Comparison of silicate minerals as sources of K for plant nutrition in sandy soil

S. M. O. MOHAMMED[a,b], K. BRANDT[b], N. D. GRAY[c], M. L. WHITE[d] & D. A. C. MANNING[c]

[a]*Soil and Water Department, Faculty of Agriculture, Sebha University, P.O. Box 19332, Sebha, Libya*

[b]*School of Agriculture, Food and Rural Development, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU,* [c]*School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU , and* [d]*School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle upon Tyne, UK, NE1 7RU*

Correspondence: D. A. C. Manning. E-mail: david.manning@ncl.ac.uk

Running head: Silicate minerals as sources of K

Key words: K, potassium, feldspar, microcline, biotite, nepheline, syenite, leek

Summary

Given the cost of conventional fertilizers and increasing demand from increasing population growth, new sources of potassium (K) for plant nutrition need to be considered. Readily soluble nutrients are rapidly lost from well-drained soils, and so it is appropriate to consider silicate minerals that release K slowly during weathering. In this paper, we compare the availability to plants grown in sandy soils of K from microcline (feldspar), biotite (mica), and nepheline syenite (nepheline + microcline) using leek (*Allium ampeloprasum* var. *porrum* L.) as a model plant. Pot experiments were carried out under controlled environmental conditions using natural and artificial soil. The performance of the minerals was compared to treatment with KCl and a negative control (no K added). Plant shoot diameter was measured weekly to assess growth rates. After 10 weeks, plant dry mass and soil and plant contents of soluble K were measured to determine offtake; mineralogical changes in biotite-treated soils were assessed. Results for artificial and natural soil differed, reflecting differences in their mineralogy. With no added K, plant growth ceased after two weeks. Growth rates were greatest for KCl, followed by biotite; linear growth continued for five weeks in the natural soil and for the entire ten weeks in the artificial soil. Growth rates with nepheline syenite (natural soil) and microcline (both soils) did not differ significantly from the negative control, but for nepheline syenite leek shoot K content was significantly greater, demonstrating availability of K from this source. X-ray diffraction analysis showed that biotite reacted to form vermiculite.

Introduction

Potassium (K) is an essential plant macronutrient that is absorbed from the root zone. Some soils can provide sufficient K for plant growth, but when the natural supply is not adequate, K fertilizers are applied. Conventionally, the major source of potassium is as chemical fertilizers prepared from mined potash salts, which can be applied directly to soils (Manning, 2010). Of these, the most common potash salt is the natural mineral sylvite (KCl), others include carnallite ($KCl.MgCl_2.6H_2O$) and polyhalite ($K_2SO_4.2CaSO_4.MgSO_4.2H_2O$). Such potash salts provide a soluble source of K that is readily available from the soil solution. The K content of potash minerals is conventionally expressed as the equivalent wt% K_2O; in the case of sylvite this is 63% K_2O. Approximately 33 million tonnes of K_2O equivalent potash salts are mined annually, predominantly from North America (Jasinski, 2011).

The price of mined potash has varied greatly in recent years. In 2008, it rose from around US$150 to US$600 per tonne, and reached US$1000 per tonne in some markets (Manning, 2010). N and P fertilizers showed similar price rises in the same period, however in 2009 both of these dropped to pre-2008 values, tracking the rise and fall in the price of oil. In contrast, the potash price is not so closely related to energy costs (Lægrid *et al.*, 1999), and reduced only to twice the pre-2008 values (approx. US$350 per tonne), with further reductions in 2013.

The relatively high price and limited geographical availability of potash has serious implications for agricultural markets that depend on imports of this fertilizer. For example, Brazil imports approximately 7 million tonnes of potash annually (Pitfield *et al*., 2010). A ten-fold reduction in the use of conventional potash since 1989 has been reported in the Czech Republic, because conventional potash has become such a comparatively expensive commodity (Madaras *et al*., 2012).

Alternative 'fixed' (poorly soluble) sources of K include the potassium silicate minerals, which in principle are widely available. For example, potassium feldspar in its pure end-member composition ($KAlSi_3O_8$) contains 17% K_2O, and was documented as a possible source of K as early as 1887 (references in Sanz Scovino & Rowell, 1988). However, recent studies of feldspars and feldspar-bearing rocks have shown that the availability of K to plants from this source is only marginally better than a K-free control, and thus this mineral cannot compete on equal terms with conventional potash salts (Harley & Gilkes, 2000). Other K-bearing silicate minerals also exist, including nepheline

((Na,K)$AlSiO_4$; a framework aluminosilicate typically with 5–10% K_2O) and micas (sheet silicates) such as biotite ($K_2Fe_6Si_6Al_2O_{20}(OH)_4$, with up to 9% K_2O). Manning (2010) explains that the critical factor in determining K availability for 'fixed' sources such as feldspars and other framework silicates is not the absolute K content but the dissolution rate of the mineral, which depends on the surface area. Thus the success of experiments using nepheline as a source of K for grass (Bakken *et al*., 1997; 2000) can be explained by nepheline's dissolution rate which, once corrected for surface area, is several orders of magnitude greater than that of potassium feldspars such as orthoclase (Manning, 2010).

Comparison of different potash sources extends beyond price and K availability alone. In some soils, readily soluble potash salts have a disadvantage in that K is removed from the root zone by drainage, and in rapidly draining, especially sandy, soils that have a small cation exchange capacity, or with high rainfall, K is lost soon after application. Leonardos *et al*. (1987; 2000) commented on the unsuitability of conventional sources of K for tropical lateritic soils, and recommended the use of potassium silicates as a means of retaining K in the root zone.

In the context of high potash prices and the need to identify alternative sources of K that are locally available or suitable for soils with poor cation exchange capacity, we have undertaken experiments to determine the availability of K derived from the feldspar microcline ($KAlSi_3O_8$), the feldspathoid nepheline ((K,Na)$AlSiO_4$; as a component of nepheline syenite) and the mica biotite ($K_2Fe_6Si_6Al_2O_{20}(OH)_4$) for the growth of leeks (*Allium ampeloprasum* var. *porrum* L., an F1 hybrid known as 'Oarsman'). These minerals differ in their crystal structure, and have different rates and mechanisms of dissolution (White & Brantley, 1995). Potassium feldspar (a framework silicate) occurs very widely in the Earth's continental crust, as microcline, orthoclase or sanidine (different crystal structures with the same chemical composition; Deer *et al*., 1992). The sheet silicate biotite is similarly widespread; biotite and feldspar occur together in granitic rocks and in some metamorphic rocks. Nepheline, a framework silicate with a greater dissolution rate than feldspar (Tole *et al*., 1986) is rare in its distribution; however, it is mined as nepheline syenite, a rock dominated by nepheline and potassium feldspar, and so is commercially available.

In this study, plant growth experiments in soils amended with K mineral sources with different dissolution behaviour were conducted using natural and artificial soil. Leek was chosen as the experimental plant for two reasons. Firstly, its anatomy (Hay & Brown, 1988; Hay & Kemp, 1992) facilitates experimental measurements. It grows as a sheaf of concentric leaves, and so the diameter of leek plants increases regularly, providing an accurate non-destructive measure of plant growth. Secondly, leek is a well-known representative of mycorrhizae-forming crop plants (Jansa *et al*. 2009) and has been used extensively for studies of mycorrhiza-enhanced uptake of minerals other than K (Sorensen *et al*. 2008), including ^{137}Cs, which behaves similarly (Rosen *et al*. 2005).

Materials and methods

Rocks and minerals

The potassium feldspar used was a commercially milled powder product supplied by Imerys Performance Minerals Ltd (Par Moor Centre, Cornwall, England, PL24 2SQ): X-ray diffraction analysis demonstrated that it was microcline. Biotite was obtained from a Newcastle University reference collection in the form of sheets and prepared by crushing in a Tema mill followed by sieving (<0.1mm). The nepheline syenite rock was a commercial milled product from North Cape Minerals AS, mined in northern Norway; X-ray diffraction analysis showed that it contained nepheline, microcline and the sodium feldspar albite

($NaAlSi_3O_8$). The materials were all sieved to <0.1mm, and their chemical compositions (Table 1) were determined by X-ray fluorescence at the Department of Geology, University of Leicester, UK. Specific surface areas (BET: Coulter 3100A using N_2 as adsorbate at 77 K) for the three minerals and their particle size distributions (laser scattering; Malvern Mastersizer 2000; Malvern Instruments Ltd, Malvern, UK) are presented in Table 2.

Table 1 *Chemical compositions of materials used in the experiments; all values in wt %. LOI stands for loss on ignition at 1200° C; n.d. denotes not determined.*

	Biotite	Microcline	Nepheline syenite
SiO_2	39.09	69.94	52.22
TiO_2	2.93	0.01	0.09
Al_2O_3	14.84	16.28	24.20
Fe_2O_3	20.74	0.06	0.16
MnO	0.33	0.00	0.01
MgO	9.97	0.00	0.00
CaO	0.31	0.38	1.62
Na_2O	0.16	2.47	8.29
K_2O	9.33	10.87	9.06
BaO	0.00	0.00	0.36
SrO	n.d.	n.d.	0.40
P_2O_5	0.00	0.01	0.11
SO_3	0.07	0.02	0.35
LOI	1.28	0.22	0.82
Total	99.05	100.24	97.59

Table 2 *Summary of surface area and particle size information for minerals used in this study. The equivalent spherical diameter parameters are the diameters at the 10% (d[0.1]), 50% (d[0.5]) and 90% (d[0.9]) points on a psd curve.*

	BET surface area	Equivalent spherical diameter parameters		
	/ $m^2 g^{-1}$	d[0.1] / µm	d[0.5] / µm	d[0.9] / µm
Microcline	2.387	1.88	12.35	34.15
Nepheline syenite	1.476	1.81	11.72	31.25
Biotite	2.686	19.09	160.7	833.3

Leek growth experiments

Two different soils were used, both with small K contents (Index 0; MAFF 1994). Artificial sandy soil was prepared according to Wallander & Wickman (1999) using a volume to volume ratio 9:1 silica sand to commercial compost (Table 3). The silica sand (97% SiO_2, Highley, 1977) was from the Woburn Bed of the Lower Greensand, Leighton Buzzard, UK, with 100% of the material passing a 600 µm sieve and retained on a 63 µm sieve. The sand was free from flaky particles, silt, clay and organic matter. The compost was Scott's Levington F2S Seed and Modular Compost, (East Riding Horticulture Ltd., http://www.eastridinghorticultureltd.co.uk). A natural soil (argillic brown sand intergrade; Avery, 1980; Entic Alfic Haplorthod/Arenic Hapludalf; USDA classification; Payton, 1980; 1988) was obtained as a bulk sample collected from the Fenton Centre, Northumberland, UK (Ordnance Survey National Grid Reference NT 966 334, within the region described by Payton, 1992), and was taken from a depth of 10–25 cm in a grassland area. The properties of both soils are presented in Table 4.

Table 3 *Summary composition of compost (Scott's Levington F2S Seed and Modular Compost).*

Component	
N-NO_3 / mg l^{-1}	145
N-NH_4 / mg l^{-1}	5
P / mg l^{-1}	200
K / mg l^{-1}	200
pH	5.5-6.0
Organic matter (%)	96
Sand (%)	4
Nominal particle size (mm)	0-3
Moisture content (%)	60-75
Micronutrient mixture	not specified

Table 4 Measured properties of soils used in the experiments.

Soil properties	Artificial soil	Natural soil
Soil texture	sand	loamy sand
N (Dumas method) / %	0.5	0.4
P (Olson method)/ mg l^{-1}	5	10
K (1M NH_4NO_3 Extractable) / mg l^{-1}	40	49
Mg (1M NH_4NO_3 Extractable) / mg l^{-1}	120	162
Ca (1M NH_4NO_3 Extractable) / mg l^{-1}	3000	955
Na (1M NH_4NO_3 Extractable) / mg l^{-1}	4	12
pH	6.5	6.4
Organic Matter (Wet Oxidation) / %	10	3.2
CEC / meq 100 g^{-1})	-	12.2

The pot experiments were carried out in a Fisons Fitotron growth chamber (Weiss Technik UK Ltd, Loughborough, UK) with a 12/12 hour light/dark photoperiod and an irradiance of 150 µmol m^{-2} s^{-1}. The pots were incubated in an 18/23° C light/dark temperature cycle, corresponding to winter/spring conditions in the Mediterranean area or temperate summer. There were four different K treatments, each applied in three different quantities designated as half, normal and double applications (Table 5) in addition to K-free controls. An additional triple application treatment was made for microcline. Each fertilizer addition was equivalent to 275 kg K_2O ha^{-1} (230 kg K ha^{-1}) as K silicate minerals or KCl (positive control) and was based on the requirements for index 0 soils for leek production (MAFF, 1994; DEFRA 2010). The mineral K treatments are denoted as follows - M: microcline (K-feldspar); B: biotite; NS: nepheline syenite; K: KCl, and C as K-free negative control. The required amount of each treatment was mixed with soil, and approximately 1 kg weighed into 14 cm diameter pots, with a capacity of approximately 0.5 l. The pots were arranged in a randomized design with three replicate pots per mineral amendment. Ammonium nitrate was applied to all pots to give an N amendment equivalent to 50 kg ha^{-1}, and phosphorus was applied in quantities equivalent to 300 kg P_2O_5 ha^{-1} (170 kg P ha^{-1}) added as calcium dihydrogen phosphate. These nutrients were added one day before the start of the experiment.

Table 5 *Application rates of fertilizer materials used in the leek experiments (275 kg K_2O ha^{-1}, equivalent to 114 mg kg^{-1} K for normal application). C is negative control, KCl denotes positive control treated with KCl and M, NS and B denote treatments with microcline, nepheline syenite and biotite respectively.*

Fertilizers	K_2O%	Application rate mg kg^{-1} soil		
		Half	Normal	Double
C	0	0	0	0
KCl	63.1	109	218	436
M	10.9	632	1265	2530
N	9.3	737	1473	2946
B	9.1	759	1518	3036

Leek seedlings were prepared by sowing seeds (purchased from http://www.nickys-nursery.co.uk) in compost two months prior to the start of the pot experiment, placed in a growth chamber and irrigated by hand to maintain optimal moisture conditions for germination. After one month, seedlings were transferred to the test soil without addition of fertilizer (control) for one month to ensure K depletion. Three leek seedlings were then planted into each replicated pot of a given soil fertilizer treatment, and the pots arranged as a split plot with three replications. The two types of soil (artificial and natural) were used in separate experiments.

The leek plants were watered with de-ionized water. To ensure a constant appropriate water potential in the soil, a capillary watering system was used according to the method developed by Thorup-Kristensen (1994). This system consisted of a Macrorhizon soil moisture sampler (Rhizosphere Research Products BV, Wageningen, Netherlands, http://www.rhizosphere.com) placed into the soil in each pot, connected by a plastic tube to a water supply placed 60 cm below the pot. The soil moisture sampler is a 9-cm sealed tube with 4.5 mm diameter consisting of a hydrophilic microfiltration membrane with a nominal pore size of 0.15–0.20 µm composed of a blend of polyvinylpyrrolidine and polyethersulfone. The soil water was in equilibrium with the water movement throughout the soil moisture sampler. This meant that there was no leaching from the pots (hence no loss of dissolved K or other nutrients), that the soil moisture conditions were relevant for field conditions and that they were identical for all the different treatments throughout growth.

All plant diameters were measured at weekly intervals at 3 cm above the soil level with a digital calliper. Increases in plant diameter observed in all the different experimental treatments were calculated by subtracting the initial diameter from all subsequent measurements, permitting results to be compared for leek seedlings with different initial sizes. Because of changes in observed rate of growth during the period of the experiment, growth rates were calculated for the observed linear period of growth between 0 and 35 days after transplantation into the experimental soil mixtures. At the end of the trial, plants were harvested and roots were washed to remove soil particles prior to separation into roots, stems and leaves, each placed separately in an aluminium tray, dried in an oven at 65° C for seven days to achieve a recorded constant weight. Biomass yields were expressed as dry weight of shoots (leaves and stems from each pot combined).

Dry mass samples were milled using a rotary mill (1 mm screen). To provide sufficient plant material for analysis, the foliage (all above-ground plant tissue, referred to as shoot) of each pot (three plants) was combined. Approximately 2 g of dried ground sample was digested by one volume of perchloric acid (60% concentration) combined with four volumes of nitric acid (approx. 70% concentration; Zhao *et al*. 1994). K was determined in the resultant digestate using either a Jenway PF7P Flame Photometer (Bibby Scientific

Limited, Stone, UK) or a Varian SpectraAA-400 Atomic Absorption Spectrophotometer (AAS; Agilent Technologies UK Ltd, Stockport, UK). A reference material (chive; *Allium schoenoprasum*; IPE sample 111, Wageningen University) was used to check the accuracy of the analysis procedure.

Unamended soils sampled prior to the experiment and soils sampled at its end were air dried, sieved (<2mm) and then extracted with 1M NH_4NO_3 (Anon., 1986; Rowell, 1994). Available K was determined in extracts either by flame photometry or AAS. X-ray diffraction was carried out using a PANalytical X'Pert Pro Multipurpose Diffractometer (MPD) with an X'Celerator detector and a secondary monochromator (PANalytical Ltd., Cambridge, UK). Scans were made over the range 2°–70°, using Cu-Kα radiation (λ = 1.54180 Å). Samples were prepared by packing approximately 500 mg of dry milled sample into 16-mm diameter steel sample wells, which rotated during analysis. Phase identification was carried out using HighScore Plus software with reference to the ICDD Powder Diffraction File 2 database (1999) and the Crystallography Open Database (February 2012).

Statistical analysis

The experiment design addresses the hypothesis that the treatments are different from the negative controls, and that this difference is in a direction and magnitude that are meaningful when compared with the positive controls. Statistical analysis of the experimental results was conducted by analysis of variance (ANOVA) of replicated treatment and control data using SPSS Statistical Software version 21. The residuals were shown to be normally distributed using the Anderson-Darling test. Tabulated data are presented as treatment means with the significance of differences between treatments and the controls (LSD) indicated by bold type (P<0.01) or italic type (P <0.1).

Results

Leek growth measurements

For all mineral treatments, leek growth initially showed continuous increase in plant diameter. For treatments supplying enough potassium to sustain growth, in the natural soil the increase levelled off after approximately five weeks, while the artificial soil supported a continuous increase in diameter throughout the ten-week duration of the experiment (Figure 1).

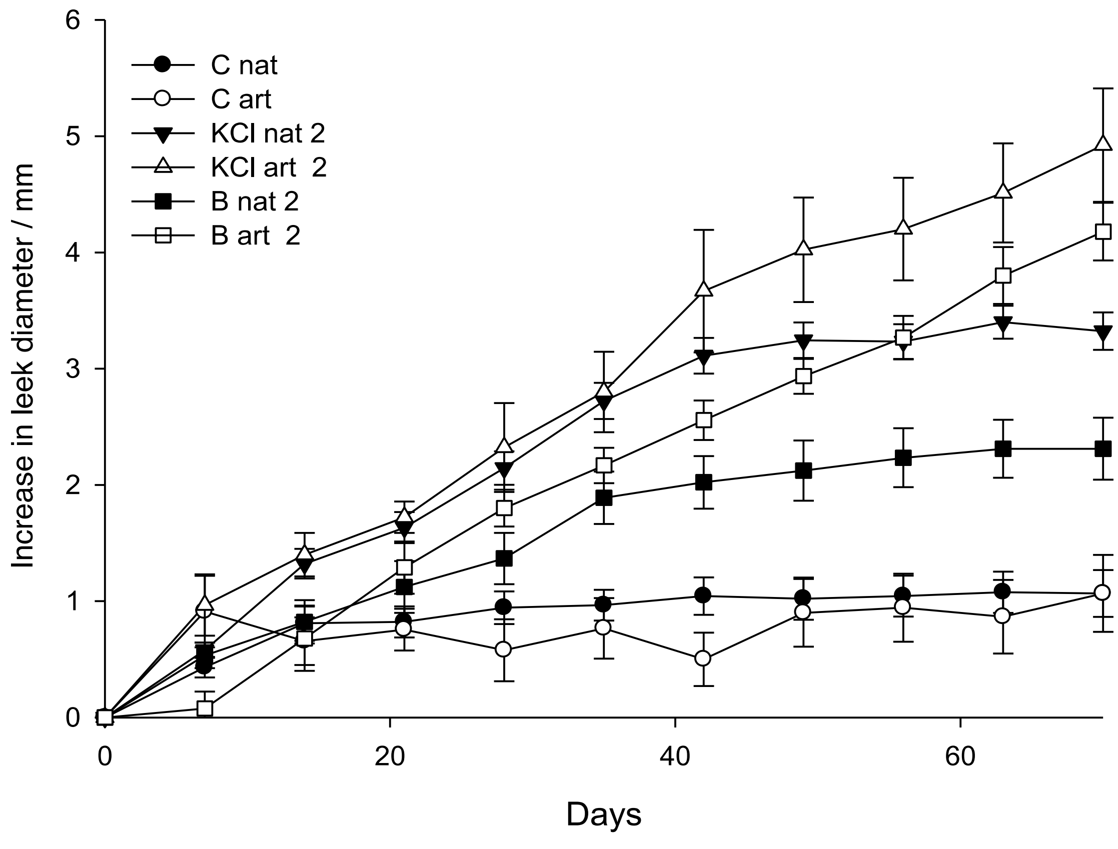

Figure 1 *Example of increase in plant neck diameter over a period of 70 days. C = negative control, KCl = treatment with KCl, B = treatment with biotite. 2 = Double treatment application. Error bars represent 1 x SEM.*

Figure 2 shows growth rates calculated from the initial 5-week period of increase in diameter for all treatments, assuming linearity. Regardless of the type of soil, addition of KCl led to growth rates that were two–three times larger than the negative control (*P*<0.01), showing that potassium was initially the limiting factor for growth in both soils.

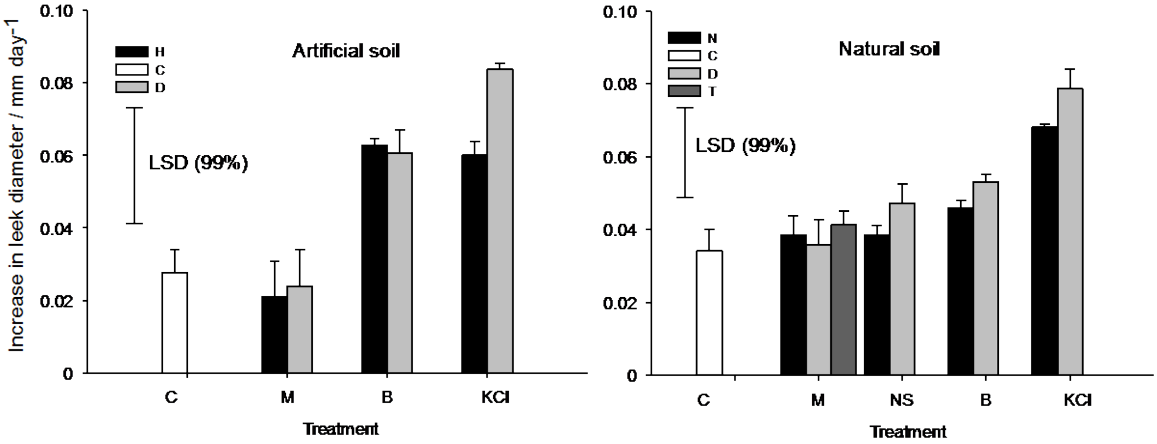

Figure 2 *Growth rates calculated from linear increase in leek neck diameters in both (A) artificial and (B) natural soil experiments from 0 to 35 days. Treatments are: C= K-free, K= potassium chloride (KCl), M= microcline, B= biotite, NS= nepheline syenite. Dose: H = half, N = normal, D = double, T = triple. A nepheline syenite treatment was not included in the artificial soil pot experiments. Error bars represent 1 x SEM. LSD bars represent the least significant mean differences calculated for treatments and controls at the 99% confidence level.*

Addition of biotite in half and double applications to the artificial soil significantly (*P*<0.01) doubled the leek growth rate compared with the negative control. However, in the natural soil the five-week growth rates with biotite were not significantly different from any of the other treatments. For both soils, the addition of biotite resulted in an increase in the maximum plant diameter at the end of the experiment (Figure 1). The effect of nepheline syenite relative to the other mineral treatments was equivocal (Figure 2). As for biotite, growth rates for nepheline syenite in the natural soil, despite appearing marginally greater, were not significantly different from the control (this treatment was not used with artificial soil). Compared with the K-free controls, the application of microcline never gave significant differences in leek growth rate. Apart from KCl in artificial soil (P<0.01), there were no significant differences in growth rate between multiple doses of the same supplement in the same soil.

When KCl and biotite treatments are compared, initial growth rate in the artificial soil with the biotite treatment were not significantly different to those observed for KCl amended experiments. In contrast, there was a significant difference between KCl and biotite for natural soil (P<0.01).

Final plant biomass yields

In both artificial and natural soils treated with KCl fertilizer, shoot dry mass yields (Table 6) were about 1.5 times and significantly (P<0.01) greater than those obtained from the K-free control. However, pairwise comparisons of the double with normal or half application dose, respectively, were not significantly different.

Table 6 *Plant yield* **(***shoot dry mass after eight weeks growth) g pot^{-1}.*

Treatment	Mean dry weight g pot^{-1}			
	Artificial soil		Natural soil	
C	3.53		2.48	
	Half dose	Double dose	Normal dose	Double dose
KCl	**5.2**	**5.8**	**3.8**	**4.8**
M	4.2	4.1	2.2	2.6
NS	-	-	2.2	2.5
B	3.8	**5.1**	3.3	*3.5*

Values in ***bold*** *indicate significant differences (P<0.01) from ANOVA followed by post hoc pairwise comparisons of treatment means with the control (LSD). Values in italics indicate borderline significance (0.01<P<0.1). SE =± 0.25 (control artificial soil, n=5), ±0.35 (artificial soil mineral treatments, n=3) and ±0.59 (all natural soils, n=3).*

Treatment with biotite (double dose in artificial soil) showed similar biomass yields to the treatment with KCl, and was found to be significantly (P<0.01) larger than controls. A double dose of biotite in the natural soil produced only a borderline (P<0.1) significant increase in biomass yield relative to the control. None of the other treatments showed any significant increase in yield compared with the controls.

Potassium concentrations in leek shoots Comparison of the KCl and biotite treatments with the control showed that K concentrations in above-ground biomass were increased significantly for all doses in the natural soil (P<0.01). In the artificial soil increases in K concentration were similarly significant for the double dose applications but not for the half dose applications. (Table 7). With nepheline syenite, K concentrations were increased (P<0.1) only for the double application to the natural soil. Treatment with microcline gave no significant difference in shoot K content when compared with the K-free control.

Table 7 *K concentrations in shoots after plant harvest.*

Treatment	K g kg^{-1} dry weight			
	Artificial soil		Natural soil	
C	13.71		15.6	
	Half dose	Double dose	Normal dose	Double dose
KCl	*21.3*	**35.9**	**27.7**	**37.0**
M	17.3	15.0	18.4	16.0
NS	-	-	19.9	*21.2*
B	19.2	**32.9**	**24.4**	**28.7**

Values in ***bold*** *indicate significant differences (P <0.01) between treatments and the control (ANOVA) followed by post hoc pairwise comparisons of means with the control (LSD)). Values in italics indicate borderline significance (0.1<P<0.01). SE = ±1.96 (control artificial soil, n=5), ±2.53 (artificial soil mineral treatments, n=3) and ±2.08 (all natural soils, n=3).*

Details of ANOVA are given in supplementary material

Potassium balance

The balance of potassium was determined to assess whether the amount of K within the harvested leek corresponded to the amounts removed from the soil during the experiment. In Table 8, K balance (B) is calculated from the formula:

$$B = (K_s + K_f) - (K_r + K_p), \quad (1)$$

where K_s is the initial amount of K in each soil, K_f the amount of added K from the fertilizer, K_r the amount of soluble K remaining in each soil at the end of the experiment, and K_p the amount of K extracted into the plant tissue (offtake). In general, in applications with small available K, offtake in plant shoots was greater than expected from the amount added, and so there was an apparent K surplus beyond the measured inputs (a negative balance). In contrast, other applications had a K deficit (a positive balance), which either reflected K that remained unavailable, or that some other factor limited K uptake (perhaps a micronutrient deficiency). The K deficit was least for biotite, and greatest for microcline.

Overall, for the characteristics measured in these experiments, the effects of the different mineral treatments were as follows. Maximum growth rates and shoot K concentration were observed for KCl, as expected. With biotite, growth rates and shoot K contents overall were similar to those observed for KCl for different soils, although smaller. Treatment with microcline showed no significant effect on any measured parameter compared with control. With nepheline syenite, the shoot K concentrations were significantly increased, but a marginal increase in growth rates relative to the control was not significant.

Weathering of biotite

X-ray diffraction analysis, although limited to initial observations on a whole untreated soil sample (no specific analysis of the clay fraction has been carried out), shows evidence for reaction of biotite during the growth experiments (Figure 3). The biotite used as a treatment in the experiments had a strong and well defined 001 peak at approximately 8.8° 2θ (d spacing 1.00 nm; Figure 3). This is clearly visible in the trace for the amended natural soil, but there is a second peak that corresponds to a similar mica already present in the soil, slightly displaced to higher 2θ from the peak for the biotite used as treatment. The soil also had a poorly defined broad peak at a lower angle, possibly corresponding to a mixed layer biotite-vermiculite. After the growth experiment, the biotite 001 peak that can be attributed to the amendment decreased in size and was poorly defined. There was a corresponding appearance of a clearly defined vermiculite 002 peak, at approximately 6° 2θ (d spacing 1.48 nm). Using the Scherrer equation, biotite crystallite size (which can be taken as an indication of the thickness of discrete packages of sheets within the mica structure) was estimated to be 1994 nm in the treated soil before the experiment, reducing to 74 nm (normal application) and 45 nm (double application) after the experiment, reflecting delamination of the layered structure.

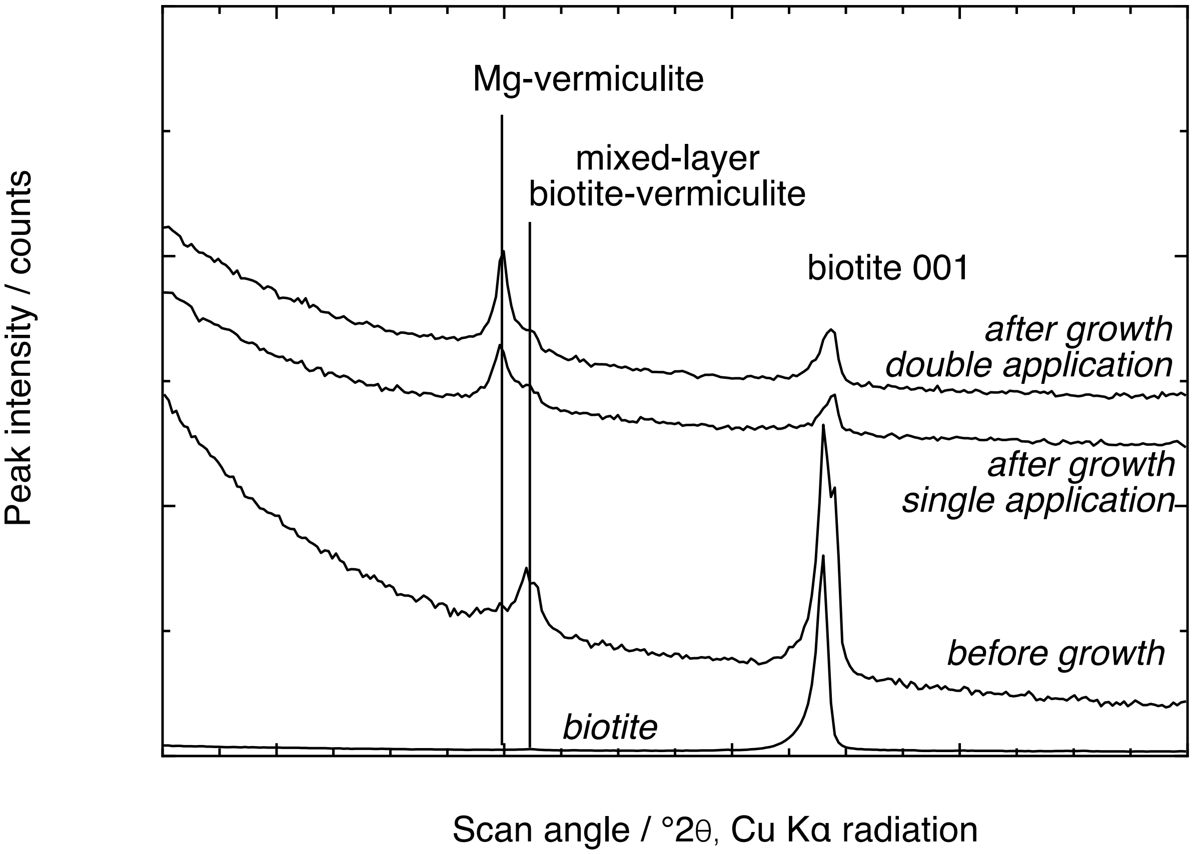

***Figure 3** X-ray diffraction scans for soil samples at low angles of 2θ, showing the biotite 001 peak, the vermiculite 002 peak and a small angle mixed layer (biotite-vermiculite) peak.*

Particle size distribution

Figure 4 shows the particle size distribution (psd) curves for both the soils and the mineral additives used in these experiments. Importantly, the nepheline syenite and the microcline had very similar psd curves, both with 99% <63 μm, which suggests that their behaviour in these experiments is directly comparable, but their BET surface areas differ (microcline 2.387

m^2 g^{-1}; nepheline syenite 1.476 m^2 g^{-1}). The biotite, in contrast, had a very wide range of particle size, extending from 10–2000µm, with only 25% <63 µm. Whereas the psd curves for the nepheline syenite and microcline were quite separate from those of the soils, the curve for biotite overlapped with that of the Fenton soil, and to a lesser extent with the artificial soil.

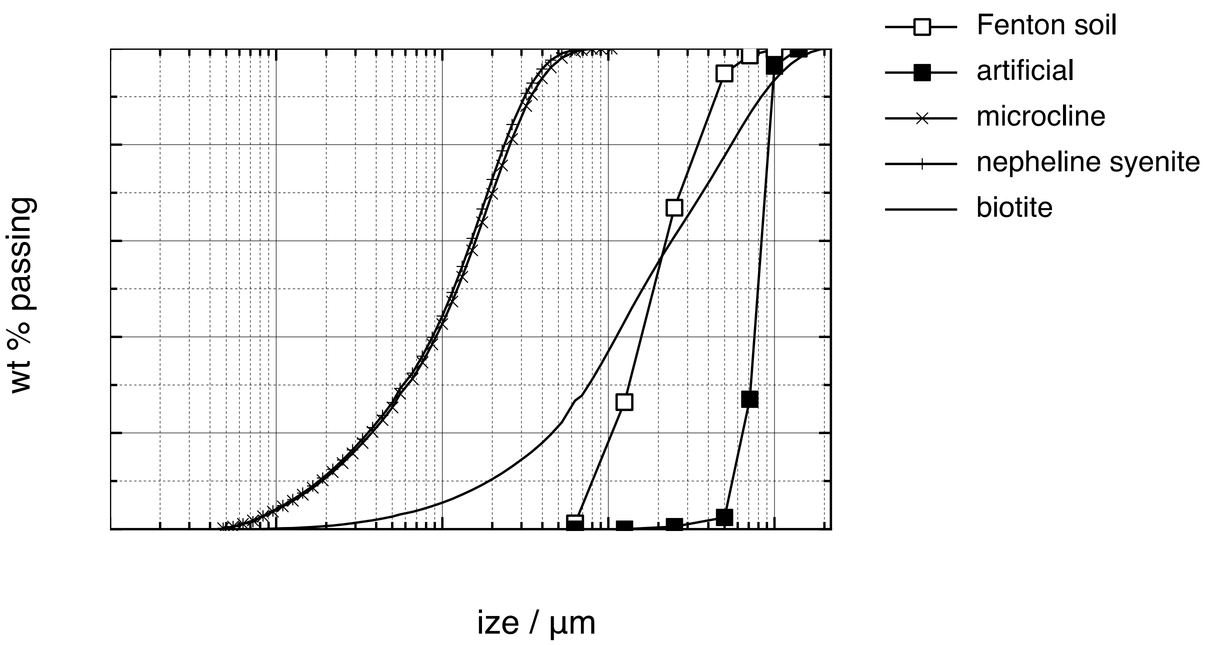

Figure 4 *Particle size distributions for microcline, nepheline syenite and biotite, and for the soils used in this study.*

Discussion

This study has shown that the ability of certain silicate mineral amendments to act as a source of the K required for plant growth appears to vary according to the natural presence or absence of K-bearing minerals within the soil. Two important factors affect the behaviour of the mineral amendments used in the experiments reported here: dissolution rate and physical form (surface area and particle size). Consideration of these then leads to discussion of the behaviour of silicate minerals within soils, as additives or as part of the natural soil composition.

Table 8 K offtake in plant foliage, measured available K and calculated K balance ($mg.pot^{-1}$) at the end of the leek experiments. A negative value for the K balance indicates values of K in offtake and as available K in excess of initial measured available K plus that added as treatment. Initial K contents for the soils are: artificial soil 20 $mg.pot^{-1}$; natural soil 25 $mg.pot^{-1}$. Single application added 114 mg K; half application added 57 mg K, and double application added 228 mg K at the start of the experiment.

	K offtake in plant material (K_p)				K remaining in soil (K_f)				K balance[1]			
Treatment	Artificial Soil		Natural Soil		Artificial Soil		Natural Soil		Artificial Soil		Natural Soil	
C	45		39		7.3		33.5		-32.4		-47.1	
	Half dose	Double dose	Normal dose	Double dose	Half dose	Double dose	Normal dose	Double dose	Half dose	Double dose	Normal dose	Double dose
KCl	*108*	**211**	**107**	**175**	8.1	**16.7**	**58.1**	**105**	-39.2	*20.3*	-25.7	-27.0
M	73	64	40	42	7.1	10.2	37.2	35.3	-1.1	**173.8**	**62.0**	**175.7**
NS	-	-	44	53	-	-	39.6	41.2	-	-	**55.2**	**159.0**
B	74	**172**	*77*	**94**	7.7	8.2	42.8	**45.5**	-4.1	**67.5**	**18.7**	**113.5**

Values in **bold** indicate significant differences (P <0.01) from ANOVA followed by post hoc pairwise comparisons of treatment means with the control (LSD). Values in *italics* indicate borderline significance (0.1<P<0.01).

SE for K offtake in plant material = ± 13.6 (control artificial soil, n=5), ±17.6 (artificial soil mineral treatments, n=3) and ±11.2 (all natural soils, n=3);

SE for K remaining in soil = ±1.4 (control artificial soil, n=5), ±1.8 (artificial soil mineral treatments, n=3) and ±5.2 (all natural soils, n=3);

SE for K balance = ±13.9 (control artificial soil, n=5), ±17.9 (artificial soil mineral treatments, n=3) and ±13.9 (all natural soils, n=3).

All values except the initial total K are as exchangeable K in NH_4NO_3 extraction.

[1]K balance is the initial total K minus the K offtake minus the available K.

Details of ANOVA are given in the Supplementary material

Mineral dissolution rate

Reported dissolution rates (Palandri & Kharaka, 2004) for microcline and biotite are similar (log rate = -10.06 mol m^{-2} s^{-1} and -9.84 mol m^{-2} s^{-1}, respectively), and seven orders of magnitude greater for nepheline (log rate = -2.73 mol m^{-2} s^{-1}). The results of the growth experiments are consistent with the premise that reaction rate alone accounts for availability of K, but only when comparing nepheline syenite and microcline (which have similar mineral structures, being aluminosilicates with a 3-dimensional framework). In particular, the BET surface area of the nepheline syenite is about 60% of the value for microcline, indicating that dissolution rate is more important than surface area as a control on K availability. The greater growth rate observed for biotite is consistent with previous work that has long shown the ability of biotite to weather in planted soils (consistent with Figure 4; Mortland *et al*., 1956; Öborn *et al.*, 2010). Biotite used in this experiment has the largest BET surface area, but also the largest equivalent spherical diameter (Table 2), which reflects the platey (non-spherical) nature of the mineral grains. It is well known that biotite weathering in soils involves an initial transformation to an expanding 2:1 clay (vermiculite), associated with dissolution and weathering (Sparks, 1999), and these physical changes are reflected in the measurement of BET surface area.

The results of other experimental studies to investigate the ability of silicate rocks to deliver K have given varying outcomes. Some studies have focused on the addition of bulk rock materials, including granite, with little evidence of response (Harley & Gilkes, 2000), and nepheline syenite, which does show a response (Bakken *et al*., 1997, 2000). Other experiments to assess the potential of silicate rocks to supply a range of nutrients, not specifically K, by application as ‘rock dust’ have shown negative results (Ramezanian *et al*., 2012). Our experiments extend previous work by demonstrating the importance of understanding (i) the differences in particle size of the mineral additives and the soil, (ii) the mineralogy and behaviour in soil environments of silicates that are considered as sources of nutrient, and (iii) the mineralogical composition of the soil that is used for the experiment.

Differences in particle size of amendment and soil

Figure 4 shows that in these experiments the particle size of the additive is very much finer than that of the soil (>100x for the microcline and nepheline syenite). The relative contributions of minerals inherently present within a soil and those in the additive will depend on differences in their surface area, given that each mineral has a specific dissolution rate (Priyono & Gilkes, 2008). The coarser grain size of the soils means that the potential influence of their constituent minerals on nutrient availability will be much less than the influence of the finer grained mineral additives. In previous studies of the use of rock powders as sources of plant nutrients, additives that were coarser than the soil have been used (Ramezanian *et al.*, 2012), effectively diluting the ability of the soil to deliver nutrients to the plant, and giving negative results.

Behaviour of silicate minerals in soils

In this study, application of microcline gave the smallest yields for leek growth, similar to results obtained with the K free control. This may be a consequence of the relatively short duration of the experiments. However, the natural control soil in any case contained some feldspar (from XRD analysis), and so in this context it was not an ideal control because the feldspar already in the soil may release K, as indicated by the relatively large initial content of available K (Table 4), and in particular by the large amounts of available K remaining in the soil after completion of the plant growth experiment (Table 8). In contrast, although the artificial soil may have contained feldspar at very small amounts (below 0.2%, corresponding to 300 mg kg^{-1} total K), the microcline application showed a slight increase in yield (statistically insignificant) compared with control, which was not seen for the natural soil (Table 6). Similarly, shoot K concentration and K offtake were greater (insignificantly) for artificial soil treated with microcline than for natural soil. Thus the observations for artificial soil suggest that the presence of finely milled feldspar may have an effect on K availability albeit a limited one. Longer term experiments using artificial or natural feldspar-free soils, with greater care to reduce variability, might be needed to show any significant effects on plant growth using microcline or other feldspars.

In this context two limitations of this pot trial compared with a similar field trial must be taken into account: (i) We chose to prevent leaching in all treatments, to reduce the complexity of the experiment and to ensure that plant growth was the only process that removed K from the soil. However this choice favoured the KCl and positive control treatments compared with how they would have performed under field conditions where leaching is a major cause of K-loss from agricultural soil. (ii) Other than K, we only supplied the macronutrients N and P to the soils and tested for the sufficient presence of Ca and Mg. We paid no particular attention to other micronutrients, which agricultural plants usually are able to extract from most soils without the need for supplementation. Commercial composts like the one used in this experiment are routinely supplemented with a complete micronutrient mixture, and we assume this is the reason that the 10% compost in the artificial soil was able to sustain linear growth throughout the 10 weeks. In contrast, the cessation of growth after 5 weeks in the natural soil probably reflected a deficiency in an unknown micronutrient, which by then had been depleted from the small volume of soil available per plant.

The results observed in this study for nepheline syenite are consistent with those from trials with grasses (Italian ryegrass, timothy and meadow fescue) over a period of three years with applications in years 1 and 2 of KCl and nepheline syenite residues from mineral processing (Bakken *et al*., 1997, 2000). Dry yields with KCl exceeded those obtained for nepheline syenite in years 1 and 2, but in year 3 similar results were obtained for both K sources, demonstrating the persistence of nepheline syenite as a slow release source of K and the likely leaching of the KCl from the soil. Given that microcline is at best a very slow provider of K, the effects observed with nepheline syenite can be attributed primarily to the presence of nepheline, in view of its greater dissolution rate.

The mineralogical composition of the soil used in plant growth experiments

In the natural soil used in the present experiment, only the KCl treatments resulted in significantly increased plant growth. For the silicate minerals the only significant effects were on K offtake and concentrations in the plants, while some of exactly the same treatments supported highly significant effects on plant growth rates in the artificial soil. In part, this observation may arise from the natural presence of the additive minerals, especially feldspar, in the soil. A consequence of Gibbs' Phase Rule (Kittrick, 1977) is that in a situation where the solution composition is controlled by dissolution of a specific mineral phase, the equilibrium composition will be constant until the mineral has been consumed completely. A plant growth experiment of the type reported here does not achieve chemical equilibrium, but the principle that the effect of increasing the amount of a specific mineral has no effect on nutrient availability is supported by failure to observe differences between microcline application rates.

The pH of the soils used in these experiments is very similar (6.5 for the artificial soil and 6.4 for the natural soil). This is close to the pH at which feldspar dissolutions rates are at a minimum (Palandri & Kharaka, 2004), indicating that the effect of treatment with microcline and nepheline syenite might well be greater for soils with lower (or higher) pH values than observed in this study.

Efficiency of K availability and nutrient balance

Calculation of K offtake shows that the leek growth removed K from the soil for all treatments; Table 8 shows the amounts of K that remain in the soil following application of the treatment and subsequent plant growth. Potassium removal is most completely observed for the application of KCl, which has the greatest offtake and also shows greatest soil available K after growth (NB no K was leached from the soil in these experiments, in contrast to natural field conditions in many regions). The ability of KCl to replenish stocks of available K is greater for the natural soil compared with the artificial soil, probably reflecting differences in soil mineralogy and hence in cation exchange capability. Treatment with biotite shows a similar effect to KCl. The half application with both soils shows that the bulk of the K supplied by biotite is reported as offtake, with some replenishment of available K in the natural soil. Treatments with nepheline syenite and microcline give small values for offtake when compared with control for the natural soil, and have little effect on final available K.

Conclusions

Growth experiments for 10 weeks using leeks in artificial and natural soils amended with bioite, microcline and nepheline syenite showed that yields obtained with biotite closely approached the maximum yields observed for KCl. Nepheline syenite gave intermediate results, and microcline the least (statistically not different from the negative control). The framework silicates released K slowly through a dissolution mechanism that involves destruction of the aluminosilicate framework, whereas biotite more rapidly released K through a combination of physical and chemical weathering, with the formation of vermiculite.

The results of this work demonstrate that K-bearing micas such as biotite are capable of acting as a relatively readily available source of plant available K appropriate for single seasons or short growing periods, particularly useful for a soil with small cation exchange capacity. Framework silicates such as nepheline and microcline have the potential to act as longer term sources of K, depending on specific local soil, agricultural and economic conditions.

One of the motivations behind this study was to contribute to the development of alternatives to conventional soluble K fertilizers for circumstances where these might be too expensive or inappropriate because of rapid nutrient leaching. However, alternative commercial products based on silicate mineral sources that include feldspar, nepheline or biotite are not readily available, although examples exist (Fortune *et al*., 2005). The work reported here emphasises the importance of the physical properties of minerals used for this purpose, such as particle size and reactive surface area, which can be increased by milling (Priyono & Gilkes, 2008). The physical form of a milled silicate rock or mineral would be similar to that of products such as agricultural lime, which is well established with appropriate equipment for its application. Additionally, the benefit of adding a potassium silicate mineral will be greatest in soils that naturally lack such minerals.

Acknowledgements

Safiya Mohammed acknowledges Libya's Minister of Higher Education and Sebha University, Libya, for financial support of this research.

References

Anon. 1986. *The Analysis Of Agricultural Materials*. Ministry of Agriculture Fisheries and Food Reference Book 427. The Stationery Office, London, UK.

Avery, B.W. 1980. *Soil Classification for England and Wales (Higher Categories)*. Soil Survey Technical Monograph No. 14. Harpenden, UK.

Bakken, A.K., Gautneb, H. & Myhr, K. 1997. The potential of crushed rocks and mine tailings as slow-releasing K fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. *Nutrient Cycling in Agroecosystems*, **47**, 41-48.

Bakken, A.K., Gautneb, H., Sveistrup, T. & Myhr, K. 2000. Crushed rocks and mine tailings applied as K fertilizers on grassland. *Nutrient Cycling in Agroecosystems*, **56**, 53-57.

Deer, W.A., Howie, R.A. & Zussman, J. 1992. *An Introduction to the Rock Forming Minerals*, 2nd ed. Longman Scientific and Technical, London, UK.

DEFRA (Department for Food, Environment and Rural Affairs) 2010. *Fertiliser Manual (RB209)*, 8th ed. The Stationery Office, Norwich.

Fortune, S., Robinson, J.S., Watson, C. A., Philipps, L., Conway, J.S. & Stockdale, E. A. 2005. Response of organically managed grassland to available phosphorus and potassium in the soil and supplementary fertilization: field trials using grass-clover leys cut for silage. *Soil Use & Management*, **21**, 370-376.

Harley, A.D. & Gilkes, R.J. 2000. Factors influencing the release of plant nutrients from silicate rock powders: a geochemical overview. *Nutrient Cycling in Agroecosystems*, **56**, 11-36.

Hay, R.K.M. & Brown, J.R. 1988. Field studies of leaf development and expansion in the leek (*Allium porrum*). *Annals of Applied Biology*, **113**, 617–625.

Hay, R.K.M. & Kemp, D.R. 1992. The prediction of leaf canopy expansion in the leek from a simple model dependent on primordial development. *Annals of Applied Biology*, **120**, 537–545.

Highley, D. E. 1977. *Silica*. Mineral Resources Consultative Committee Mineral Dossier no. 18, Her Majesty's Stationery Office, London, UK.

Jansa, J., Oberholzer, H.-R. & Egli, S. 2009. Environmental determinants of the arbuscular mycorrhizal fungal infectivity of Swiss agricultural soils. *European Journal of Soil Biology*, **45**, 400-408.

Jasinski, S.M. 2011. *Mineral Commodity Summaries (2011) Potash*; http://minerals.usgs.gov/minerals/pubs/commodity/potash.

Kittrick, J. A. 1977. Mineral equilibria and the soil system. In: *Minerals in Soil Environments* (eds J. B. Dixon & S. B Weed), pp 1-25. Soil Science Society of America, Madison, Wisconsin, USA.

Lægrid, M., Bøckman, O.C. & Kaarstad, O. 1999. *Agriculture, Fertilizers and the Environment*. CABI Publishing. Wallingford, UK.

Leonardos, O.H., Fyfe, W.S. & Kronberg, B.I. 1987. The use of ground rocks in laterite systems – an improvement to the use of conventional soluble fertilizers. *Chemical Geology*, **60**, 361-370.

Leonardos, O.H., Theodoro, S.H. & Assad, M.L. 2000. Remineralization for sustainable agriculture: A tropical perspective from a Brazilian viewpoint. *Nutrient Cycling in Agroecosystems*, **56**, 3-9.

Madaras, M., Mayerová, M., Kulhánek, M., Koubová, M. & Faltus, M. 2012. Waste silicate minerals as potassium sources: a greenhouse study on spring barley. *Archives of Agronomy & Soil Science*, **59**, 671-683.

MAFF 1994. *Fertiliser Recommendations For Agricultural And Horticultural Crops (RB209)*. The Stationery Office. London, UK.

Manning, D.A.C. 2010. Mineral sources of potassium for plant nutrition. A review. *Agronomy for Sustainable Development*, **30**, 281-294.

Mortland, M.M., Lawton, K. & Uehara, G. 1956. Alteration of biotite to vermiculite by plant growth. *Soil Science*, **82**, 477-481.

Öborn, I., Edwards, A.C. & Hillier, S. 2010. Quantifying uptake rate of potassium from soil in a long-term grass rotation experiment. *Plant & Soil*, **335**, 3-19.

Palandri, J.L. & Kharaka, Y.K. 2004. *A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling*. U.S. Geological Survey Open File Report 2004-1068, Menlo Park, USA.

Payton, R.W. 1980. Soils of the Milfield Plain, Northumberland. *Proceedings of the Northern England Soils Discussion Group*, **16**, 1-52.

Payton, R.W. 1988. The characteristics and genesis of frangipans in British soils. PhD thesis, University of Newcastle upon Tyne, UK.

Payton, R.W. 1992. Fragipan formation in argillic brown earths (fragiadalfs) of the Milfield Plain, North-East England. *Journal of Soil Science*, **43**, 621-644.

Pitfield, P.E.J., Brown, T.J. & N E Idoine, N.E. 2010. *Mineral information and statistics for the BRIC countries* 1999 –2008. British Geological Survey, Keyworth, Nottingham.

Priyono, J. & Gilkes, R.J. 2008. High-energy milling improves the effectiveness of silicate rock fertilizers: A glasshouse assessment. *Communications in Soil Science & Plant Analysis*, **39**, 358-369.

Ramezanian, A., Dahlin, A.S., Campbell, C.D., Hillier, S., Mannerstedt-Fogelfors, B. & Öborn, I. 2013. Addition of a volcanic rockdust to soils has no observable effects on plant yield and nutrient status or on soil microbial activity. *Plant & Soil*, **367**, 419–436.

Rosen, K., Zhong, W.L. & Martensson, A. 2005. Arbuscular mycorrhizal fungi mediated uptake of Cs-137 in leek and ryegrass. *Science of the Total Environment*, **338**, 283-290.

Rowell, D.L. 1994. *Soil Science: Methods & Applications*. Longman Scientific and Technical, London, UK.

Sanz Scovino, J.I. & Rowell, D.L. 1988. The use of feldspars as potassium fertilizers in the savannah of Columbia. *Fertilizer Research*, **17**, 71-83.

Sorensen, J.N., Larsen, J. & Jakobsen, I. 2008. Pre-inoculation with arbuscular mycorrhizal fungi increases early nutrient concentration and growth of field-grown leeks under high productivity conditions. *Plant & Soil*, **307**, 135-147.

Sparks, D.L. 1999. Bioavailability of soil potassium. In: *Handbook of Soil Science* (ed. M. E. Sumner), pp D38-D53. CRC Press, Boca Raton, USA.

Thorup-Kristensen, K. 1994. An easy pot incubation method for measuring nitrogen mineralization from easily decomposable organic material under well defined conditions. *Fertilizer Research*, **38**, 239-247.

Tole, M.P., Lasaga, A.C., Pantano, C. & White, W.B. 1986. The kinetics of dissolution of nepheline ($NaAlSiO_4$). *Geochimica et Cosmochimica Acta*, **50**, 379-392.

Wallander, H. & Wickman, T. 1999. Biotite and microcline as potassium surces in ectomycorrhizal and non-mycorrhizal Pinus sylvestris seedlings. *Mycorrhiza*, **9**, 25-32.

White, A.F. & Brantley, S.L. 1995. *Chemical weathering rates of silicate minerals. Reviews in Mineralogy* , **31**, Mineralogical Society of America, Washington, USA.

Zhao, F., McGrath, S.P. & Crosland, A.R. 1994. Comparison of 3 wet digestion methods for the determination of plant sulphur by inductively coupled plasma–atomic emission spectroscopy (ICP AES). *Communications in Soil Science & Plant Analysis*, **25**, 407-418.

Supplementary Table 1. ANOVA of average leek growth rates

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	.0106	.00176	10.80	<0.001
Within treatments	14	.0023	.000163		
Total	20	.0129			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	9	.00584	.00065	6.88	<0.001
Within treatments	20	.00188	.00009		
Total	29	.00772			

Supplementary Table 2. Average leek growth rate **(**leek diameter)

Treatment	Average growth of leek diameter mm d^{-1}			
	Artificial soil		Natural soil	
C	0.028		0.034	
	Half dose	Double dose	Normal dose	Double dose
KCl	**0.060**(	**0.083**	**0.068**	**0.078**
M	0.021	0.024	0.038)	0.047
N	-	-	0.038	0.047
B	**0.063**	**0.061**	0.046	0.053*

Values in **bold** indicate significant differences (>99% confidence) from ANOVA followed by post hoc pairwise comparisons of treatment means with the control (LSD). ***** indicates borderline significance (90-99% confidence).SE = ±0.007 (artificial soil) and ±0.006 (natural soil)

Supplementary Table 3. ANOVA of average Plant yield **(**shoot dry mass after 8 weeks growth)

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	15.45	2.58	7.16	.001
Within treatments	17	6.11	.360		
Total	23	21.56			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	9	17.622	1.958	4.85	.002
Within treatments	20	8.071	.404		
Total	29	25.692			

Supplementary Table 4. ANOVA of K concentrations in shoots after plant harvest

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	1510.11	251.69	13.12	<.001
Within treatments	16	306.84	19.1778		
Total	22	1816.96			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	9	1378.94	153.22	11.83	<.001
Within treatments	20	259.11	12.96		
Total	29	1638.05			

Supplementary Table 5. ANOVA of K offtake

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	76082.61	12680.44	13.70	<.001
Within treatments	16	14805.63	925.35		
Total	22	90888.24			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	8	49576.62	6197.08	16.53	<.001
Within treatments	18	6747.00	374.83		
Total	26	56323.62			

Supplementary Table 6. ANOVA of K remaining in soil

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	217.03	36.17	3.92	.013
Within treatments	16	147.76	9.24		
Total	22	364.79			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	8	11860.20	1482.53	16.21	<.001
Within treatments	18	1646.21	91.46		
Total	26	13506.42			

Supplementary Table 7. ANOVA of K balance

Artificial soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	6	105312.31	17552.05	18.20	<.001
Within treatments	16	15430.10	964.38		
Total	22	120742.41			
Natural soil experiments					
Source	Degrees of freedom	Sum of squares	Mean square	*F* ratio	*P*
Between treatments	8	161480.23	20185.03	34.81	<.001
Within treatments	18	10437.08	579.84		
Total	26	171917.31			