

6 Plant Growth Experiments

6.1 Introduction

The previous chapter examined dissolution of attrition milled silicate minerals in a simple, closed system. The dissolution of these minerals in soils during plant growth involves more complex processes. Soil minerals are involved in chemical reactions that control the levels of nutrients in the soil solution and influence plant nutrition (Lindsay, 1979). Although soil minerals buffer ion concentrations in solution through adsorption/desorption processes, these readily available exchangeable nutrients may be exhausted by plants within a few growing seasons, and in exportive agricultural systems require replenishment from soil minerals (Pal et al., 2001; Sparks and Huang, 1985). The removal of nutrients such as K, Ca, Mg and Si by plant roots constantly depletes the soil solution, resulting in modifications to solution equilibrium and increased mineral dissolution (Hinsinger, 1998; Hinsinger et al., 2001).

The glasshouse experiment described in this chapter assesses the capacity of milled minerals to supply nutrients to ryegrass and clover. In each case, the effectiveness of minerals as sources of nutrients was compared with soluble sources of these nutrients.

6.2 Materials and Methods

6.2.1 Mineral Preparation

Specimens of microcline, biotite and hornblende were prepared in a small attritor mill as described in Section 3.2.3.

6.2.2 Experimental Design

The experiment was designed to determine the influence of milling and application rate of silicate minerals to soil on plant growth and nutrient uptake. A factorial experimental design was created with four application rates of each mineral for each milling time to determine the ability of (i) microcline to supply K, (ii) biotite to supply K and Mg, and (iii) hornblende to supply Mg and Ca for plant growth, i.e. 4 milling times x 4 application rates x 5 nutrient sources. Additional treatments consisting of three rates of soluble fertiliser containing K, Mg or Ca plus a nil treatment were also included. This large full factorial

design was followed as it was anticipated that high application rates of minerals may influence soil properties including pH so that toxicities or deficiencies of other nutrient elements might occur thereby confounding plant nutrient uptake data for some treatments.

6.2.3 Soil Preparation

To maximise the influence of plant uptake on mineral dissolution during plant growth, chemically inert silica sand was chosen as a soil medium for the glasshouse study. Non-draining pots were prepared with 1kg of sand per pot weighed into plastic bags. A suite of soluble fertilisers containing N, P, Cu, Zn, Mn, Fe, Co, Mo and B were supplied to all pots prior to the experiment to ensure that these were non-limiting for the growth of ryegrass and clover. N was reapplied every two weeks and the other basal nutrients were reapplied after each harvest (every four weeks). The amount of each application (modified from Robson and Snowball, 1989) was: 66mg NH_4NO_3 (23 mg N kg^{-1}), 185mg $\text{NH}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (20mg P kg^{-1}), 2mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5mg Cu kg^{-1}), 2mg $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (1.0mg Zn kg^{-1}), 8mg $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (2.6mg Mn kg^{-1}), 13mg $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (2.6mg Fe kg^{-1}), 0.3mg $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.06mg Co kg^{-1}), 0.2mg $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.08mg Mo kg^{-1}), 0.7mg H_2BO_3 (0.12 mg B kg^{-1}).

In addition to a nil treatment, solutions containing K, Mg and Ca, were prepared with $\text{K}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and additional pots containing three levels of one of these soluble reference fertiliser were applied initially and at each harvest, (*Table 6.1*).

Table 6.1: Amounts of soluble nutrients applied as reference treatments at the start of the experiment and after each harvest.

Nutrient	Nil Treatment	Rate 1	Rate 2	Rate 3
		(mg nutrient) (kg soil) ⁻¹		
K	0	22.5	45	90
Mg	0	0.5	1.0	2.0
Ca	0	10	20	40

Minerals were applied at four rates and thoroughly mixed through the soil. The lowest mineral application rates were based on the assumption derived from the dissolution experiments that about one-third of the mineral may dissolve during the experiment. Consequently, the lowest rate of minerals were applied at rates to provide three times as much nutrient in the mineral as initially supplied by the highest rate of soluble fertiliser.

Mineral application rates are presented in *Table 6.2* and corresponding nutrient application rates are presented in *Table 6.3*. Basal K, Mg and Ca were also applied with the minerals, omitting the element that was being investigated for that mineral.

Table 6.2: Mineral application rates

Nutrient	Mineral	Rate 1	Rate 2 (g mineral)	Rate 3 (kg soil) ⁻¹	Rate 4
K	Microcline	2.90	5.80	11.6	23.2
K	Biotite	3.50	7.00	14.0	28.0
Mg	Biotite	0.08	0.16	0.32	0.64
Mg	Hornblende	0.06	0.12	0.24	0.48
Ca	Hornblende	1.54	3.08	6.16	12.3

Table 6.3: Nutrient application rates

Nutrient	Mineral	Rate 1	Rate 2 (mg nutrient)	Rate 3 (kg soil) ⁻¹	Rate 4
K	Microcline, Biotite	270	540	1080	2160
Mg	Biotite, Hornblende	6.0	12.0	24.0	48.0
Ca	Hornblende	120	240	480	960

Soluble fertilisers were applied and allowed to dry prior to being thoroughly mixed into the soil. The minerals were mixed into the soil before it was wetted to field capacity and allowed to stand for 7 days prior to sowing. There was no replication as data analysis was based on comparison of complete response curves rather than on comparison of individual treatments.

6.2.4 Cropping Technique, Harvest and Analysis

The experiment was performed in a glasshouse under ambient conditions. Fifteen Italian ryegrass seeds (*Lolium multiflorum* cv Richmond) and 10 germinated subterranean clover seeds (*Trifolium subterranean* cv Dalkeith) were sown in each pot, and thinned to 10 and 5 uniform plants respectively after emergence. Soil water was maintained at 90% field capacity and pots were regularly randomised. Plants were initially harvested after six weeks and then every four weeks, with up to nine harvests being collected. Shoots were cut approximately 2 cm from the soil surface, oven-dried at 60°C, and weighed to give dry biomass. The ground shoots were pressed into a pellet with boric acid as a backing material and K, Mg, Ca, P, Si, Zn, Cu, Mn, Cl, S, and Na determined by X-ray

fluorescence spectrometry (XRF). Plant roots were not included in this analysis as plants died at different times, resulting in decay of some roots by final harvest. In addition, the small mineral particles became attached to the densely matted root mass, making it impossible to clean the roots.

6.2.5 Soil Sampling and Analysis

Soil samples were collected at each harvest by collected one soil core of approximately 10 cm³. The samples were air-dried and passed through a 1mm sieve before analysis. The pH and electrical conductivity of a 1:5 soil/water suspension were determined for each pot. Cations were extracted by 1:50 soil/unbuffered 0.1M Ag(TU)⁺ suspension (Rayment and Higginson, 1992) and analysed for K (microcline, biotite), Mg (biotite, hornblende) and Ca (hornblende) by atomic adsorption spectrometry (AAS). The cations are referred throughout this chapter as exchangeable and refer to all readily removed cations whether they be extractable, exchangeable or structural cations.

Mineral samples were recovered from soils by dry sieving with a 90µm sieve after cropping for X-ray diffraction (XRD) analysis to determine mineralogical changes resulting from plant growth. Minerals were collected for each milling time from pots where microcline had been added at 11.6 g kg⁻¹, biotite at 14.0 g kg⁻¹ and hornblende 12.3 g kg⁻¹. These pots were chosen for ease of mineral recovery, their similar application rates, the range of plant growth values and for the range of conditions where the exchangeable pool was exhausted and not exhausted. Microcline and hornblende samples were prepared as random powder samples and biotite samples were prepared as oriented plates. Diffraction patterns were collected with a Philips PW-3020 diffractometer equipped with a diffracted beam graphite monochromator using Cu Kθ radiation generated at 50kV and 20mA with a fixed divergence slit of 1° and a fixed receiving slit of 0.1°. Continuous scans were collected between 5 and 60° 2θ at a speed of 0.02° 2θ sec⁻¹.

6.2.6 Analysis of Data

The nutrient content of dried herbage for the first harvest, calculated by multiplying the nutrient concentration in the dried tops by the yield of the dried tops, was plotted against the level of nutrient applied to enable the calculation of agronomic effectiveness of the milled silicate minerals relative to soluble fertilisers (RE) as described by Bolland and

Baker (2000). Due to curvature of the response functions, RE was calculated by dividing the initial linear slope for silicate mineral fertilisers (0 and two lowest application rates) by the linear slope for soluble fertiliser. Using this criterion, if RE is <1.00 then a mineral fertiliser is less effective than a soluble fertilisers.

Due to the development of elevated metal concentration for some treatments receiving soluble fertilisers, calculation of RE after the first harvest was not possible. In addition, most clover plants did not survive past the second harvest due to nutrient deficiency. Thus, the agronomic relative effectiveness (RE) of silicate minerals was determined from the relationship between the total nutrient content in ryegrass plants that did not experience metal toxicity and the level of nutrient applied. Over the range of data of the experiment, the Mitscherlich equation provided the best description of data summary where minerals were applied at rates greater than 1 g kg⁻¹:

$$y = a - be^{-cx} \quad \text{Equation 6.1}$$

where y is the nutrient element content of dried tops (mg kg⁻¹), x is the level of nutrient applied (mg kg⁻¹), coefficient a is an estimate of the maximum content plateau (mg kg⁻¹), b is the content response, and c describes the curvature of the relationship between plant content and level of nutrient applied. The initial slope can be approximated by bc from fitted curves (Bolland and Baker, 2000), and is used to estimate the relative effectiveness of milling for each mineral for longer growing periods.

A linear equation was used to describe this relationship where biotite and hornblende were applied at rates less than 1 g kg⁻¹:

$$y = a'x + b' \quad \text{Equation 6.2}$$

where y and x are the same as above, and a' is the slope. Comparison of a' values gives an estimate of the relative effectiveness of different milling times for each mineral.

The relationship between Ag(TU)⁺ exchangeable K, Mg and Ca in the soil and the level of nutrient applied were adequately described by a linear equation:

$$y = a''x + b'' \quad \text{Equation 6.3}$$

where y is the exchangeable cation concentration (mg kg⁻¹ soil), x is the level of nutrient applied (mg kg⁻¹ soil), and the slope a'' ((mg exchangeable nutrient)/(mg nutrient applied)⁻¹) provides a measure of exchangeability (Bolland and Baker, 2000). Exchangeable

cations are expressed as mg kg^{-1} during this work to allow for ease of comparison between nutrient uptake and exchangeable nutrients. The $\text{RE}_{\text{exchangeable}}$ values were calculated by dividing the exchangeability values for the silicate minerals by the exchangeability values for the appropriate soluble fertiliser.

6.3 Results and Discussion

A summary of all plant and soil analytical data is in Appendix 2. The appendix has been annotated to indicate plant concentrations that may have either deficient or toxic concentrations based on criteria published by Reuter and Robinson (1997) and these values are used for discussions in this section. The ryegrass cultivar used in this experiment (*Lolium multiflorum* cv Richmond) is used in Western Australian pastures and is adapted to low nutrient status soils. As such, the deficient values used in the following section and Appendix 2 may not be accurate. They do, however, provide a guideline to present and discuss the experimental data.

6.3.1 Initial Nutrient Uptake, Relative Effectiveness and Soil Chemistry

Figures 6.1 and 6.2 show the nutrient element content of ryegrass and clover for all application rates of both mineral and soluble fertilisers for the first harvest collected 43 days after sowing (DAS). Clover growth was much less than that of ryegrass, and the uptake of K and Mg by ryegrass was at least twice that of clover, regardless of the source of these nutrients. Nutrient uptake increased for both ryegrass and clover with increased application of soluble fertiliser, except for clover Mg content at the highest application rate of MgSO_4 . Nutrient uptake by ryegrass generally increased with increasing application rate and milling time of silicate minerals. For clover, there were no uniform trends in the relationships between nutrient content and amounts of nutrient applied as silicate minerals; nutrient content of clover generally increased with application rate and milling time for the two lowest application rates, while this trend reversed at higher mineral application rates.

The nutrient uptake trends are summarized below:

- **K:** K deficiency symptoms were observed in ryegrass shoots for the nil K treatment and the lowest application rate of K_2SO_4 , all treatments of M0, and the lowest rate of M1. K deficiency, as defined by Reuter and Robinson (1997), also occurred in clover shoots for the nil K treatment, the three lowest rates of M0 and the lowest

rate of M1. Biotite was able to supply sufficient K to ryegrass and clover for all milling times and application rates.

- **Mg:** Mg deficiency symptoms were observed in ryegrass shoots in all treatments with MgSO₄, CaCl₂ and K₂SO₄, although Mg deficiency was only observed in clover shoots for the nil Mg treatment and the lowest rate of MgSO₄. This suggests that the concentration of the soluble source of Mg chosen was insufficient for adequate plant growth. For pots with soluble Mg omitted, biotite and hornblende was able to supply sufficient Mg for ryegrass growth at the highest B6, H6 and H24 rate and the three highest B24 rate. Where soluble Mg was added to pots amended with biotite and hornblende, sufficient Mg was supplied by these minerals to overcome deficiency levels.
- **Ca:** Ca deficiency symptoms were observed only in ryegrass shoots grown in the nil Ca treatment.

Other nutrients were also monitored during the experiment and based on the criteria of Reuter and Robinson (1997) the following observations can be made:

- **P:** P deficiency occurred in clover plants grown in pots amended with milled microcline, biotite and hornblende applied at rates greater than 1 g kg⁻¹. P deficiency also occurred in ryegrass grown at the highest rates of B24 and H24.
- **S:** S deficiency occurred in both ryegrass and clover shoots when grown in pots amended with milled microcline and biotite.
- **Cl:** Cl toxicity occurred in clover from several treatments. No single trend was observed for Cl toxicity in clover. Cl uptake for both ryegrass and clover when grown in pots amended with hornblende at greater than 1 g kg⁻¹ was much lower than all other treatments, due to the absence of CaCl₂.
- **Trace Elements:** Zn toxicity occurred in clover for all soluble fertilizer reference treatments, pots amended with M0 and H0, and all treatments where biotite and hornblende were applied at rates less than 1 g kg⁻¹. Mn toxicity occurred in clover grown with the nil Ca treatment, the lowest rate of CaCl₂, and H0 at rates greater than 1 g kg⁻¹. Some Zn, Cu and Mn deficiencies may have existed in both ryegrass and clover, generally in the highest rates of minerals milled for 6 and 24 hours.

- **Si:** Si uptake in ryegrass generally increased with milling time and application rate. Si concentrations in clover samples were below the method detection limit (0.24% Si).

The relative effectiveness values for silicate minerals compared with soluble fertilisers (RE) are presented in *Tables 6.4* (ryegrass) and *6.5* (clover). In all cases, silicate mineral fertilisers were much less effective than soluble fertilisers (mineral RE ranged from 0.01 – 0.29), although the actual recovery of water-soluble fertilisers was very poor (15-28%). Mineral RE generally increased systematically with milling time, except for RE based on K content of ryegrass for soil amended with biotite, Ca content in ryegrass for soil amended with hornblende, and Mg and Ca contents of clover for soils amended with hornblende.

Table 6.4: Value of the initial slope (mg mg⁻¹) of a linear equation fitted to the relationship between nutrient content of ryegrass herbage, 43 DAS and amount of nutrient applied and RE, calculated from slope values.

Nutrient	Fertilizer	Milling Time	Initial Slope	R ²	RE	Percent Recovery	
K	K ₂ SO ₄		0.281	0.99	1.00	28%	
		Microcline	Initial	0.002	1.00	0.006	0.2%
			1 hour	0.014	0.95	0.050	1.4%
			6 hour	0.018	0.84	0.064	1.8%
			24 hour	0.022	0.86	0.079	2.2%
	Biotite	Initial	0.037	0.83	0.131	3.7%	
		1 hour	0.038	0.97	0.136	3.8%	
		6 hour	0.010	0.85	0.036	1.0%	
		24 hour	0.034	0.99	0.121	3.4%	
	Mg	MgSO ₄		0.218	0.97	1.00	22%
Biotite			Initial	0.017	0.77	0.076	1.7%
			1 hour	0.016	0.96	0.072	1.6%
			6 hour	0.027	0.96	0.126	2.7%
			24 hour	0.049	0.95	0.223	4.9%
Hornblende		Initial ¹	--	--	--	--	
		1 hour	0.010	0.97	0.045	1.0%	
		6 hour	0.017	0.99	0.077	1.7%	
		24 hour	0.017	1.00	0.079	1.7%	
Ca		CaCl ₂		0.154	1.00	1.00	15%
	Hornblende	Initial ¹	--	--	--	--	
		1 hour	0.001	0.75	0.009	0.1%	
		6 hour ¹	--	--	--	--	
		24 hour	0.002	0.89	0.012	0.2%	

1. Non-linear relationship

Table 6.5: Values of the initial slope (mg mg^{-1}) of linear equations fitted to the relationship between nutrient content of clover herbage, 43 DAS and amount of nutrient applied and RE calculated from slope values.

Nutrient	Fertilizer	Milling Time	Initial Slope	R ²	RE	Percent Recovery	
K	K ₂ SO ₄		0.059	1.00	1.00	5.9%	
		Microcline	Initial	0.001	0.98	0.010	0.1%
			1 hour	0.004	1.00	0.060	0.4%
			6 hour	0.003	0.98	0.046	0.3%
			24 hour	0.008	0.97	0.136	0.8%
	Biotite	Initial	0.002	0.98	0.039	0.2%	
		1 hour	0.002	0.44	0.028	0.2%	
		6 hour	0.002	0.73	0.033	0.2%	
		24 hour	0.006	0.99	0.095	0.6%	
	Mg	MgSO ₄		0.197	1.00	1.00	20%
Biotite			Initial	0.005	0.84	0.028	0.5%
			1 hour	0.007	0.75	0.033	0.7%
			6 hour	0.008	0.89	0.042	0.8%
			24 hour	0.057	1.00	0.291	5.7%
Hornblende		Initial ¹	--	--	--	--	
		1 hour	0.003	0.81	0.014	1.4%	
		6 hour	0.004	0.85	0.020	2.0%	
		24 hour	0.004	0.99	0.022	2.2%	
Ca		CaCl ₂		0.094	0.98	1.00	9.4%
	Hornblende		Initial	0.002	1.00	0.024	0.2%
			1 hour	0.005	0.73	0.055	0.5%
			6 hour	0.003	0.91	0.032	0.3%
			24 hour	0.002	0.77	0.024	0.2%

1. Non-linear relationship

Soil pH-H₂O amended with milled minerals after 7 days of incubation showed varying responses with respect to mineralogy, application rate and milling time (Figure 6.3). For application rates greater than 1g kg^{-1} , pH values increased with application rate and milling. The largest differences between milled minerals was for hornblende where pH values of soil amended with H0 ranged from 6.5 to 6.7, while pH values for soil amended with H24 ranged from 7.7 to 9.5, i.e. an increase of between 1 and 3 pH units. The soil pH values with hornblende applied at rates of 1.54g kg^{-1} were greater than those for microcline applied at 23.2g kg^{-1} for each milling time. Similar values occurred for biotite and hornblende amended soils, although biotite was applied at rates 2.3 times higher than for hornblende. For biotite and hornblende applied at rates less than 1g kg^{-1} , there was no

systematic effect on soil pH due to differences in milling time or application rate. In general, the pH of soils amended with milled minerals was higher than for the nil treatment except for some microcline treatments.

Exchangeable cation values of soils at the commencement of the experiment for all application rates of both mineral and soluble fertilisers (*Figure 6.4*) increased with both milling time and application rate. Fits to a linear equation for K_2SO_4 and $CaCl_2$ were used to calculate $RE_{\text{exchangeable}}$. The $RE_{\text{exchangeable}}$ values for K and Ca (*Table 6.6*) indicate that although the effectiveness of silicate minerals increased with milling time, all minerals were less effective than soluble fertilisers to supply exchangeable cations. Exchangeable Mg concentrations at the start of the experiment were below the method detection limit (0.012 mg L^{-1}) in soil samples treated with $MgSO_4$ and all biotite and hornblende treatments except for B6 and H24 at the highest application rates and for B24 at all but the lowest application rate (*Figure 6.4*). As a result, $RE_{\text{exchangeable}}$ could not be calculated.

6.3.2 Long-term Nutrient Uptake and Relative Effectiveness

Less than half of the pots were harvested for clover twice due to plant mortality. Analytical results for clover that was collected from the second harvest indicate that nutrient deficiencies of several elements were responsible for poor re-growth after the first harvest. Consequently, only ryegrass results are presented for the longer-term growth periods.

Up to six harvests of ryegrass were collected from the reference pots and up to nine harvests of ryegrass were collected from pots amended with silicate mineral fertilisers. It should also be noted that K_2SO_4 was added inadvertently to the pots containing M0 and M1 after the fourth harvest. By this time, plant growth had ceased in the pots containing M0, and data for subsequent harvests obtained for pots containing M1 are not reported. In addition ryegrass for B1 applied at 7.00 g kg^{-1} , died due to lack of watering after the third harvest. There are also no data for H24 applied at 0.24 g kg^{-1} due to an error in pot preparation.

Table 6.6: Value of the slope of linear equations fitted to the relationship between the amount of $Ag(TU)^+$ exchangeable K and Ca extracted from the soil and the levels of K and Ca applied (coefficient a'' , Equation 6.3), and $RE_{exchangeable}$ values calculated from the a'' coefficients.

Fertilizer	Milling Time	a''	R^2	$RE_{exchangeable}$
K_2SO_4		0.87	0.93	1.00
Microcline-K	Initial ¹	0.00	--	0.00
	1 hour	0.06	0.96	0.07
	6 hours	0.11	0.90	0.13
	24 hours	0.13	0.89	0.15
Biotite-K	Initial	0.08	0.96	0.09
	1 hour	0.11	0.97	0.13
	6 hours ²	0.28	0.99	0.32
	24 hours ²	0.44	0.99	0.51
$CaCl_2$		1.05	0.88	1.00
Hornblende-Ca	Initial ³	--	--	--
	1 hour	0.04	0.57	0.04
	6 hours	0.11	0.94	0.10
	24 hours	0.17	0.96	0.16

1. All values were 0 mg kg^{-1} .
2. Four values used to calculate the linear equation.
3. Non-linear relationship.

Due to the changes in soil properties as a result of addition of milled silicate minerals, particularly to this large increase in pH in some instances, and the increase in solutes due to addition of soluble nutrients, it was anticipated that some plants would be influenced by salt or metal toxicity/deficiency over the long-term growth period. Using values published by Reuter and Robinson (1997) as a guide, toxic concentrations of Zn, Cu, Mn and Cl may have occurred and these data are highlighted in Appendix 2 and are shown on the summary figures (*Figures 6.5, 6.6 and 6.7*) as hollow symbols.

Analytical data for ryegrass from the reference pots indicated the possible occurrence of trace element and chloride toxicities by the third harvest (98 DAS). This was accompanied by a reduction in plant growth. As a result, results for the long-term uptake from the reference pots have not been used in interpretation of data.

A summary of the long-term nutrient uptake trends is presented below:

- **Microcline K:** K deficiency was observed predominately in ryegrass shoots grown in pots amended with M0 and M1, leading to ryegrass death generally after 129

days of growth (*Figure 6.5*). K deficiency in these pots may have been due to Zn, Cu, Mn and/or Cl toxicity. The K uptake curves for M6 and M24, especially at the higher application rates, showed continuing K uptake throughout the course of the experiment without K deficiency or trace element toxicity. High concentrations of Cl in plants occurred for the later harvests.

- **Biotite K:** Ryegrass grown in biotite treated pots persisted throughout the course of the experiment (*Figure 6.5*). K deficiency was not observed until harvest 6 (184 DAS) and even then only at the lowest rate of B0. Possible deficiency at subsequent harvests only occurred at the lowest application rate of B6 and B24, and plant death may have been due to salt and/or trace element toxicity rather than to K deficiency.
- **Biotite and Hornblende Mg:** Mg deficiency in ryegrass probably occurred for the first harvest and continued for subsequent harvests, resulting in low Mg uptake values (*Figure 6.6*). The uptake curves for both minerals follow a similar trend, although Mg concentrations in ryegrass grown on biotite were about twice that of hornblende. Some plants however were able to obtain sufficient Mg for the fourth (129 DAS) and fifth (156 DAS) harvests. B24 and H24 applied at the highest rate were able to sustain sufficient Mg levels in ryegrass for 184 days of growth. Salt and metal toxicity appear to have become prevalent by the third harvest (98 DAS), and were probably responsible for the death of ryegrass plants with sufficient Mg in shoots for later harvests.
- **Hornblende Ca:** Although Ca was taken up by ryegrass for most pots amended with hornblende throughout the course of the experiment (268 days), less than 8% of the applied Ca was utilised by ryegrass during this experiment. The Ca uptake response curves (*Figure 6.7*) indicate that although uptake was greater for milled than unmilled hornblende, there was little response to increasing milling time or application rate. There were also no symptoms of Ca deficiency in these pots suggesting that sufficient Ca was being obtained by the ryegrass. Ryegrass death did occur as a result of Ca deficiency in pots amended with H0 at the three lowest rates and H1 at the lowest rate, although it is possible that trace element toxicity occurred where unmilled hornblende was applied.

Data for plants that may have contained toxic concentrations of Cu, Zn or Mn were discarded from further analysis. These data include the ryegrass data for the reference pots where possible metal toxicities were observed by the third harvest. Over the range of data, the Mitscherlich equation provided the best summary of ryegrass K and Ca contents summed over all harvests versus the level of nutrient applied. The initial slope of the fitted curve bc was used to determine the relative fertiliser effectiveness (RE) of the minerals (Table 6.7).

Table 6.7: Values of coefficients of the Mitscherlich (Equation 6.1) equation fitted to the relationship between the total nutrient content for all harvests of ryegrass and level of nutrient applied. RE was determined from the initial slope (bc).

Nutrient	Mineral	Milling Time	a ($mg\ kg^{-1}$)	b ($mg\ kg^{-1}$)	c ($\times 10^{-3}$)	R^2	RE (bc)
K	Microcline	Initial	11.9	11.7	0.17	0.98	0.002
		1 hour	179	185	0.36	0.97	0.067
		6 hour	178	183	1.35	0.98	0.247
		24 hour	180	183	1.98	0.99	0.362
K	Biotite	Initial	135	129	2.16	0.93	0.279
		1 hour	156	150	1.52	0.83	0.228
		6 hour	181	176	1.86	0.98	0.327
		24 hour	205	207	2.16	0.99	0.447
Ca	Hornblende	Initial	8.47	5.75	0.19	0.93	0.001
		1 hour	15.0	13.0	1.43	0.95	0.019
		6 hour	12.0	9.38	4.03	0.99	0.038
		24 hour	12.0	9.21	8.04	0.97	0.074

A summary of trends in RE is presented below:

- **K:** Unmilled microcline (M0) was almost ineffective as a K-source regardless of application rate, while unground biotite (B0) did supply some K to ryegrass. A much greater plant K uptake plateau (coefficient a in Table 6.7) was achieved for pots amended with B0 (135 mg K) than with M0 (11.9 mg K) and the initial slope of the K content response curve was two orders of magnitude greater for biotite than for microcline. Milling improved the effectiveness for both microcline and biotite with systematic responses to milling time (Figure 6.5, Table 6.7). Although a similar K content asymptote was reached for both minerals milled for 6 and 24 hours, the initial slope for microcline was always less than that for biotite. Thus

although milling greatly improved the RE of microcline, biotite is more effective than microcline for any given milling time.

- **Mg:** Mg uptake by ryegrass increased linearly with application rate for both biotite and hornblende (*Figure 6.6*). The slopes of the linear relationships between Mg content and application rate were used to calculate relative effectiveness (*Table 6.8*). For both biotite and hornblende, RE increased with increased milling, although for any given milling time, biotite was more effective than hornblende. The effect of milling was greatest for biotite with B24 being 3 times more effective than B1, while the effectiveness of hornblende only increased by 64% for the same milling period.

Table 6.8: Values of coefficients of linear equations fitted to the relationship between the sum of ryegrass nutrient content for all harvests versus level of nutrient applied (mg mg^{-1}).

Nutrient	Mineral	Milling Time	a' (mg mg^{-1})	R^2
Mg	Biotite	Initial	0.006	0.18
		1 hour	0.061	0.99
		6 hour	0.134	0.96
		24 hour	0.183	0.98
Mg	Hornblende	Initial	0.000	0.01
		1 hour	0.054	0.96
		6 hour	0.057	0.98
		24 hour	0.085	0.99

- **Ca:** Although milled hornblende was more effective than unmilled hornblende and the RE increased systematically with increased milling time (*Table 6.7*), this response was small (*Figure 6.7*) and the RE values were all less than 0.074 indicating that hornblende appears to be a poor source of Ca for ryegrass. As mentioned above, there were no visual symptoms of Ca deficiency for ryegrass grown on milled minerals

6.3.3 Long-term Soil Chemical Behaviour in Relation to Plant Growth

Values of soil pH decreased due to plant growth (*Figure 6.8*) and this trend has been observed by other workers (Hinsinger, 1998). Soil pH values were lowered by between 0.6 and 3.2 pH units during the experiment, and final pH values ranged from 4.7 (M1, 23.2g kg⁻¹) to 6.9 (H24, 12.3g kg⁻¹). There is a close relationship between the total combined biomass of ryegrass and clover and the reduction in pH over 268 days (*Figure 6.9*). When all minerals are combined, there is a weak linear relationship ($R^2 = 0.55$) between changing pH values and biomass. The relationship improves when individual minerals are considered separately indicating that this trend is influenced by mineralogy, presumably reflecting the different liming capacities of the minerals. The slope of the linear regression of this relationship is an indication of the amount of biomass required to lower the pH by 1 unit. Approximately twice as much biomass is required in soil amended with microcline and biotite than in soil amended with hornblende. However, approximately twice as much microcline and biotite than hornblende was applied. Thus on a unit weight of mineral basis, all three minerals have the same pH buffering potential as a result of plant growth.

Depletion of the initial exchangeable nutrient pool occurred for all minerals as a result of plant growth. To determine if non-exchangeable (structural) forms of K and Ca were used by ryegrass and clover, the relationship between exchangeable cations and the sum of nutrient content in shoots from all harvests is shown in *Figure 6.10*. Lines with a slope of 1 are drawn on these graphs indicating the complete uptake of initial exchangeable cations. This is, however, an underestimate of the amount of nutrient in the plant, as it does not take into account the amount in the roots. Points falling above this line indicate those plants that have used more than the exchangeable pool and therefore further dissolution of minerals has occurred. Points below the line are those plants that have yet to exhaust the exchangeable cations within the soil.

- **Microcline K:** Nonexchangeable microcline K was utilised only for M0 and M1. The pool of exchangeable K was not exhausted by ryegrass and clover for soil amended with M6 and M24, with ryegrass continuing for 268 days without signs of K deficiency.

- **Biotite K:** Nonexchangeable K from biotite was utilised by plants at lower application rates of B0, B1 and B6. B0 applied at the lowest application rate had exchangeable K concentrations after 7 days of incubation below the method detection limit (0.065 mg L^{-1}) but was still able to release 85 mg of K to be taken up by plants, indicating the ability of plants to extract K from micas (Mengel and Rahmatullah, 1994; Pal et al., 2001).
- **Biotite and Hornblende Mg:** All exchangeable and some nonexchangeable Mg was used by plants, due primarily to the very low initial exchangeable Mg values. For those pots where exchangeable Mg concentrations were below the method detection limit (not shown in *Figure 6.10*), ryegrass was still able to persist for approximately 3 months after sowing due to its ability to extract Mg from hornblende and biotite.
- **Ca:** Exchangeable Ca was sufficient to supply all Ca utilised by plants for all milling times or application rates and there was no indication of deficient symptoms in the ryegrass shoots.

At the point of plant death, exchangeable cation concentrations had been depleted to near zero concentrations. All pots were maintained at 90% field capacity after plant death to determine subsequent mineral dissolution. This was best observed for samples collected at the end of the experiment from treatments of biotite and hornblende for Mg uptake as these pots generally had a longer incubation time and plant death occurred for all treatments. Exchangeable Mg concentrations at the end of the experiment (*Figure 6.11*) generally increased from their values at the time of plant death.

6.3.4 Mineralogical Changes

To determine any mineralogical changes as a result of plant uptake of nutrients, minerals were recovered from pots that had application rates of approximately 10 g kg^{-1} . Complete, unsmoothed X-ray diffraction patterns are compiled in Appendix 2. Smoothed traces of the low 2θ region of these patterns are shown in *Figures 6.12*, *6.13* and *6.14*. Plant growth and soil chemistry details are included on the XRD patterns as are d -spacings of reflections that are present only after cropping when compared with the patterns prior to cropping.

XRD patterns for microcline from cropped soil (*Figure 6.12*) indicate the development of a peak at between 7.6 and 7.9\AA that may be attributed to the formation of either gypsum

(CaSO₄.H₂O) or brushite CaHPO₄.H₂O (isostructural minerals) resulting from precipitation of constituents of the soluble fertilisers. There was no other evidence of mineral transformation of microcline as a result of cropping, even where non-exchangeable K was utilised by the plants.

XRD patterns for biotite as oriented plate samples (*Figure 6.13*) do not show the development of the peak between 7.6 and 7.9Å present in the microcline samples. The (001) biotite peaks were characterised by a general peak broadening when compared with the uncropped sample, and this was accompanied by the development of weak, broad reflections at *d*-spacings of 14.7 and 12.0 Å for B1 and at 12.4Å for B6. In the former sample, all the initial exchangeable K was utilised and ryegrass growth continued throughout the duration of the experiment, while in the latter sample, the initial pool of exchangeable K was not completely utilised during the experiment. The peaks observed in B1 can be attributed to vermiculite (14.7Å) and mixed biotite-vermiculite (12.0Å). Such mineralogical changes have been reported during plant growth of Italian ryegrass with mica as a K source (Hinsinger and Jaillard, 1993). The 12.4Å peak observed for B6 may be attributed to the formation of mixed-layer biotite-vermiculite. Biotite mineral transformations are due primarily to replacement of interlayer K by hydrated Mg or Ca ions. These mineral transformations were not observed for oriented plates samples of B0 and B24, despite most nonexchangeable K being utilised by ryegrass for B0. The K from B0 may have been released due to an acid-mediated dissolution of biotite as the pH in the soils was 0.5 to 1 unit lower than the other treatments.

The only change observed in the random powder XRD samples of hornblende (*Figure 6.14*) was the development of a reflection at 7.6Å for H1, H6 and H24, attributed to the formation of either gypsum or brushite. In all cases, most of the initial exchangeable Ca was not utilised during plant growth and could have been incorporated into these minerals.

6.4 General Discussion

6.4.1 Milled Minerals as Fertilisers

Milled minerals are unlikely to be as effective as soluble fertilisers in the short term, and should not be considered as simple substitutes. However, these minerals do rapidly release some of their nutrient content and also act as slow release fertilisers. Soils amended with biotite and highly milled microcline were quite effective in supplying K and although not

tested in this experiment, it is expected that milled minerals would provide greater production than single applications of soluble fertilisers.

The increase in exchangeable cations after plant death also indicates long-term fertiliser potential. Mineral dissolution is enhanced by changes in soil chemistry including the addition of root exudates (Hinsinger et al., 1993; Hinsinger and Jaillard, 1993) and the mass-action effect of nutrient removal via plant uptake (Hinsinger et al., 2001) increases the nutrient supply over periods of several years.

Despite their lower relative effectiveness than soluble fertilisers, milled minerals may have a role in agriculture:

□ **K Minerals**

Biotite provided considerable amount of K to plants and milling did not greatly increase the RE of biotite. In contrast, microcline was the most responsive mineral to milling with K uptake by plants increasing with milling time. Biotite as a source of K was more responsive to application rate than milling time. This result is consistent with previous work where feldspars or rocks containing K in feldspars such as granite are ineffective K fertilisers while rocks with most K in biotite such as mica schist had more plant available K (Bakken et al., 1997; Bakken et al., 2000; Bolland and Baker, 2000; Sanz Scovino and Rowell, 1988). This difference can be attributed to the existence of exchangeable interlayer K in biotite whereas K in feldspar is predominately structural. As feldspars are the most abundant source of K in rocks (Huang, 1989), a technique that allows the release of some K from feldspars will be potentially useful in regions where soluble sources of K are unavailable. Milling may also be appropriate for dioctahedral micas such as muscovite that are considered to be poor sources of K (Kalinowski and Schweda, 1996; Nagy, 1995). Potential sources of K that may be greatly improved by milling include siliceous igneous rocks such as granites and metamorphic rocks such as gneiss and migmatite.

□ **Mg Minerals**

Based on the results presented here, biotite is up to twice as effective as hornblende at supplying Mg. Previous plant growth experiments examining the release of Mg to plants by soils have focused primarily on clay minerals, with Rice and Kamprath (1968) suggesting that the dominant Mg reserves in soils are the nonexchangeable Mg in the crystal lattice of mica, montmorillonite, illite, chlorite and vermiculite while non-layer silicate minerals in soils appear to be even less effective sources of Mg than clay

minerals. Indeed, Longstaff and Graham (1951) observed Mg deficiency in soybeans where hornblende was the main source of Mg. Exhaustion cropping experiments using clays as sources of Mg indicate, however, that these non-exchangeable sources of Mg cannot sustain normal plant growth (Kidson et al., 1975; Salmon and Arnold, 1963) which has been attributed to the strength of the combined ionic-covalent bonding in the octahedral layer. Christenson and Doll (1973) have also attributed the decreasing availability of Mg in bentonite and chlorite during growth experiments to oxidation of octahedral Fe that is known to reduce the solubility of layer silicates. A sufficient supply of Mg to plants from silicate rocks has been reported by Chittenden et al., 1964 (1967; McNaught and Gdanitz, 1952). High application rates of those rocks were used, and generally the rocks had high Mg contents. For example, McNaught and Gdanitz (1952) used serpentine with 35% MgO at a rate of approximately 37 t ha⁻¹ while in the present experiment the highest application rate was equivalent to 640 kg ha⁻¹ of biotite containing 13.5% MgO.

□ **Ca Minerals**

Although uptake of Ca by ryegrass increased with the application of milled hornblende when compared to the unmilled hornblende, there was no systematic response to milling time. This observation, combined with the persistence of much exchangeable Ca in soil during the experiment, suggests that Ca deficiency was not limiting plant growth. Although the high soil pH values observed at the start of the experiment (*Figure 6.3*) can inhibit plant growth and lead to deficiencies of nutrients including P, Zn and Mn (Marschner, 1995), only P deficiency was encountered at the highest rate of H24 for the first harvest, which was overcome by the second harvest. Mineral dissolution can be reduced by ions and molecules present in solution that can modify the surface energy and thereby alter surface processes (Banfield and Hamers, 1997). Bonifacio et al. (2001) has reported that H₂PO₄⁻ strongly affects the dissolution of serpentine in contrasting ways depending on all reactions occurring between phosphate, mineral surfaces and solution species. At the highest P concentrations, they found that precipitation of calcium phosphates occurred at the mineral surface, covering it and protecting it from dissolution. Either gypsum (CaSO₄.H₂O) or brushite (CaHPO₄.2H₂O) (isostructural minerals) were detected in XRD patterns of hornblende recovered after cropping, so precipitation of the Ca salts may have influenced Ca uptake. Although the causes of low Ca uptake by ryegrass during this experiment

cannot be ascertained, this observation does highlight the complex interactions between minerals and plants in soils.

Crop species is also an important consideration in determining the value of silicate mineral fertilisers as shown by the persistence of ryegrass compared with clover in this experiment. Grasses in general have lower external K requirements and where soil exchangeable K is depleted, clover yields decrease at a faster rate than for grasses, this effect being readily demonstrated in pot experiments with mixed pasture systems (Steffens, 1986). Ryegrass has previously been shown to be a strong competitor with clover for soil K (Mengel and Steffens, 1985) and Mg (Salmon and Arnold, 1963). Steffens (1986) proposed that K release from nonexchangeable sources depend on the K concentration of the soil solution; the lower the K concentration, the higher the net release of K from the nonexchangeable pool. Springob and Richter (1998) found that in an illitic loess material, K release began at K concentrations of $10\mu\text{M}$ and increased exponentially below $3\mu\text{M}$. The lower external requirement of ryegrass may accelerate the K depletion process, making it a more efficient user of nonexchangeable K. Grasses may also be capable of exploiting soil K more effectively than clover due to their highly fibrous, extensive root morphology (Evans, 1977; Mengel and Steffens, 1985). Management practices involving silicate mineral fertilisers may also require the use of grasses in the first season(s) after application to alter soil and rhizosphere chemistry and enhance mineral dissolution in preparation for including plants with higher external requirements in subsequent seasons.

6.4.2 Milled Minerals as Soil Ameliorants

Several workers have proposed the use of silicate minerals and rocks as soil ameliorants rather than fertilisers (Coroneos et al., 1996; Gillman, 1980; Gillman et al., 2001; Hinsinger et al., 1996; Mersi et al., 1992). Silicate minerals have been proposed as a liming agent, especially in area of high rainfall where the benefits of lime or dolomite additions can be short-lived (Coventry et al., 2001) or where the use of lime increases the risk of dissolved organic carbon mobilization and excessive nitrification (Hildebrand and Schack-Kirchner, 2000). Other benefits of adding finely ground rocks include increasing ion exchange capacity (Gillman, 1980; Gillman et al., 2001) and improving physical properties such as increasing water holding capacity in sandy soils and increasing coarse pore volume to improve structure in clayey soils (Kahnt et al., 1986).

The acid neutralising (liming) capacity of the milled minerals was evaluated during this experiment. The inverse of the slope of a linear relationship between soil pH values prior to cropping and mineral application rate (*Figure 6.3*) was used to determine the amount of mineral (g kg^{-1}) required to raise the pH of the soil by 1 pH unit (*Table 6.9*). Milling improved the acid neutralizing capacity of all minerals, with hornblende being the most effective, requiring the equivalent of 4 ton ha^{-1} after 1 hour of milling to raise the soil pH by one unit. When compared to CaCO_3 , however (*Table 6.9*), these materials are still less effective than lime with H24 having a lime equivalence of only 11%.

Table 6.9: Estimation of the amount of milled mineral and CaCO_3 (g kg^{-1}) required to raise the pH of soil by 1 pH unit and corresponding lime equivalence.

Mineral	Milling Time	Mineral Required (g kg^{-1})/pH unit	R ²	Lime Equivalence
CaCO_3		0.26	1.00	100%
Microcline	Initial	119	0.32	0.2%
	1 hour	39	0.88	0.7%
	6 hour	22	0.72	1.2%
	24 hour	14	0.99	1.9%
Biotite	Initial	20	0.99	1.3%
	1 hour	15	1.00	1.7%
	6 hour	9.9	0.95	2.6%
	24 hour	7.1	0.87	3.7%
Hornblende	Initial	60	0.57	0.4%
	1 hour	3.7	0.98	7.0%
	6 hour	2.6	0.94	10.0%
	24 hour	2.3	0.94	11.3%

Although not studied directly, the ameliorative effect of silicate minerals on trace metal concentrations in plants was indicated by the plant analyses. All pots received the same amount of trace metals, yet concentrations of metals in plants differed with different mineral treatments. In general, the lower the application rate of silicate minerals and the shorter milling time, the larger the contents of Cu, Mn and Zn in plants. Thus the plants in the reference pots contained high concentrations of trace metals. High concentrations of trace metals in plants did not occur for pots amended with hornblende. The activity of Cu^{2+} , Zn^{2+} and Mn^{2+} in soil solution decreases as pH increases (Lindsay, 1979), thereby reducing uptake of these elements by plants (Marschner, 1995). Trace metals in ryegrass grown on hornblende-amended pots increased substantially only after pH-H₂O values fell

below 5.0, despite large applications of trace metals during the course of the experiment. In addition to the effect from soil pH, the high surface area of the milled minerals substantially increased the surface area of the soils thereby potentially increasing sorption of Cu, Zn and Mn and reducing uptake by plants. The application of Si has been linked to amelioration of Mn and Al toxicities (Epstein, 1999). In the present research, each pot received the same amounts of N, P and trace element fertilisers, but different amounts of Si were added depending on the application rate of the silicate minerals. As with the other nutrient elements, Si uptake by plants increased with increasing milling time and may have affected uptake of trace metals.

6.4.3 Estimating Mineral Application Rates and Milling Parameters

The application of silicate mineral fertilisers has historically been based on anecdotal evidence or trial and error. Proponents of such materials generally recommend application rates of between 5 and 20 t ha⁻¹, yet guidelines behind such recommendations are not detailed. Some consideration, however, is given to mineralogy and mafic rocks are preferred to siliceous (felsic) rocks (e.g. basalt over granite) and fine-grained rocks are preferred over coarse-grained rocks (e.g. volcanic over plutonic). There are no clear guidelines to estimating appropriate application rates or optimal material characteristics (e.g. grain size). Several published studies have investigated different grain size fractions and not surprisingly arrived at different estimates of the effectiveness of silicate mineral fertilisers (Blum et al., 1989a; Niwas et al., 1987; Wang et al., 2000). The results generally indicate that plant growth improves with the use of finer grain sizes, however, optimal sizes have not been identified. Comparisons between published studies are difficult due to the poor specifications of properties of materials. Coventry et al. (2001) determined the optimum particle-size for ground basalt based on the surface charge characteristics of the milled rock in what appears to be the first systematic attempt to optimise preparation parameters. They concluded firstly that a particle size <0.250mm was optimal based on the maximum release of exchangeable cations by a 0.1 M BaCl₂/NH₄Cl solution, and secondly that there was a lower particle size (32 µm) below which no further increase in surface charge was attained. In subsequent plant growth experiments on highly weathered soils in North Queensland, only two rates of application were used; 2.5 and 25 t ha⁻¹ and although plant growth and nutrient uptake improved at the higher application rate, there again was no systematic attempt to optimise application rate.

The relationship between the sum of plant nutrient content and the application of minerals may be used to evaluate the appropriate mineral application rates (*Figure 6.15*). Application rates less than 1 t ha^{-1} (biotite and hornblende Mg) produce a linear increase in content with increasing rates. K content from microcline indicates that this linear relationship continues to between 5 and 10 ton ha^{-1} , followed by a slight increase to 20 ton ha^{-1} , which would support the anecdotal evidence. These responses, however, are for milled minerals, with unmilled minerals showing minimal response to application rate, indicating factors other than simply application rates.

Dissolution studies on the milled minerals used in this study (Chapter 5) indicate that BET surface area is highly predictive of mineral dissolution of the milled silicates and the release of nutrients from silicate minerals is a surface mediated process. Plant growth kinetics can be modelled based on the uptake rate of nutrients against time from a freely available source of nutrients. This model does not consider the slow surface dissolution of minerals. Mineral dissolution rates are generally related to surface area (Banfield and Hamers, 1997). In interpreting dissolution experiments, the rate of mineral dissolution is normalised to a m^2 mineral basis. In the plant growth experiment, minerals were applied at various rates with various surface areas and thus provided a wide range of total surface area values. Nutrient uptake rate can be considered in terms of m^2 of area provided by applied minerals present in 1 kg of soil.

Si is the only element that is common to all three minerals and may be considered an indicator of the rate of mineral dissolution as determined by Si uptake. Si uptake rates were calculated from the slope of the linear relationship between Si content at harvest and time for shoots that did not experience metal toxicity. When all the minerals are considered as a single population, a near linear relationship exists between Si uptake rate and m^2 of surface area of mineral applied is up to approximately 300 m^2 (*Figure 6.16*). Above this surface area value, there is no increased uptake rate with increased mineral surface area per pot, indicating that this value may represent the upper limit of useful application of silicate mineral fertiliser beyond which there was no nutritional benefit of additional application. The closeness of the fit of data for all three minerals to the single plot suggests that BET measured surface area is highly predictive of plant uptake or nutrients of milled minerals.

Silicon may not be truly indicative of the mechanisms of plant uptake. A comparison of nutrient element uptake with surface area of applied mineral (*Figure 6.17*) indicates that

although Si uptake increase up to approximately 300 m² kg soil⁻¹, K uptake increases to up to 100 m² kg soil⁻¹ for Mg uptake increases linearly with surface area up to at least 60 m² kg soil⁻¹ and for Ca there is no uptake increase above 20 m² kg soil⁻¹.

Based on these calculations of optimal surface areas, the associated application rate of silicate minerals to very sandy soils such as those used in this experiment can be calculated (*Table 6.10*). Dissolution is however likely to be much greater in different soils (e.g. very acid, clayey) and the surface area based application rates may need to be varied. These calculations are based on single minerals rather than mineral assemblages as found in rocks. Application rates will need to be higher if based on whole rock compositions where dilution with minerals such as quartz occurs. These predictions provide no estimation of the residual value of ground silicate rocks so that the required frequency of reapplication is unknown. Surface area can, however, provide a unifying parameter to begin firstly comparing different experimental conditions and secondly to predict and possibly engineer silicate mineral fertilisers for optimal use.

Table 6.10: Specific surface area (S) as determined by the BET gas adsorption method (m² g⁻¹) of minerals milled for various times and corresponding application rates to achieve an increase of surface area of 40, 60, 100 and 300 m² when added to 1 kg of soil. These rates correspond to field application rates of t ha⁻¹. Insufficient sample of H24 was available for measurement of S.

Mineral	Milling Time	S (m ² g ⁻¹)	Application Rate (g kg ⁻¹ ≈ t ha ⁻¹)			
			≈ 40 m ² kg ⁻¹	≈ 60 m ² kg ⁻¹	≈ 100 m ² kg ⁻¹	≈ 300 m ² g ⁻¹
Microcline	Initial	3.9	10	15	26	77
	1 hour	8.3	4.8	7.2	12	36
	6 hour	23	1.7	2.6	4.3	13
	24 hour	48	0.8	1.2	2.1	6.2
Biotite	Initial	3.6	11	17	28	83
	1 hour	18	2.3	3.4	5.7	17
	6 hour	63	0.6	1.0	1.6	4.8
	24 hour	95	0.4	0.6	1.1	3.2
Hornblende	Initial	2.8	14	21	36	107
	1 hour	16	2.4	3.7	6.1	18
	6 hour	61	0.7	1.0	1.6	4.9

Although a promising preparatory technique, the use of milled silicate minerals under field conditions is unknown. Similar experiments utilising rock phosphates in glasshouse

conditions have been “of uncertain relevance under field conditions” (Bolland et al., 1997). The processing and application of very fine material, as well as associated costs, still present major limitations to the practical use of this material.

6.4.4 Limitations of Methodology

The large factorial design of the experiment was required to evaluate whether attrition milling could improve the effectiveness of silicate minerals as fertilisers, and to determine appropriate milling times and application rates, if any, that may be useful during cropping. Although the results show that this technique is promising, there are many limitations to this experiment:

- The difference between the application rates of soluble fertilisers and silicate minerals were too large to draw adequate conclusions, and longer growth periods of soluble fertiliser control pots are required to evaluate the long-term relative effectiveness of milled silicate minerals.
- Single applications of soluble fertilisers are also required to compare the long-term relative effectiveness of silicate minerals.
- Different soil types are required to further evaluate responses to silicate mineral application rate, and better predict soil conditions that are suitable for application of this material.
- The experiment did not consider the influence of organic matter, soil microorganisms or mycorrhizal fungi on mineral dissolution.

6.5 Summary

The uptake of K, Mg and Ca by ryegrass and clover from soil amended with microcline, biotite and hornblende that had been subjected to attrition milling was measured in a glasshouse experiment for up to 268 days, producing the following major findings:

- Attrition milling greatly enhanced the agronomic effectiveness of silicate minerals as sources of K, Ca, Mg;
- The relative effectiveness of individual silicate minerals increased with milling time;

- Over a 6-week growth period silicate minerals, regardless of milling time, were far less effective than soluble fertilisers in supplying these nutrients for plant growth;
- Sustained plant growth (up to 268 days) was attained in several treatments of milled minerals indicating the long-term benefits of milled minerals;
- Plant death generally associated with exhaustion of the exchangeable cation pool, which was then replenished under “fallow” conditions;
- Soil pH values greatly increased following the addition of milled silicates prior to plant growth. These pH values were greatly reduced (up to 2 pH units) by growing ryegrass and clover;
- Ryegrass more efficiently utilises nutrients supplied by minerals than clover; and
- The surface area of the applied minerals may be the best predictor of growth performance irrespective of mineral species.

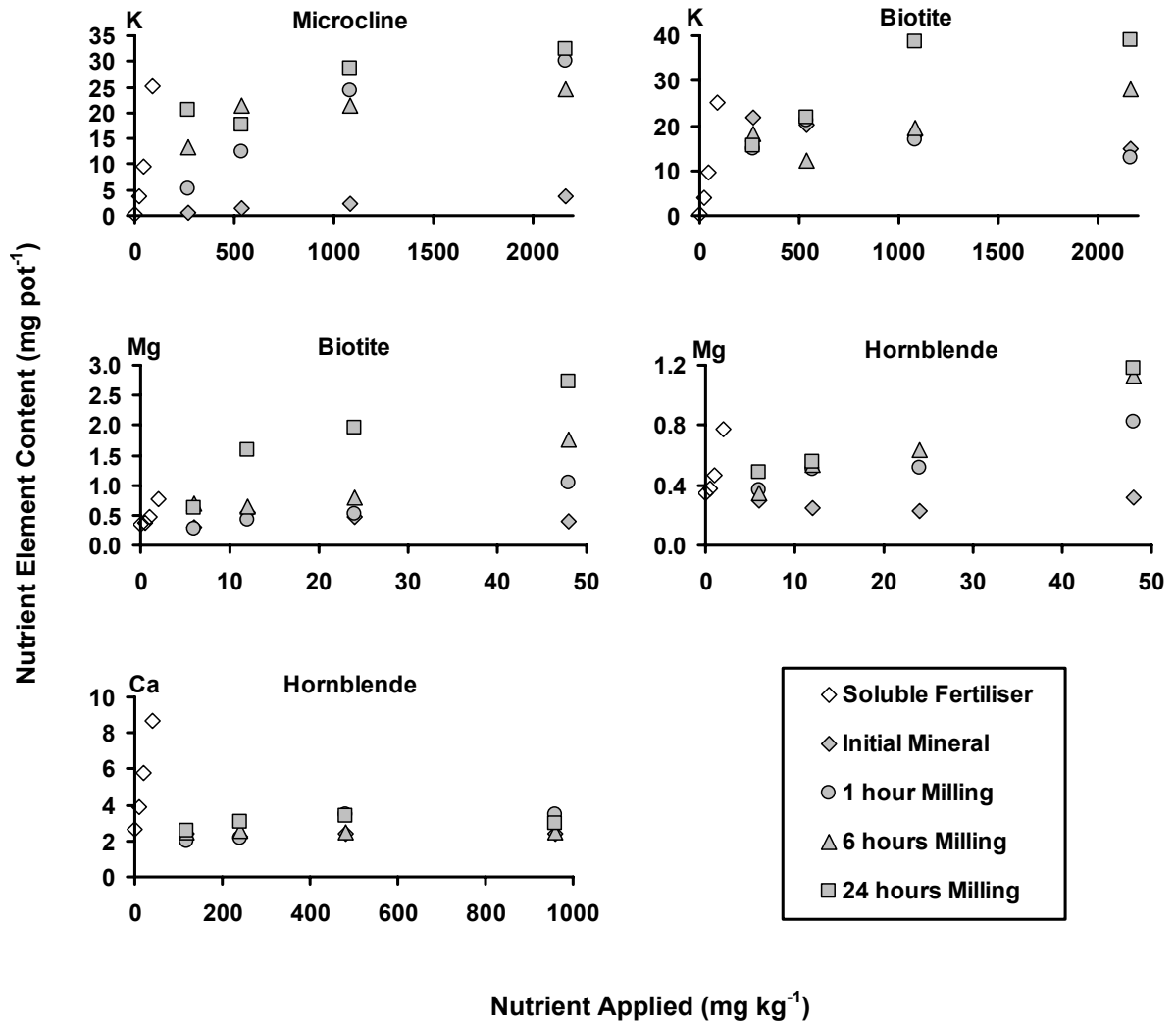


Figure 6.1: Relationships between nutrient content of ryegrass herbage 43 DAS and the level of nutrient applied to soil as either soluble fertiliser (K_2SO_4 , $MgSO_4$ or $CaCl_2$) or milled silicate mineral.

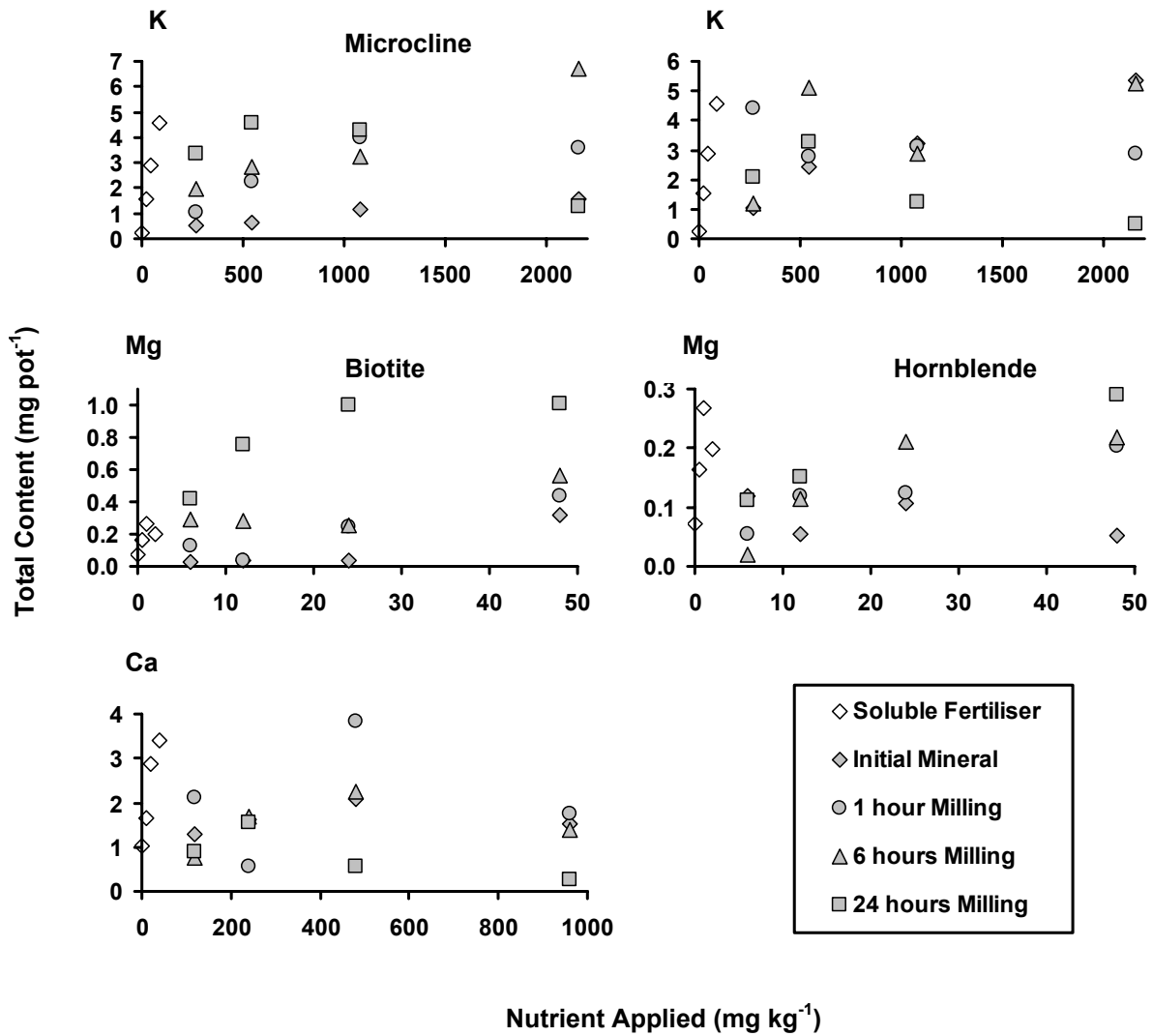


Figure 6.2: Relationships between nutrient content of clover herbage 43 DAS and the level of nutrient applied to soil as either soluble fertiliser (K_2SO_4 , $MgSO_4$ or $CaCl_2$) or milled silicate mineral.

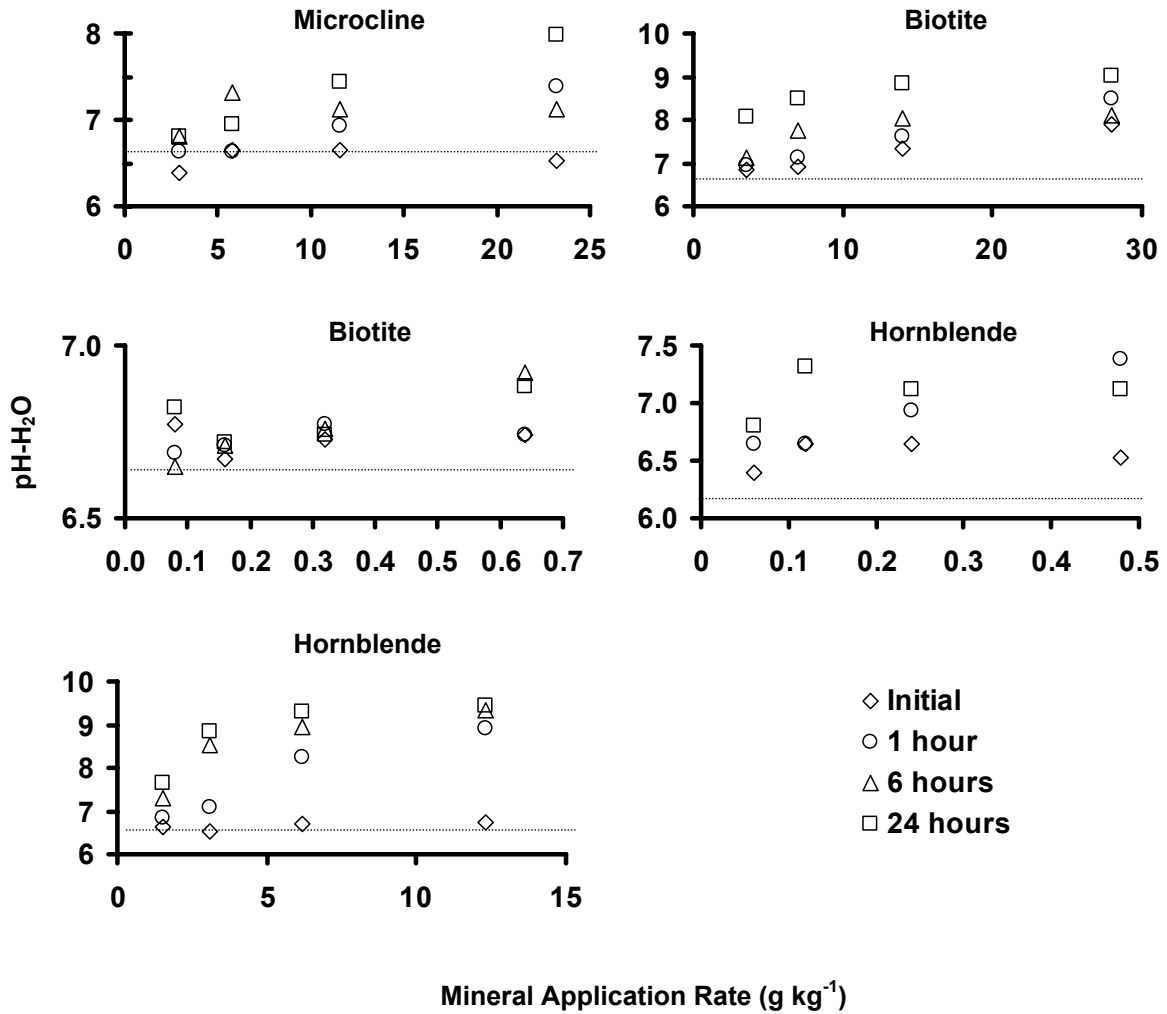


Figure 6.3: $pH-H_2O$ values of soil amended with various rates of milled silicate minerals after incubation for 7 days. Dashed line is $pH-H_2O$ value of soil for the nil treatment.

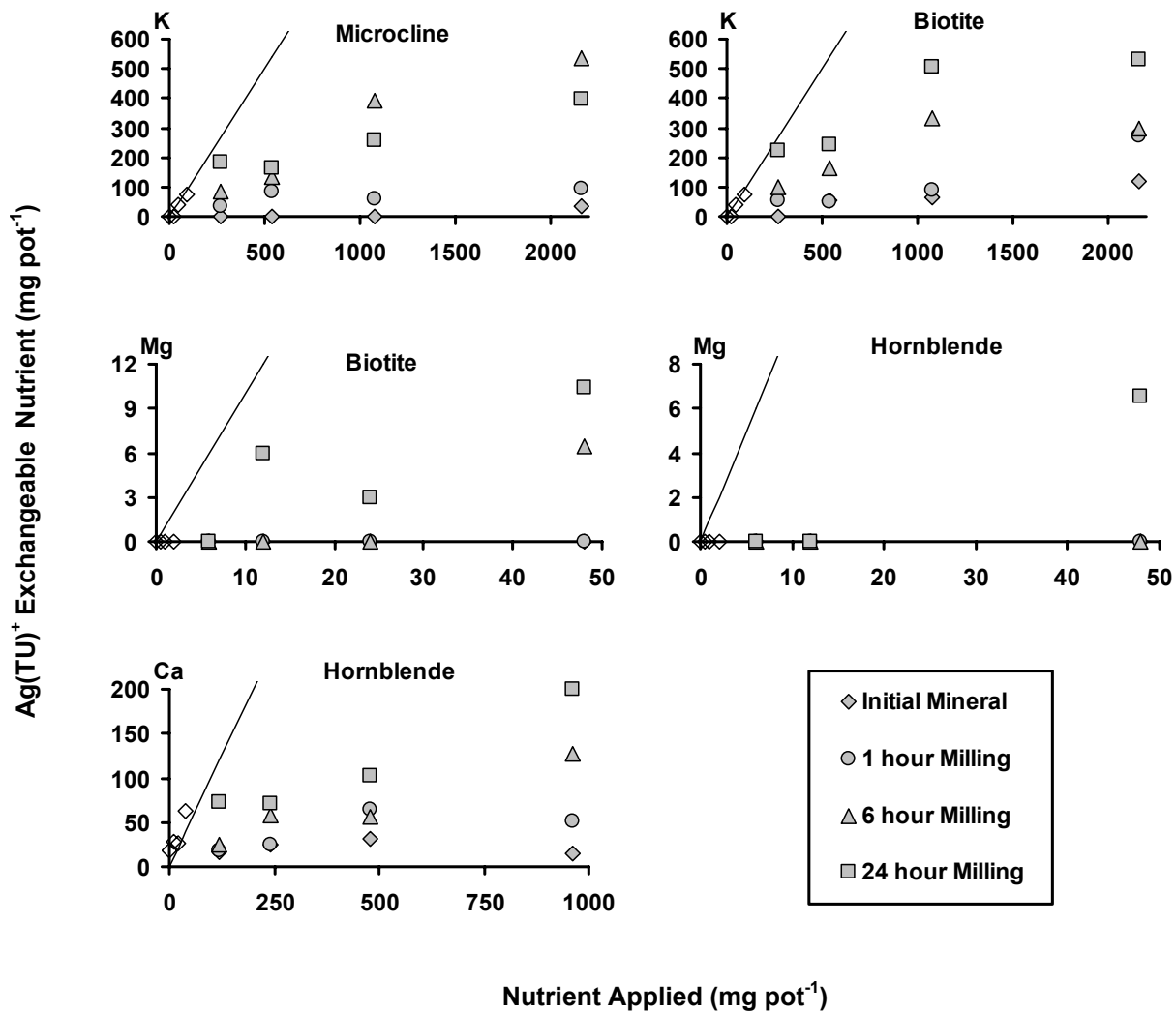


Figure 6.4: Relationship between $Ag(TU)^+$ exchangeable nutrient element concentration for soil versus the level of nutrient applied as either soluble fertiliser (K_2SO_4 , $MgSO_4$ or $CaCl_2$) or milled silicate mineral after 7 days of incubation. Lines have slope = 1, indicating all of the nutrient applied is $Ag(TU)^+$ exchangeable.

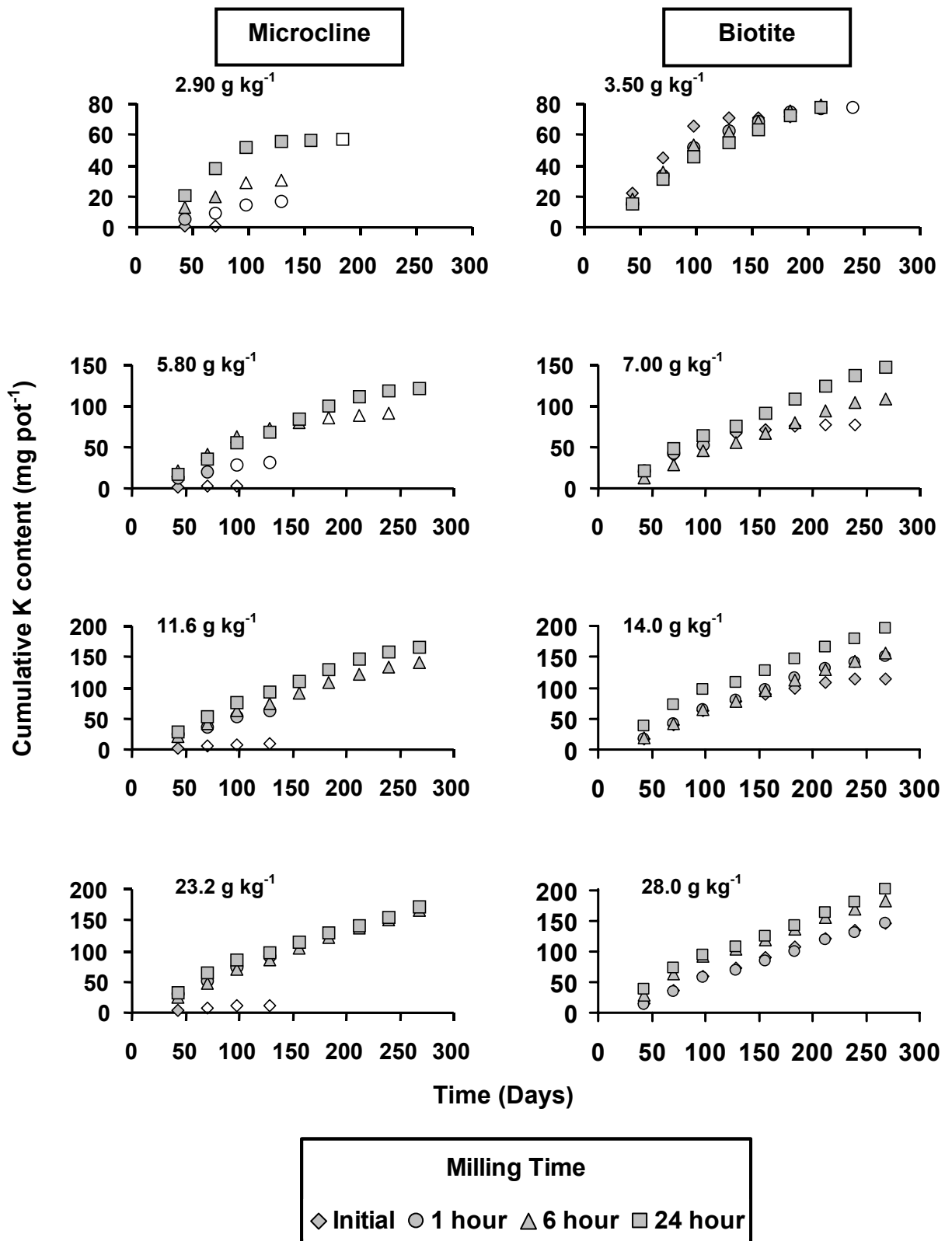


Figure 6.5: Cumulative K uptake by ryegrass from milled microcline and biotite. Hollow symbols indicate plants that may have experienced Cu, Zn or Mn toxicity.

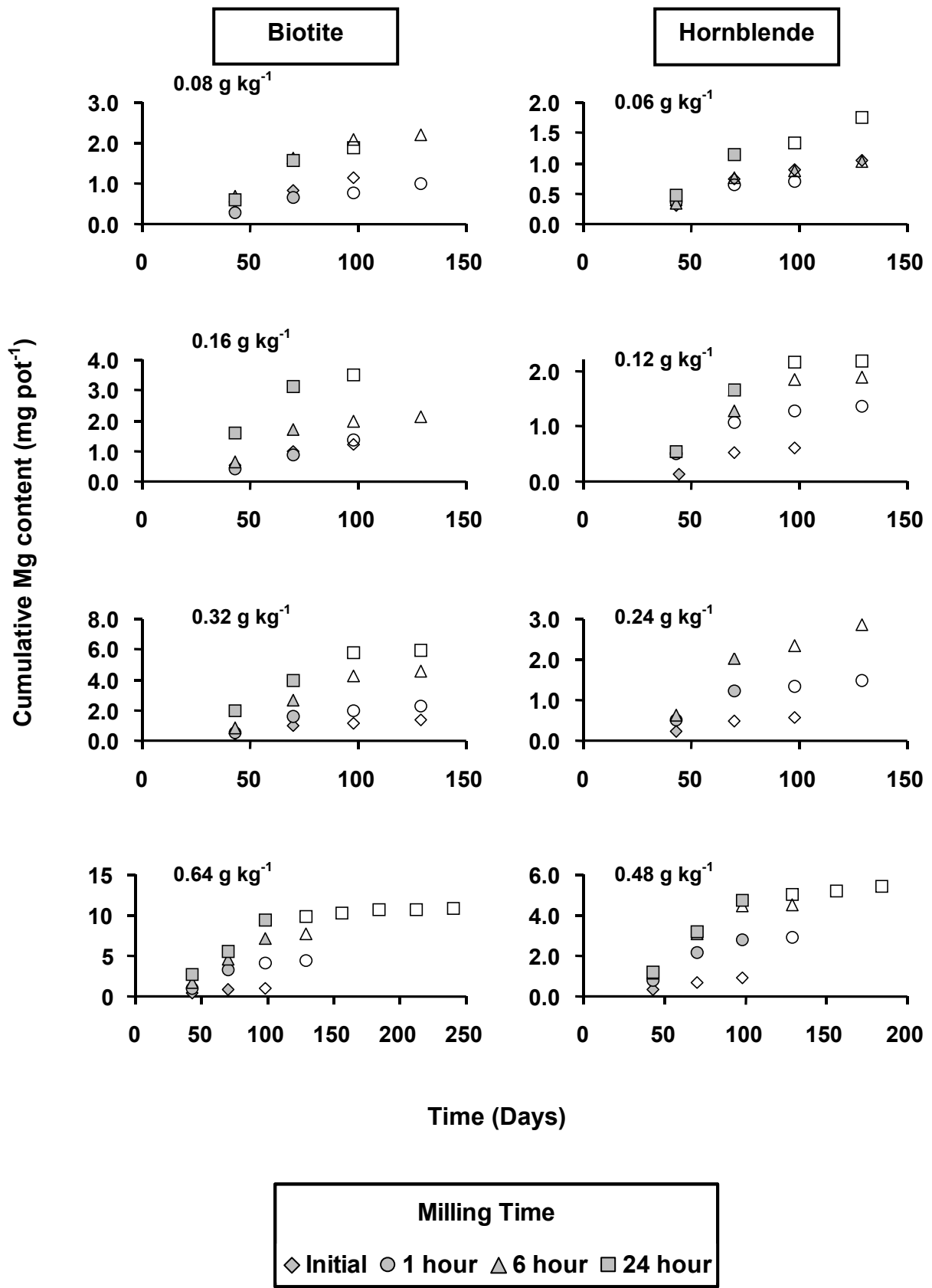


Figure 6.6: Cumulative Mg uptake by ryegrass from milled biotite and hornblende. Hollow symbols indicate plants that may have experienced Cu, Zn or Mn toxicity.

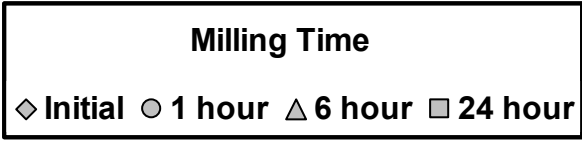
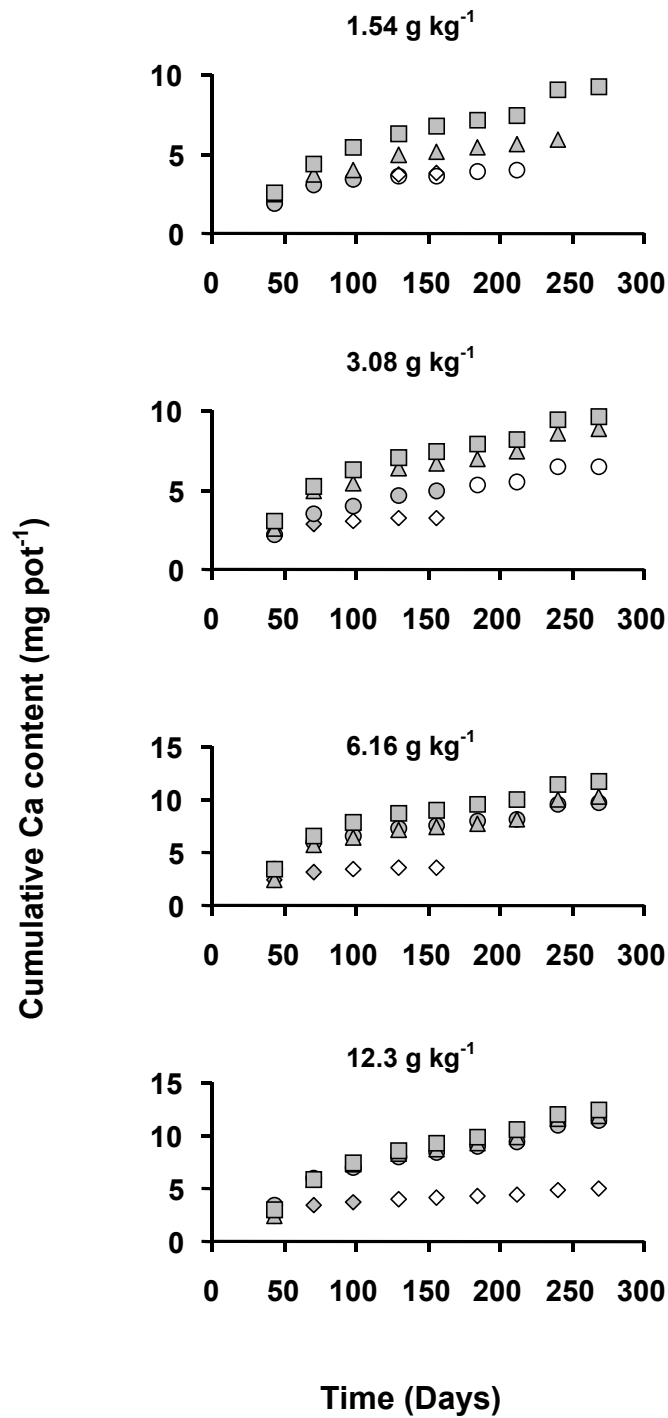


Figure 6.7: Cumulative Ca uptake by ryegrass for hornblende. Hollow symbols indicate plants that may have experienced Cu, Zn and Mn toxicity.

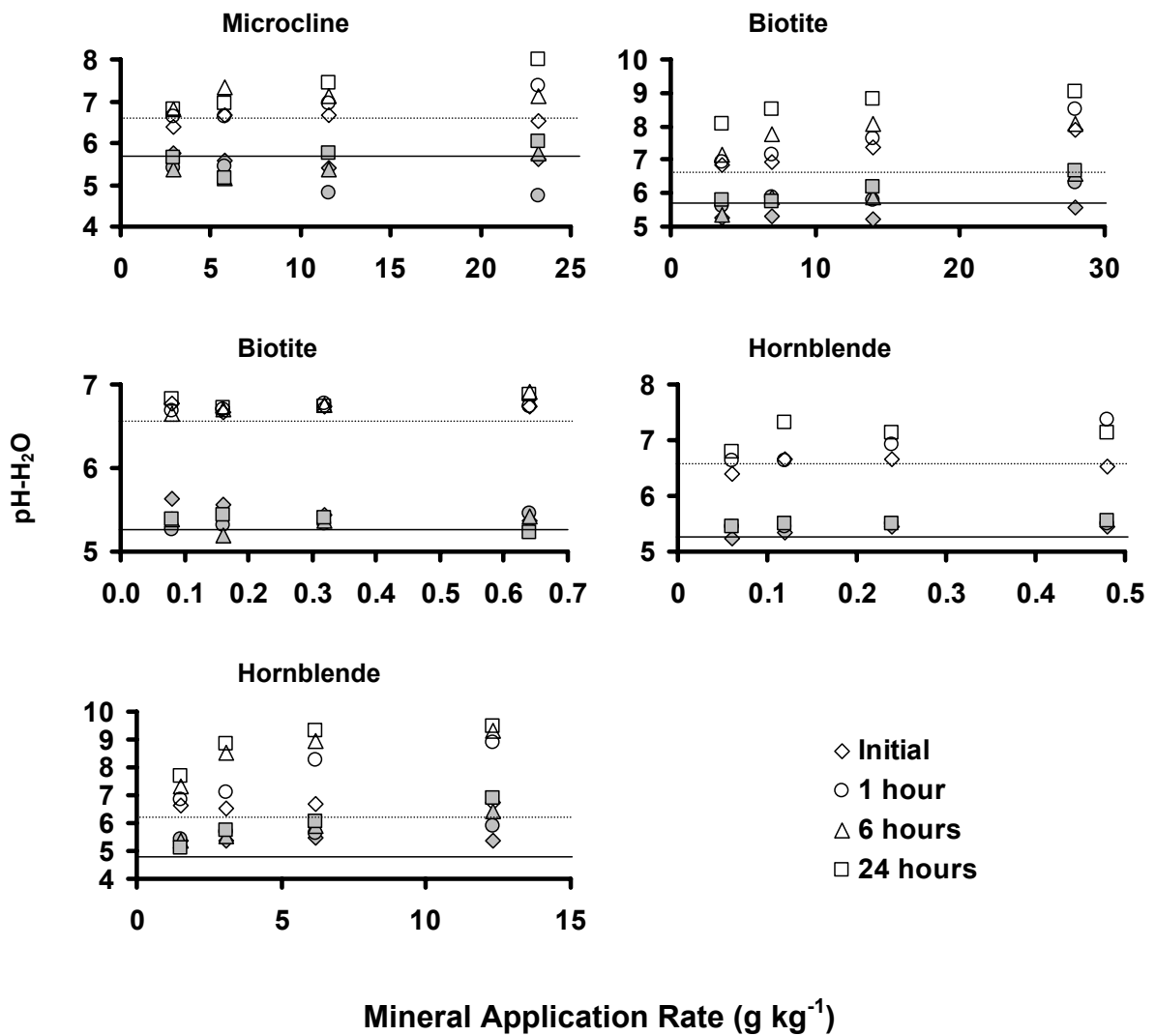


Figure 6.8: $pH-H_2O$ values of soil amended with various rates of milled silicate minerals measured before (open circles) and after (shaded circles) cropping with ryegrass and subterranean clover. The dashed line is the $pH-H_2O$ value after 7 days of incubation and the solid line is the $pH-H_2O$ value after cropping for the nil treatment.

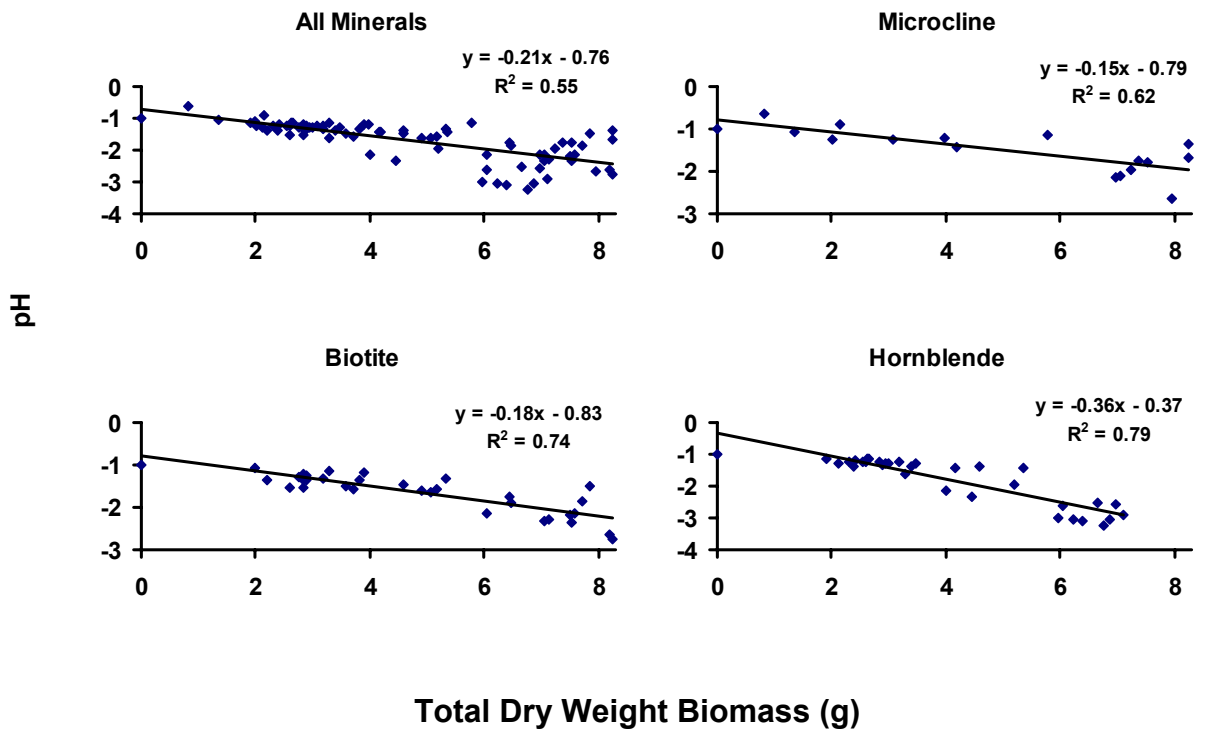


Figure 6.9: Relationship between the total dry biomass of ryegrass and clover herbage and the reduction in pH-H₂O values (Δ pH) of soil amended with milled silicate minerals from the start and end of a glasshouse experiment.

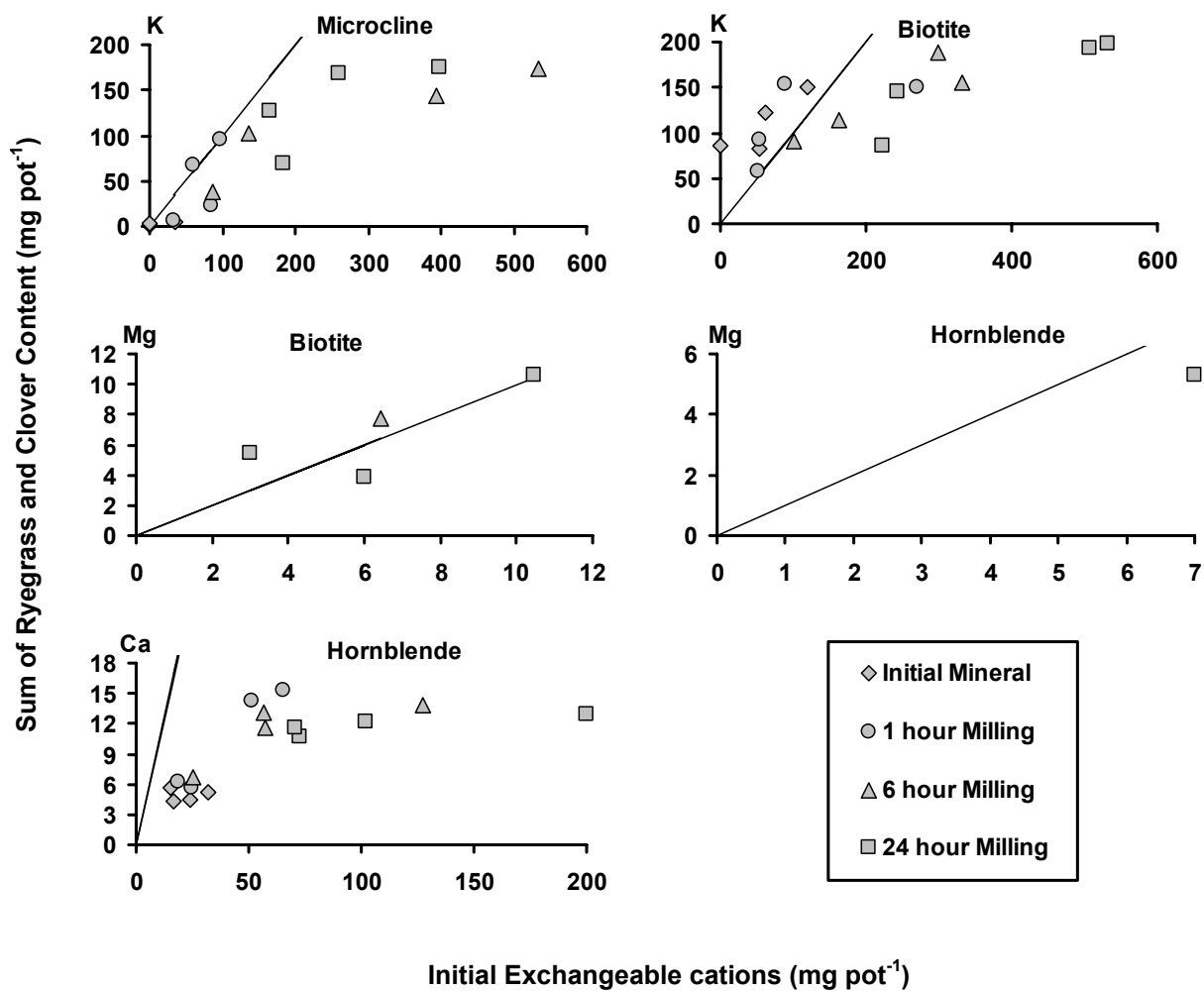


Figure 6.10: Relationship between initial $Ag(TU)^+$ exchangeable cations in soil amended with milled silicate minerals and the sum of the cation contents of ryegrass and clover herbage. Samples with exchangeable Mg < method detection limit not included. Lines have slope = 1, indicating the complete uptake of initial exchangeable cations.

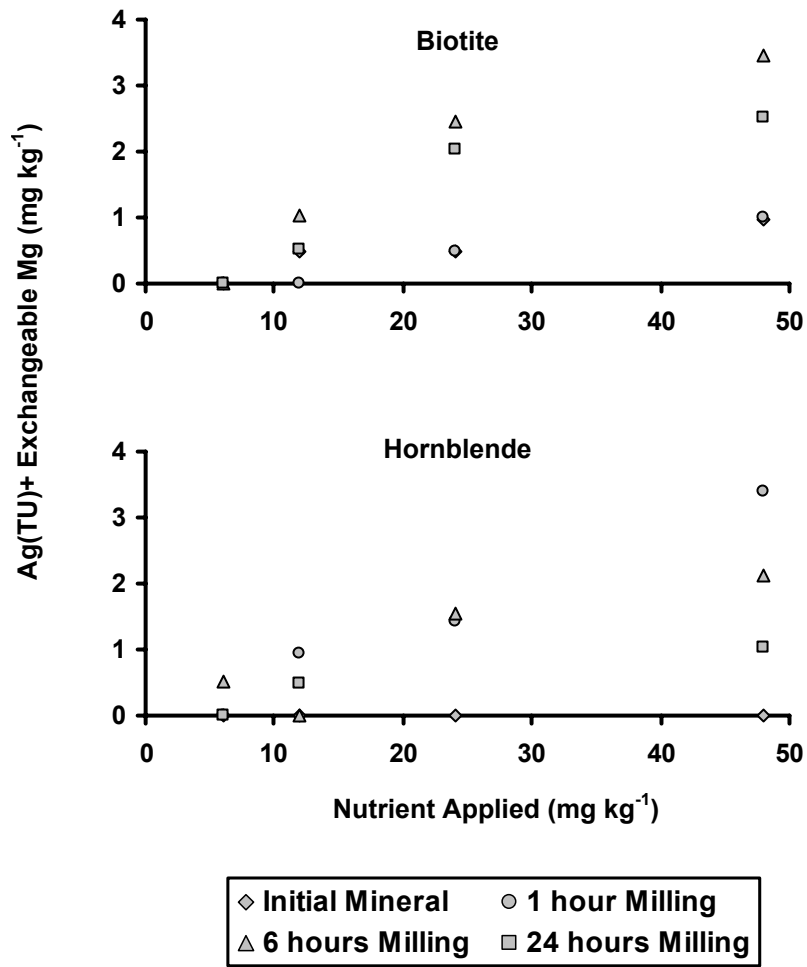


Figure 6.11: Relationship between final Ag(TU)^+ exchangeable Mg and the levels of Mg applied as milled biotite and hornblende applied to soil. Samples were collected 268 DAS and pots were incubating for periods of between 28 and 170 days after plant death.

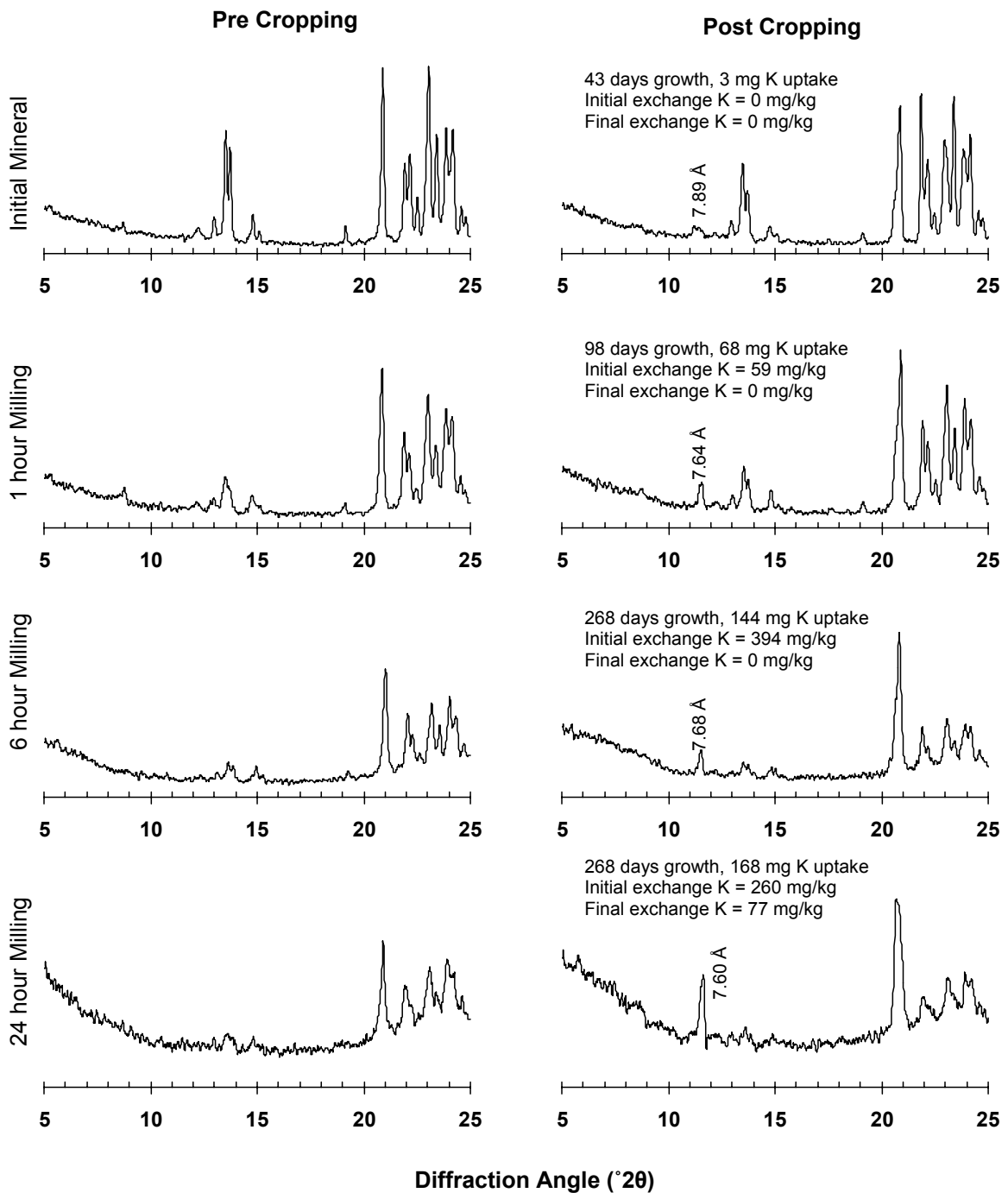


Figure 6.12: The low 2θ region of random powder X-ray diffraction patterns of milled microcline applied at 11.6 g kg^{-1} , sample taken before and after cropping. Curves were smoothed by a 9-point moving average and the intensities of patterns for each milling time are at the same scale without offset along the y-axis. Uptake values refer to the sum of ryegrass and clover shoot contents. Initial exchange concentrations were measured after 7 days of incubation and prior to sowing. Final exchange concentrations were measured either at the point of plant death or at the end of the experiment. Values of d-spacings are for peaks for compounds that formed during the experiment.

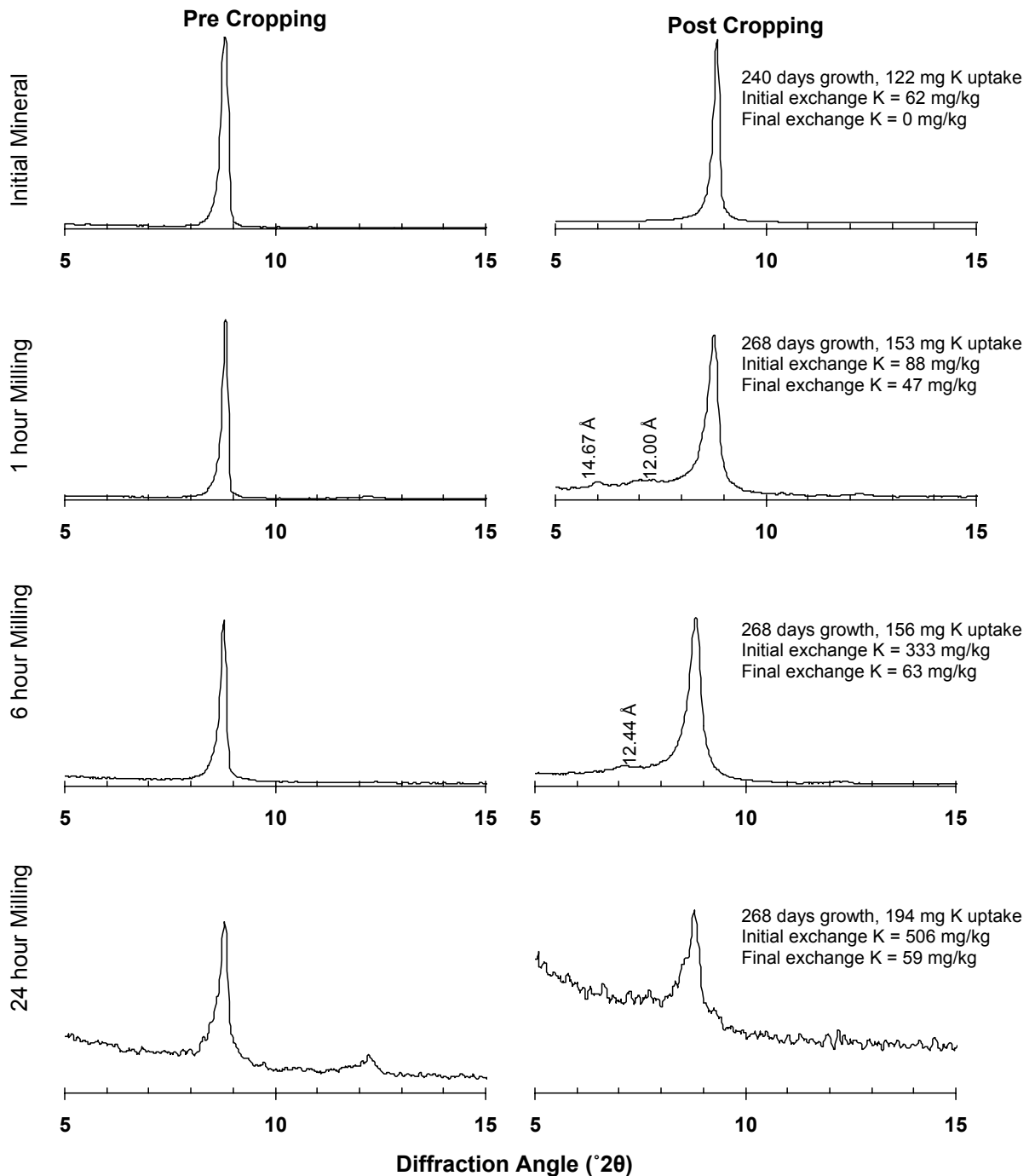


Figure 6.13: The low 2θ region of oriented plate X-ray diffraction patterns of milled biotite applied at 14.0 g kg^{-1} , samples taken before and after cropping. Curves were smoothed by a 9-point moving average and the intensities of patterns are set to depict the maximum intensity of the (001) peak. Uptake values refer to the sum of ryegrass and clover shoot contents. Initial exchange concentrations were measured after 7 days of incubation and prior to sowing. Final exchange concentrations were measured either at the point of plant death or at the end of the experiment. Values of d-spacings are for peaks for compounds that formed during the experiment.

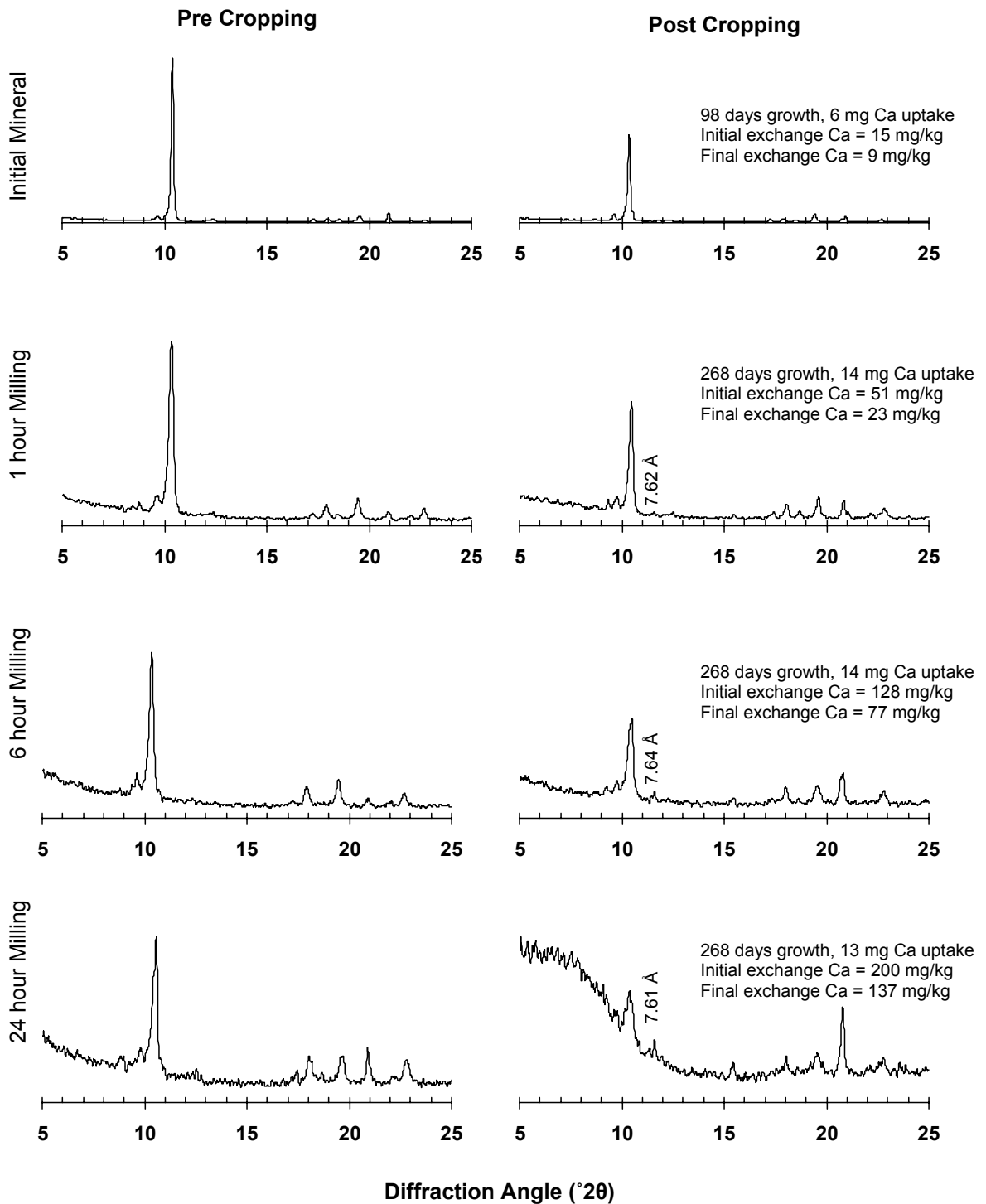


Figure 6.14: The low 2θ region of random powder X-ray diffraction patterns of milled hornblende applied at 12.3 g kg^{-1} , samples taken before and after cropping. Curves were smoothed by a 9-point moving average and the intensities of patterns for each milling time are at the same scale without offset along the y-axis. Uptake values refer to the sum of ryegrass and clover shoot contents. Initial exchange concentrations were measured after 7 days of incubation and prior to sowing. Final exchange concentrations were measured either at the point of plant death or at the end of the experiment. Values of d-spacings are for peaks for compounds that formed during the experiment.

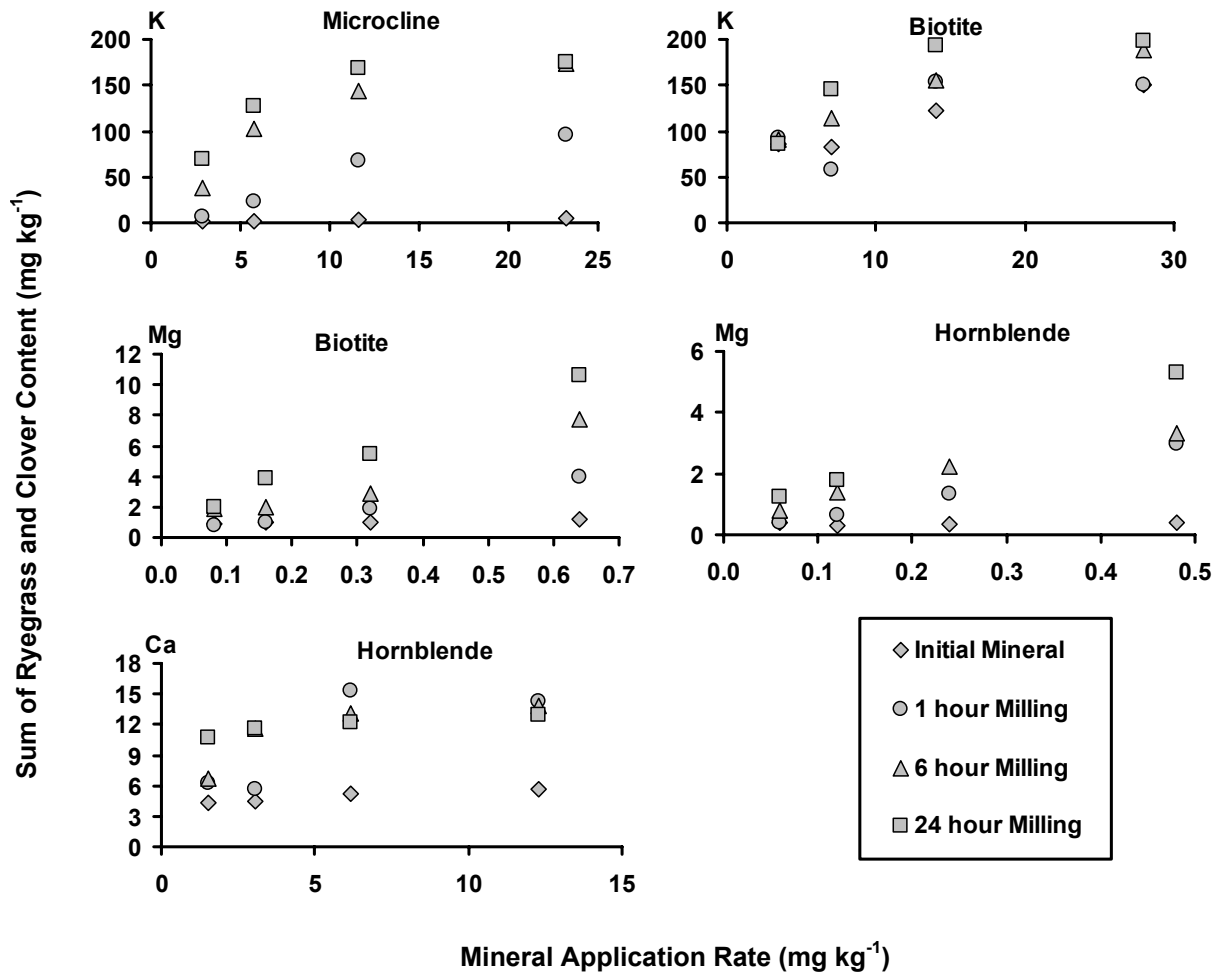


Figure 6.15: Relationship between the sum of ryegrass and clover content and the application rate of milled silicate minerals.

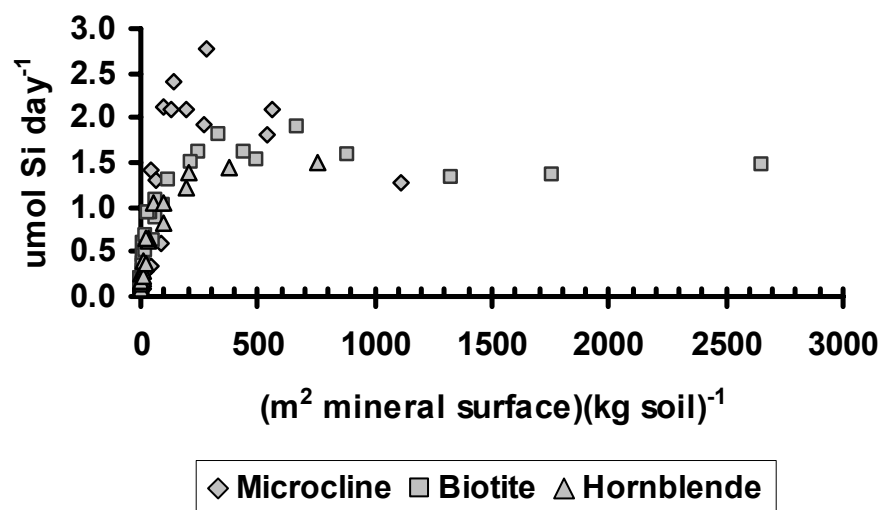


Figure 6.16: Relationship between Si uptake rate and total surface area of the amount of milled mineral added to 1kg of soil.

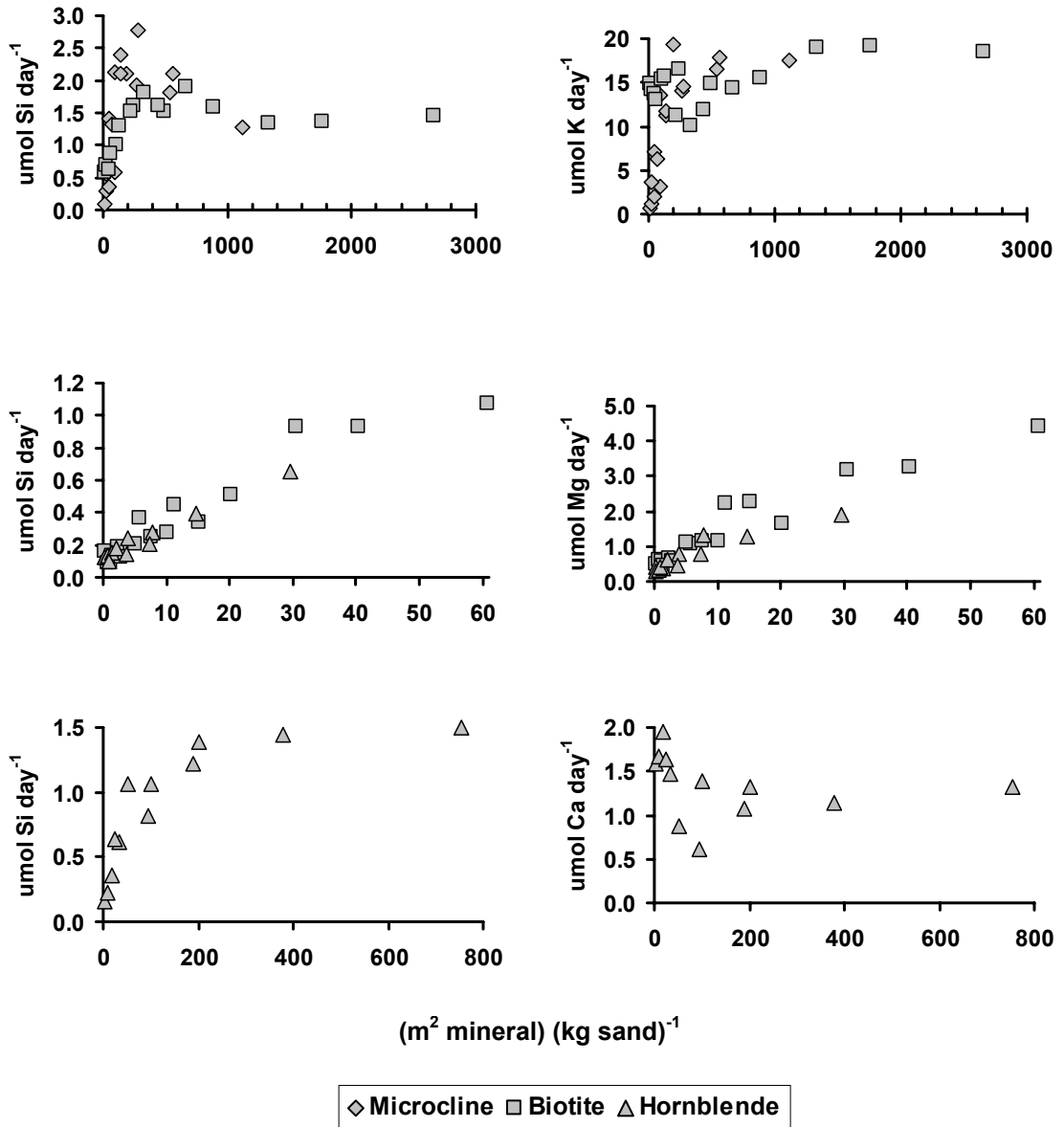


Figure 6.17: Relationships between nutrient uptake rate and total surface area of the amount of milled mineral added to 1kg of soil.