soil reaction (Turner 1993) due to the liming effect of SRF. Ryegrass may grow on a variety of soil types and best growth is on soils with pH range between 5.5 and 7.0 (Valenzuela and Smith 2002) or 7.5 (Hannaway *et al.* 1999). At lower pH, Al toxicity may be a problem, while higher pH may promote chlorosis due to Fe and Mn deficiencies (Hannaway *et al.* 1999).

The initial pH of soil WP-6 was about 4.0, and application of basalt and dolerite SRFs increased the soil pH by about 0.4 – 1.0 units (see Figure 5.10), while soil pH was not increased by the +$CaCl_2$ treatment which may explain the mortality of plants for the +$CaCl_2$ treatment. It is probable that the large response of plants grown on soil WP-6 to the application of basalt and dolerite SRFs was mostly due to the liming effect rather than to the supply of Ca from SRFs.

For soil MR-5 (Figure 5.2), there was no to little responses in plant yield and Ca uptake to the application of Ca fertilizers, there were statistically significant effects for the +basalt SRF treatment on these plant variables (see Appendix B1). The initial amount of exchangeable Ca for soil MR-5 was relatively high, i.e., about 2.57 $cmol_c$/kg (≈ 514 mg/kg) and pH was about 5.6 (see Table 5.1). In this instance the liming effects of ground basalt and dolerite applications were small (i.e., increased soil pH by 0 - 0.4 units, see Figure 5.10) and the soil was not so acidic as to affect growth of ryegrass. Consequently the application of Ca as SRFs to soil MR-5 had little or no effect on plant growth.

In summary, the application of basalt and dolerite SRFs as Ca fertilizers at rates of about 4 – 16 g SRF/kg (≈ 333 – 1332 mg total Ca/kg) greatly increased cumulative yield and cumulative Ca uptake of ryegrass grown on an acidic and Ca-deficient soil WP-6, but these effects were absent or minor for plants grown on the less acidic and relative Ca-rich soil MR-5.

Mg Experiment

Most of plants grown on soil WP-6 for all treatments with Mg fertilizers did not survive. Thus, the effects of Mg fertilizers on cumulative yield and cumulative Mg uptake of plants for soil WP-6 can not be statistically determined. As mentioned in the discussion for Ca experiment, the main limiting factor for the growth of ryegrass on soil WP-6 was probably the very low soil pH. Application rates of basalt or dolerite SRF up to 0.96 g SRF/kg or 32 mg of total Mg/kg were too small to increase soil pH to the levels suitable for ryegrass (see Figure 5.11) which are 5.0 – 7.8 (Valenzuela and Smith 2002).

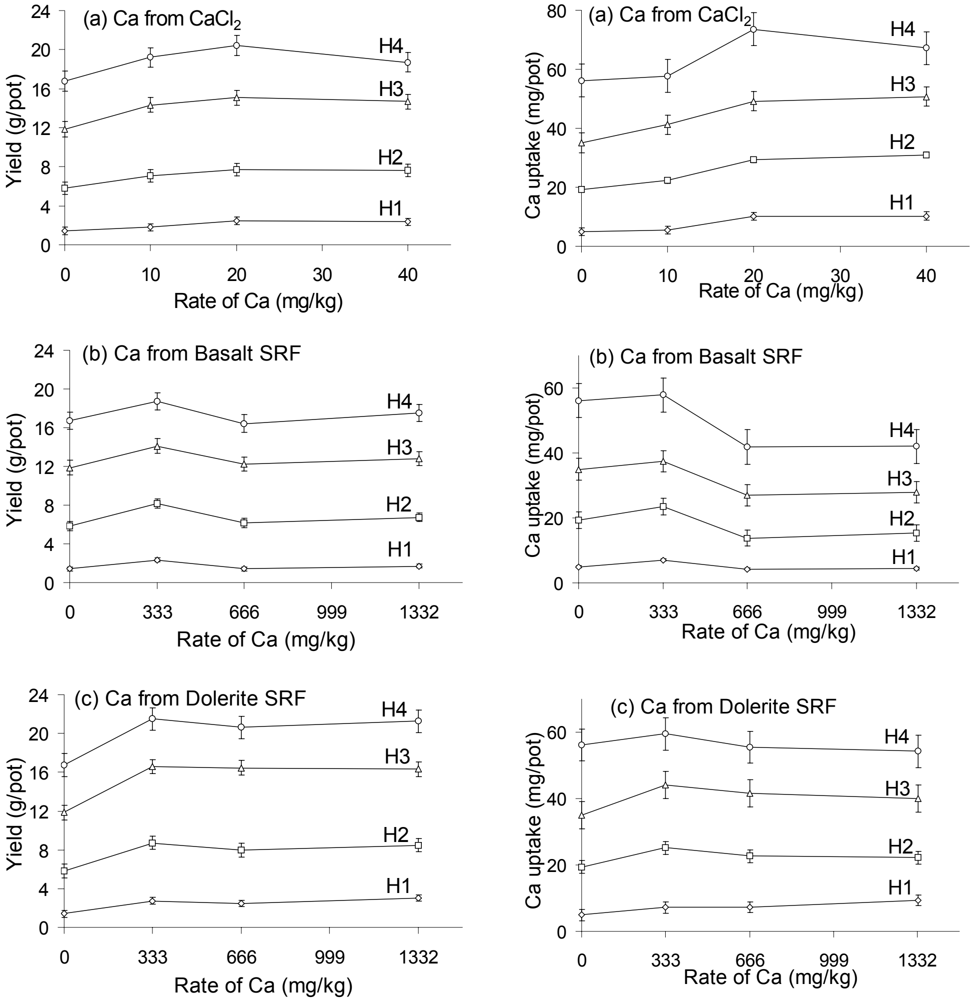


Figure 5.2. Effects of the application of Ca as $CaCl_2$, basalt SRF, and dolerite SRF on cumulative yield (oven-dried plant tops) and cumulative Ca uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) of ryegrass grown on soil MR-5. Error bars are the standard error of mean.

For soil MR-5 (see Figure 5.4), the application of Mg fertilizers had little or no effect on cumulative plant yield and cumulative Mg uptake. The exchangeable Mg for soil MR-5 at the commencement of the experiment was about 0.57 $cmol_c$/kg (≈ 114 mg/kg) (see Table 5.1) and this amount of Mg was sufficient for optimum growth of ryegrass for 12 months during which time the plants utilized about 70 mg Mg/pot (cumulative uptake for H4, Figure 5.4) or 61 % of the exchangeable Mg.

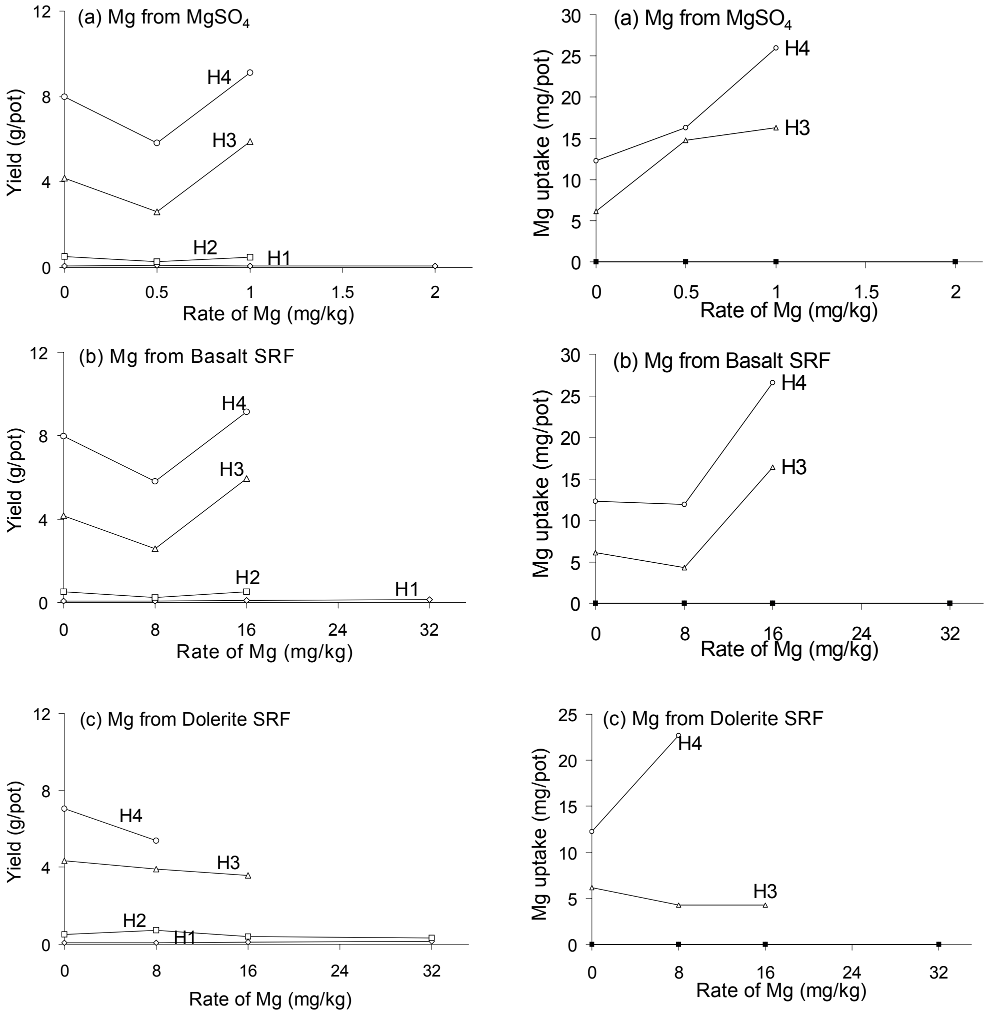


Figure 5.3. Effects of the application of Mg as $MgSO_4$, basalt SRF, and dolerite SRF on cumulative yield (oven-dried plant tops) and cumulative Mg uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) of ryegrass grown on soil WP-6. Most plants for this treatment died.

K Experiment

The plots of cumulative yield and cumulative K uptake versus the application rate of K fertilizers are presented in Figures 5.5 and 5.6. Ryegrass grown on soil BSN-1 and SCP-11 grew well for the first 3 months. However, K deficiency symptoms appeared after the first cut for the $+K_2SO_4$ treatment associated with low concentrations of K in dry tops (i.e., 0.1 – 0.4 %, see Appendix B12). For the +SRF treatments, values of cumulative K uptake for the first cut were about 3 fold larger than those for the $+K_2SO_4$ treatment. However, these high values of K uptake for

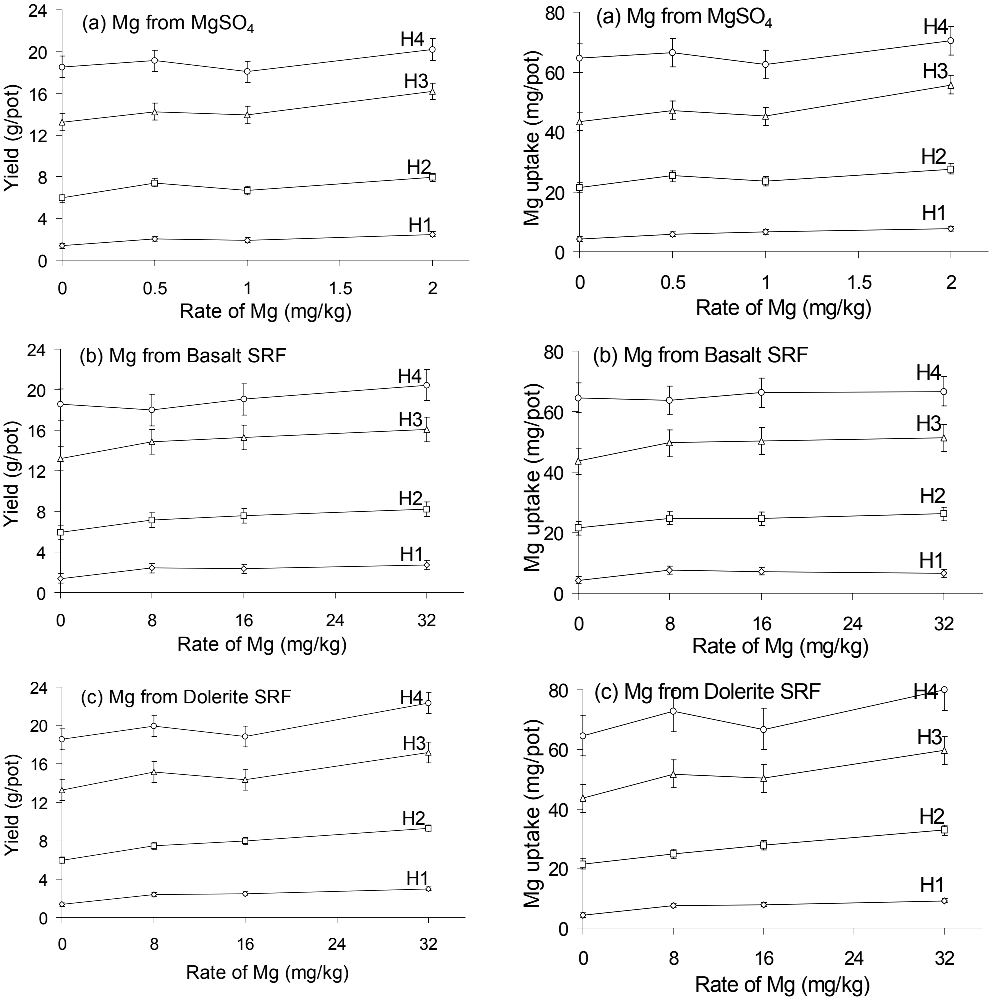


Figure 5.4. Effects of the application of Mg in forms of (a) MgSO$_4$, (b) basalt SRF, and (c) dolerite SRF on cumulative yield (oven-dried plant tops) and cumulative Mg uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) for ryegrass grown on soil MR-5. Error bars are the standard error of mean.

the +SRF treatment were not associated with large increases in yield as all the plants were K-sufficient.

As shown in Figures 5.5 and 5.6, for the first cuts there were only small increases in cumulative yield for all K fertilizers (not statistically significant for the +K-feldspar treatment, see Appendix B1). There were large increases in cumulative K uptake with increasing application rate of all K fertilizers, and for K_2SO_4 where about 50 % of added K was utilized by the plants. By the 2nd harvest (H2) for + K_2SO_4, most K had been utilized by plants so that there was little additional K uptake for H3 and H4. This was not the case for the two SRFs where additional K

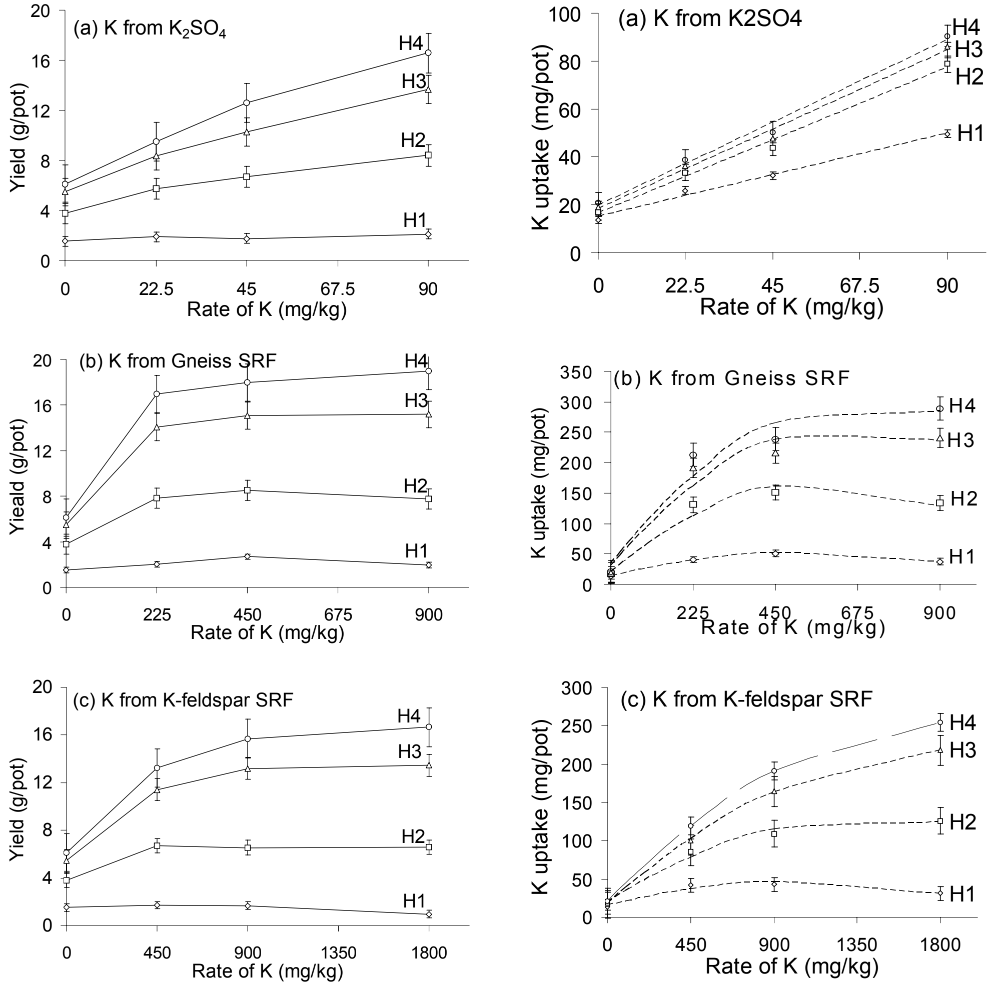


Figure 5.5. Effects of the application of K as K_2SO_4, gneiss SRF, and K-feldspar SRF on cumulative yield (oven-dried plant tops) and cumulative K uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) of ryegrass grown on soil BSN-1. The broken lines are drawn from best fit equations (Table 5.5) describing relationships between application rates of K fertilizers and cumulative K uptake. These lines were used to calculate the relative agronomic effectiveness (RAE) of SRFs (section 5.3.2). Error bars are the standard error of mean.

was utilized by plants for H2 – H4. In summary, application of silicate rock K-fertilizers increased plant yield and K uptake for ryegrass grown on soils BSN-1 and SCP-11 that were deficient in K (i.e., exchangeable K values were 0.78 and 1.08 $cmol_c/kg$ respectively, see Table 5.1).

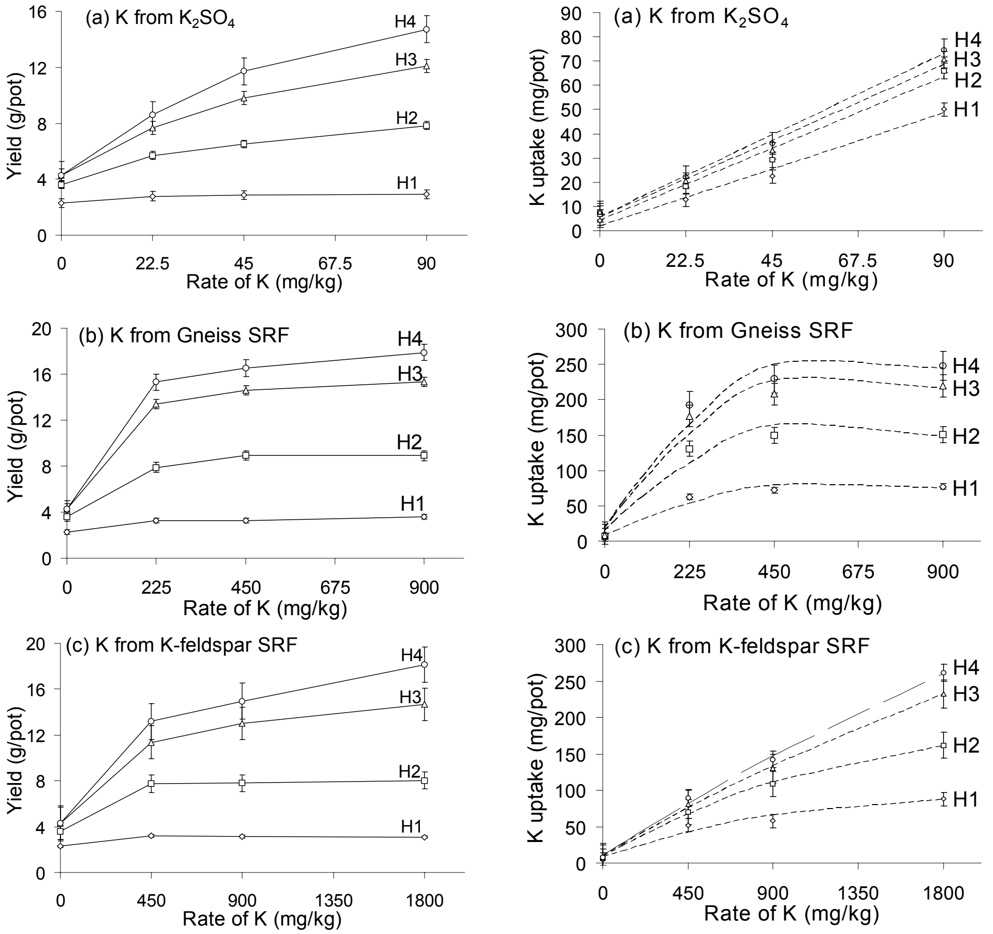


Figure 5.6. Effects of the application of K as K_2SO_4, gneiss SRF, and K-feldspar SRF on cumulative yield (oven-dried plant tops) and cumulative K uptake for the 1st, 2nd, 3rd, and 4th harvests (H1, H2, H3, and H4) of ryegrass grown on soil SCP-11. The broken lines are drawn from best fit equations (Table 5.5) describing relationships between application rate of K fertilizers and cumulative K uptake. These lines were used to calculate the relative agronomic effectiveness (RAE) of SRFs (section 5.3.2). Error bars are the standard error of mean.

5.3.2. Concentration of Plant Nutrients in Dry Tops

The application of SRFs may greatly affect concentrations of the major nutrients applied (Ca, Mg, and K), but may also affect the concentrations in plants of non treatment nutrients (Na, Cu, Zn, Mn, Fe, Si, P, S, and Cl). It is possible that these effects are due to pH change which may have caused plant nutrition disorders (deficiency or toxicity) in this experiment. The results of analysis of variance for effects of the application rate of fertilizers on concentrations of nutrients in dry tops of ryegrass are presented in Appendix B3.

For Ca experiment using soil WP-6, the effect of application of Ca as $CaCl_2$ on nutrient concentration in dry tops could not be identified due to insufficient data (most plants died). For the +basalt SRF and +dolerite SRF treatments, the concentration of Ca in dry tops of plants (for H1 – H4, Appendix B4) was doubled (i.e., from about 0.1 % to about 0.2 %) by increasing the application rate of Ca from 333 to 1332 mg/kg. Concentrations of Zn and Mn in dry tops of H2 – H4 increased by about 2 - 3 fold with the increase of application rates of Ca as basalt and dolerite SRFs. Concentrations of these nutrients reached very high levels, i.e., more than 20 and 200 mg/kg respectively for Zn and Mn, but were below toxic levels (< 40 mg/kg for Zn and < 1230 mg/kg for Mn) (Pinkerton *et al.* 1997). There was no simple trend in the concentration of other nutrients in dry tops in response to the application of Ca fertilizers.

For Ca experiment using soil MR-5, there was no significant effect of the application of Ca fertilizers on the concentration of nutrients in dry tops, except for the concentrations of Cl and Si. Concentration of Cl in dry tops of plants increased with increasing rate of $CaCl_2$ applied. Concentration of Si in dry tops (H1 – H4) receiving Ca as basalt and dolerite SRFs were 2 - 3 fold higher than for plants for the nil Ca or +$CaCl_2$ treatments. Presumably this was due to the large supply of soluble Si due to dissolution of these SRFs. For Mg experiment using soil MR-5, there was no significant effect of the application of Mg fertilizers on the concentration of nutrients in dry tops.

For K experiment, the concentration of K in dry tops of plants grown on soils BSN-1 and SCP-11 increased with increasing application rate of K fertilizers. For the +K_2SO_4 treatment, this effect occurred only for plant tops from H1 – H2, whereas for the +SRF treatments it occurred for H1 – H4. Concentrations of other nutrients (i.e., Ca, Mg, P, Cl, Cu, and Zn) in dry tops for most harvests decreased with increasing application rate of all K fertilizers. Antagonistic interactions of Ca and Mg with K have been reviewed by Munson (1968) and Marschner (1986) in which high concentrations of K inhibit the uptake and physiological availability of Ca and Mg for plants. The application rate of SRF as K fertilizers increased the concentration of Si in dry tops as a consequence of large amounts of Si released from these SRFs.

The great increase of plant-available Si in soils due to dissolution of SRFs indicates an advantage for the use of SRFs for plants that required Si (e.g., grasses). Large amounts of plant-available Si in soil may stimulate plant growth and the quality of plant products (Epstein 1999), reduce toxicity effects of Mn (Marschner 1986) for several plant species, reduce Al-induced inhibition of corn roots (Ma *et al.* 1996; Corrales *et al.* 1997), and increase resistance of plants to the attack of several pathogens (Volk *et al.* 1958). Coventry *et al.* (2001) associated the beneficial effects of plant-available Si from application of Minplus^{TM} (crushed basalt) to the reduction of Al toxicity in acidic soils.

Nutrient deficiency or toxicity in the ryegrass was identified by comparing the concentration of nutrients in dry tops to the critical values proposed by Pinkerton *et al*. (1997) (Appendix B4 – B12). Concentration of P in dry tops of ryegrass from the present experiment was generally lower than the P-deficient level (0.13 %) proposed by Pinkerton *et al*. (1997), except for most plants grown on soil SCP-11. However, there were no foliar symptoms of P-deficiency as described by Turner (1993). The low P concentration in dry tops may be partly due to insufficient supply of P in soils which was supplied as basal fertilizers, but other workers (Hinsinger *et al.* 1996; Pal *et al.* 2001; Harley, 2002) have used the same basal P application rate or similar soils for growing ryegrass and have not reported P deficiency. Andrew and Robin (1971) found that native grass taken from low P soils was less responsive to application of P compared to grasses from other soils. The ryegrass used in this experiment is a high P efficient cultivar (*Lolium multiflorum* cv Richmond) that was developed for use for the highly P deficient soils in south-western Australia, so that a lower critical level is appropriate (but unknown). This explanation is consistent with the observation that the highest yields in this experiment were provided by plants grown on soil MR-5, but these plants had low concentrations of P (< 0.1 %) in dry tops.

The plants grown on soil WP-6 receiving Ca as basalt and dolerite applications were deficient in Ca during 12 months of growing periods (see Appendices B4 – B5). In addition, the plants for H2 and H3 were also deficient in Cu (< 4 mg/kg). It was observed that the plants growing on soil WP-6 were shorter with thicker leaves than plants growing on soil MR-5. Concentration of nutrients in dry tops of plants growing on soil MR-5, including those for the controls, +Ca and +Mg fertilizer treatments (Appendixes B4 – B7) were at adequate levels.

For K experiment, the plants grown on soils BSN-1 and SCP-11 were mostly deficient in K (Appendices B10 and B12) after the first 3 months (H2 - H4). This nutritive disorder was accompanied by high concentrations of Na (i.e., > 1.5 % for the nil K treatment) and Cl (i.e., > 2 % for the +K-feldspar SRF treatment) in plant tops. Yellowish-green leaves which is a typical symptom of K deficiency (Turner 1993; Grundon *et al.* 1997) were common for plants in experiment C, and were associated with chlorosis which might be due to Na toxicity (Pinkerton *et al.* 1997). These nutritive disorders were so severe that after the 3rd harvest the plants grown on the nil K (control) soil SCP-11 died. The replacement of K by Na in plant tops was observed by Marschner *et al.* (1981) for sugar beet, and this mechanism was apparent in this present experiment (see Appendices B9 and B11 for the nil K and +K_2SO_4 treatments) so that plants severely deficient in K had higher concentrations of Na in their tops.

In summary of this review of the general nutrition status of the experimental plants, the application of SRFs increased concentrations of the nutrients applied in dry tops of ryegrass grown on soils which were deficient in the test nutrients. Plant response was sometimes associated with either a decrease or increase in the concentration of other nutrients which sometimes extended to nominally deficient or toxic levels.

5.3.3. Relative Agronomic Effectiveness (RAE) of SRFs

Although plants on soil WP-6 responded well to the application of Ca as basalt and dolerite SRFs, no RAE values could be calculated due to the death of most plants supplied with the reference ($CaCl_2$) fertilizer. The application of Ca and Mg fertilizers to soil MR-5 had minor effects on nutrient uptake so that response functions were poorly defined. Based on Figures 5.3 and 5.5, the RAE values for basalt and dolerite as Ca and Mg fertilizers were about 6 %.

These SRFs act more as liming materials than as Ca or Mg fertilizers for plant growing on acidic soils (e.g. soil WP-6 with pH about 4.0), but these effects were minor for plant growing nearly neutral and Ca-rich soil (e.g., soil MR-5 with pH about 5.6). The best growth of ryegrass is on soils with pH range of 5.5 – 7.5 (Hannaway *et al.* 1999; Valenzuela and Smith 2002).

Table 5.5. The best fit equations describing relationships between cumulative uptake of K (Y, mg K/kg) and application rate of K fertilizers (X, mg K/kg) and RAE values. The RAE value is defined as ratio of slope of the equation for SRF relative to that for K_2SO_4 at the application rate (X) of 90 mg K/kg.

Fertilizer	Harvest	Equation	RAE (%)
		Soil BSN-1	
K_2SO_4	H1	$Y = 15.1 + 0.39 X$ ($R^2 = 0.99$)	100
	H2	$Y = 16.6 + 0.68 X$ ($R^2 = 1.00$)	100
	H3	$Y = 18.2 + 0.74 X$ ($R^2 = 0.99$)	100
	H4	$Y = 19.9 + 0.77 X$ ($R^2 = 1.00$)	100
Gneiss	H1	$Y = 14.1 + 0.14 X – 129\ 10^{-5} X^2$ ($R^2 = 1.00$)	43
	H2	$Y = 20.3 + 0.50 X – 425\ 10^{-5} X^2$ ($R^2 = 0.96$)	86
	H3	$Y = 30.4 + 0.70 X – 519\ 10^{-5} X^2$ ($R^2 = 0.95$)	107
	H4	$Y = 34.3 + 0.75 X – 526\ 10^{-5} X^2$ ($R^2 = 1.00$)	110
K-feldspar	H1	$Y = 15.5 + 0.06 X – 289\ 10^{-5} X^2$ ($R^2 = 0.92$)	17
	H2	$Y = 19.8 + 0.15 X – 521\ 10^{-5} X^2$ ($R^2 = 0.99$)	24
	H3	$Y = 18.3 + 0.21 X – 558\ 10^{-5} X^2$ ($R^2 = 1.00$)	30
	H4	$Y = 20.1 + 0.25 X – 666\ 10^{-5} X^2$ ($R^2 = 1.00$)	34
		Soil SCP-11	
K_2SO_4	H1	$Y = 2.1 + 0.52 X$ ($R^2 = 0.99$)	100
	H2	$Y = 4.1 + 0.66 X$ ($R^2 = 0.99$)	100
	H3	$Y = 5.4 + 0.70 X$ ($R^2 = 0.99$)	100
	H4	$Y = 5.9 + 0.74 X$ ($R^2 = 0.99$)	100
Gneiss	H1	$Y = 7.8 + 0.24 X – 185\ 10^{-5} X^2$ ($R^2 = 0.95$)	53
	H2	$Y = 14.5 + 0.52 X – 412\ 10^{-5} X^2$ ($R^2 = 0.95$)	90
	H3	$Y = 17.8 + 0.71 X – 548\ 10^{-5} X^2$ ($R^2 = 0.96$)	116
	H4	$Y = 18.4 + 0.78 X – 588\ 10^{-5} X^2$ ($R^2 = 0.96$)	119
K-feldspar	H1	$Y = 8.2 + 0.08 X – 225\ 10^{-5} X^2$ ($R^2 = 0.95$)	17
	H2	$Y = 8.3 + 0.14 X – 327\ 10^{-5} X^2$ ($R^2 = 0.99$)	23
	H3	$Y = 9.9 + 0.15 X – 158\ 10^{-5} X^2$ ($R^2 = 1.00$)	22
	H4	$Y = 10.6 + 0.17 X – 150\ 10^{-5} X^2$ ($R^2 = 1.00$)	23

The best fit equations describing response curves for cumulative K uptake versus application rate of K fertilizers with their values of RAE are presented in Table 5.5. As shown in this table, gneiss was about half as effective as K_2SO_4 for growing ryegrass up to 6 months (H1 – H2), but was slightly more effective for plants harvested at 9 and 12 months (H3 – H4). This interpretation should be treated with some caution as the plants supplied with K_2SO_4 had removed most (≈ 3/4) of applied K from soil by H2. K-feldspar was much less effective than K_2SO_4 for all growth periods.

5.3.4. Internal Efficiency (IE) of Nutrient Elements

Various confounding effects may occur when comparisons are made between fertilizers of quite different composition and particularly for fertilizers that provide several nutrient elements, dissolve at very different rates and which may have various liming effects. One way of testing data for the presence of these confounding effects is to determine if plant yield and plant nutrient (test nutrients) content data conform to a single curve (relationship) for all the fertilizers under comparison. These relationships are often called 'internal efficiency' (Yang *et al.* 2003; Pathak *et al.* 2003) or 'physiological efficiency' (Sahrawat *et al.* 1997) curves as they provide an indication of the efficiency with which increments of nutrient uptake (content) produce increments of plant growth (response). The trends in IE were identified by plotting the yield of dry shoot versus uptake of nutrient concerned for each growing period (H1 – H4), and plots are presented in Figures 5.7 – 5.9. The plots for experiments A (using soil MR-5) and B (using soils WP-6 and MR-5) were excluded from this analysis due to the minor response of plants to applications of fertilizers.

The slopes of these plots indicate the values of the parameters IE as defined in this thesis, and these values (as indicated in Figures 5.8 and 5.9) change with application rate of fertilizers. To provide appropriate estimates for relative internal effectiveness (RIE) of SRF over that of the reference fertilizer (only for K experiment), the IE value for K_2SO_4 was defined as the mean IE values for the application rates of 0 (control) to 90 mg K/kg soil (e.g., the slopes of broken lines shown in Figures 5.8 and 5.9), whereas the IE value for SRF was defined as the initial slope of the curve for application rates of 0 (control) to 225 mg K as gneiss

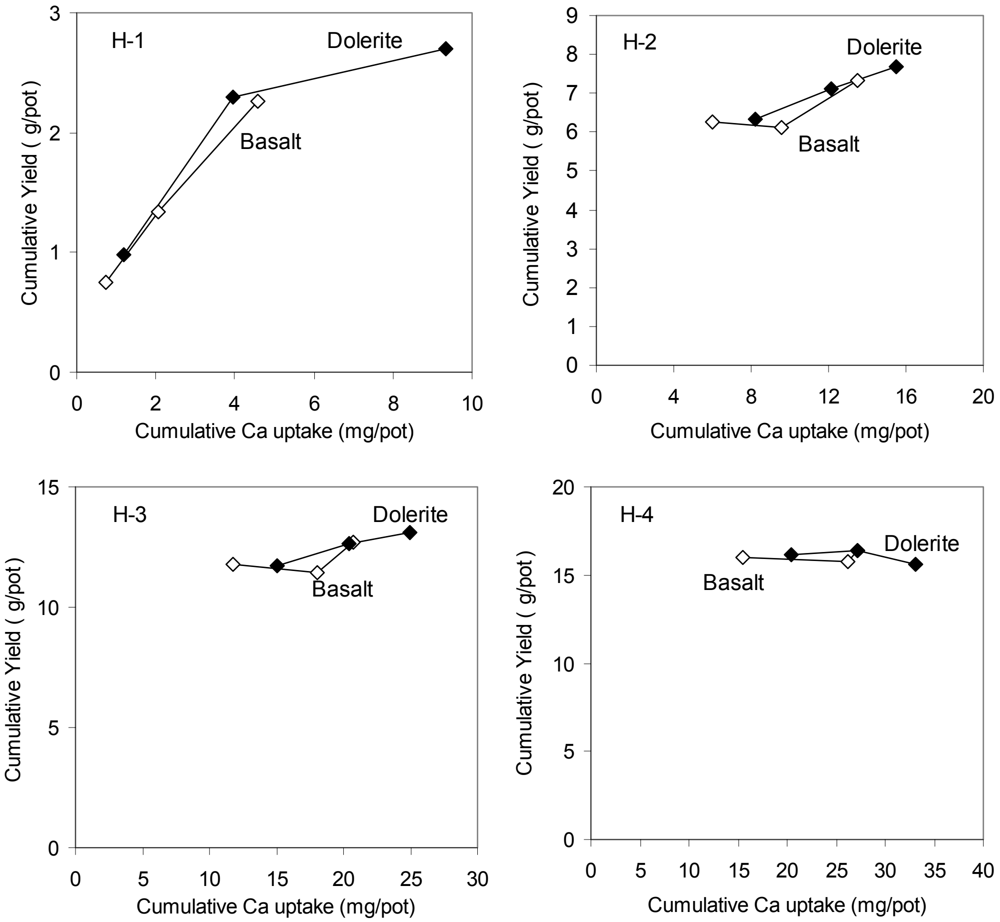


Figure 5.7. Plots of yield versus Ca uptake for each harvest (H1 – H4) of plants grown on soil WP-6 receiving Ca fertilizers (Ca experiment). The plots for nil Ca and +$CaCl_2$ was not presented due to insufficient data (most plants for the nil Ca and +$CaCl_2$ treatments dead).

SRF/kg soil and to 450 mg K as K-feldspar SRF/kg soil. The IE values for K experiment are presented in Table 5.6.

As shown in Figure 5.7, the IE values of H1 for basalt and dolerite SRFs were similar, which was about 0.4 (g dry tops/mg Ca uptake), and IE tends to decrease with increasing application rate of the Ca fertilizers. The IE values for H2 – H4 were about zero to negative, indicating that for applications of basalt and dolerite SRFs at rates greater than 333 mg Ca/kg soil to soil WP-6 increased Ca uptake but did not increase yield H2 – H4 (see Figure 5.1).

As discussed in earlier sections, the main limiting factor for plant growth on soil WP-6 was the low pH of the soil rather than it being deficient in Ca. Some of the applied basalt and dolerite SRFs may have rapidly dissolved releasing about

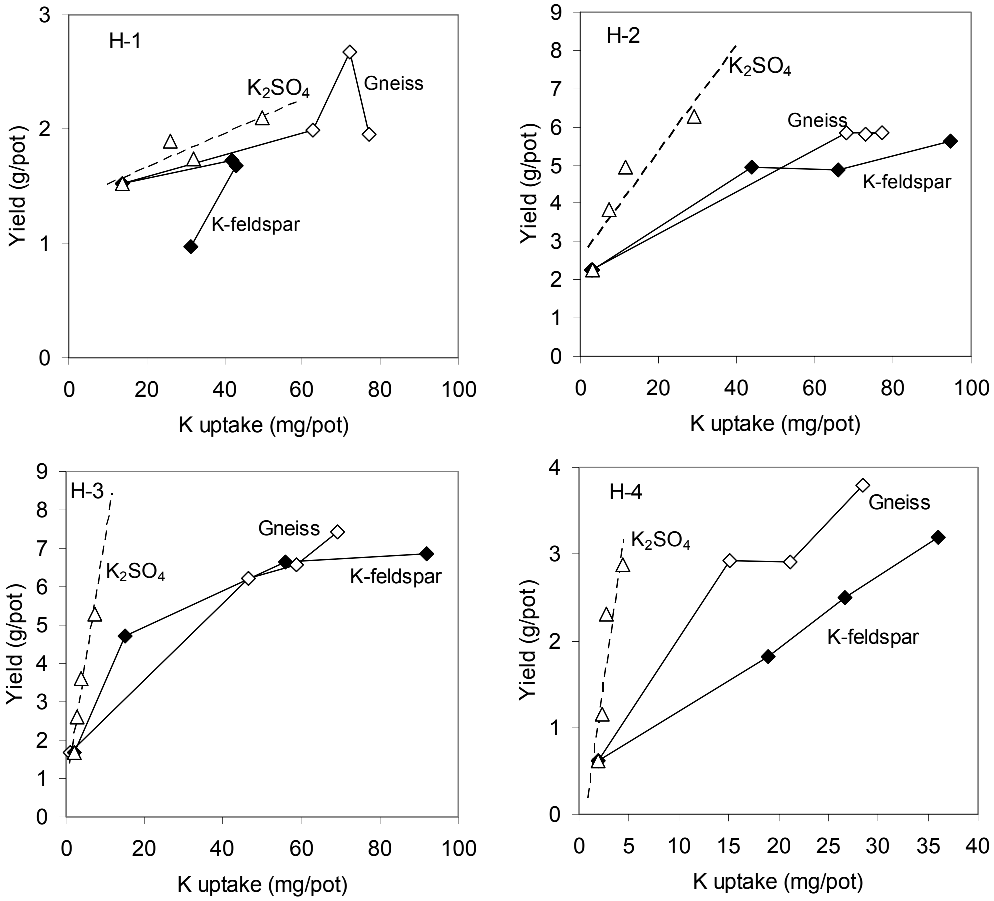


Figure 5.8. Plots of yield versus K uptake of each harvest (H1 – H4) for plants grown on soil BSN-1 receiving K fertilizers.

10 % of total Ca (see Figure 4.1, Chapter 4) during the first 3 months while also increasing soil pH. For a longer growing period, more Ca was released from Ca-SRF which was associated with an increase in soil pH which may also have increased microbial activity and released initially soil-fixed Ca (e.g., OM-Ca) to plants (Gillman 1980). Consequently, a large amount of Ca was taken up by plants. This large Ca uptake, however, did not increase plant yield which actually decreased, which was probably due partly to the confounding effect of SRF reducing Cu uptake to deficient level (see section 5.3.2.).

For K experiment (see Figures 5.8 - 5.9 and Table 5.6), the IE values for H1 are in the order gneiss $\geq$ K_2SO_4 > K-feldspar (BSN-1) and K-feldspar $\geq$ gneiss > K_2SO_4 (SCP-11). With increasing growing period, the IE values for K_2SO_4 become much higher than for both K-SRFs.

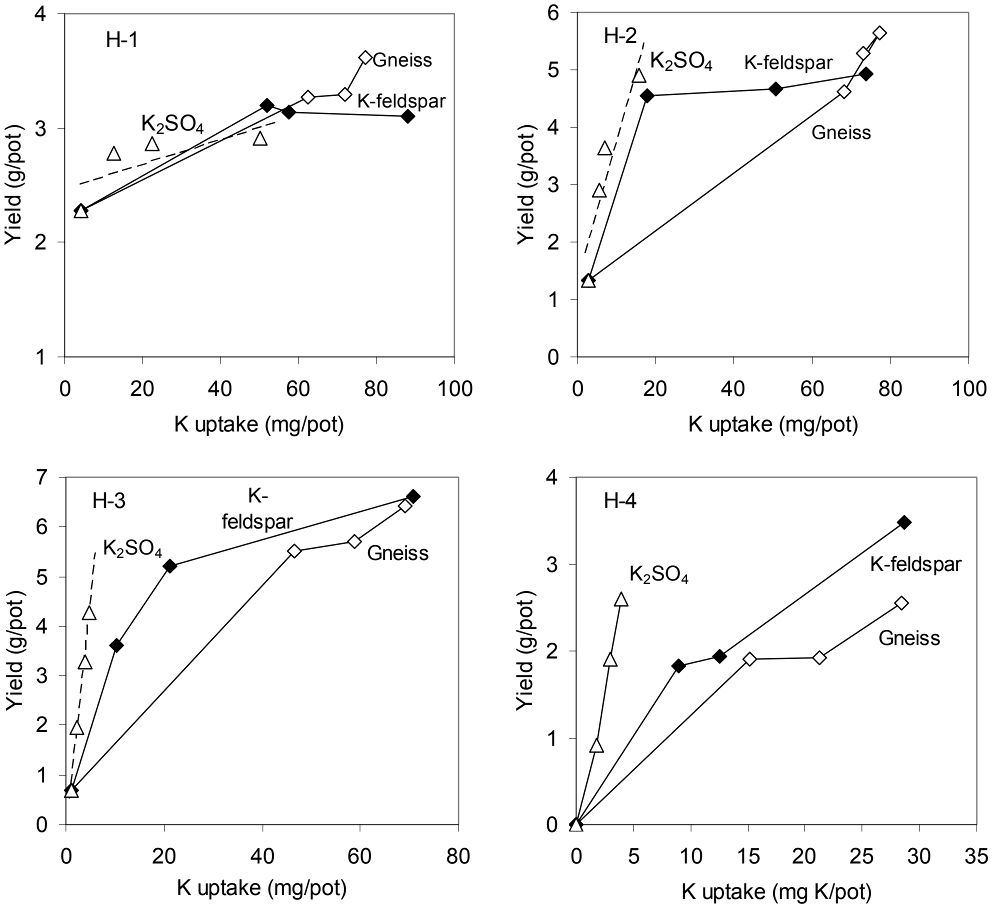


Figure 5.9. Plots of yield versus K uptake of each harvest (H1 – H4) for plants grown on soil SCP-11 receiving K fertilizers.

Table 5.6. Internal efficiency (IE) and relative internal efficiency (RIE) for application of K fertilizers calculated based on initial slope of response curves in Figures 5.8 and 5.9.

Harvest	IE (g dry shoot/mg K uptake)			RIE (%)		
	+K_2SO_4	Gneiss	K-feldspar	+K_2SO_4	Gneiss	K-feldspar
			SoilBSN-1			
H1	0.0148	0.0174	0.0072	100	118	49
H2	0.1025	0.0548	0.0668	100	53	65
H3	0.5570	0.0998	0.2313	100	18	42
H4	0.8550	0.1723	0.0695	100	20	8
			SoilSCP-11			
H1	0.0108	0.0170	0.0192	100	157	178
H2	0.2444	0.0502	0.2115	100	21	87
H3	0.9503	0.1061	0.3108	100	11	33
H4	0.6565	0.1251	0.2048	100	19	31

Values of IE are commonly used to provide information on the relative efficiency of genotypically different plants in utilizing a nutrient/fertilizer (Baligar *et al.* 2001; Yang *et al.* 2003; Pathak *et al.* 2003; Sahrawat *et al.* 1997), in which experiments the plants under comparison receive the same amounts of nutrient/fertilizer. In this present research, however, the same plants were grown, so the differences in IE values mostly reflect the external and sometimes confounding effects discussed above.

During the first 3 months, the plants grown on soils BSN-1 and SCP-11 were sufficient in K, so there was less response in plant yield to the application of K-fertilizers although there was an increase in K uptake (low IE values). For growing periods of 3 – 12 months, the plants receiving K_2SO_4 were severely deficient in K due to rapid depletion of K in the first 3 months so that the plants were highly responsive in yield to K uptake, thus the IE values increased with increasing growing period. In contrast, the plants receiving ground gneiss and K-feldspar applications were less severely deficient in K (for H2 – H4) due to additional K dissolving from applied K-SRFs during this growth period. Moreover, dissolution of K-SRFs produced a liming effect (increased soil pH) which may have increased the amount of K released from indigenous soil K reserves. In summary, the internal efficiency for K_2SO_4 was higher than for ground gneiss and K-feldspar applications for plants grown on soils deficient in K. This relatively lower IE values for K-SRF application was due to the large supply of K and the liming effect of the applied K-SRFs. Moreover, the confounding effects of K-SRF application including reduced uptake of several plant nutrients as discussed in section 5.3.2 may also have contributed to these low IE values.

5.3.5. Extractable Nutrients, pH, and EC of Residual Soils

The effects of silicate rock application on the soils used in this glasshouse experiment include changes in CH_3COONH_4-extractable nutrients, pH, and EC. The amounts of extractable nutrients in the soils at the end of experiment (= 12 month incubation), soil pH_{H_2O} and EC were determined and are plotted as functions of the application rate of fertilizers in Figures 5.10 – 5.12.

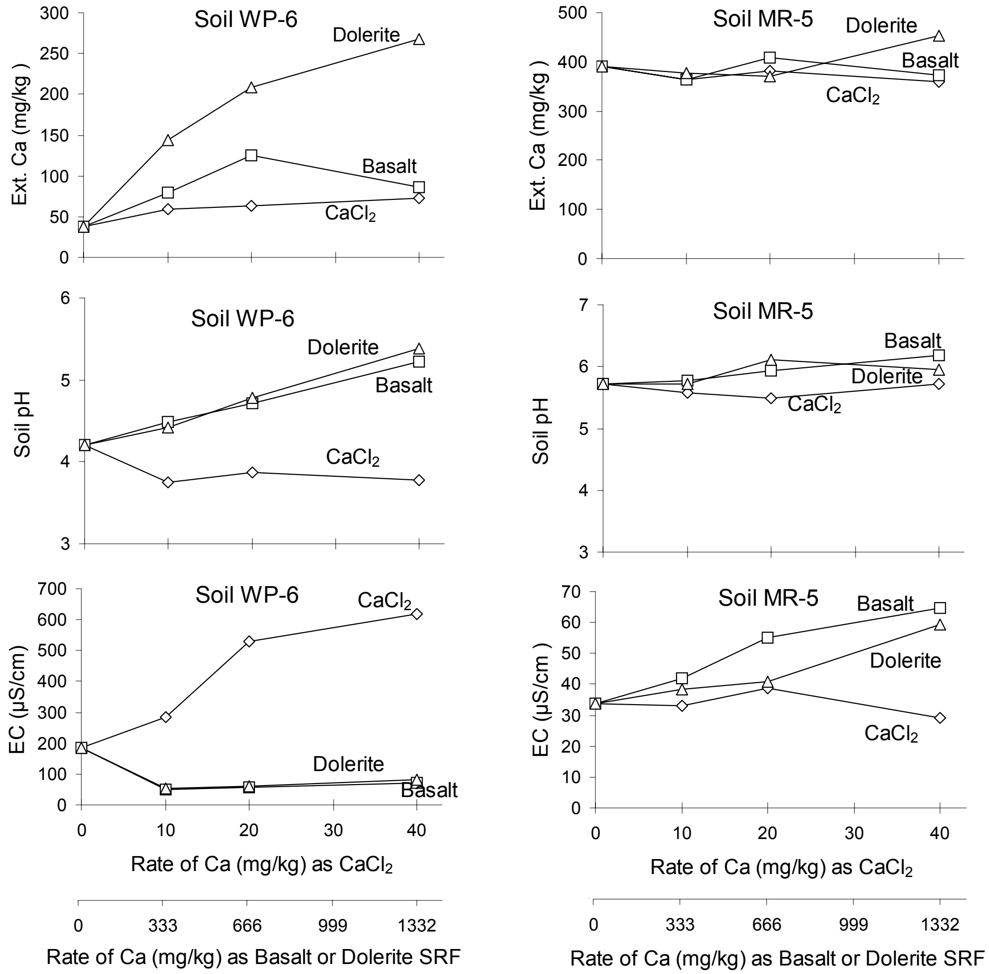


Figure 5.10. The amount of CH_3COONH_4-extractable Ca, pH and EC of soils WP-6 and MR-5 after the 4th harvest as affected by application rate of Ca fertilizers.

Extractable Nutrients

For Ca experiment with soil WP-6, the amounts of extractable Ca increased with increasing amounts of Ca fertilizers applied (Figure 5.10). The increases in extractable Ca were much larger for the +SRF relative to +$CaCl_2$ treatments but the application rates of $CaCl_2$ were much smaller. The plots of the increases in extractable Ca versus Ca applied are approximately linear so that the "relative effectiveness (RE)" values of the three Ca fertilizers can be calculated the initial slopes of these curves and are 100 % (for the +$CaCl_2$), 37 % (for the +dolerite SRF) and 15 % (for the +basalt SRF). The larger RE value for dolerite SRF relative to basalt SRF indicates greater dissolution of Ca from dolerite SRF than from basalt SRF in soil WP-6 during the 12 months of plant growth (discussed in section 5.3.6).

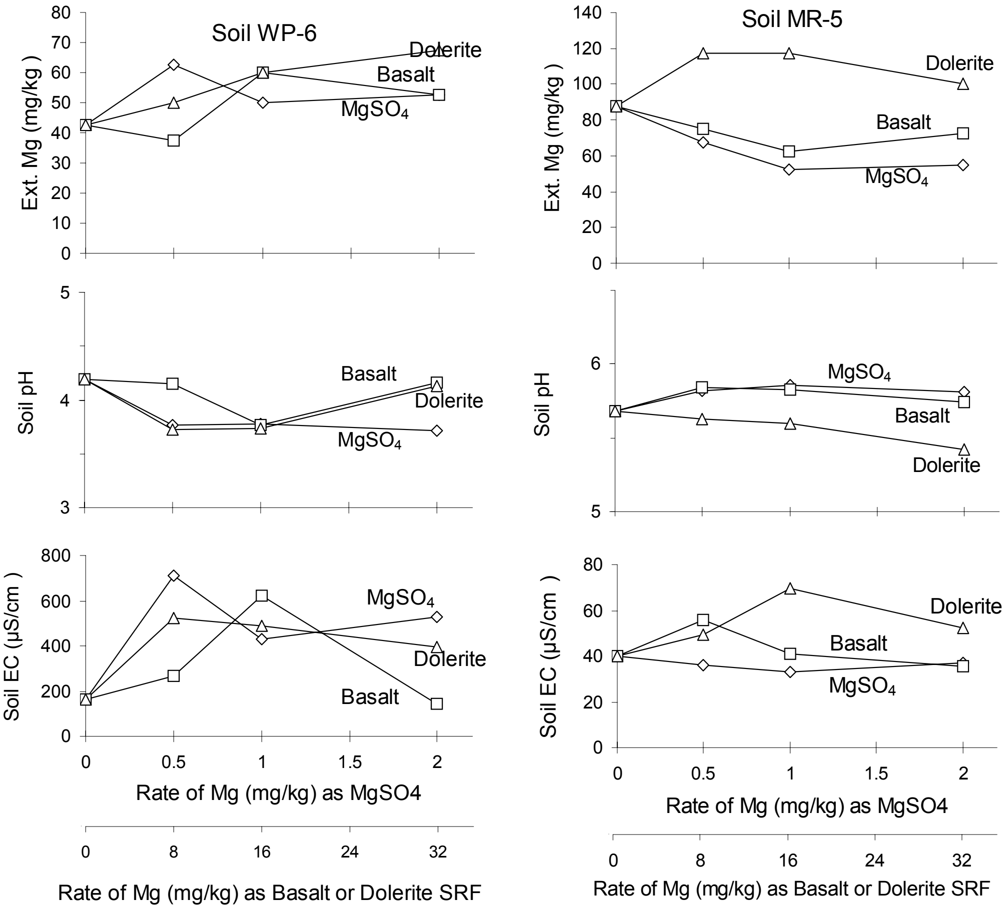


Figure 5.11. The amount of CH_3COONH_4-extractable Mg, pH and EC of soils WP-6 and MR-5 after the 4th harvest as affected by application rate of Mg fertilizers.

For Ca experiment with soil MR-5 there was no systematic effect of the application of Ca fertilizers on the amounts of extractable Ca in soil MR-5. There was no systematic effect of the application of Mg fertilizers on the amounts of extractable Mg in soils WP-6 and MR-5. Therefore, values of RE for the Mg fertilizers could not be determined.

The application of K as gneiss SRF greatly increased the amounts of extractable K in soils BSN-1 and SCP-11, there were smaller increases for K_2SO_4 and K-feldspar. The RE values calculated from initial slopes are in the order gneiss SRF (1170 %) > K_2SO_4 (100 %) > K-feldspar SRF (71 %) for soil BSN-1, and gneiss SRF (2960 %) > K_2SO_4 (100 %) > K-feldspar SRF (80 %) for soil SCP-11. The much greater RE values for gneiss SRF than for K-feldspar SRF are due to greater dissolution of gneiss than K feldspar SRF in the soils (see section 5.3.5).

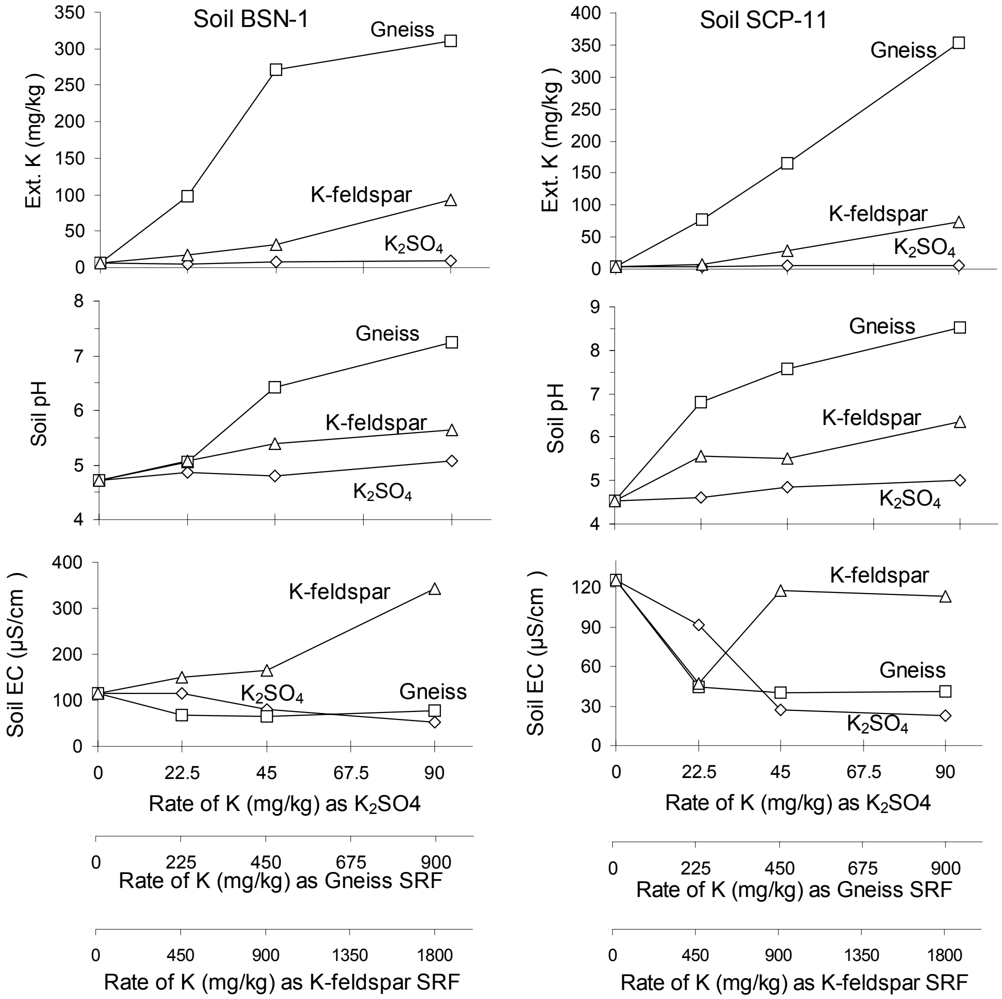


Figure 5.12. The amount of CH_3COONH_4-extractable K, pH and EC of soils BSN-1 and SCP-11 after the 4th harvest as affected by application rate of K fertilizers.

Soil pH

The applications of basalt and dolerite SRFs increased pH of soil WP-6 by about 0.2 – 1.0, whereas the application of $CaCl_2$ decreased pH of this soil by about 0.3 (Figure 5.10). There was a minor effect of the application of these Ca fertilizers on the pH of soil MR-5. Thus, the liming effects of these Ca-SRFs were greater for highly acidic soil WP-6 than for the less acidic soil MR-5. The apparent reduction in pH due to $CaCl_2$ addition for soil WP-6 is probably due to the “salt effect” on the activity (concentration) of H^+ in soil solution and the water extract (McLean, 1982) and does not indicate a real decrease in pH.

The application rates of Mg fertilizers were so low that their effect on soil pH at the end of experiment was minor. In marked contrast, the application of K as gneiss and K-feldspar SRFs greatly increased soil pH, whereas the application of K as K_2SO_4 did not affect soil pH. Soil pH increased by up to about 2.5 and 3.5 respectively for soils BSN-1 and SCP-11 receiving gneiss. The maximum increase of soil pH due to the K-feldspar was about 1.5 for both soils. However, the efficiency of K-feldspar SRF as a liming material (ratio of increase of soil pH/application rate expressed as unit mass of the SRF) was 2 – 5 times higher than that of gneiss SRF. These results are consistent with the findings of the laboratory experiments described earlier (see Figure 4.3 in Chapter 4).

Soil EC

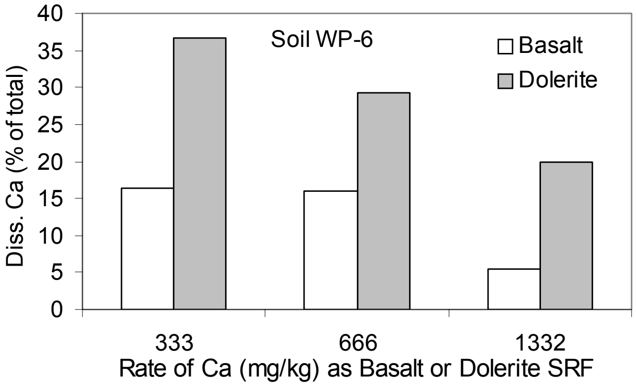
For experiment A with soil WP-6, the application of $CaCl_2$ increased the EC of soil by about 400 μS/cm, but the applications of basalt and dolerite decreased the EC of soil WP-6. Most plants grown on soil WP-6 receiving $CaCl_2$ did not survive so that $CaCl_2$ added to this soil and other soluble nutrients from basal fertilizers (added after each harvest) remained in the soil. Consequently, the EC of soil at the end of experiment for the $CaCl_2$ treatments increased greatly and was much higher than the soil EC for the Ca-SRF treatments. For soil MR-5, the application of Ca fertilizers had no or little effect on the EC of the soil. The applications of Mg fertilizers had no effect on the EC of soils WP-6 and MR-5.

For experiment C using soil BSN-1, the application of K as K-feldspar SRF increased soil EC by about 375 μS/cm, but there was no effect for gneiss SRF and K_2SO_4. The plants for the nil K treatment for soil SCP-11 did not survive after the 3rd harvest, so that the basal fertilizer salts added to the soil after the 3rd harvest remained in the soil causing a higher EC value (i.e., about 120 μS/cm) relative to initial EC value (i.e., 21 μS/cm, see Table 5.1) for soil SCP-11. In summary, the trends of EC values versus the application rate of K fertilizers for soil SCP-11 seem to be similar to those for soil BSN-1 as described above.

5.3.6. Quantity of Nutrients Dissolved from SRF in the Soil

To provide estimates of dissolution of SRFs in the soil which reflects the benefits of milling in improving the effectiveness of SRFs, two main assumptions were applied: (1) the amounts of plant-available nutrient initially in the soil for the control treatment were equal to the cumulative nutrient uptake (H4) +

CH_3COONH_4-extractable nutrient in soil at the end of experiment and (2) there was no fixation of nutrients (by soil) from applied fertilizers during the experiment. The calculation of the dissolved nutrients from SRFs is presented in Appendix B13, and the percentages of nutrient dissolved from SRFs are presented in Figure 5.13.



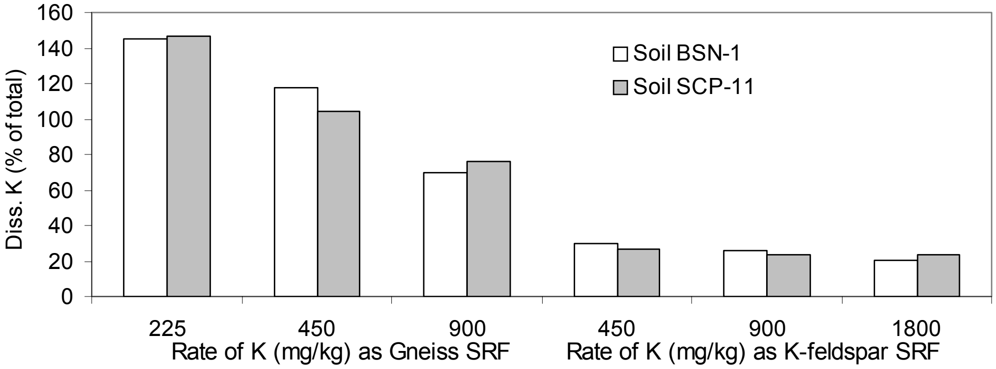


Figure 5.13. The percentages of dissolved Ca and K from SRFs in the soil for the glasshouse experiment of 12 months. Detailed calculations used to provide the values in this figure are presented in Appendix B13.

As shown in Figure 5.13, the percentage dissolution of applied nutrients from SRFs decreased but the quantities of dissolved nutrients increased (see Appendix B13) with increasing application rate. This decrease in percentage of nutrients dissolved from SRFs may be due partly to the increase of soil pH (liming effect). An identical result has been observed for rock phosphate (RP) fertilizer (Kanabo and Gilkes 1988) where the increase in pH and decrease in exchangeable acidity due to initial dissolution of RP decreases the subsequent dissolution of RP. This negative feed back mechanism does not operate for potassium chloride and other fertilizer salts that simply require water (and not soil acidity) to dissolve. A consequence of the reduction of percentage SRF dissolution as application rate of

SRFs increases is that the relative agronomic effectiveness of SRFs (e.g., relative to KCl) is rate dependent (i.e., there is no constant substitution or relative effectiveness value).

The percentages of Ca dissolved for basalt SRF was about half of that for dolerite SRF, and the percentages of K dissolved for gneiss SRF was about 3 - 5 fold higher than for K-feldspar SRF. These trends are consistent with results of laboratory experiments (Chapters 3 and 4), and dissolution of SRFs in the soil-plant system was larger than in soils alone (see Chapter 4) or in a dilute organic acid (see Chapter 3) presumably due to plant root-induced dissolution (Hinsinger and Gilkes 1995, 1997; Hinsinger *et al.* 2001), and the mass action effect of plants removing dissolved elements (Ca, Mg, K) from solution thereby promoting additional dissolution. Dissolution of K from gneiss SRF at an application rate of 225 mg K/kg was about 100 %, and the additional soil K (equivalent to about 47 % of added K in gneiss SRF) was released as a consequence of increasing soil pH (liming effect) including organic matter mineralization and release of OM-K. In case of K-feldspar SRF, the dissolution of K was much lower than for gneiss SRF. Dissolved K for gneiss SRF was probably originated mostly from biotite (see Table 2.1 in Chapter 2). This more soluble K from biotite than feldspars (microcline) may be due to K release from biotite is by simple exchange of the interlayer cation and congruent dissolution is not required (Rick 1968; Feigenbaum *et al.* 1981; Bakken *et al.* 1997). Dissolution of K from K-feldspar SRF may be increased by applying a longer milling time (e.g., 90 min, see Figure 2.11 in Chapter 2). Clearly, high-energy milling greatly improved dissolution of nutrients from SRFs, thereby increasing the agronomic effectiveness of most the SRFs used in this experiment.

5.4. Conclusions

A main objective of this research was to identify if the increased amounts of plant nutrient elements released from SRFs due to milling, as shown in the laboratory experiments (Chapters 3 and 4), will translate into an improved agronomic effectiveness of SRFs. A second main objective was to determine the soil types for which the application of SRFs will be most beneficial.

The application of basalt and dolerite SRFs at rates of 333 - 1332 mg of total Ca/kg soil (≈ 4.44 – 16.67 t SRF/ha) was much more effective than $CaCl_2$ for ryegrass grown on an acidic and/or Ca-deficient soil (WP-6), but was not effective for plants grown on a less acidic and/or relatively Ca-rich soil (MR-5). The effects of basalt and dolerite SRF applications were indicated by increases in plant yield, Ca concentration, and Ca uptake of dry tops, the amount of Ca extractable in 1*M* CH_3COONH_4, and increasing soil pH, with increasing application rate. In this instance, the SRFs acted primary as liming materials instead of Ca sources for promoting increased plant growth. Consequently, the applications of basalt and dolerite SRFs at relatively low rates, i.e., about 0.4 – 1 g SRF/kg soil (≈ 0.4 – 1.0 t/ha) as Mg fertilizers did not significantly increase soil pH, consequently they did not affect plant growth for both acidic (WP-6) and less acidic (MR-5) soils.

The application of gneiss and K-feldspar SRFs to the K-deficient soils increased plant yield, K concentration and K uptake of plant tops, amounts of K extractable in 1*M* CH_3COONH_4, and soil pH. The agronomic effectiveness of gneiss milled for one hour was nearly as great as K_2SO_4 indicating that ground gneiss could be used as a K fertilizer although the depletion of the soluble reference K fertilizer means that this result must be treated with caution. K-feldspar SRF was much less effective than gneiss SRF due mostly to the relatively low dissolution of K-feldspar SRF in the soil. The dissolution data reported in earlier chapter indicates that the agronomic effectiveness of K-feldspar SRF may be improved by employing a longer milling time (90 min).

Results of this present experiment indicate that all SRFs tested were suitable for use as soil ameliorants. In addition to being sources of plant nutrient elements (including Si), the SRFs are quite effective liming materials. These results are consistent with findings by Leonardos *et al.* (1987), Gillman (1980), Gillman *et al.* (2001, 2002), and Coventry *et al.* (2001) who added basalt dust to tropical soils. Other workers (Sanz Scovino and Rowell 1988) used gneiss dust, and Bakken *et al.* (2000) used several K-bearing minerals as K fertilizers. In summary it appears that application of SRFs will be most advantageous for amending strongly acidic and nutritionally impoverished soils.

Milling greatly improved the agronomic effectiveness of SRFs in supplying K relative to values reported for other pot experiments (Coroneos *et al.* 1996; Hensinger *et al.* 1996) for field experiments with granite dust (Bolland and Baker 2000) and mine tailings (Bakken *et al.* 1997, 2000) and feldspars (Sanz Scovino and

Rowell 1988). In these published experiments the sources of K were relatively coarse particles. Clearly, high-energy milling provides a simple method for manufacturing effective SRFs.

Chapter 6

SUMMARY, LIMITATIONS, AND RECOMMENDATIONS

6.1. Summary of Findings

High-energy milling of silicate rocks to produce silicate rock fertilizers (SRFs) reduced particle size, enhanced amorphism, and increased the release of structural cations from the rocks to solution, but in some cases the effects of milling were minor. Dry milling appears to be more effective than wet (rock/water ratio of 1/3) milling. Although agglomeration occurred for some dry-milled rocks, it did not reduce the surface area or exchangeable cations (K, Na, Ca, and Mg). Based on the total exchangeable cation data, the optimum milling times were 30 - 90 min, depending on rock type. The use of NaCl and KCl as milling additives did not enhance the properties of the SRFs.

Dissolution of SRF in 0.01*M* acetic-citric acid and in the soil reflected the changes in SRF properties due to milling. The general trends of SRF dissolution in the acid and soil were similar to published results of dissolution experiments by other workers (Huang and Keller 1970; Welch and Ullman 1996; Blake and Walter 1999; Oelkers and Scott, 2001; Oelkers and Gislason 2001; Harley 2002). The acid preferentially dissolved basic cations over Si (incongruent dissolution) and dissolved more amorphous and/or structurally disordered relative to crystalline materials. The proportions of rapidly dissolved elements, which may be indicative of the quantities of plant-available nutrients, varied between rock types and ranged from about 2 % (for initially milled rock dusts) to 70 % (for 120 min dry-milled rock dusts) of total content. In most cases this proportion for monovalent cations (Na and K) was about 2 – 3 fold higher than for divalent cations (Ca and Mg). Incubation of SRFs in soils resulted in a significant liming effect (increase of pH) with a minor salinity effect. The extent of dissolution of SRFs in the soil for up to 10-month incubation could be accurately predicted by the SRFs dissolved in 0.01*M* acetic-citric acid in 1 h. Neither SRFs nor soil properties were highly predictive of dissolution of basic cations from SRFs in soils, although equations including % sand, % clay, and exchange acidity of the soils are quite predictive of dissolution. The poor relationships between the extent of SRFs dissolved in soils and soil properties are similar to the findings by Hughes and Gilkes (1994) for dissolution of rock phosphates in soils.

Results of the glasshouse experiment indicate that application of Ca in basalt and dolerite SRFs at rates of 333 – 1332 mg of total Ca/kg soil (≈ 4 – 16 t SRF/ha) greatly increased plant yield and Ca uptake of ryegrass grown on highly acidic and/or Ca deficient soils, but did not do so for plants grown on less acidic and/or relatively Ca-rich soils. The large effects on plants were due mainly to the increase in soil pH rather than to increased Ca supply from the SRFs. Application of these SRFs at much lower rates (≈ 0.2 – 1 t/ha) as Mg fertilizers had only minor effects on pH and consequently on plant growth and nutrient uptake. The applications of milled gneiss SRF at the rates of 225 – 1332 mg of total K/kg soil (≈ 25 – 100 t SRF/ha) and K-feldspar SRF (5 – 20 t/ha) greatly increased plant growth and K uptake on soils deficient in K. Milled gneiss SRF was nearly as effective as K_2SO_4 for use as a K fertilizer based on total content of K in dry tops of plants, but ground K-feldspar SRF was not effective. However, most of the reference soluble K fertilizers had been consumed early in the experiment so was not an adequate reference treatment and these high application rates of K-SRFs also caused a large confounding effect due mainly to the increase in soil pH which affected the internal efficiency of K. Consequently the relative effectiveness values presented in this thesis can only be regarded as indicative. It is however apparent that milling greatly improves the effectiveness of SRFs relative to values reported by other researchers (Coroneos *et al.* 1996; Hinsinger *et al.* 1996; Bolland and Baker 2000; Bakken *et al.* 1997, 2000; Sanz Scovino and Rowell 1988) who used relatively coarse particles of silicate rock dusts in their experiments.

The general findings of this research are mostly consistent with those by the other researchers cited in this thesis. SRFs may be used as soil ameliorant for highly acid and nutrient deficient soils. SRFs have the capability to supply the nutrients required for plant growth and SRFs also act as liming materials. Consequently, large effects of SRFs on plant growth and soil properties occurred when they were applied to acidic and/or nutritionally poor soils. The beneficial effects of SRFs were greatly improved by high-energy milling of the SRFs and this should become a standard practice for commercial SRFs. Although no long term plant growth measurements were obtained, it is likely that the residual values (RV) of SRFs will be considerable as dissolution occurs over a long period.

6.2. Limitations and Recommendations for Future Researches

These results were based on laboratory and glasshouse experiments, and further research is needed. This should include identification of optimum milling methods (e.g., maximum benefits and minimal milling costs) at an industrial scale, followed by field experiments on diverse soils and plants to determine RE and RV values. Importantly, a cost-benefit evaluation for manufacturing SRFs is a major requirement prior to establishing a SRF industry. The optimum milling times will depend on (1) type of rock or minerals, for which ferromagnesian silicates require shorter milling time (≤ 10 min) than for feldspars or potassic-rock materials (1 – 1.5 hours), (2) milling method, for which dry milling is recommended, and (3) milling energy which may associated to the ball/sample ratio and intensity (rpm), in addition to milling time.

Applying tonnes of ‘superfine-rock dust’ over large areas may also create an environmental dust problem that could adversely affect the status of SRF as an environmentally sound fertilizer. Silicate dusts are known to be associated with respiratory disease and especially dust that contains quartz. It may be possible to granulate SRF without significantly reducing the rates at which nutrients are released from SRF to soil solution. It may also be possible to combine SRF with compost, manures, biofertilizers and/or organic substances to increase the effectiveness of SRF. These opportunities should be evaluated by additional research. There is closely parallel stream of research on rock phosphate (PR) fertilizers (with manure, compost, etc.) that will provide a guide to carrying out the proposed research.

Experimental evaluations of the agronomic effectiveness of SRFs, including in this present research, are based on a single nutrient which the silicate rock/mineral being a source of the plant nutrient. The true effectiveness of SRF should be assessed on the basis of SRF being a multinutrient fertilizer. Glasshouse and field studies should be carried out comparing the effectiveness of silicate rock mixtures versus multinutrient-chemical fertilizers. Many igneous and metamorphic rocks contain S, P, Fe, Mn and several micronutrients and these may be well matched to the plant nutrient requirement for multinutrient deficient (and acidic) soils which are abundant in tropical areas and on ancient land surfaces.

6.3. Promoting the Use of SRF for Appropriate Agricultural Systems

SRF as a soil ameliorant must also be considered for its capability as a remedial material to overcome specific agricultural and environmental problems such as those associated with utilization of acid and acid sulphate soils and saline/sodic soils, reclamation of degraded lands due to mining activities and deforestation. Therefore, future research may also need to address the evaluations of the potential of SRF for use as (1) a liming material for acid sulphate soils, (2) a Ca source for acid and sodic soils, and (3) a rejuvenating material for nutrient depleted and degraded lands.

As indicated by this present research, the application of SRFs has longer beneficial effects on plant growth and nutrient status of plant and soil, in contrast to the relatively short term-immediate effects of chemical fertilizers. Consequently, the application of SRFs to plantations and trees crops is probably more appropriate than for seasonal-food crops, but this interpretation needs to be evaluated through experimental results.

The concept of organic farming currently includes the use of SRFs and has been accepted worldwide with organic farming products being of considerable importance in Europe, North America, Australia, and New Zealand. The combination of SRF with compost and other organic matter ameliorants used in organic farming may have synergetic interactions to improve the beneficial effects of both materials for use as fertilizers. SRF supplies nutrients and increases soil pH which enhances microorganism activity in decomposing organic materials; while organic acids resulting from microbial activities may enhance dissolution of SRF. This combination of nutrient sources is probably a most suitable alternative for many developing countries that spent scarce dollars to import chemical fertilizers, as both SRF and organic fertilizers can be locally produced. A specific case is for small land-farming systems in highly populated countries. The low-farming capital could be a major constraint to the success of organic farming programs using the ‘new fertilizer product – SRF’, thus governments may need to provide ‘cost-free SRF’, at least in the early stages of implementation of the program.

SRF is recommended for use as a fertilizer or soil ameliorant for agricultural land in the humid-tropical areas where weathering and nutrient leaching are intensive resulting in acidic and infertile soils. Moreover, the favourable soil moisture for plant growth enables intensive cropping in these areas during the whole year. As soils remain moist so that dissolution of SRFs will be enhanced. At present commonly only highly soluble chemical fertilizers (i.e., N, P and/or K) are applied and rapid depletion of plant nutrients from the soils can not be avoided. To some extent chemical fertilizers (especially N) produce additional soil acidity which is undesirable for these acid soils. Sustainable agriculture in these areas requires continuous replacement of nutrients being leached and removed by crops from the soils, and this requirement may be satisfied by applying SRFs. Government programs promoting the use of SRFs in such farming systems are needed, i.e., through extension programs, field demonstrations and implementing economic and social-reward policies for SRF users including organic farmers.

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Publications derived from this thesis:

1. The use of high-energy milling with reactive additives to improve the release of nutrients from silicate rock fertilizers (J. Priyono, R.J. Gilkes, and P. McCormick). Proceeding of the 17th WSCC, Bangkok, Thailand, 2002.
2. XRD patterns of intensively milled silicate rocks (J. Priyono and R.J. Gilkes). Proceeding of the AXAA/WASEM conference, Wooroloo – WA, 19 – 21 September 2003.
3. Dissolution of milled-silicate rock fertilizers in the soil (J. Priyono and R.J. Gilkes, 2004), *Australian Journal of Soil Research* **42**: 441 - 448.

APPENDICES

Appendix A1. Total elemental composition of milled-silicate rocks determined using XRF

Type of	Milling		Oxide (%)											Element ($\mathrm{cmol_c/kg}$)										
Silicate Rocks	Cond.	Time (min)	Fe_2O_3	MnO	TiO_2	CaO	K_2O	SO_3	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	Fe	Mn	Ti	Ca	K	S	P	Si	Al	Mg	Na
Basalt	Dry	Initial	11.3	0.18	1.8	11.1	0.2	0.05	0.19	48.0	19.2	6.1	2.1	281	4.9	88.1	283	3.8	3.9	13.2	3197	1127	304	67.6
		10	11.5	0.17	1.7	10.9	0.2	0.05	0.18	48.9	18.4	6.0	2.1	287	4.8	85.5	279	3.8	3.8	13.0	3259	1080	299	67.3
		30	11.7	0.17	1.7	10.8	0.2	0.05	0.18	49.8	17.6	5.9	2.1	292	4.8	83.0	275	3.8	3.8	12.8	3319	1034	293	67.1
		60	12.1	0.17	1.6	10.5	0.2	0.05	0.18	51.5	16.1	5.7	2.1	302	4.6	78.2	267	3.7	3.7	12.4	3433	947	283	66.6
		90	12.1	0.17	1.6	10.6	0.2	0.04	0.17	51.6	16.0	5.7	2.0	302	4.7	78.3	270	3.7	3.1	12.2	3437	939	283	65.6
		120	12.1	0.17	1.6	10.7	0.2	0.03	0.17	51.6	15.8	5.7	2.0	302	4.7	78.3	273	3.6	2.4	12.0	3442	930	283	64.6
	Wet	10	12.1	0.18	1.6	11.1	0.2	0.01	0.16	51.0	15.7	5.8	2.1	303	4.9	79.1	284	4.0	0.8	11.1	3399	926	291	67.3
		30	12.5	0.18	1.6	11.0	0.2	0.01	0.16	50.9	15.7	5.8	2.1	314	5.0	78.7	281	3.9	0.4	11.1	3393	921	288	66.2
		60	13.0	0.18	1.6	10.9	0.2	0.00	0.16	50.8	15.6	5.7	2.0	325	5.0	78.2	277	3.8	0.0	11.2	3387	916	284	65.1
		90	13.8	0.18	1.6	11.1	0.2	0.01	0.15	50.0	15.5	5.6	2.0	345	4.9	79.9	283	3.8	0.8	10.2	3331	913	278	63.2
		120	13.7	0.17	1.5	10.5	0.2	0.00	0.16	50.3	15.7	5.7	2.1	342	4.8	75.7	268	3.7	0.0	11.5	3354	922	286	68.8
Dolerite	Dry	Initial	15.2	0.21	1.9	11.4	0.4	0.12	0.13	49.9	13.2	6.3	1.2	381	5.9	94.4	290	7.9	8.7	8.9	3328	779	316	39.1
		10	15.2	0.21	1.9	11.3	0.4	0.11	0.12	50.2	13.2	6.3	1.2	380	5.8	93.7	287	7.7	8.6	8.8	3344	777	314	38.9
		30	15.3	0.21	1.9	11.2	0.4	0.11	0.12	50.0	13.3	6.3	1.2	382	5.8	93.8	286	7.7	8.5	8.7	3335	780	315	38.9
		60	15.3	0.21	1.9	11.2	0.4	0.11	0.11	50.1	13.3	6.3	1.2	383	5.8	93.6	285	7.6	8.5	7.9	3339	781	315	37.7
		90	15.3	0.21	1.9	11.1	0.4	0.11	0.13	50.1	13.3	6.3	1.2	384	5.8	93.1	283	7.5	8.3	8.9	3342	782	314	38.6
		120	15.4	0.21	1.9	11.0	0.3	0.11	0.14	50.2	13.3	6.3	1.2	384	5.8	92.7	280	7.4	8.2	9.8	3345	783	313	39.5
	Wet	10	17.1	0.22	1.8	11.1	0.3	0.07	0.14	48.7	12.8	6.3	1.3	429	6.1	92.1	283	7.3	5.4	9.7	3249	752	317	41.5
		30	17.2	0.22	1.8	11.1	0.3	0.07	0.14	48.7	12.8	6.4	1.3	429	6.1	92.0	283	7.3	5.4	9.7	3246	753	318	41.6
		60	17.1	0.22	1.8	11.1	0.3	0.07	0.14	48.9	12.7	6.3	1.3	427	6.1	92.3	283	7.4	5.5	9.6	3257	750	315	41.3
		90	17.4	0.22	1.8	11.0	0.3	0.07	0.14	48.3	12.9	6.5	1.3	434	6.1	91.2	282	7.0	5.2	9.8	3221	760	324	42.1
		120	17.6	0.22	1.8	10.8	0.3	0.07	0.12	48.7	13.0	6.1	1.2	441	6.2	90.3	276	6.9	5.4	8.6	3249	762	307	37.9
Gneiss	Dry	Initial	2.6	0.02	0.3	2.0	1.1	0.00	0.08	74.0	15.0	0.7	4.1	66	0.6	15.7	51.3	23.2	0.0	5.9	4934	884	37.2	131.1
		10	3.5	0.02	0.3	2.0	1.1	0.00	0.09	73.4	14.9	0.7	4.0	87	0.7	15.6	51.0	23.1	0.0	6.1	4892	874	36.9	130.0
		30	4.3	0.03	0.3	2.0	1.1	0.00	0.09	72.8	14.7	0.7	4.0	108	0.7	15.5	50.7	23.0	0.0	6.3	4850	864	36.6	129.0
		60	6.0	0.03	0.3	2.0	1.1	0.00	0.10	71.5	14.4	0.7	3.9	151	0.9	15.3	50.1	22.7	0.0	6.7	4765	845	36.0	126.9
		90	8.7	0.04	0.3	1.9	1.0	0.00	0.10	69.4	13.9	0.7	3.8	219	1.0	15.0	49.0	22.3	0.0	7.0	4630	816	35.0	123.4
		120	9.5	0.04	0.3	1.9	1.0	0.00	0.11	68.9	13.7	0.7	3.8	238	1.2	15.0	48.9	22.3	0.0	7.5	4593	805	34.8	122.5
	Wet	10	4.8	0.03	0.3	2.0	1.1	0.00	0.09	72.5	14.6	0.7	3.9	119	0.9	15.4	50.1	22.9	0.0	6.5	4835	860	36.9	125.1
		30	6.5	0.04	0.3	2.0	1.1	0.00	0.09	71.1	14.2	0.7	3.9	163	1.0	15.3	50.2	23.0	0.0	6.3	4743	837	35.9	126.1
		60	8.4	0.04	0.3	2.0	1.1	0.00	0.09	69.7	13.8	0.7	3.9	210	1.2	15.3	50.4	23.2	0.0	6.1	4644	812	34.9	127.0
		90	10.9	0.05	0.3	1.9	1.0	0.00	0.10	67.5	13.8	0.7	3.7	272	1.5	14.8	47.7	21.8	0.0	6.7	4502	813	35.4	120.3
		120	12.8	0.06	0.3	1.8	1.0	0.00	0.07	66.4	13.3	0.7	3.5	321	1.8	14.4	46.1	20.6	0.0	5.2	4429	780	36.7	114.3

Appendix A1 (continuous)

Type of	Milling		Oxide (%)											Element (cmol$_c$/kg)										
Silicate Rocks	Cond.	Time (min)	Fe_2O_3	MnO	TiO_2	CaO	K_2O	SO_3	P_2O_5	SiO_2	Al_2O_3	MgO	Na_2O	Fe	Mn	Ti	Ca	K	S	P	Si	Al	Mg	Na
K-feldspar	Dry	Initial	0.0	0.00	0.1	0.1	11.6	0.00	0.22	66.5	19.1	0.0	2.5	0.5	0.0	2.7	1.4	246.0	0.0	15.3	4435	1121	0.00	81.1
		10	0.1	0.00	0.1	0.1	11.0	0.00	0.22	65.0	20.9	0.0	2.6	3.2	0.0	2.7	1.6	233.6	0.0	15.8	4332	1231	0.00	84.8
		30	0.2	0.00	0.1	0.1	11.4	0.00	0.22	67.0	18.3	0.0	2.8	4.5	0.0	2.7	1.4	243.1	0.0	15.7	4465	1077	0.00	89.4
		60	1.1	0.00	0.1	0.1	10.8	0.00	0.21	65.2	20.1	0.0	2.4	28.7	0.0	2.6	1.3	229.8	0.0	14.7	4349	1181	0.00	78.2
		90	1.2	0.00	0.1	0.1	11.3	0.00	0.18	65.5	19.3	0.0	2.4	31.0	0.0	2.7	1.6	239.9	0.0	12.8	4366	1135	0.00	77.5
		120	1.9	0.00	0.1	0.1	10.8	0.00	0.25	66.1	18.6	0.0	2.2	48.2	0.0	2.6	1.4	229.1	0.0	17.9	4409	1095	0.00	71.0
	Wet	10	0.8	0.00	0.1	0.1	11.0	0.00	0.20	66.4	19.0	0.0	2.4	19.5	0.0	2.6	1.6	234.9	0.0	14.1	4430	1116	0.00	78.9
		30	1.2	0.00	0.1	0.1	10.9	0.00	0.20	66.3	18.8	0.0	2.4	31.1	0.0	2.6	1.5	231.6	0.0	14.4	4420	1108	0.00	77.8
		60	1.7	0.00	0.1	0.1	10.7	0.00	0.21	66.2	18.7	0.0	2.4	42.6	0.0	2.6	1.3	228.4	0.0	14.6	4410	1101	0.00	76.7
		90	2.3	0.00	0.1	0.1	10.2	0.00	0.21	65.7	18.8	0.0	2.6	56.5	0.0	2.5	1.3	217.3	0.0	14.4	4383	1108	0.00	85.3
		120	2.8	0.00	0.0	0.0	9.7	0.00	0.20	65.4	18.9	0.0	2.9	69.5	0.0	2.4	1.2	206.9	0.0	14.3	4358	1113	0.00	93.4
Basalt + NaCl	Dry	120	11.9	0.18	1.5	10.2	0.1	0.00	0.16	50.9	15.7	5.9	3.4	297	4.9	77.3	260	3.1	0.0	11.6	3395	923	295	108.9
	Wet	120	13.5	0.18	1.5	10.0	0.1	0.01	0.16	49.8	15.6	6.0	3.1	337	5.0	75.0	256	3.1	0.8	11.1	3319	919	299	101.2
Basalt + KCl	Dry	120	11.8	0.17	1.5	10.1	1.1	0.00	0.18	51.2	15.8	6.0	2.2	295	4.7	76.4	257	22.5	0.0	12.7	3413	927	299	72.3
	Wet	120	13.4	0.17	1.5	9.9	1.1	0.01	0.17	49.8	15.6	6.0	2.4	334	4.8	73.8	252	22.8	0.8	12.1	3323	918	302	77.0
Basalt + K-feldspar	Dry	120	7.1	0.09	0.8	5.2	5.1	0.00	0.18	59.3	17.5	2.8	2.1	177	2.5	41.0	132	108.8	0.0	12.7	3950	1027	138	66.4
	Wet	120	8.1	0.09	0.8	5.1	5.2	0.00	0.17	58.1	17.4	2.8	2.2	202	2.6	39.9	130	110.9	0.0	12.2	3874	1025	141	71.2
Dolerite + NaCl	Dry	120	15.6	0.21	1.8	10.3	0.3	0.14	0.15	49.3	13.0	6.4	2.7	391	5.9	89.7	264	6.6	10.8	10.9	3286	766	320	87.3
	Wet	120	17.9	0.23	1.7	10.2	0.3	0.09	0.14	47.9	12.7	6.3	2.6	448	6.4	87.4	260	6.2	7.0	9.5	3191	746	313	83.6
Dolerite + KCl	Dry	120	15.4	0.21	1.9	11.0	0.3	0.11	0.14	50.2	13.3	6.3	1.2	384	5.8	92.7	280	7.4	8.2	9.8	3345	783	313	39.5
	Wet	120	16.8	0.20	1.7	10.0	0.9	0.09	0.12	48.7	13.9	6.2	1.4	420	5.5	85.6	256	19.5	7.0	8.3	3246	816	308	45.4
Dolerite + K-feldspar	Dry	120	9.3	0.12	1.0	5.4	5.7	0.03	0.18	57.2	15.8	3.3	2.1	232	3.2	47.7	139	121.0	2.4	12.6	3810	928	166	66.2
	Wet	120	10.8	0.13	0.9	5.4	5.4	0.02	0.16	56.3	15.6	3.3	2.0	269	3.5	47.1	139	114.9	1.6	11.2	3752	916	165	64.2
Gneiss + NaCl	Dry	120	8.5	0.04	0.3	1.9	1.0	0.00	0.14	68.4	13.9	0.7	5.0	212	1.2	15.0	49	22.1	0.0	9.7	4562	817	36	162.5
	Wet	120	11.5	0.06	0.3	1.8	1.0	0.00	0.10	66.3	13.5	0.8	4.7	287	1.8	14.5	47	20.5	0.0	6.8	4419	795	38	152.2
Gneiss + KCl	Dry	120	9.1	0.04	0.3	1.8	2.2	0.00	0.13	68.5	13.9	0.7	3.4	227	1.1	14.4	45	46.6	0.0	9.0	4563	818	36	110.3
	Wet	120	12.3	0.06	0.3	1.7	2.0	0.00	0.09	66.1	13.5	0.8	3.2	307	1.6	13.8	43	43.1	0.0	6.3	4410	794	38	103.0

[1] Average values of 4 replicates, normalized to total oxides of 100 %

Appendix A2. The quantities of dissolved elements from milled-basalt dust in 0.01*M* acetic-citric acid

Milling		Dissolution Time (day)							Dissolution Time (day)						
Cond.	Time (min)	0.042	1	3	7	14	28	56	0.04	1	3	7	14	28	56
					Ca (cmol$_c$/kg)							**Ca (% of total in rock)**			
	Initial	10.6	11.2	12.6	15.9	22.1	22.7	23.4	2.7	2.8	3.2	4.0	5.6	5.7	5.9
Dry	10	17.3	21.3	27.1	34.4	41.3	46.0	44.4	4.4	5.4	6.9	8.8	10.6	11.8	11.4
	60	48.4	51.0	57.9	68.9	78.1	78.1	78.1	12.9	13.6	15.5	18.4	20.9	20.9	20.9
	120	68.5	69.4	78.9	89.4	98.9	97.5	95.0	17.9	18.1	20.6	23.4	25.9	25.5	24.8
	10	17.9	19.9	24.1	30.4	36.6	40.6	40.2	4.5	5.0	6.1	7.6	9.2	10.2	10.1
Wet	60	36.1	37.7	47.5	57.2	65.3	68.3	66.5	9.3	9.7	12.2	14.7	16.8	17.6	17.2
	120	48.6	51.8	61.4	74.7	80.9	83.4	79.0	13.0	13.8	16.4	19.9	21.6	22.3	21.1
					Mg (cmol$_c$/kg)							**Mg (% of total in raock)**			
	Initial	18.6	42.7	47.0	49.7	50.2	51.7	56.4	6.1	14.0	15.5	16.3	16.5	17.0	18.5
Dry	10	29.1	46.7	50.7	53.8	57.7	57.0	68.0	9.7	15.6	17.0	18.0	19.3	19.1	22.8
	60	63.5	64.5	66.3	72.7	76.5	82.3	96.5	22.4	22.8	23.4	25.7	27.0	29.1	34.1
	120	76.2	80.5	81.8	88.6	98.7	106.0	122.4	26.9	28.4	28.9	31.3	34.9	37.4	43.3
	10	34.1	41.5	45.8	49.2	49.8	53.1	59.3	11.7	14.3	15.7	16.9	17.1	18.2	20.4
Wet	60	36.8	48.5	57.7	63.0	66.2	73.8	88.1	13.0	17.1	20.3	22.2	23.3	26.0	31.1
	120	43.0	58.2	69.0	77.2	78.8	95.9	106.6	15.1	20.4	24.2	27.0	27.6	33.6	37.3
					Na (cmol$_c$/kg)							**Na (% of total in rock)**			
	Initial	2.2	3.7	4.2	5.0	5.6	8.5	11.0	3.2	5.5	6.2	7.3	8.2	12.6	16.3
Dry	10	7.0	7.2	8.2	10.7	13.5	20.3	24.2	10.3	10.7	12.1	15.9	20.0	30.1	36.0
	60	20.7	17.8	20.8	25.4	30.9	33.1	40.3	31.1	26.8	31.2	38.1	46.4	49.6	60.5
	120	27.8	29.5	31.5	33.0	38.3	43.6	50.1	43.1	45.6	48.7	51.0	59.2	67.4	77.5
	10	3.1	3.8	5.1	6.9	9.0	13.8	18.3	4.7	5.7	7.6	10.2	13.4	20.5	27.1
Wet	60	9.2	9.3	11.7	16.3	19.6	29.5	37.6	14.2	14.3	18.0	25.0	30.1	45.3	57.7
	120	11.3	13.7	17.6	22.1	23.1	30.1	35.8	16.4	19.8	25.5	32.1	33.6	43.8	52.0
					K (cmol$_c$/kg)							**K (% of total in rock)**			
	Initial	0.2	0.9	0.9	1.0	1.1	1.2	1.4	4.5	23.4	24.7	26.3	27.9	32.4	35.8
Dry	10	0.6	0.8	1.1	1.3	1.5	1.6	1.7	16.3	22.1	27.6	32.9	40.5	40.8	45.3
	60	1.8	2.1	2.2	2.3	2.6	2.9	2.8	49.5	57.6	58.1	62.4	69.2	77.8	76.2
	120	2.1	2.6	2.5	2.7	2.9	3.0	3.3	57.2	71.1	70.6	75.8	80.8	84.4	90.6
	10	0.7	0.8	0.9	1.0	1.2	1.2	1.4	16.8	20.8	22.8	26.0	29.8	31.0	35.0
Wet	60	1.0	1.1	1.1	1.4	1.5	1.7	1.8	26.3	29.7	30.0	36.6	39.2	44.5	48.2
	120	1.3	1.5	1.5	1.7	1.8	2.1	2.2	35.1	39.2	40.3	46.8	48.9	55.7	58.1
					Al (cmol$_c$/kg)							**Al (% of total in rock)**			
	Initial	11.4	25.1	35.0	49.5	62.3	80.2	135.1	1.0	2.2	3.1	4.4	5.5	7.1	12.0
Dry	10	31.2	61.3	89.6	124.0	165.9	183.3	258.7	2.9	5.7	8.3	11.5	15.4	17.0	24.0
	60	145.6	173.0	220.1	276.1	332.2	411.0	445.7	15.4	18.3	23.2	29.1	35.1	43.4	47.0
	120	229.0	254.9	309.6	351.9	411.3	496.3	526.7	24.6	27.4	33.3	37.9	44.2	53.4	56.6
	10	33.1	49.5	75.0	100.0	145.2	155.8	232.1	3.6	5.4	8.1	10.8	15.7	16.8	25.1
Wet	60	83.0	113.6	161.2	203.6	256.8	282.7	369.8	9.1	12.4	17.6	22.2	28.0	30.9	40.4
	120	129.2	159.8	212.0	260.6	319.0	348.9	429.2	14.0	17.3	23.0	28.3	34.6	37.8	46.6
					Si (cmol$_c$/kg)							**Si (% of total in rock)**			
	Initial	17.6	42.4	62.0	107.6	132.8	200.8	268.0	0.6	1.3	1.9	3.4	4.2	6.3	8.4
Dry	10	31.5	64.2	89.7	153.9	173.4	243.3	306.9	1.0	2.0	2.8	4.7	5.3	7.5	9.4
	60	194.4	209.1	243.0	332.1	392.4	441.3	518.1	5.7	6.1	7.1	9.7	11.4	12.9	15.1
	120	333.6	351.9	427.2	491.7	516.3	566.4	640.2	9.7	10.2	12.4	14.3	15.0	16.5	18.6
	10	36.0	45.6	71.4	100.8	145.2	211.2	264.9	1.1	1.3	2.1	3.0	4.3	6.2	7.8
Wet	60	86.7	97.5	137.7	183.3	243.6	333.6	413.4	2.6	2.9	4.1	5.4	7.2	9.8	12.2
	120	144.6	163.2	210.3	267.6	333.3	400.8	506.1	4.3	4.9	6.3	8.0	9.9	12.0	15.1
					Fe (cmol$_c$/kg)							**Fe (% of total in rock)**			
	Initial	29.2	63.5	74.7	80.1	81.2	73.4	83.0	6.9	15.0	17.7	19.0	19.2	17.4	19.7
Dry	10	79.6	108.5	114.6	118.9	124.6	166.3	168.8	18.5	25.2	26.7	27.6	29.0	38.7	39.2
	60	132.1	132.6	138.8	147.9	157.2	136.6	138.8	29.2	29.3	30.6	32.7	34.7	30.2	30.6
	120	183.8	188.8	203.8	206.8	218.3	204.4	209.5	40.6	41.7	45.0	45.7	48.2	45.1	46.3
	10	68.0	79.8	88.7	93.5	99.9	96.4	99.4	15.0	17.6	19.5	20.6	22.0	21.2	21.9
Wet	60	142.0	159.4	171.4	180.3	187.5	186.7	188.6	29.2	32.7	35.2	37.0	38.5	38.3	38.7
	120	208.4	227.9	242.4	252.1	260.6	255.3	259.3	40.7	44.5	47.3	49.2	50.8	49.8	50.6

Appendix A3. The quantities of dissolved elements from milled-dolerite dust in 0.01*M* acetic-citric acid

Milling		Dissolution Time (day)							Dissolution Time (day)						
Cond.	Time (min)	0.042	1	3	7	14	28	56	0.04	1	3	7	14	28	56
					Ca (cmol$_c$/kg)						**Ca (% of total in rock)**				
Dry	Initial	7.6	9.3	14.8	16.7	17.0	18.8	21.0	1.9	2.3	3.6	4.1	4.2	4.6	5.2
	10	22.7	25.4	30.3	37.1	43.1	46.9	45.9	5.7	6.3	7.5	9.2	10.7	11.7	11.4
	60	56.5	59.6	65.9	74.6	82.1	83.0	83.5	14.2	14.9	16.5	18.7	20.6	20.8	20.9
	120	94.4	94.6	101.5	110.9	111.1	113.6	103.7	24.1	24.1	25.9	28.3	28.3	29.0	26.4
Wet	10	12.4	15.3	18.7	23.8	28.9	32.4	31.9	3.1	3.9	4.7	6.0	7.3	8.2	8.1
	60	22.9	27.4	32.7	39.5	46.1	49.2	47.4	5.8	6.9	8.3	10.0	11.6	12.4	12.0
	120	30.6	37.4	41.2	49.4	56.3	58.3	56.4	7.9	9.7	10.7	12.8	14.6	15.1	14.6
					Mg (cmol$_c$/kg)						**Mg (% of total in raock)**				
Dry	Initial	7.2	9.3	9.6	14.3	16.5	19.1	24.8	2.3	2.9	3.0	4.5	5.2	6.1	7.8
	10	28.1	31.7	37.9	42.5	49.0	57.9	74.4	8.9	10.1	12.1	13.5	15.6	18.4	23.7
	60	82.0	84.0	93.5	103.3	122.2	121.0	137.5	26.0	26.7	29.7	32.8	38.8	38.4	43.7
	120	131.5	140.7	147.8	168.3	182.2	188.3	206.4	42.0	44.9	47.2	53.7	58.1	60.1	65.8
Wet	10	10.6	13.0	15.8	19.8	23.6	29.7	37.2	3.3	4.1	5.0	6.2	7.4	9.4	11.7
	60	18.6	23.1	28.1	35.2	40.7	50.2	62.3	5.9	7.3	8.9	11.2	12.9	15.9	19.8
	120	25.7	33.0	40.4	45.8	54.3	65.5	92.8	8.4	10.8	13.2	14.9	17.7	21.3	30.2
					Na (cmol$_c$/kg)						**Na (% of total in rock)**				
Dry	Initial	0.4	0.6	1.7	1.6	1.8	3.1	4.5	0.9	1.6	4.5	4.1	4.7	7.8	11.4
	10	2.6	3.3	4.2	5.7	7.1	9.7	12.3	6.7	8.5	10.7	14.5	18.3	25.0	31.6
	60	8.4	9.0	10.7	12.4	13.1	19.1	22.1	22.1	24.0	28.4	33.0	34.8	50.6	58.6
	120	16.7	17.0	19.0	20.3	22.7	30.7	35.0	42.3	42.9	48.0	51.3	57.5	77.8	88.6
Wet	10	1.0	1.3	2.2	3.0	4.0	5.9	8.1	2.5	3.1	5.2	7.1	9.6	14.3	19.4
	60	2.2	3.0	4.4	6.0	7.1	10.2	12.5	5.3	7.4	10.5	14.5	17.3	24.6	30.3
	120	3.7	4.5	6.2	7.7	9.1	12.9	15.3	9.9	11.9	16.3	20.2	24.1	34.1	40.4
					K (cmol$_c$/kg)						**K (% of total in rock)**				
Dry	Initial	2.4	2.7	2.8	2.9	3.3	4.1	4.1	30.0	33.9	35.4	37.2	41.3	51.6	51.6
	10	3.6	3.7	3.8	3.9	4.2	4.6	5.2	46.8	48.3	49.5	51.2	53.9	60.3	67.7
	60	4.7	4.8	4.9	5.1	5.5	6.0	6.3	62.4	63.4	65.0	67.6	71.7	78.6	83.3
	120	5.5	5.7	6.0	6.1	6.4	7.0	7.2	74.3	76.8	80.5	82.7	86.1	94.1	96.9
Wet	10	2.8	2.9	2.9	3.3	3.7	3.9	4.0	38.1	39.2	39.2	45.5	50.8	53.7	54.9
	60	3.0	3.1	3.2	3.6	3.8	4.3	4.6	40.1	41.9	42.6	48.5	51.6	58.5	62.7
	120	3.5	3.4	3.4	3.9	4.1	4.4	4.8	50.7	48.7	48.7	55.8	60.0	63.6	70.0
					Al (cmol$_c$/kg)						**Al (% of total in rock)**				
Dry	Initial	11.9	20.3	30.2	43.4	72.6	73.6	124.4	1.5	2.6	3.9	5.6	9.3	9.4	16.0
	10	56.6	72.2	94.3	118.3	161.7	197.4	264.8	7.3	9.3	12.1	15.2	20.8	25.4	34.1
	60	133.4	158.8	181.0	207.8	256.8	306.7	348.7	17.1	20.3	23.2	26.6	32.9	39.3	44.6
	120	211.1	241.2	271.4	305.8	342.5	391.0	420.2	27.0	30.8	34.7	39.1	43.8	50.0	53.7
Wet	10	18.5	37.3	49.5	73.1	108.0	127.7	177.7	2.5	5.0	6.6	9.7	14.4	17.0	23.6
	60	43.0	67.4	90.1	116.4	160.7	181.0	245.5	5.7	9.0	12.0	15.5	21.4	24.1	32.7
	120	59.0	88.7	117.4	146.1	189.0	232.8	283.2	7.7	11.6	15.4	19.2	24.8	30.6	37.2
					Si (cmol$_c$/kg)						**Si (% of total in rock)**				
Dry	Initial	31.6	42.4	65.2	82.8	110.4	161.2	210.4	0.9	1.3	2.0	2.5	3.3	4.8	6.3
	10	131.6	146.8	186.8	236.4	309.6	396.0	511.2	3.9	4.4	5.6	7.1	9.3	11.8	15.3
	60	326.8	386.4	443.2	514.4	562.4	644.0	802.8	9.8	11.6	13.3	15.4	16.8	19.3	24.0
	120	445.6	521.2	569.6	617.2	726.0	748.8	872.8	13.3	15.6	17.0	18.4	21.7	22.4	26.1
Wet	10	50.8	76.0	98.0	131.6	184.4	251.6	332.0	1.6	2.3	3.0	4.1	5.7	7.7	10.2
	60	107.2	131.6	168.0	230.0	307.6	391.6	498.0	3.3	4.0	5.2	7.1	9.4	12.0	15.3
	120	152.8	181.6	231.6	292.8	402.8	465.6	616.8	4.7	5.6	7.1	9.0	12.4	14.3	19.0
					Fe (cmol$_c$/kg)						**Fe (% of total in rock)**				
Dry	Initial	17.4	24.4	31.1	39.4	48.8	51.2	52.5	3.0	4.3	5.4	6.9	8.5	9.0	9.2
	10	72.6	82.5	99.1	115.4	133.7	146.3	161.8	12.7	14.5	17.4	20.3	23.5	25.7	28.4
	60	189.4	197.7	220.2	238.4	260.4	266.5	287.1	33.0	34.4	38.3	41.5	45.3	46.4	50.0
	120	281.3	292.0	316.1	340.2	356.3	350.9	358.9	48.8	50.6	54.8	59.0	61.8	60.8	62.2
Wet	10	45.0	52.2	62.7	73.7	86.8	95.6	97.0	7.0	8.1	9.7	11.5	13.5	14.9	15.1
	60	122.1	133.9	149.5	166.3	186.2	168.8	180.3	19.1	20.9	23.3	26.0	29.0	26.3	28.1
	120	178.7	195.8	210.5	233.3	254.5	255.0	255.0	27.0	29.6	31.9	35.3	38.5	38.6	38.6

Appendix A4. The quantities of dissolved elements from milled-gneiss dust in 0.01*M* acetic-citric acid

Milling		Dissolution Time (day)							Dissolution Time (day)						
Cond.	Time (min)	0.042	1	3	7	14	28	56	0.04	1	3	7	14	28	56
					Ca (cmol$_c$/kg)							**Ca (% of total in rock)**			
	Initial	3.8	5.3	5.3	5.7	6.2	5.9	5.3	5.3	7.3	7.4	8.0	8.6	8.2	7.4
Dry	10	6.3	7.4	7.6	8.5	9.3	10.1	10.8	8.8	10.4	10.6	11.9	13.1	14.1	15.1
	60	8.1	9.4	9.4	10.8	12.0	12.8	13.0	11.6	13.3	13.4	15.4	17.1	18.3	18.5
	120	11.2	14.0	14.3	15.8	17.2	18.2	19.1	16.4	20.4	20.9	23.1	25.1	26.6	27.9
	10	5.4	5.8	5.9	6.6	7.4	8.0	7.6	7.6	8.3	8.4	9.4	10.5	11.3	10.9
Wet	60	6.2	7.3	7.7	8.8	9.6	10.4	11.1	8.8	10.4	10.9	12.4	13.6	14.7	15.7
	120	8.2	8.4	8.7	10.4	11.0	12.1	12.4	12.7	13.0	13.4	16.1	17.0	18.8	19.1
					Mg (cmol$_c$/kg)							**Mg (% of total in raock)**			
	Initial	3.0	5.8	6.5	9.9	13.8	19.7	25.1	8.1	15.7	17.5	26.6	37.1	52.8	67.4
Dry	10	14.3	17.2	22.4	27.9	31.7	32.6	36.8	38.9	46.6	60.9	75.8	86.0	88.5	99.9
	60	40.0	41.1	41.6	41.5	42.0	43.3	38.9	100	100	100	100	100	100	100
	120	37.3	37.2	37.3	37.1	37.7	35.9	35.6	100	100	100	100	100	100	100
	10	4.3	5.5	8.0	11.1	14.9	20.5	25.3	11.8	15.1	21.6	30.1	40.5	55.8	68.6
Wet	60	7.5	9.6	12.7	16.2	19.8	25.6	28.2	21.5	27.4	36.3	46.2	56.5	73.1	80.5
	120	9.3	12.0	15.2	18.1	20.8	24.8	26.9	25.4	32.8	41.4	49.4	56.8	67.8	73.6
					Na (cmol$_c$/kg)							**Na (% of total in rock)**			
	Initial	0.7	0.8	0.9	0.9	1.0	2.5	2.3	0.5	0.6	0.7	0.7	0.7	1.9	1.7
Dry	10	6.4	7.2	7.5	8.2	8.9	11.9	14.0	5.0	5.6	5.8	6.3	6.8	9.1	10.8
	60	16.3	17.6	19.2	19.2	21.0	29.2	31.9	12.8	13.8	15.1	15.1	16.5	23.0	25.1
	120	41.3	44.5	46.3	49.7	50.5	51.0	60.0	34	36	38	41	41	42	49
	10	1.2	1.4	1.6	2.0	2.5	3.7	5.5	1.0	1.1	1.3	1.6	2.0	3.0	4.4
Wet	60	7.2	7.3	7.3	8.5	9.0	13.6	15.4	5.7	5.7	5.7	6.7	7.1	10.7	12.1
	120	11.3	12.0	12.7	14.1	15.0	19.6	26.4	9.9	10.5	11.1	12.3	13.2	17.2	23.1
					K (cmol$_c$/kg)							**K (% of total in rock)**			
	Initial	1.0	1.0	0.9	1.1	1.2	1.3	1.4	4.1	4.4	4.1	4.9	5.1	5.5	6.0
Dry	10	3.2	3.3	3.5	3.8	3.8	4.1	4.5	13.9	14.2	15.2	16.3	16.3	17.8	19.5
	60	9.0	9.2	9.4	9.7	9.8	10.3	10.7	39.8	40.7	41.2	42.6	43.2	45.5	47.3
	120	12.1	12.2	12.3	12.5	12.8	13.8	14.1	54.3	54.5	55.0	55.9	57.4	61.9	63.0
	10	1.3	1.3	1.4	1.5	1.6	1.8	1.9	5.5	5.8	6.3	6.5	6.9	7.8	8.3
Wet	60	1.8	2.6	2.4	2.9	3.0	3.4	3.6	7.6	11.0	10.4	12.3	13.0	14.6	15.5
	120	3.6	3.7	3.8	4.1	4.3	4.7	5.0	17.4	17.7	18.3	20.0	20.7	22.9	24.1
					Al (cmol$_c$/kg)							**Al (% of total in rock)**			
	Initial	7.7	11.0	14.3	22.7	47.7	60.6	98.0	0.9	1.2	1.6	2.6	5.4	6.9	11.1
Dry	10	38.3	51.5	65.5	74.1	105.2	141.5	170.3	4.4	5.9	7.5	8.5	12.0	16.2	19.5
	60	117.4	133.9	142.3	150.9	177.6	186.3	259.3	13.9	15.9	16.8	17.9	21.0	22.1	30.7
	120	190.4	203.6	222.4	229.0	258.3	269.2	345.0	23.6	25.3	27.6	28.5	32.1	33.4	42.9
	10	8.3	15.6	23.3	29.9	62.7	78.5	124.2	1.0	1.8	2.7	3.5	7.3	9.1	14.4
Wet	60	27.1	40.0	51.0	59.9	95.2	117.1	167.2	3.3	4.9	6.3	7.4	11.7	14.4	20.6
	120	48.2	63.2	75.9	90.9	122.7	147.4	199.0	6.2	8.1	9.7	11.7	15.7	18.9	25.5
					Si (cmol$_c$/kg)							**Si (% of total in rock)**			
	Initial	16.4	21.6	25.6	31.2	50.8	84.8	103.6	0.3	0.4	0.5	0.6	1.0	1.7	2.1
Dry	10	60.0	75.6	104.4	126.8	162.0	216.4	279.6	1.2	1.5	2.1	2.6	3.3	4.4	5.7
	60	218.8	217.6	232.4	260.0	288.8	328.8	411.2	4.6	4.6	4.9	5.5	6.1	6.9	8.6
	120	324.4	363.6	375.6	435.6	495.2	498.4	569.6	7.1	7.9	8.2	9.5	10.8	10.9	12.4
	10	18.8	28.8	37.2	58.4	71.6	122.0	165.2	0.4	0.6	0.8	1.2	1.5	2.5	3.4
Wet	60	67.2	76.4	89.6	118.8	152.8	208.0	263.2	1.4	1.6	1.9	2.6	3.3	4.5	5.7
	120	114.4	141.2	164.4	199.2	230.0	287.2	340.0	2.6	3.2	3.7	4.5	5.2	6.5	7.7
					Fe (cmol$_c$/kg)							**Fe (% of total in rock)**			
	Initial	10.3	20.8	21.9	29.5	40.7	41.0	39.9	10.4	21.0	22.1	29.8	41.1	41.4	40.3
Dry	10	75.0	83.0	95.9	105.8	115.7	121.1	123.2	57.4	63.6	73.4	81.0	88.6	92.7	94.3
	60	110.1	113.0	114.9	116.5	119.2	120.0	133.4	48.6	49.9	50.7	51.4	52.6	52.9	58.9
	120	318.8	318.8	321.4	324.1	326.8	329.5	333.8	89.3	89.3	90.0	90.8	91.5	92.3	93.5
	10	58.9	63.8	70.2	77.1	88.1	93.5	97.5	33.0	35.7	39.3	43.2	49.4	52.4	54.6
Wet	60	245.4	275.9	292.0	302.7	313.4	310.7	316.6	77.9	87.6	92.7	96.1	99.5	98.7	100
	120	375.0	294.6	468.8	487.5	495.5	586.6	605.4	77.9	61.2	97.4	100	100	100	100

Appendix A5. The quantities of dissolved elements from milled-K-feldspar dust in 0.01*M* acetic-citric acid.

Milling		Dissolution Time (day)							Dissolution Time (day)						
Cond.	Time (min)	0.042	1	3	7	14	28	56	0.04	1	3	7	14	28	56
					Na (cmol$_c$/kg)						**Na (% of total in rock)**				
	Initial	0.1	0.1	0.1	0.1	0.3	0.7	1.1	0.1	0.1	0.1	0.1	0.3	0.9	1.3
Dry	10	3.0	3.3	3.6	4.0	4.4	5.5	8.5	3.6	3.9	4.2	4.7	5.2	6.5	10.0
	60	9.0	9.9	10.2	10.7	11.2	13.9	15.8	11.6	12.7	13.0	13.7	14.3	17.8	20.2
	120	19.0	19.7	20.6	23.9	24.1	25.9	25.9	27	28	29	34	34	36	36
	10	0.7	0.9	1.0	1.2	1.6	2.2	3.2	0.9	1.1	1.3	1.5	2.0	2.8	4.0
Wet	60	4.4	4.7	5.3	6.0	6.4	9.1	9.9	5.8	6.1	6.9	7.8	8.3	11.8	12.9
	120	9.3	9.0	7.0	7.8	8.6	9.9	12.4	10.0	9.6	7.5	8.4	9.2	10.6	13.3
					K (cmol$_c$/kg)						**K (% of total in rock)**				
	Initial	1.0	1.1	1.2	1.5	1.9	2.7	3.3	0.4	0.4	0.5	0.6	0.8	1.1	1.3
Dry	10	15.6	16.2	17.0	17.9	19.1	22.9	25.1	6.7	7.0	7.3	7.6	8.2	9.8	10.7
	60	45.1	48.3	50.2	50.6	52.0	56.9	59.8	19.6	21.0	21.8	22.0	22.6	24.8	26.0
	120	86.0	89.7	94.8	95.6	96.5	99.5	98.0	37.5	39.1	41.4	41.7	42.1	43.4	42.8
	10	4.5	5.0	5.5	6.1	7.0	9.1	10.6	1.9	2.1	2.3	2.6	3.0	3.9	4.5
Wet	60	21.2	22.0	24.5	25.8	28.5	32.0	32.9	9.3	9.6	10.7	11.3	12.5	14.0	14.4
	120	29.1	30.8	33.6	35.9	38.4	42.5	42.7	14.1	14.9	16.3	17.3	18.6	20.5	20.6
					Al (cmol$_c$/kg)						**Al (% of total in rock)**				
	Initial	2.5	5.8	6.7	16.5	36.8	44.8	45.5	0.2	0.5	0.6	1.5	3.3	4.0	4.1
Dry	10	37.3	45.3	51.0	57.6	88.2	120.9	152.2	3.0	3.7	4.1	4.7	7.2	9.8	12.4
	60	117.4	128.2	147.1	176.7	190.9	196.1	265.3	9.9	10.9	12.4	15.0	16.2	16.6	22.5
	120	223.4	237.5	259.6	270.9	311.0	342.0	387.3	20.4	21.7	23.7	24.7	28.4	31.2	35.4
	10	11.4	15.2	30.9	48.6	69.3	77.3	97.3	1.0	1.4	2.8	4.4	6.2	6.9	8.7
Wet	60	51.5	57.1	74.0	103.3	132.9	149.9	188.2	4.7	5.2	6.7	9.4	12.1	13.6	17.1
	120	69.3	83.5	95.7	129.6	168.7	184.3	251.1	6.2	7.5	8.6	11.6	15.2	16.5	22.6
					Si (cmol$_c$/kg)						**Si (% of total in rock)**				
	Initial	0.4	2.0	9.2	12.0	9.2	36.0	50.4	0.0	0.0	0.2	0.3	0.2	0.8	1.1
Dry	10	34.0	36.8	49.2	78.4	112.4	182.8	238.8	0.8	0.8	1.1	1.8	2.6	4.2	5.5
	60	124.4	134.4	161.2	200.8	249.2	346.0	406.0	2.9	3.1	3.7	4.6	5.7	8.0	9.3
	120	185.6	211.2	252.8	322.4	374.8	459.6	570.0	4.2	4.8	5.7	7.3	8.5	10.4	12.9
	10	11.6	11.6	17.2	32.0	52.0	96.8	134.0	0.3	0.3	0.4	0.7	1.2	2.2	3.0
Wet	60	42.0	52.8	74.4	94.8	100.8	210.8	282.4	1.0	1.2	1.7	2.1	2.3	4.8	6.4
	120	53.2	70.4	91.6	124.4	165.6	246.4	332.8	1.2	1.6	2.1	2.9	3.8	5.7	7.6

Appendix A6. Congruency ratio (CR) for dissolution of milled-basalt dust in 0.01*M* acetic-citric acid, calculated using Eq. (3.3).

Milling		Dissolution Time (day)						
Condition	Time (min)	0.042	1	3	7	14	28	56
					$CR_{(Ca)}$			
Dry	0	1.95	1.10	0.91	0.78	0.69	0.61	0.54
	10	4.11	2.11	1.68	1.41	1.21	1.05	0.91
	60	4.48	2.23	1.75	1.45	1.25	1.07	0.92
	120	3.69	2.09	1.71	1.47	1.30	1.15	1.01
Wet	10	5.73	2.43	1.81	1.44	1.19	0.99	0.82
	60	10.30	3.62	2.52	1.90	1.51	1.21	0.96
	120	15.30	4.89	3.29	2.43	1.89	1.47	1.15
					$CR_{(Mg)}$			
Dry	0	0.34	0.63	0.79	0.93	1.07	1.23	1.42
	10	0.14	0.32	0.43	0.53	0.64	0.77	0.92
	60	0.12	0.28	0.37	0.46	0.55	0.66	0.79
	120	0.20	0.43	0.57	0.71	0.84	1.00	1.19
Wet	10	17.21	5.33	3.55	2.59	2.01	1.55	1.20
	60	12.67	4.05	2.73	2.01	1.57	1.22	0.95
	120	8.89	4.29	3.33	2.74	2.34	1.99	1.70
					$CR_{(Na)}$			
Dry	0	0.88	1.13	1.23	1.32	1.39	1.47	1.56
	10	0.48	0.96	1.22	1.47	1.71	2.00	2.33
	60	1.89	1.18	1.00	0.88	0.79	0.71	0.64
	120	0.43	0.95	1.25	1.54	1.83	2.18	2.59
Wet	10	1.23	1.64	1.81	1.95	2.08	2.21	2.36
	60	1.43	2.09	2.38	2.64	2.87	3.12	3.39
	120	4.08	3.27	3.03	2.85	2.72	2.59	2.46
					$CR_{(K)}$			
Dry	0	18.00	9.25	7.34	6.15	5.31	4.59	3.97
	10	15.57	7.75	6.09	5.05	4.34	3.72	3.20
	60	8.13	4.90	4.11	3.59	3.21	2.87	2.57
	120	12.72	7.19	5.90	5.07	4.47	3.95	3.48
Wet	10	14.65	6.22	4.63	3.68	3.05	2.53	2.10
	60	4.48	2.88	2.47	2.19	1.99	1.80	1.64
	120	5.45	3.50	3.00	2.66	2.42	2.19	1.99
					$CR_{(Al)}$			
Dry	0	0.46	0.71	0.83	0.94	1.03	1.14	1.25
	10	2.10	1.97	1.93	1.90	1.87	1.85	1.82
	60	3.74	3.19	3.02	2.89	2.80	2.70	2.61
	120	2.17	2.38	2.46	2.53	2.58	2.64	2.69
Wet	10	3.39	2.80	2.62	2.49	2.39	2.29	2.20
	60	7.03	4.37	3.71	3.26	2.94	2.65	2.39
	120	6.03	3.99	3.46	3.10	2.83	2.59	2.37

Appendix A7. Congruency ratio (CR) for dissolution of milled dolerite in 0.01*M* acetic-citric acid, calculated using Eq. (3.3).

Milling		Dissolution Time (day)						
Condition	Time (min)	0.042	1	3	7	14	28	56
		$CR_{(Ca)}$						
Dry	0	8.52	3.29	2.37	1.84	1.49	1.21	0.98
	10	6.71	2.51	1.79	1.37	1.11	0.89	0.72
	60	5.13	2.25	1.69	1.36	1.13	0.95	0.79
	120	4.29	2.28	1.83	1.54	1.34	1.17	1.02
Wet	10	7.52	2.81	2.00	1.54	1.24	1.00	0.81
	60	9.82	3.34	2.30	1.72	1.36	1.08	0.85
	120	14.03	4.21	2.77	2.01	1.54	1.19	0.91
		$CR_{(Mg)}$						
Dry	0	1.85	1.44	1.32	1.23	1.17	1.10	1.04
	10	1.30	1.26	1.25	1.24	1.23	1.22	1.21
	60	2.52	1.95	1.79	1.67	1.58	1.50	1.41
	120	2.28	2.14	2.09	2.06	2.03	2.00	1.97
Wet	10	1.39	1.19	1.12	1.08	1.04	1.00	0.97
	60	1.55	1.37	1.31	1.27	1.23	1.20	1.16
	120	0.68	0.94	1.04	1.14	1.22	1.31	1.40
		$CR_{(Na)}$						
Dry	0	1.56	1.66	1.70	1.73	1.75	1.78	1.80
	10	2.77	2.52	2.44	2.38	2.33	2.28	2.23
	60	1.01	1.58	1.84	2.07	2.28	2.52	2.77
	120	0.38	1.02	1.43	1.86	2.31	2.86	3.55
Wet	10	1.46	1.65	1.73	1.79	1.84	1.89	1.94
	60	2.64	2.40	2.32	2.26	2.21	2.17	2.12
	120	2.42	2.35	2.32	2.30	2.29	2.27	2.25
		$CR_{(K)}$						
Dry	0	11.80	7.81	6.77	6.07	5.54	5.07	4.63
	10	0.55	0.93	1.13	1.30	1.46	1.65	1.85
	60	0.71	1.04	1.18	1.31	1.42	1.55	1.68
	120	1.16	1.40	1.49	1.57	1.64	1.71	1.78
Wet	10	8.26	4.82	4.00	3.46	3.08	2.74	2.43
	60	2.40	2.25	2.20	2.16	2.13	2.10	2.08
	120	0.71	0.97	1.08	1.18	1.26	1.35	1.45
		$CR_{(Al)}$						
Dry	0	2.39	2.47	2.49	2.51	2.53	2.55	2.57
	10	3.00	2.64	2.53	2.44	2.38	2.31	2.25
	60	2.51	2.35	2.30	2.26	2.23	2.20	2.17
	120	2.56	2.41	2.35	2.31	2.28	2.25	2.22
Wet	10	4.35	3.38	3.09	2.89	2.73	2.59	2.45
	60	3.70	2.97	2.75	2.59	2.47	2.35	2.24
	120	4.72	3.33	2.95	2.69	2.49	2.31	2.14

Appendix A8. Congruency ratio (CR) for dissolution of milled gneiss in 0.01*M* acetic-citric acid, calculated using Eq. (3.3).

Milling		Dissolution Time (day)						
Condition	Time (min)	0.042	1	3	7	14	28	56
		CR $_{(Ca)}$						
Dry	0	40.80	9.20	5.49	3.68	2.66	1.92	1.39
	10	8.89	4.15	3.19	2.60	2.20	1.87	1.58
	60	78.04	16.51	9.64	6.36	4.53	3.23	2.30
	120	9.51	5.55	4.60	3.99	3.54	3.15	2.80
Wet	10	25.53	7.18	4.63	3.30	2.50	1.89	1.44
	60	20.86	7.33	5.10	3.86	3.07	2.44	1.94
	120	2.89	2.17	1.97	1.83	1.71	1.61	1.51
		CR$_{(Mg)}$						
Dry	0	79.10	54.07	47.40	42.81	39.40	36.25	33.36
	10	163.64	61.25	43.57	33.51	27.03	21.80	17.59
	60							
	120							
Wet	10	59.96	37.27	31.61	27.83	25.09	22.61	20.38
	60	75.59	37.63	29.55	24.53	21.06	18.08	15.52
	120	32.66	19.67	16.50	14.41	12.89	11.54	10.33
		CR$_{(Na)}$						
Dry	0	0.01	0.05	0.10	0.16	0.24	0.36	0.54
	10	0.37	0.63	0.76	0.88	0.99	1.11	1.25
	60	5.23	4.19	3.88	3.66	3.48	3.32	3.16
	120	1.15	1.58	1.76	1.92	2.05	2.20	2.36
Wet	10	0.31	0.53	0.64	0.74	0.84	0.94	1.06
	60	0.45	0.80	0.97	1.13	1.28	1.45	1.64
	120	0.08	0.35	0.59	0.87	1.21	1.68	2.32
		CR$_{(K)}$						
Dry	0	2.73	1.75	1.50	1.34	1.21	1.10	1.00
	10	1.79	1.53	1.45	1.39	1.34	1.29	1.25
	60	10.44	4.88	3.75	3.06	2.59	2.19	1.86
	120	0.22	0.55	0.75	0.96	1.17	1.43	1.75
Wet	10	4.13	2.19	1.76	1.49	1.29	1.13	0.98
	60	50.83	13.42	8.46	5.93	4.43	3.31	2.48
	120	1.28	1.32	1.33	1.34	1.35	1.36	1.37
		CR$_{(Al)}$						
Dry	0	3.54	4.28	4.57	4.81	5.01	5.22	5.45
	10	4.17	3.79	3.67	3.58	3.50	3.43	3.36
	60	3.02	3.32	3.43	3.52	3.59	3.67	3.75
	120	0.26	0.76	1.11	1.47	1.87	2.36	2.99
Wet	10	4.00	4.13	4.18	4.21	4.24	4.27	4.30
	60	3.98	3.98	3.98	3.98	3.98	3.98	3.98
	120	1.76	2.42	2.70	2.94	3.15	3.38	3.62

Note: values of CR$_{(Mg)}$ for dry-milled gneiss for 60 and 120 minutes were very large due to nearly 100 % of Mg was dissolved from the rock within 1 days of dissolution period, and the values were not presented.

Appendix A9. Congruency ratio (CR) for dissolution of milled K-feldspar in 0.01*M* acetic-citric acid, calculated using Eq. (3.3).

Milling		Dissolution Time (day)						
Condition	Time (min)	0.042	1	3	7	14	28	56
		$CR_{(Na)}$						
Dry	0	0.07	0.24	0.37	0.51	0.67	0.87	1.14
	10	0.09	0.22	0.29	0.37	0.45	0.55	0.67
	60	0.40	0.71	0.86	1.01	1.14	1.29	1.46
	120	9.13	4.13	3.14	2.54	2.14	1.80	1.51
Wet	10	0.65	1.01	1.18	1.33	1.46	1.61	1.78
	60	2.85	2.95	2.98	3.00	3.02	3.05	3.07
	120	1.87	1.87	1.87	1.87	1.87	1.87	1.87
		$CR_{(K)}$						
Dry	0	0.68	0.74	0.77	0.79	0.81	0.82	0.84
	10	1.60	0.93	0.78	0.67	0.60	0.53	0.47
	60	2.03	1.58	1.44	1.35	1.28	1.21	1.14
	120	5.72	2.36	1.73	1.37	1.13	0.93	0.76
Wet	10	1.51	1.56	1.58	1.59	1.61	1.62	1.63
	60	9.70	5.31	4.31	3.67	3.22	2.82	2.47
	120	9.45	4.86	3.86	3.23	2.79	2.41	2.09
		$CR_{(Al)}$						
Dry	0	1.23	2.63	3.43	4.20	4.96	5.86	6.92
	10	3.42	2.06	1.73	1.51	1.35	1.21	1.08
	60	2.12	2.12	2.12	2.12	2.12	2.12	2.12
	120	1.74	1.74	1.74	1.74	1.74	1.74	1.74
Wet	10	6.84	6.63	6.56	6.50	6.46	6.41	6.37
	60	13.81	9.15	7.93	7.10	6.49	5.93	5.42
	120	4.08	4.08	4.08	4.08	4.08	4.08	4.08

Appendix A10. The percentages of dissolved (Ca + Mg)[1] from basalt and dolerite SRFs in soils after incubation for the first hour (rapidly dissolved), 2 and 10 months (designed as E_0, E_{2M}, and E_{10M} respectively), which were calculated as CH_3COONH_4-exractable (Ca + Mg) for soil-SRF mixture minus that for control soil (nil SRF), relative to total of (Ca + Mg) in 1 g SRF added.

		Basalt SRF												Dolerite SRF											
No	Soil	E_0 (%)				E_{2M} (%)				E_{10M} (%)				E_0 (%)				E_{2M} (%)				E_{10M} (%)			
	Code	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120
1	ALB-1	-1.73	1.44	3.11	2.30	8.39	4.87	17.50	17.53	5.15	1.99	11.31	18.13	2.48	3.29	8.22	10.89	1.60	4.84	16.29	23.42	4.04	11.02	23.33	28.97
2	ALB-5	-1.58	-3.87	10.73	0.65	1.91	2.26	12.71	15.82					-1.93	-8.01	-4.49	3.14	0.14	0.35	3.96	7.60				
3	DEN-2	1.03	4.64	9.88	3.64	1.24	18.31	25.62	18.31					1.93	-1.42	4.44	6.52	2.81	5.25	10.97	17.94				
4	DEN-4	-7.22	0.61	0.96	-6.36	6.22	5.80	10.35	12.44					1.66	2.94	10.52	10.31	3.17	4.35	12.82	14.69				
5	DEN-7	-2.38	-0.04	3.91	1.58	5.18	10.34	11.04	8.71					2.24	1.74	7.12	11.58	3.25	4.08	11.20	14.03				
6	KTG-6	-2.67	2.54	1.58	1.37	16.38	21.64	36.86	45.15					12.19	14.91	20.26	21.03	17.49	17.70	25.83	34.03				
7	WP-6	-0.04	2.45	4.58	2.31	1.61	6.61	16.27	19.32	1.78	7.60	13.03	14.98	-0.68	0.16	5.95	7.57	-0.16	3.71	11.48	16.84	3.70	6.14	17.32	17.82
8	MR-6	-0.33	2.58	8.33	3.37	1.94	3.18	10.82	7.47	0.50	2.81	11.02	9.99	0.93	0.87	5.92	8.71	0.43	2.61	12.39	13.90	0.11	3.02	12.56	16.54
9	SCP-3	-1.63	-0.19	9.27	-1.34	2.68	5.70	22.01	6.72					0.31	-0.71	5.07	4.24	-1.01	0.41	7.15	7.86				
10	SCP-4	-1.27	7.51	13.44	14.39	8.53	4.80	14.57	28.88					-0.51	3.51	12.24	8.05	1.10	4.99	8.51	11.69				
11	SCP-5	10.39	12.85	14.96	12.38	20.02	24.78	44.16	36.36					12.53	10.50	16.77	19.29	18.28	21.26	32.72	39.42				
12	SCP-6	0.61	3.81	6.23	2.21	7.01	5.57	11.48	14.30					1.77	-0.35	5.05	4.78	1.17	8.70	6.80	18.36				
13	SCP-11	5.01	5.47	16.65	8.83	6.42	8.69	20.12	16.30	10.40	12.58	22.95	18.99	-1.57	-5.83	8.10	3.05	5.32	7.38	16.88	12.58	13.67	16.45	25.65	20.85
14	PTN-3	-3.62	1.90	1.81	7.29	10.82	12.68	17.46	18.01					6.15	5.72	10.09	10.76	6.92	9.50	17.12	19.35				
15	PTN-4	0.93	4.16	6.36	8.49	-12.30	-9.78	-2.30	-6.33	1.11	4.29	11.54	10.73	-2.11	-1.81	3.93	8.89	0.71	4.34	13.56	15.61	-0.07	4.92	14.67	18.89
16	PTN-5	0.56	1.44	3.99	1.74	5.74	7.72	15.98	20.36	1.98	11.02	14.66	21.30	-11.47	-9.54	-5.46	-6.52	4.95	7.77	17.06	20.97	4.30	13.32	19.21	26.16
17	BSN-1	2.77	4.70	11.84	7.36	0.68	4.28	11.64	4.60	0.83	2.20	8.48	7.38	-2.51	-0.09	6.27	7.71	0.26	4.13	10.53	12.95	0.67	3.13	13.18	14.84
18	BSN-4	2.34	1.51	2.56	2.81	8.48	7.53	14.72	27.90	15.68	18.87	23.18	34.48	-2.41	-1.41	4.81	5.57	1.06	5.37	16.33	18.15	11.63	22.47	30.44	29.04
19	DP-1	-2.75	2.99	11.10	10.94	10.72	9.05	26.65	22.79	9.36	12.95	24.38	24.05	12.91	16.22	20.47	17.20	0.04	6.19	13.38	14.86	9.82	14.80	21.92	28.77
20	DP-6	11.06	14.64	20.49	15.11	14.00	10.94	21.23	18.49	12.01	14.85	23.03	26.94	-1.95	-1.31	0.24	2.85	-0.13	4.70	8.11	8.56	7.89	12.21	14.75	19.91
21	BTN-2	-2.53	-1.74	3.07	4.54	11.90	13.71	17.06	23.23					25.67	32.42	30.53	35.40	1.87	4.73	12.45	16.62				
22	BTN-3A	-1.03	5.74	7.58	7.72	3.38	3.57	3.84	10.89					-1.03	0.64	4.69	4.33	-6.39	1.35	10.58	11.06				
23	BTN-3B	-0.34	-0.36	2.54	0.45	4.49	9.65	8.05	20.52					-13.01	-10.62	-0.59	0.35	-11.22	-7.57	9.92	6.63				
	Mean	0.24	3.25	7.61	4.86	6.32	8.34	16.86	17.77	5.88	8.92	16.36	18.70	1.81	2.25	7.83	8.94	2.25	5.48	13.31	16.40	5.58	10.75	19.30	22.18
	Std Dev	4.12	4.20	5.35	5.23	6.48	7.03	9.97	10.67	5.54	5.98	6.26	8.39	8.10	9.32	8.17	8.36	6.15	5.61	6.23	7.78	4.93	6.40	5.93	5.53

[1] Mean values of triplicate measurements

Appendix A11. The percentages of dissolved (K + Na)[1] from gneiss and K-feldspar SRFs in soils after incubation for the first hour (rapidly dissolved), 2 and 10 months (designed as E_0, E_{2M}, and E_{10M} respectively), which were calculated as CH_3COONH_4-exractable (K + Na) for soil-SRF mixture minus that for control soil (nil SRF), relative to total of (K + Na) in 1 g SRF added.

		Gneiss SRF												K-feldspar SRF											
No	Soil	E_0 (%)				E_{2M} (%)				E_{10M} (%)				E_0 (%)				E_{2M} (%)				E_{10M} (%)			
	Code	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120	T0	T10	T60	T120
1	ALB-1	4.52	7.90	14.17	33.08	7.11	13.00	27.67	48.34	8.01	11.37	31.75	53.66	0.95	5.12	13.73	25.89	0.18	7.51	24.51	37.22	13.27	16.11	41.33	42.65
2	ALB-5	20.87	25.54	35.96	54.83	27.13	28.09	43.65	64.23					10.06	14.16	26.98	39.02	8.93	14.32	33.02	43.55				
3	DEN-2	-1.68	0.85	6.68	26.45	9.30	19.07	24.67	49.65					1.01	4.37	18.31	25.26	1.01	6.06	21.72	32.22				
4	DEN-4	4.01	7.05	19.59	35.50	20.74	25.28	33.16	57.80					2.78	7.07	16.59	29.32	2.02	9.36	24.42	36.85				
5	DEN-7	-4.13	4.38	15.04	32.67	7.75	14.44	31.08	36.74					-1.22	2.92	13.21	29.12	2.93	6.41	18.15	29.32				
6	KTG-5	-4.65	-2.94	5.61	8.15	43.28	43.50	51.34	87.71					0.52	0.00	11.43	24.09	1.22	1.82	18.18	28.32				
7	WP-6	-0.52	4.31	15.51	32.04	5.56	11.82	31.48	41.78	7.30	7.51	22.39	49.93	-1.13	2.54	14.22	27.16	2.93	7.79	18.77	32.39	2.17	17.34	38.28	49.28
8	MR-6	-0.13	6.27	19.92	28.73	3.81	9.86	23.66	42.54	5.56	8.36	21.12	31.22	0.73	6.12	15.71	31.32	2.60	6.69	20.58	34.56	-2.57	3.77	26.59	43.35
9	SCP-3	-9.75	-8.16	0.60	13.26	1.03	2.35	12.10	27.97					-0.21	4.08	12.37	22.86	-3.85	0.88	11.85	26.09				
10	SCP-4	-1.72	-3.40	10.43	29.42	5.56	10.97	24.13	43.30					-1.74	2.17	15.88	25.39	4.28	4.84	8.73	22.09				
11	SCP-5	-2.26	-3.46	11.43	31.63	4.91	5.68	16.44	39.64					-0.21	3.89	13.44	24.73	-1.22	0.63	4.51	17.99				
12	SCP-6	-4.07	-1.96	10.09	24.10	3.75	7.64	18.78	50.00					2.57	5.68	14.03	28.76	-0.46	0.16	6.14	21.96				
13	SCP-11	2.91	2.22	13.03	31.42	2.39	8.88	22.39	40.06	7.62	10.71	28.94	39.36	-0.21	3.58	15.88	28.26	-1.90	4.27	7.95	18.29	7.25	11.06	20.29	36.59
14	PTN-3	-4.20	-6.07	5.35	16.30	1.23	5.88	9.76	24.45					0.67	4.08	13.31	27.29	1.83	3.55	9.16	24.73				
15	PTN-4	-0.45	1.31	11.10	33.70	4.20	9.86	20.79	40.88	2.71	12.02	22.19	39.02	-1.90	3.58	15.81	28.22	1.16	0.16	5.62	21.33	2.90	5.50	16.75	46.08
16	PTN-5	-1.42	4.44	11.83	27.35	5.23	9.86	21.19	39.50	1.61	10.97	26.00	27.97	-1.22	1.98	12.01	25.02	0.49	-0.09	4.81	22.49	-0.89	6.94	23.15	51.48
17	BSN-1	-4.26	0.85	9.29	26.31	1.03	6.34	28.94	36.53	-3.29	21.42	28.74	43.09												
18	BSN-4	-4.46	-2.81	8.56	22.38	6.78	11.56	17.65	39.36	6.33	10.84	14.64	26.10												
19	DP-1	-3.62	1.24	4.08	19.82	4.97	12.02	21.72	41.78	5.17	13.59	20.99	45.72	-2.42	2.98	10.52	21.99	-2.11	-5.18	3.83	17.46	0.86	12.69	34.61	44.39
20	DP-6	-11.05	-6.99	4.68	21.55	1.49	8.75	15.91	33.49	4.84	9.86	19.25	35.29	-4.40	0.91	10.91	20.56	0.24	-0.97	0.52	14.80	9.72	11.84	35.32	42.52
21	BTN-2	-3.17	3.33	11.50	28.04	5.56	9.54	22.26	36.40					-1.74	3.05	14.42	26.62	-0.34	4.33	17.47	29.42				
22	BTN-3A	-7.75	-0.20	11.03	27.56	7.17	13.59	26.74	43.30					1.59	4.02	12.05	23.36	0.55	5.78	13.57	24.06				
23	BTN-3B	0.71	1.11	15.78	25.55	33.20	30.50	43.65	89.99					0.06	7.51	12.63	32.89	2.54	5.72	18.57	33.29				
	Mean	-1.58	1.51	11.79	27.38	9.27	13.85	25.62	45.89	4.59	11.67	23.60	39.14	-1.58	1.51	11.79	27.38	9.27	13.85	25.62	45.89	4.09	10.65	29.54	44.54
	Std Dev	6.21	6.83	7.14	9.06	11.05	9.57	10.13	16.02	3.45	3.84	5.19	9.18	2.82	2.92	3.50	4.10	2.64	4.29	8.54	7.60	5.48	4.90	9.05	4.56

[1] Mean values of triplicate measurements

Appendix B1. Results of analysis of variance for the effects of application rate of fertilizers on cumulative yield and cumulative uptake of nutrients for each harvest (H1 – H4). The mean values are presented in Figures 5.1 – 5.6.

Soil & Nutrient	Fertilizer & LSD	Cumulative Yield (g/pot)				Cumulative Uptake (mg/kg)			
		H1	H2	H3	H4	H1	H2	H3	H4
WP-6	Ca-Basalt	S	S	S	S	S	S	S	S
(Ca)	$LSD_{0.05}$	0.13	0.21	0.48	0.46	0.22	1.15	2.58	3.22
	Ca-Dolerite	S	S	S	S	S	S	S	S
	$LSD_{0.05}$	0.14	0.52	1.10	0.92	2.29	2.54	2.60	5.37
	$CaCl_2$	S	S	S	S	S	S	S	S
	$LSD_{0.05}$	0.29	0.49	0.58	0.78	1.82	3.29	4.39	7.37
MR-5	Ca-Basalt	S	S	S	NS	S	S	S	S
(Ca)	$LSD_{0.05}$	0.15	0.35	0.57	-	0.49	2.88	4.40	6.97
	Ca-Dolerite	S	S	S	S	NS	S	NS	NS
	$LSD_{0.05}$	0.25	0.53	0.55	0.88	-	5.01	-	-
	$MgSO_4$	S	S	S	NS	S	S	S	S
	$LSD_{0.05}$	0.18	0.30	0.57	-	1.09	2.17	4.05	-
MR-5	Mg-Basalt	NS	S	NS	NS	NS	NS	NS	NS
(Mg)	$LSD_{0.05}$		0.54	-	-	-	-	-	-
	Mg-Dolerite	S	S	NS	S				NS
	$LSD_{0.05}$	0.18	0.27	-	0.82	0.90	2.20	6.18	-
	K_2SO_4	NS	S	S	S	S	S	S	S
	$LSD_{0.05}$	-	0.66	0.86	1.24	2.09	4.47	4.30	5.85
BSN-1	Gneiss	S	S	S	S	S	S	S	S
(K)	$LSD_{0.05}$	0.19	0.69	0.90	1.20	6.57	16.60	21.41	25.02
	K-feldspar	NS	S	S	S	S	S	S	S
	$LSD_{0.05}$	-	0.46	0.70	1.23	12.24	22.98	25.64	15.17
	K_2SO_4	S	S	S	S	S	S	S	S
	$LSD_{0.05}$	0.08	0.21	0.35	0.74	3.63	4.38	4.39	5.87
SCP-11	Gneiss	S	S	S	S	S	S	S	S
(K)	$LSD_{0.05}$	0.15	0.32	0.31	0.54	5.06	14.66	20.37	26.13
	K-feldspar	NS	S	S	S	S	S	S	S
	$LSD_{0.05}$	-	0.57	1.08	1.19	8.48	13.77	16.53	16.76

S : significant at $\alpha = 0.05$.

NS : not significant at $\alpha = 0.05$.

LSD: least significant different.

Appendix B2. Results of analysis of variance for the effects of the application rate of fertilizers on concentration of plant nutrients in dried tops of ryegrass for each harvest (H1 – H4).

Soil	Fertilizer	Na (%)				Cu (mg/kg)				Zn (mg/kg)				Mn (mg/kg)				Fe (mg/kg)				Si (%)			
		H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4
	$CaCl_2$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Basalt	S(+)	NS	NS	NS	S(-)	NS	NS	NS	S(-)	S(+)	S(+)	S(+)	S(+)	S(+)	S(+)	NS	NS	NS	NS	NS	S(-)	S(+)	S(+)	S(+)
WP-6	LSD$_{0.05}$	0.04				1.0				4.0	2.7	4.0	5.9	27	51	51						0.32	0.25	0.23	0.13
	Dolerite	NS	NS	NS	NS	NS	NS	NS	NS	S(-)	S(+)	S(+)	S(+)	S(+)	S(+)	S(+)	NS	NS	NS	NS	NS	S(-)	S(+)	S(+)	S(-)
	LSD$_{0.05}$									6.3	3.3	4.9	11.7	28	67	96						0.21	0.25	0.21	0.24
	CaCl2	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	LSD$_{0.05}$																								
MR-5	Basalt	NS	NS	NS	S(+)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S(+)	S(+)	S(+)	S(+)
	LSD$_{0.05}$				0.11																	0.20	0.06	0.15	0.28
	Dolerite	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S(+)	S(+)	S(+)	S(+)
	LSD$_{0.05}$																					0.07	0.11	0.11	0.42
	$MgSO_4$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WP-6	Basalt	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Dolerite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	MgSO4	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
MR-5	Basalt	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	Dolerite	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	K_2SO_4	S (-)	S(-)	S(-)	NS	S(-)	S(-)	S(-)	S(-)	NS	S(-)	S(-)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	LSD$_{0.05}$	0.05	0.28	0.35		0.9	2.1	2.9	3.5		3.4	9.2													
	Gneiss	NS	S(-)	S(-)	NS	NS	S(-)	S(-)	NS	NS	S(-)	S(-)	NS	S(-)	S(-)	NS	NS	NS	NS	NS	NS	S(+)	S(+)	S(+)	S(+)
BSN-1	LSD$_{0.05}$		0.19	0.35			1.3	3.5			2.6	8.3		25	46							0.15	0.13	0.18	0.26
	K-feldspar	S(+)	S(-)	S(-)	S(+)	S(+)	S(-)	S(-)	NS	NS	S(-)	S(-)	NS	NS	NS	NS	NS	NS	NS	NS	NS	S(+)	S(+)	S(+)	NS
	LSD$_{0.05}$	0.15	0.10	0.32	0.31	2.2	1.7	2.3			5.0	9.1										0.16	0.08	0.08	
	K_2SO_4	S(-)	S(-)	NS	NS	NS	S(-)	NS	NS	NS	S(+)	S(+)	NS	NS	NS	NS	NS	NS	S(-)	NS	NS	NS	S(-)	S(-)	S(-)
	LSD$_{0.05}$	0.06	0.37				1.4				20.4	65.7							22				0.06	0.06	0.40
SCP-11	Gneiss	S(-)	S(+)	NS	NS	NS	S(-)	S(-)	NS	NS	S(-)	S(-)	NS	S(-)	S(-)	NS	NS	NS	S(-)	S(-)	NS	S(+)	S(+)	S(+)	NS
	LSD$_{0.05}$	0.10	0.13				1.6	1.9			4.9	20.0		31	56				13	73		0.13	0.20	0.24	
	K-feldspar	S(±)	S(±)	NS	S(+)	S(+)	S(-)	S(±)	NS	NS	S(-)	S(±)	NS	NS	NS	NS	NS	NS	S(-)	NS	NS	S(+)	S(+)	S(+)	NS
	LSD$_{0.05}$	0.17	0.09		0.33	1.7	2.1	1.8			25.3	31.3							18			0.09	0.27	0.22	

S: significant ($p < 0.05$), followed by LSD$_{0.05}$ (least significant different at $\alpha = 5$ %); NS: not significant

Signs (+), (-), and (+) are for nutrient concentrations that significantly increase, decrease, increase then decrease (quadratic trends), respectively, with increasing the application rate of fertilizers.

Note: for soil WP-6, the values for H1 – H4 control (nil Ca) and +$CaCl_2$ treatments were excluded from analysis of variance.

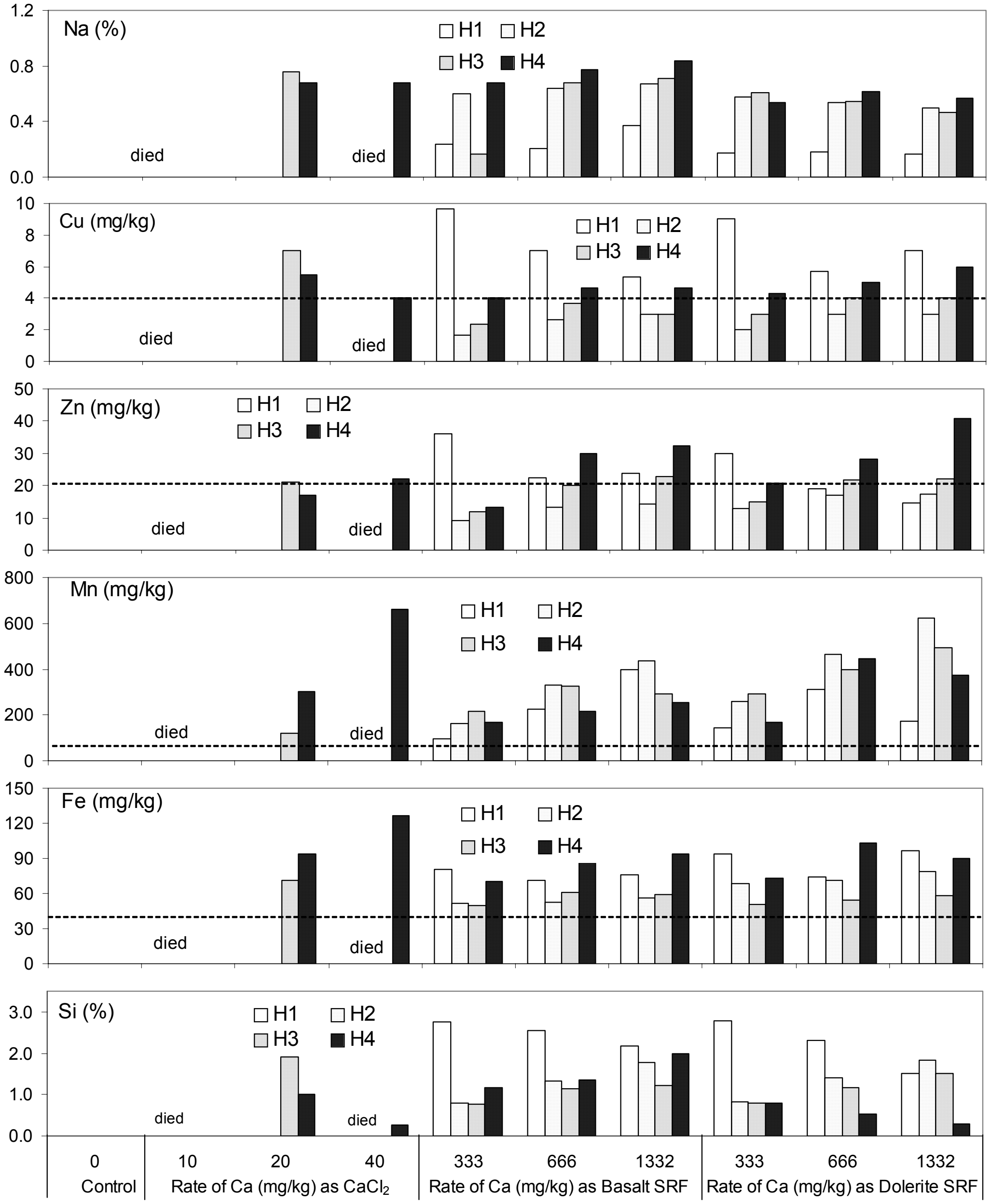
Appendix B2. (continuous)

Soil	Fertilizer	Ca (%)				Mg (%)				K (%)				P (%)				S (%)				Cl (%)			
		H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4
	$CaCl_2$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Basalt	S(+)	S(+)	S(+)	S(+)	NS	NS	NS	NS	S(-)	NS	NS	NS	NS	NS	NS	NS	S(-)	NS	NS	NS	NS	NS	NS	NS
WP-6	$LSD_{0.05}$	0.02	0.02	0.02	0.03					0.13								0.06							
	Dolerite	S(+)	NS	NS	S(+)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S(-)	NS	NS	NS	NS	NS	NS	NS
	$LSD_{0.05}$	0.02			0.02													0.07							
	$CaCl_2$	S(+)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	S(+)	S(+)	S(+)	NS
	$LSD_{0.05}$	0.06																				0.21	0.05	0.02	
MR-5	Basalt	S(-)	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	$LSD_{0.05}$	0.04																							
	Dolerite	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	$MgSO_4$	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
WP-6	Basalt	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Dolerite	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	$MgSO_4$	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
MR-5	Basalt	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	Dolerite	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
	K_2SO_4	NS	S(-)	S(-)	NS	S(-)	S(-)	S(-)	NS	S(+)	S(+)	NS	NS	NS	S(-)	S(-)	NS	NS	NS	S(-)	NS	NS	S(-)	S(+)	NS
	$LSD_{0.05}$		0.10	0.10		0.04	0.06	0.06		0.56	0.06				0.05	0.06				0.05			0.25	0.56	
BSN-1	Greks	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	S(+)	S(+)	S(+)	S(+)	NS	S(-)	S(-)	NS	NS	S(-)	S(-)	NS	NS	S(-)	S(-)	NS
	$LSD_{0.05}$	0.03	0.06	0.08	0.16	0.05	0.05	0.1	0.08	0.38	0.27)	0.11	0.11		0.05	0.04			0.04	0.04			0.19	0.38	
	K-feldspar	S(-)	S(-)	S(-)	NS	S(-)	S(-)	S(-)	S(-)	S(+)	S(+)	S(+)	S(+)	S(+)	S(-)	S(-)	NS	S(+)	S(-)	S(-)	NS	S(+)	S(-)	S(-)	S(+)
	$LSD_{0.05}$	0.06	0.06	0.06		0.05	0.04	0.05	0.07	0.37	0.31	0.06	0.76	0.01	0.05	0.02		0.04	0.04	0.05		0.29	0.24	0.26	0.61
	K_2SO_4	S(-)	S(-)	S(-)	NS	S(-)	S(-)	NS	NS	S(+)	NS	NS	NS	S(-)	S(-)	NS	S(+)	NS	NS	NS	NS	S(-)	S(-)	NS	NS
	$LSD_{0.05}$	0.14	0.18	0.30		0.02	0.13			0.13				0.13	0.07		0.10					0.14	0.39		
SCP-11	Greks	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	NS	S(+)	S(+)	S(+)	S(+)	S(-)	S(-)	S(-)	NS	S(+)	S(-)	S(-)	NS	S(-)	S(-)	NS	NS
	$LSD_{0.05}$	0.04	0.13	0.22	0.20	0.02	0.07	0.03		0.21	0.18	0.19	0.22	0.02	0.03	0.09		0.01	0.05	0.02		0.19	0.20		
	K-feldspar	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	S(-)	NS	S(+)	S(+)	S(+)	S(+)	S(-)	S(-)	S(-)	NS	S(+)	S(-)	S(-)	NS	S(+)	NS	NS	NS
		0.06	0.19	0.24	0.24	0.02	0.08	0.06		0.19	0.11	0.13	0.12	0.02	0.05	0.11		0.02	0.05	0.02		0.36			

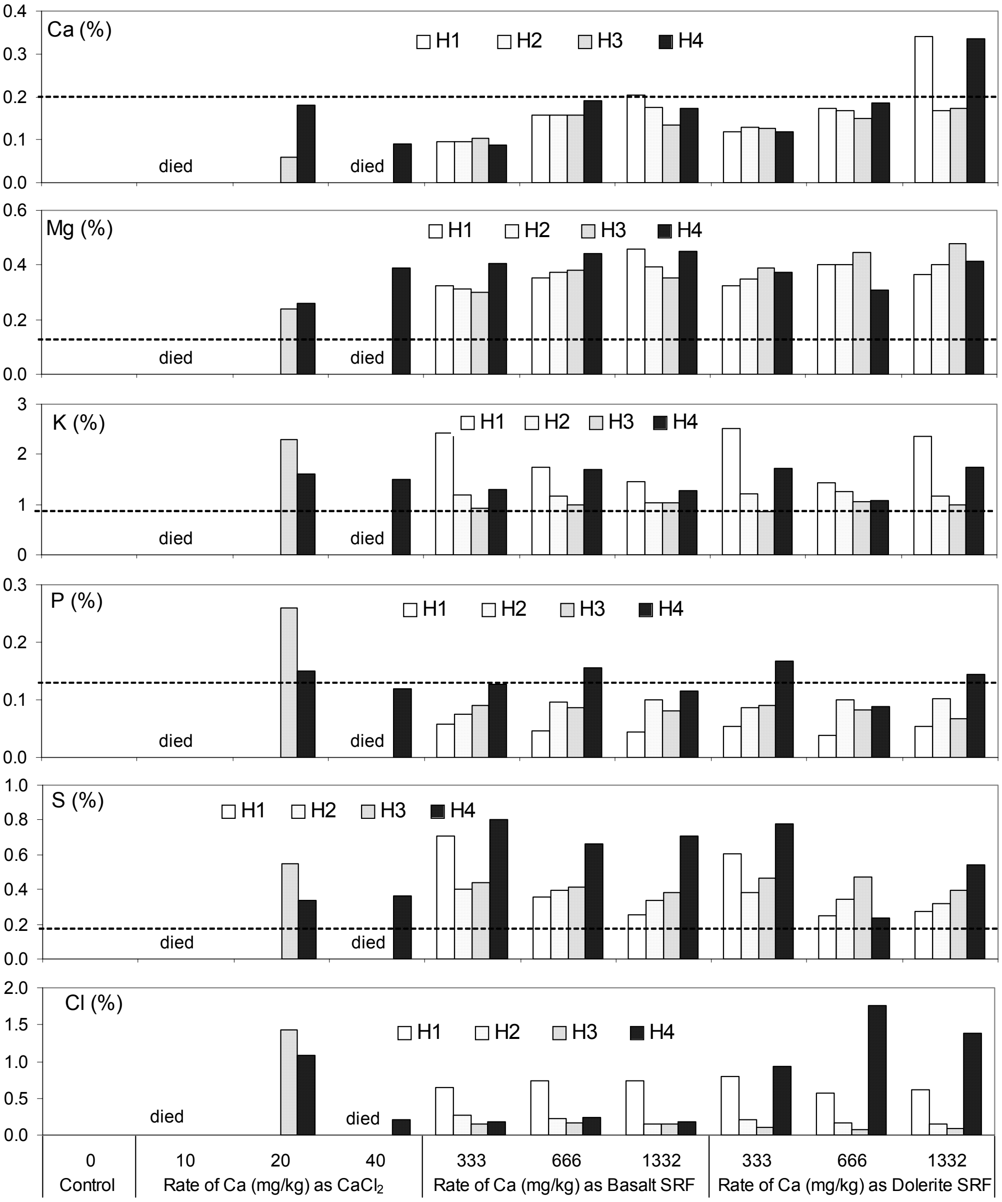
S: significant ($p < 0.05$), followed by $LSD_{0.05}$ (least significant different at $\alpha = 5\ \%$); NS: not significant

Signs (+), (-), and (+) are for nutrient concentrations that significantly increase, decrease, increase then decrease (quadratic trends), respectively, with increasing the application rate of fertilizers.

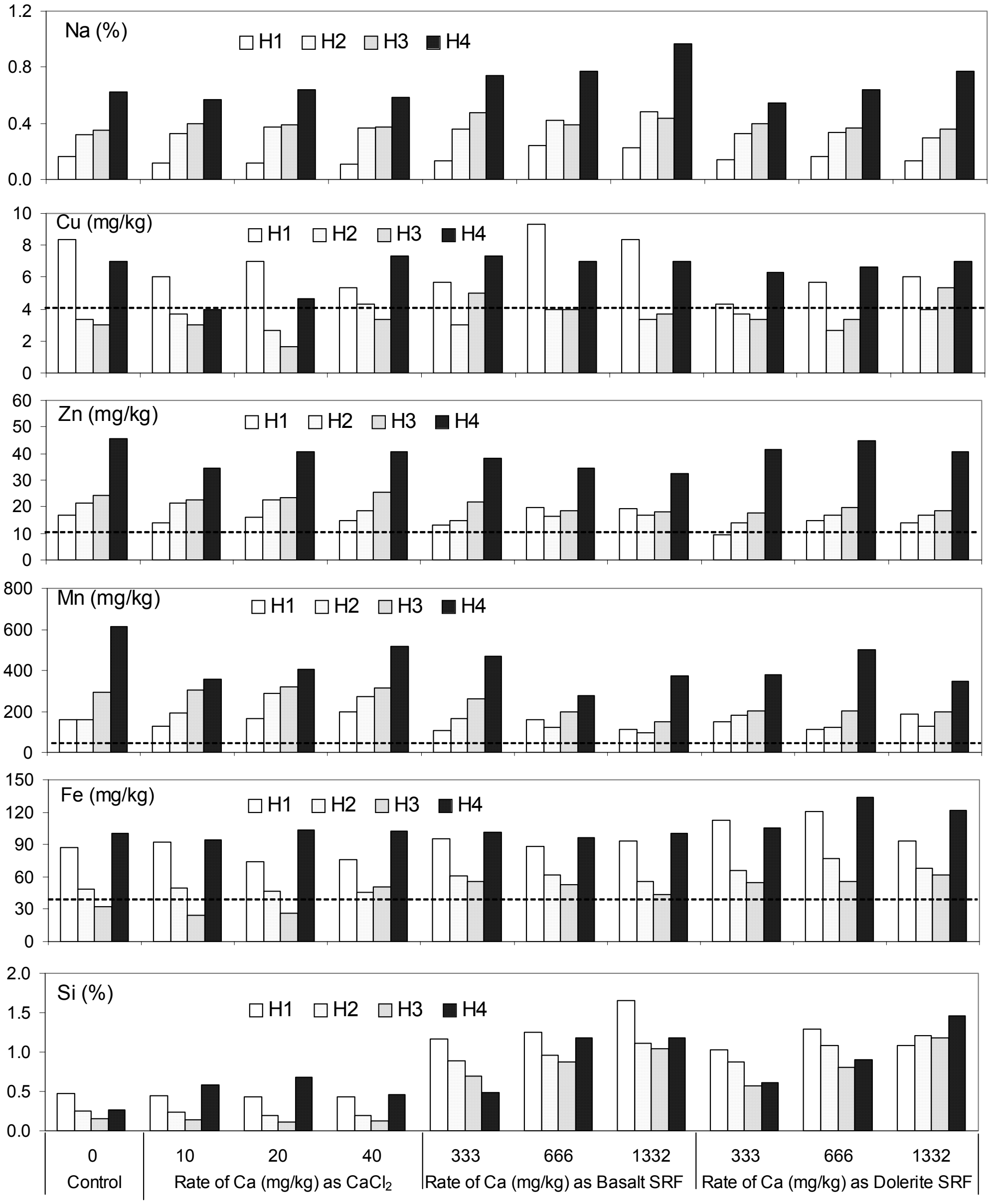
Note: for soil WP-6, the values for H1 – H4 control (nil Ca) and +$CaCl_2$ treatments were excluded from analysis of variance.



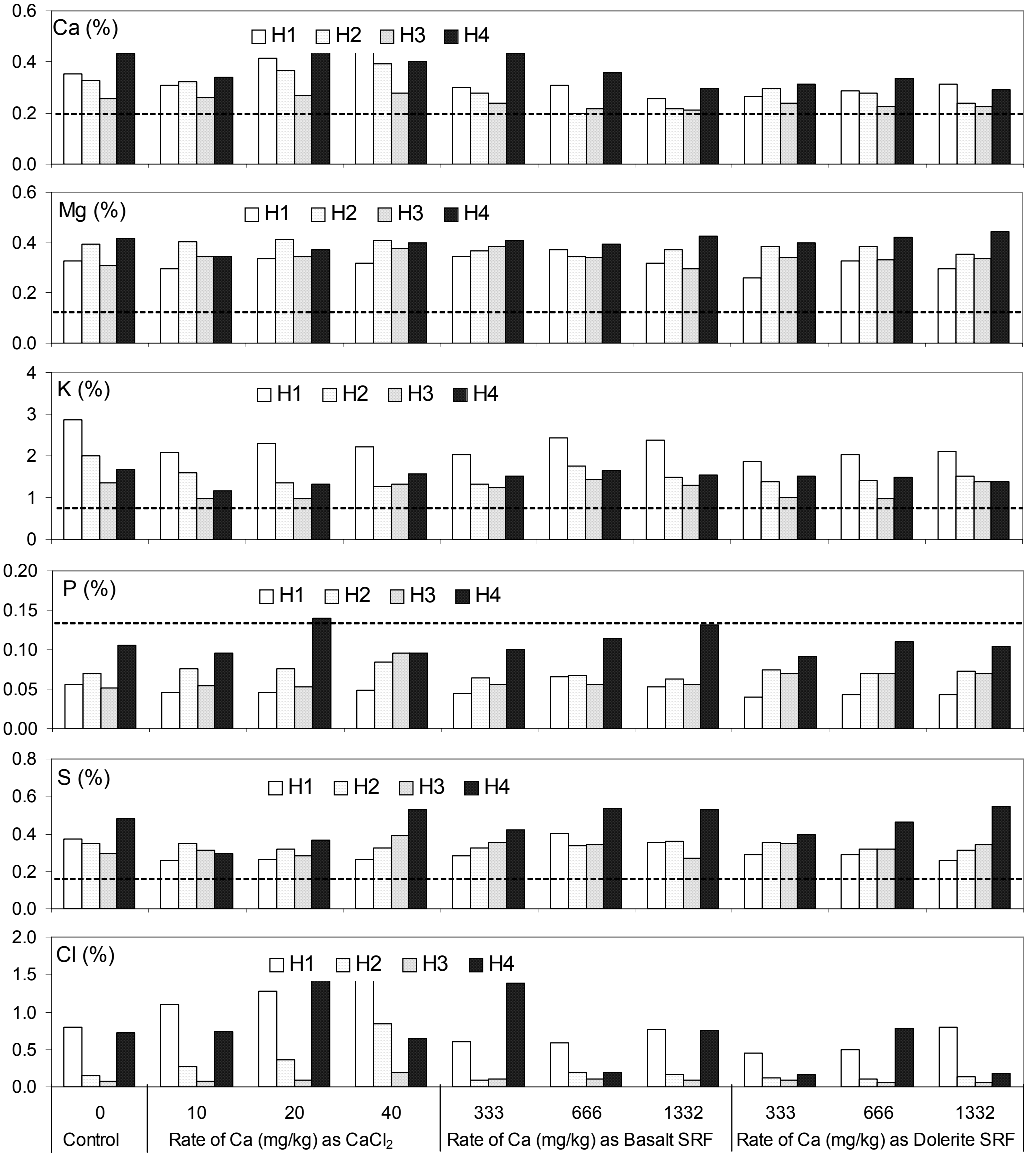
Appendix B3. Mean concentrations of Na, Cu, Zn, Mn, Fe, and Si in oven-dried tops of ryegrass grown on soil WP-6, as a function of the application rate of Ca fertilizers. Plants for the control, +10 and +20 (H4) mg Ca/kg as $CaCl_2$ died, the amounts of dry shoot (H1-H2) for the treatments of +20 and +40 mg Ca/kg as $CaCl_2$ were too small for elemental analysis (data for nutrient concentrations for these treatment are not available). The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



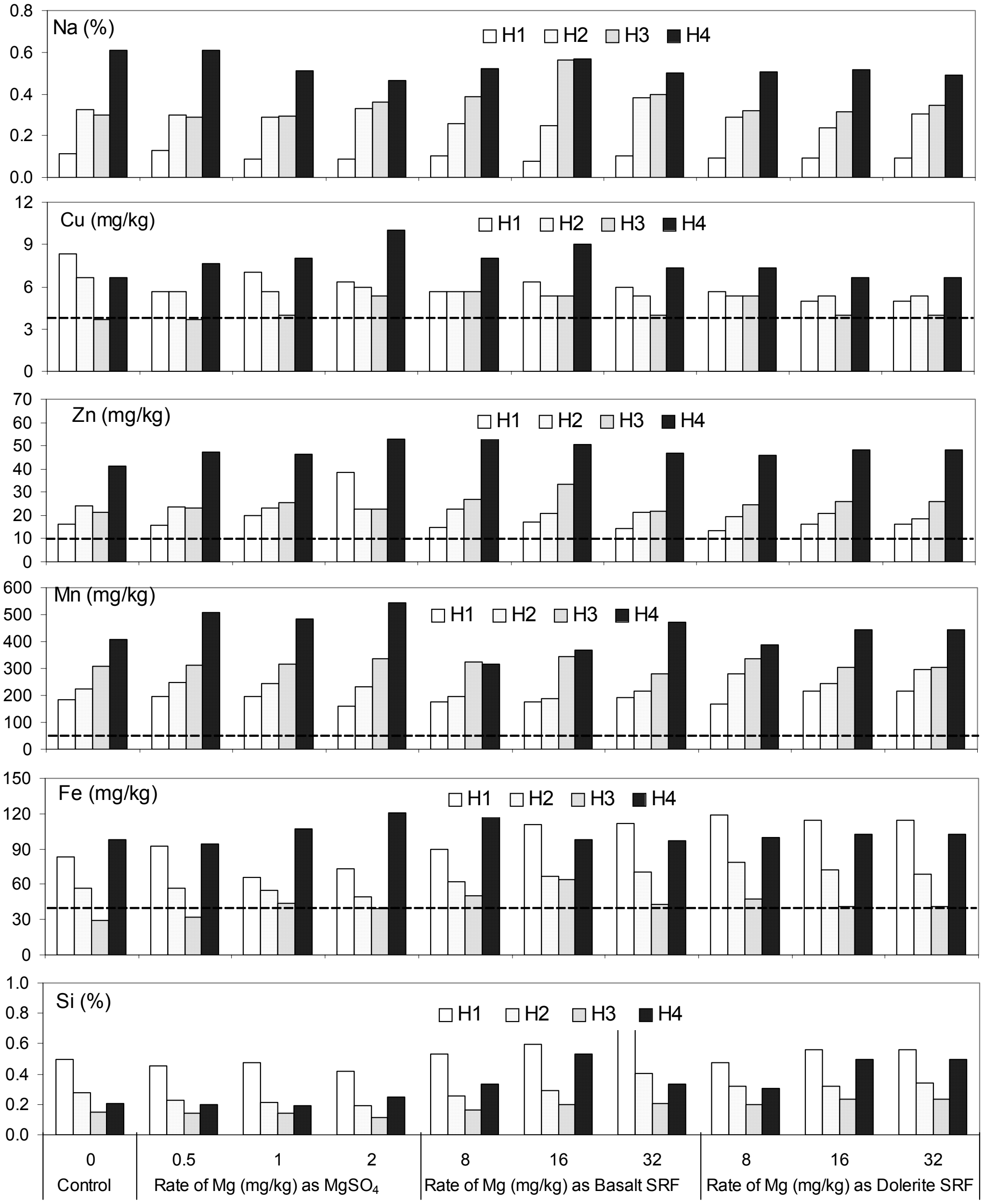
Appendix B4. Mean concentrations of Ca, Mg, K, P, S, and Cl in oven-dried of ryegrass grown on soil WP-6, as a function of the application rate of Ca fertilizers. Plants for the control, +10 and +20 (H4) mg Ca/kg as $CaCl_2$ died, the amounts of dry shoot (H1-H2) for the treatments of +20 and +40 mg Ca/kg as $CaCl_2$ were too small for elemental analysis (data for nutrient concentration for these treatments are not available). The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



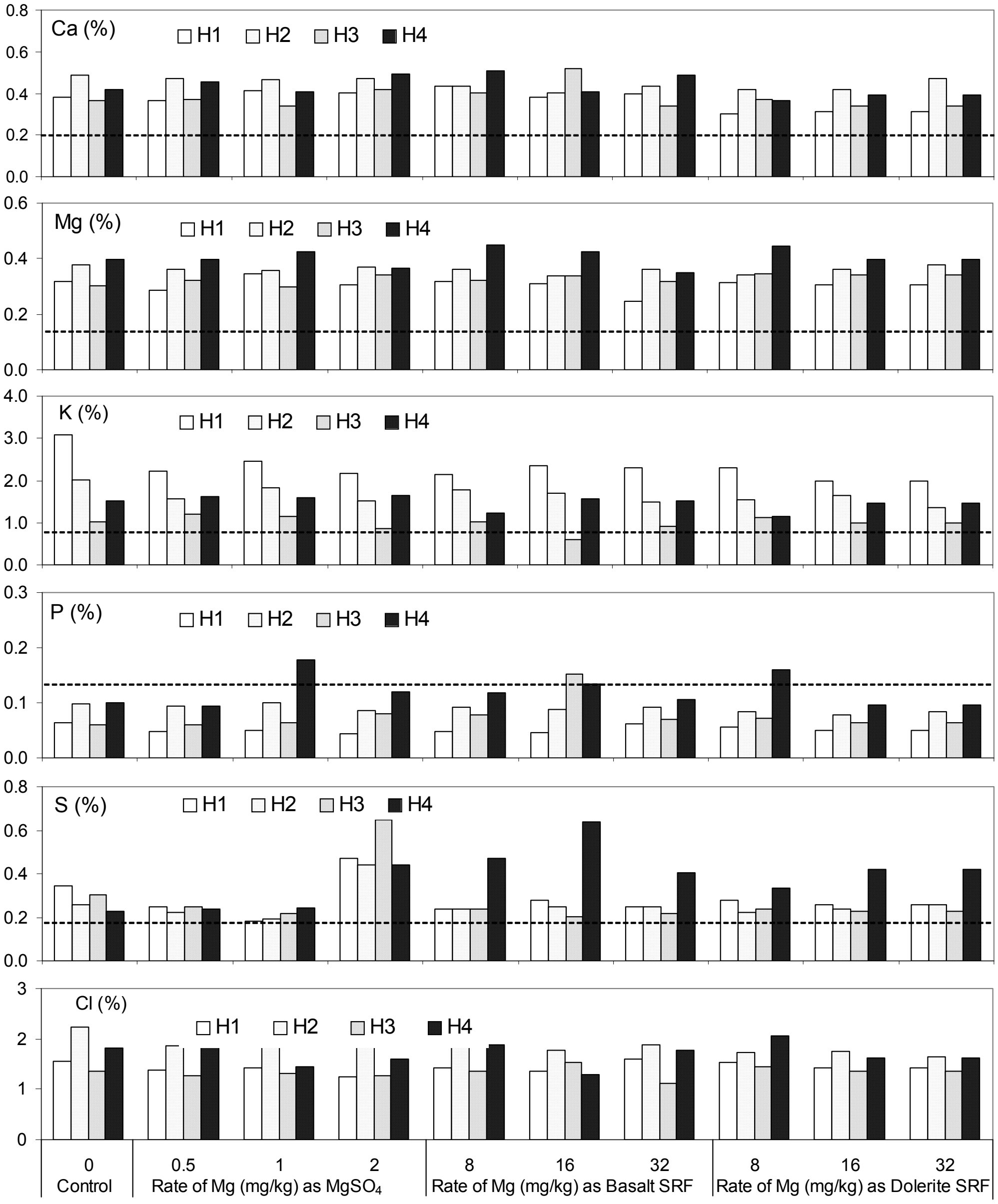
Appendix B5. Mean concentrations of Na, Cu, Zn, Mn, Fe, and Si in oven-dried tops of ryegrass grown on soil MR-5, as a function of the application rate of Ca fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



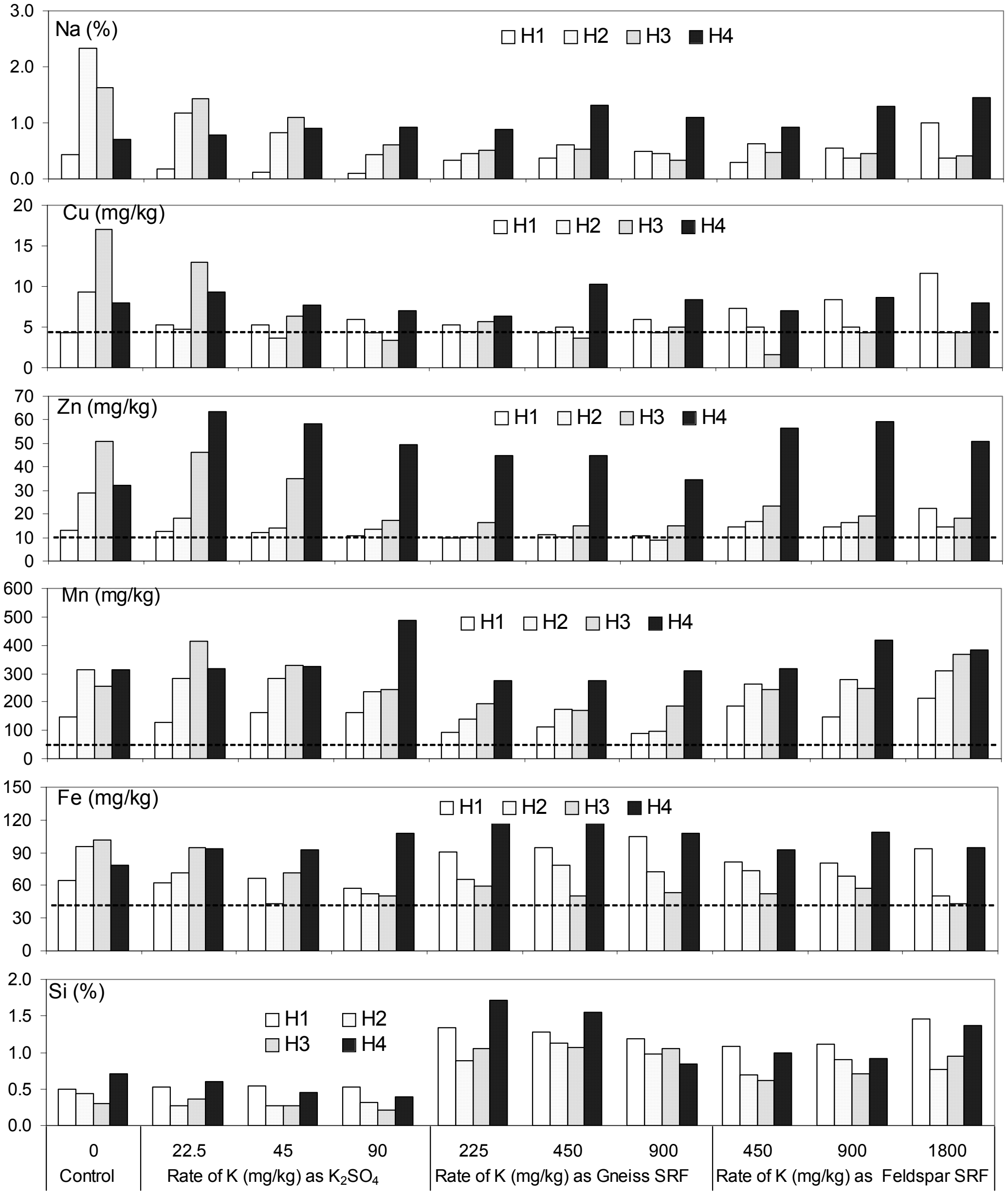
Appendix B6. Mean concentrations of Ca, Mg, K, P, S, and Cl in oven-dried tops of ryegrass grown on soil MR-5, as a function of the application rate of Ca fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



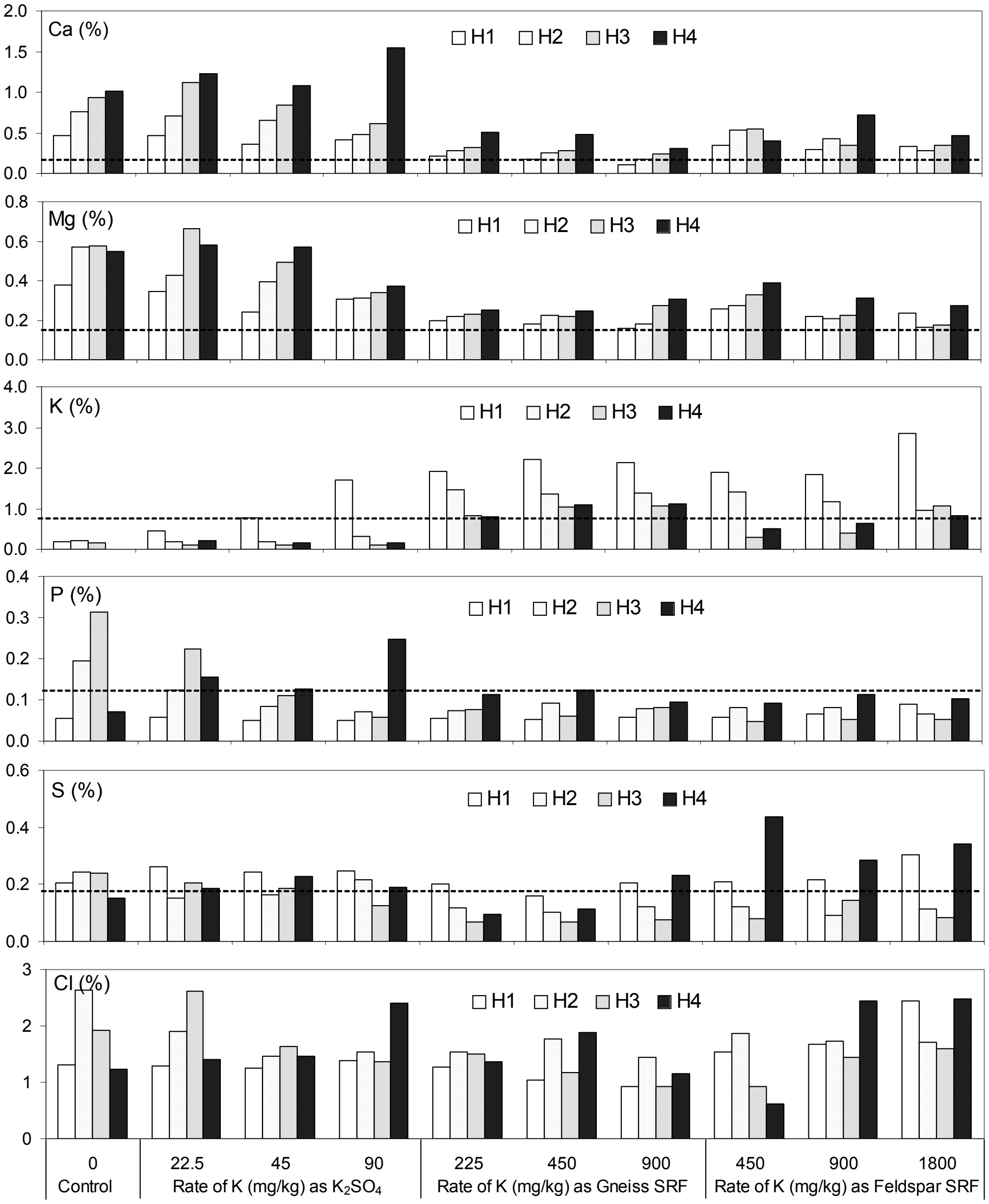
Appendix B7. Mean concentrations of Na, Cu, Zn, Mn, Fe, and Si in oven-dried tops of ryegrass grown on soil MR-5, as a function of the application rate of Mg fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



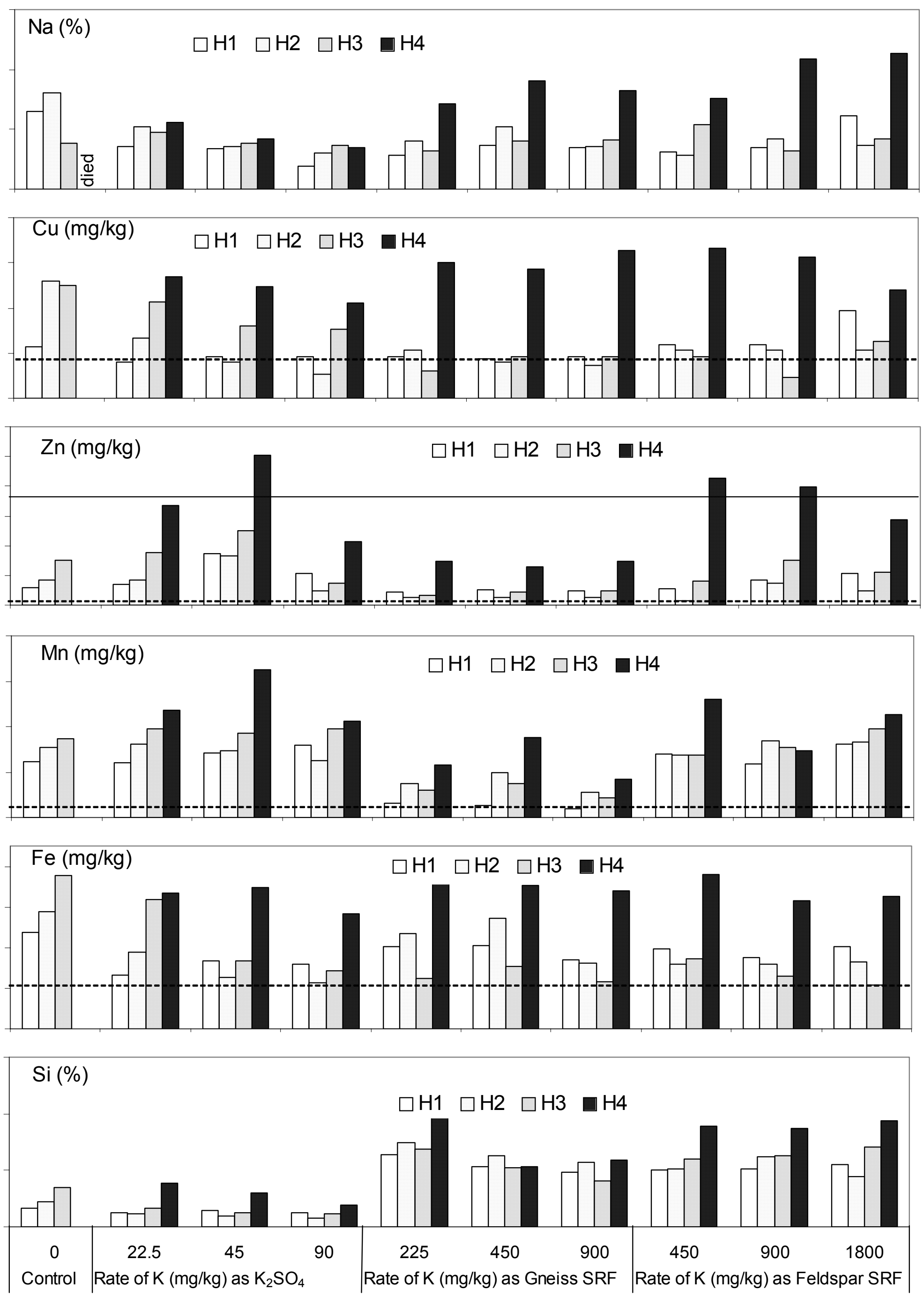
Appendix B8. Mean concentrations of Ca, Mg, K, P, S, and Cl in oven-dried tops of ryegrass grown on soil MR-5, as a function of the application rate of Mg fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



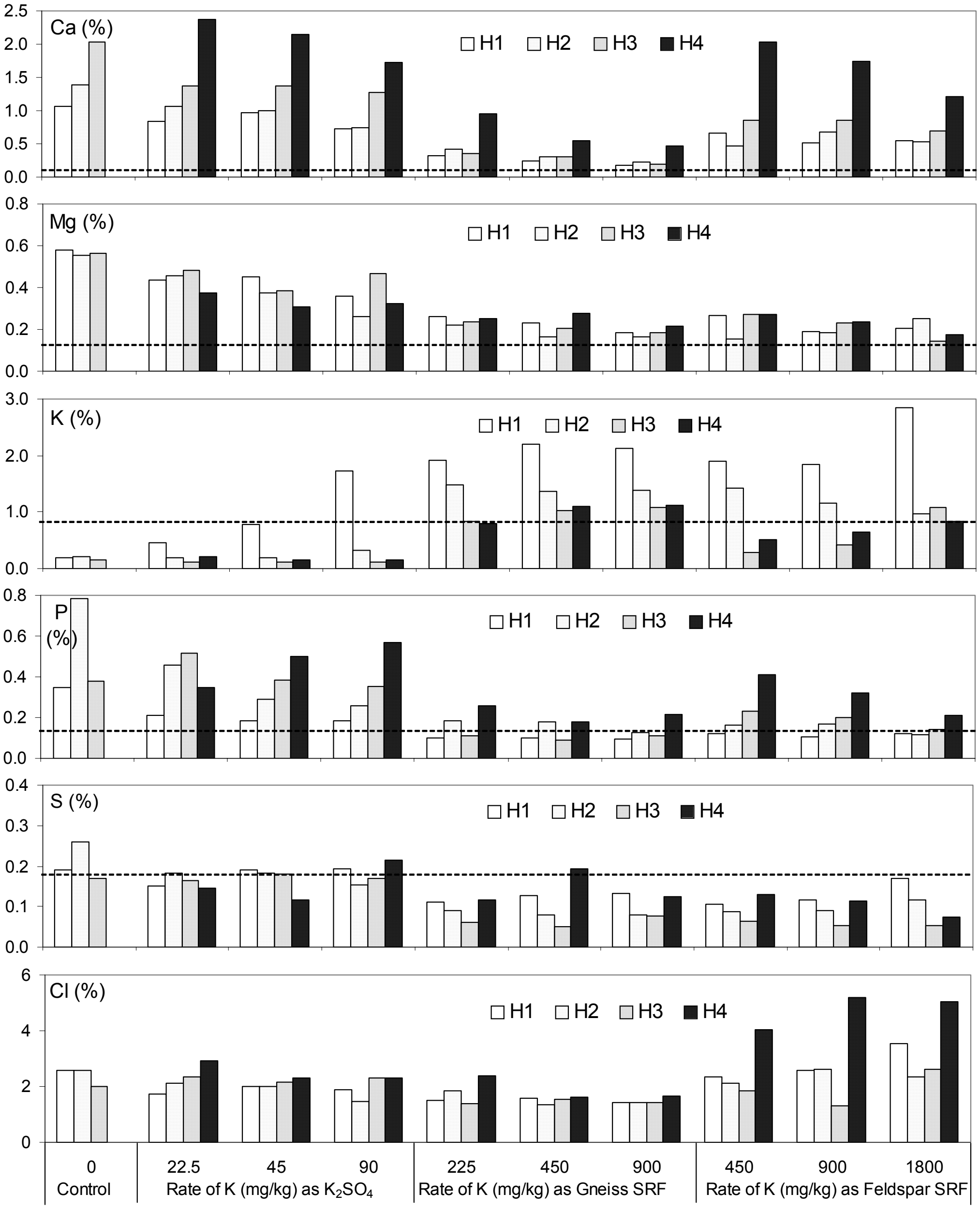
Appendix B9. Mean concentrations of Na, Cu, Zn, Mn, Fe, and Si in oven-dried tops of ryegrass grown on soil BSN-1, as a function of the application rate of K fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



Appendix B10. Mean concentrations of Ca, Mg, K, P, S, and Cl in oven-dried tops of ryegrass grown on soil BSN-1, as a function of the rate of K fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.



Appendix B11. Mean concentrations of Na, Cu, Zn, Mn, Fe, and Si in oven-dried tops of ryegrass grown on soil SCP-11, as a function of the rate of K fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients, and the full lines are for toxic levels in ryegrass (Pinkerton *et al.* 1997).



Appendix B12. Mean concentrations of Ca, Mg, K, P, S, and Cl in oven-dried tops of ryegrass grown on soil SCP-11, as a function of the application rate of K fertilizers. The broken lines are for critical values for deficient levels in ryegrass (Pinkerton *et al.* 1997) but are probably higher than applies to the cultivar used in this research which is highly efficient in utilizing nutrients.

Appendix B13. Calculation of the dissolution of nutrient from SRFs in the soil for Ca experiment on soil WP-6 and K experiment on soils BSN-1 and SCP-11.

Soil &	App. Rate	Uptake (mg/pot)		Ext. Nutr.	Plant-Avail.Nutr.	Dissolved Nutrient	
Treatment	(mg/kg)	Tops	Root	(mg/kg)	(mg/kg)	(mg/kg)	%
	(A)	(B)	(C)	(D)	(E)	(F)	(G)
<u>WP-6</u>							
Control	0			38	38		
Basalt	333	12		80	92	54	16
(Ca)	666	20		125	145	107	16
	1332	25		86	112	74	6
Dolerite	333	16		144	160	122	37
(Ca)	666	24		208	233	195	29
	1332	34		268	302	264	20
<u>BSN-1</u>							
Control	0	21		6	27		
K_2SO_4	22.5	39	6	6	45	17	76
	45	50	14	8	58	31	69
	90	90	17	10	100	73	81
Gneiss	225	213	43	98	354	327	145
(K)	450	239	48	271	557	530	118
	900	289	58	310	657	630	70
K-feldspar	450	120	24	18	161	134	30
(K)	900	191	38	31	261	234	26
	1800	254	51	94	399	372	21
<u>SCP-11</u>							
Control	0	8		4	11		
K_2SO_4	22.5	22	8	3	25	14	62
	45	36	16	5	56	30	67
	90	75	22	5	80	69	77
Gneiss	225	192	71	78	341	330	147
(K)	450	229	85	166	480	469	104
	900	248	92	353	693	682	76
K-feldspar	450	89	33	8	130	119	26
(K)	900	142	53	29	224	213	24
	1800	261	97	74	431	420	23

Calculation procedure (Appendix B13):

1. Values in column B were taken from data of cumulative uptake H4 (Figures 5.1, 5.5, and 5.7); values in column D were from Figures 5.10 and 5.12.
2. Values in column E = B + C + D; F = $E_{(treated)} - E_{(control)}$; G = F/A x 100 %.
3. For K experiment: if 100 % of K was dissolved from K_2SO_4, the values in column F for the $+K_2SO_4$ will be equal to its values in column A. Using this assumption, the nutrient content in plant roots (column C) for the $+K_2SO_4$ will be equal to $[(A + E_{control}) - E_{treated}]$and the results are as presented in the table (highlighted values in column C). The mean percentages of these values (K content in plant roots for + K_2SO_4) relative to K content in plant tops are 20 and 37 %, respectively for soils BSN-1 and SCP-11. These mean values of ratio of % K content in [roots/tops] are used to calculate the values of K content in plant roots (column C) for gneiss and K-feldspar applications, i.e., 20 % x B (for soil BSN-1) and 37 % x B (for soil SCP-11). The values in column C for other treatments were not calculated, so that dissolved Ca from basalt and dolerite would be about 2 – 4 % underestimated.