



Testing the ability of plants to access potassium from framework silicate minerals



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HIGHLIGHTS

- Plant growth in artificial soil has derived K from potassium feldspar as well as mica.
- Use of mica (phlogopite) as a source of K gives response similar to KCl control.
- The observed growth response in both cases increases with increasing mineral dose.
- K content in plant tissue increases with dose, and confirms a mineral source for K.
- The results highlight the potential of feldspar, in syenite rock, as a source of K for tropical soils.

GRAPHICAL ABSTRACT



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ABSTRACT

The availability of K, essential for plant growth, from syenite (a silicate rock in which potassium feldspar is the dominant mineral; >90 wt%), and phlogopite mica has been demonstrated using carefully designed plant growth pot experiments in which the only added source of K was the mineral of interest, with no loss of nutrients through drainage. Using pure quartz sand as a soil, both growth (increase in diameter) of leek plants and K-content of the plant material showed a dose-dependent positive response to the application (114–43000 mg K/pot) of milled syenite with increases in plant diameter of 0.5–0.7 mm/week, increasing with application rate. Phlogopite mica (114–6000 mg K/pot) supported the highest observed increase in diameter (approx. 1 mm/week) and plant K-content, both similar to that observed for a positive control (KCl). These experiments demonstrate that plants can obtain K for growth from milled syenite, in which feldspar is the dominant K-bearing mineral, and confirm previous observations that micas can be an effective source of K.

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1. Introduction

For healthy growth, all plants require a range of major and trace nutrients. With the exception of nitrogen, the ultimate source of all

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nutrients is the geological mineral assemblage that occurs within a soil. The function of soil minerals varies, with (for example) congruent dissolution of apatite providing P, and cation exchange on clay surfaces controlling K and N (as ammonium) within the soil solution.

This paper focuses on the availability of K for plant growth, and demonstrates for the first time that K is available for plant growth when potassium feldspar (KAlSi_3O_8) is the dominant source of K in a soil. Potassium feldspar occurs widely in (especially temperate) soils, yet is regarded as inert on the timescale of crop production given its slow rate of dissolution as determined in the laboratory and low K yields in conventional laboratory tests of K availability (Harley and Gilkes, 2000; Manning, 2010a; White and Brantley, 1995). Other widely occurring potassium silicate minerals include micas, which have long been known to act as sources of K through cation exchange and weathering reactions (Sparks and Huang, 1985; Mohammed et al., 2014). Similarly, there is long-standing evidence that nepheline-bearing rocks (including nepheline syenites; nepheline is also an aluminosilicate mineral, a feldspathoid) may be effective as sources of K for plant growth (Ciceri et al., 2015). Conventionally, potassium fertilisers are based on soluble salts, derived from the natural mineral sylvite (KCl) or sulfates such as polyhalite ($\text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$) and carnallite ($\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$).

Globally, inputs of K to soils from all sources (including crop residues) are much less than the amount removed through the harvesting of crops (Sheldrick et al., 2002). Nutrient balance studies show that if this deficit was an accurate representation of the need for K to support crop growth, then the requirement for supplementation with K would be far greater than the need for P or N, which more often are in balance (Sheldrick et al., 2002). Indeed, if all K removed annually by crops had to be replaced to fill the 'potash gap' (Manning, 2015), world mined production of potash would need to double. The ability of many soils to sustain reasonable yields without annual supply of K thus indicates that their content of plant available K may be replenished from sources already present in the soil (Mohammed et al. 2014).

At present, global production of K fertilisers is about 33.5 million tonnes K_2O equivalent annually (Jasinski, 2014), typically mined from deposits of natural K chloride and sulfate salts, some of which contain other nutrients. 99% of world potash is mined from just 12 countries, dominated by Canada (Rittenhouse, 1979), and whole continental regions have insignificant (e.g. Africa, Australasia), or low production (e.g. South America). The price of K fertilisers reached US\$1000/tonne in 2009 (Manning, 2010a), reducing to US\$350–400/tonne more recently. In addition to paying the commodity price and for value added during processing, farmers must pay high associated transport and distribution costs. Additionally, K from sources such as KCl is highly soluble and can be rapidly lost through leaching, so (depending on the soil) it may need to be replaced for every growing season.

To supply the K required for crop growth it is therefore important to consider novel inputs in addition to conventional sources, given constraints on price and availability. K silicate minerals including feldspar and mica contain up to 16 wt% and 11 wt% K_2O respectively, and have been used in a number of studies (Ciceri et al., 2015). In particular, Leonardos et al. (1987) present a convincing case for the use of silicate minerals as sources of K for deeply weathered tropical soils, where leaching of conventional salt-based fertilisers often removes nutrients even before they can be used by the growing plants. But although some trials have given positive results (e.g. Bakken et al., 1997, 2000; Sanz-Scovino and Rowell, 1988; Mohammed et al., 2014; Manning, 2010b), other trials have failed to do so (e.g. Bolland and Baker, 2000; Harley and Gilkes, 2000; Hinsinger et al., 1996), and the generally low price, historically, of conventional K fertilisers has reduced the need for alternatives.

A critical aspect of the use of novel sources of K is the unambiguous demonstration that K within a plant is derived from a known source. In this paper, we report the design and results of experiments in which we show that K can be derived from (a) milled syenite rock in which

potassium feldspar is present as the dominant K-bearing mineral, or (b) mica (the mineral phlogopite). We believe that this is the first time that K availability from a feldspathic rock to plants has been demonstrated experimentally, and our results support the future design and use of silicate minerals as fertilisers particularly in deeply-leached tropical soils in which oxide minerals predominate.

2. Materials and methods

Plant growth experiments were carried out using closed system pot trials in which there was no through drainage that would permit unknown loss of nutrients from the pot, and in which the dominant source of K was the silicate mineral of interest. An artificial soil was used, based on a high purity silica sand ('Sibelco RHT': >99% quartz and >99% 125–710 μm grain size, www.sibelco.eu), which was mixed with 20% organic matter (Irish moss peat – fine, Recipe no 822, East Riding Horticulture, www.eastridinghorticultureltd.co.uk) by volume, corresponding to approximately 3% by weight and adding potentially 4–8 mg K (based on supplier's specification) equally to each pot. The K sources were syenite (12.8% K_2O) supplied by Terrativa SA (Belo Horizonte, Brazil) and phlogopite mica (10.19% K_2O) supplied by LKAB minerals (product PD900; www.lkabminerals.com). The syenite was supplied milled, and the phlogopite was supplied as flakes (approx. 5 mm or less) and was milled using a TEMA mill prior to use. Both were sieved to <0.150 μm . The chemical compositions of the materials used (Table 1) were determined by X-ray fluorescence spectroscopy using a Panalytical PW2404 wavelength-dispersive sequential X-ray spectrometer (School of Geosciences, Edinburgh University). Major elements were determined on fused glass discs, 40 mm-diameter, prepared from approximately 0.9 g of sample powder mixed with 4.5 g lithium metaborate flux and fused in Pt-5%Au crucibles at 1100 °C. Mineralogically (based on petrography), the syenite is composed of >90% K-feldspar (microcline), with <10 wt% each of pyroxene, amphibole and accessory minerals, all of which are K-free, and biotite. X-ray diffraction (Supplementary material) did not detect biotite (or any other mica) in the syenite used in these experiments; this technique would normally detect the (001) reflection of micas at >1 wt%.

In addition, the particle size distribution of the materials used was determined using a Malvern Mastersizer 2000 (Malvern Instruments Ltd., Malvern, UK); the results show 90% of the milled syenite was <150 μm , and 90% of the milled phlogopite was <60 μm (Supplementary material; Fig. S2). Particle surfaces were observed using a Carl Zeiss SIGMA HD VP Field Emission scanning electron microscope combined with an Oxford AZtec ED X-ray analysis system to confirm mineral identification (School of Geosciences, Edinburgh University).

Characterised by ourselves, these commercial materials were chosen to ensure (as far as possible) use of tightly specified materials that are available from commercial sources for future experiments or commercial use.

Table 1

Chemical composition of mineral materials used in the experiments. The three syenite samples are replicates of the material used.

wt%	Phlogopite	Syenite 1	Syenite 2	Syenite 3	Sand
SiO_2	41.97	62.55	62.60	62.77	98.89
Al_2O_3	9.54	16.26	16.30	16.40	0.13
Fe_2O_3	9.05	2.81	2.81	2.80	0.26
MgO	24.16	0.69	0.70	0.72	0.23
CaO	0.62	2.11	2.16	2.15	0.03
Na_2O	0.02	1.50	1.52	1.52	n.d.
K_2O	10.2	12.78	12.79	12.70	0.019
TiO_2	0.18	0.31	0.31	0.33	0.031
MnO	0.04	0.07	0.07	0.07	n.d.
P_2O_5	0.12	0.19	0.20	0.20	0.012
LOI	3.82	0.50	0.35	0.33	0.13
Total	99.85	99.75	99.81	99.98	99.71

There were ten different K treatments (Table 2): four different doses of milled syenite, 3 doses of phlogopite, 2 doses of KCl and a K-free control treatment, each with ten replicates (pots). Each 13 cm pot with 1 kg capacity was labelled with a 3-digit code obtained from a random number generator, arranged in a randomized design, giving a total of one hundred pots.

Leek (*Allium ampeloprasum* L. var., 'Oarsman' F1 (A.L. Tozer Ltd., www.tozerseeds.com)) was chosen as the trial plant. Its growth as a sheaf of concentric leaves (Hay and Kemp, 1992; Tsouvaltzis et al., 2010) allows periodic measurement of the increase in diameter, facilitating measurement of growth without killing the plants to determine biomass. Leek seeds were sown in moist compost in a greenhouse three months before starting the trials, and were watered by hand twice a week to deplete the stores of potassium and other nutrients. The seedlings were carefully rinsed with tap water to remove as much compost as possible from the roots, and then wrapped in paper towel to absorb excess water. Plants were sorted according to size in 2 groups (small and large), and two seedlings were selected for each pot, one of each size, pairing the largest plants with the smallest plants to minimise variation in combined size. The diameter, height, and weight were recorded before being planted in the pot. Each pot was placed on an individual saucer to prevent transfer of water or nutrients from one pot to the other, and the pot experiment was carried out in an unheated greenhouse for a period of 10 weeks, between April and July, providing a soil temperature regime representative of subtropical or tropical regions.

Once a week, each pot was provided with 200 ml of a K-free Hoagland's nutrient solution containing all required nutrients except K (modified from Johnson et al., 1957; Supplementary Information Table S1).

A constant water tension was applied to each pot by supplying de-ionized water through a capillary irrigation system (Hydrospike HS-300; www.hydrospike.com), which ensured that the water availability would be appropriate for plant growth under field conditions irrespective of the composition of the soil (Thorup-Kristensen 1994). This irrigation system involved a ceramic spike positioned into the soil in each pot, attached by a watering tube to a water reservoir placed approx. 60 cm below the pots. The surface of the reservoir was allowed to recede by no > 10 cm by refilling to initial height at least once every week. The water in the reservoir was replaced once every month to prevent growth of algae, which may clog the tip of the watering tube. With this system the moisture condition was identical for all the treatments, irrespective of differences in water use by plants of different sizes (Thorup-Kristensen 1994), and there was no through drainage.

The diameter of each plant 1 cm above the soil surface was measured weekly, using a digital caliper (Mohammed et al., 2014). The increase in plant diameter since planting was calculated by subtracting the initial diameter (T_0) from each of the subsequent measurements (T_n). Signs of nutrient deficiency in the leaves, such as yellow leaves and chlorosis, were recorded.

Table 2
Application rates of K fertilisers used in the pot trial experiment.

g mineral/pot	mg K/pot
Syenite (12.8% K ₂ O)	
406	43,000
56.8	6000
7.87	830
1.08	114
Phlogopite (10.2% K ₂ O)	
71.0	6000
9.84	830
1.35	114
KCl (63% K ₂ O)	
0.22	114
0.11	57.0

After 10 weeks, the whole plants were harvested and the roots were washed gently to remove soil particles, excess water was removed using paper towels. The shoots and roots were placed in separate aluminium trays, dried in an oven at 65 °C for 4 days and the dry biomass recorded.

After 2 h additional drying (to facilitate milling), the dried samples were ground in an electric coffee mill. Dried shoots from the two plants from each pot were combined into one sample per pot. Approximately 2 g of ground plant material per sample was then analysed for K, Na, Ca and Mg. The dried samples were digested in a mixture of concentrated HNO₃ and HCl (1:2). Element concentration in the acid digest was determined after suitable dilution for each sample by atomic absorption spectrometry (Varian SpectraAA-400). Chive (*Allium schoenoprasum* L.; WEPAL-IPE sample 111, Wageningen University) was used as a plant reference material, to verify the accuracy of the analysis. The K content of the reference was found to be 21.1 g/kg (n = 3; standard deviation = 0.7 g/kg) compared to the declared consensus value of 22.6 g/kg (n = 128; standard deviation = 1.36 g/kg).

For statistical analysis, the trial had one factor: fertiliser. There were ten fertiliser treatments, including the controls, each with 10 replicates and ten sampling times. The plants in 11 pots (0–3 in each treatment) appeared to be affected by disease, which resulted in very low biomass (<30% of the average within the treatment), the data from these pots were treated as outliers and omitted from the statistical analysis. Growth rate was calculated for each plant as the slope of the change in diameter across all 10 weeks if R² > 0.85 (this was fulfilled for one or both plants in all pots with healthy plants). The offtake was calculated as the K concentration in foliage multiplied by the foliage dry mass per pot (since the amount of root material was insufficient for measurement of K). The results were tested by analysis of variance (ANOVA) using General Linear Models in Minitab 17 Statistical software, assessing for normal distribution and considering p-values < 0.05 significant.

3. Results and discussion

The observed increase in leek diameter depended on the mineral treatment. It was greatest for the positive control containing KCl, and for the treatment containing phlogopite mica 6000 mg pot⁻¹ (Fig. 1). Treatment with different amounts of syenite gave results between the negative control and the positive control, with the change in diameter increasing with greater application rates (R² 0.23, p < 0.0008).

For all treatments an increase in the diameter was observed, reaching a maximum at the end of the experiment (Fig. 1). Plants were able to mobilise K from both syenite and phlogopite, showing increased rates of growth compared with the negative control for all

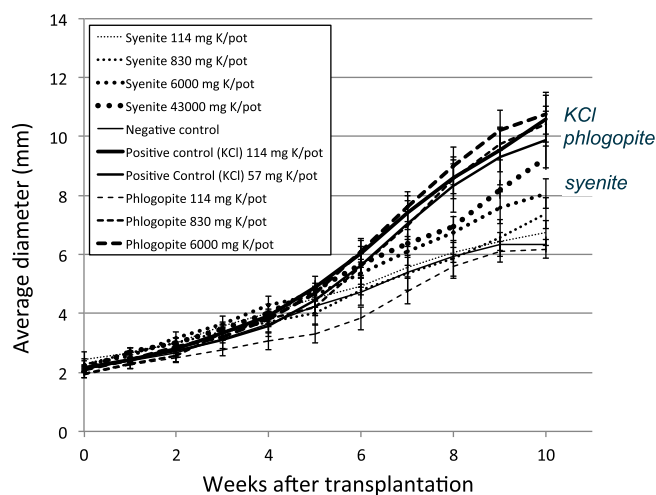


Fig. 1. Variation in the plant diameter over a period of 10 weeks in the pot trial for the nepheline syenite and phlogopite mica. Data are the mean value of 10 replicates. Error bars represent 1 × SEM.

but the lowest applications (Fig. 2). The phlogopite treatment gave results similar to the KCl control, as observed in other studies using micas (Mohammed et al., 2014). Importantly, the growth rates for the treatments with syenite were significantly ($p < 0.00001$) correlated ($R^2 = 0.3179$) with the log of the syenite dose, and, the rates for the treatments with 830, 6000 and 43,000 mg K/pot were statistically different from the negative control ($p < 0.007$, $p < 0.001$ and $p < 0.001$ respectively), demonstrating that some of the K from the syenite was available for uptake by plants.

When considering the K concentration in the plant (Fig. 3), significant differences were seen between treatments. K concentration in the treatment with maximum dose of syenite was higher than the negative control ($p < 0.001$), and proportional with syenite dose across all treatments ($R^2 0.797$, $p < 0.00001$). The phlogopite mica treatments (with the exception of the lowest dose treatment; $p > 0.6$) differed from the negative control. The K concentrations for the maximum dose of syenite and the KCl treatment were not statistically different ($p < 0.9$). In the maximum dose for the phlogopite mica, the K content was much greater than all other treatments of syenite and phlogopite mica, and greater than observed for the KCl treatment ($p < 0.01$).

Calculation of offtake (plant K concentration \times dry mass; Fig. 4) again shows clearly that K was taken up from syenite treatments; it also shows for all treatments that no K was released from other sources than the added minerals, as applications of K were never exceeded by offtake. A comparison of Figs. 2 and 4 demonstrates that growth was completely inhibited for treatments that provided < 8 mg plant-available K per pot (negative control, and the lowest dose of syenite and phlogopite, respectively), while treatments providing 8–29 mg per pot showed partial K-limitation, and the growth in remaining treatments was unaffected by K-availability within the timescale of the experiment. Sufficient K was present in the negative control and lowest dose applications of syenite and phlogopite to give offtake of approximately 8 mg K/pot; this is consistent with the availability of K from the peat compost added in identical quantity to each pot, but may also reflect the K present within the plant following initial growth in compost prior to planting in the trial pots.

The results described above were obtained from experiments that lasted only 10 weeks, so while they demonstrate that the plants were able to access some K from milled syenite to sustain growth, and equally clearly demonstrated that large amounts of syenite had no toxic effects on the plants, they did not allow assessment of the rate of degradation of the syenite beyond what may be the contribution from an accessible surface layer or the fine particles that coat grain surfaces, both created by mechanical impact during the milling

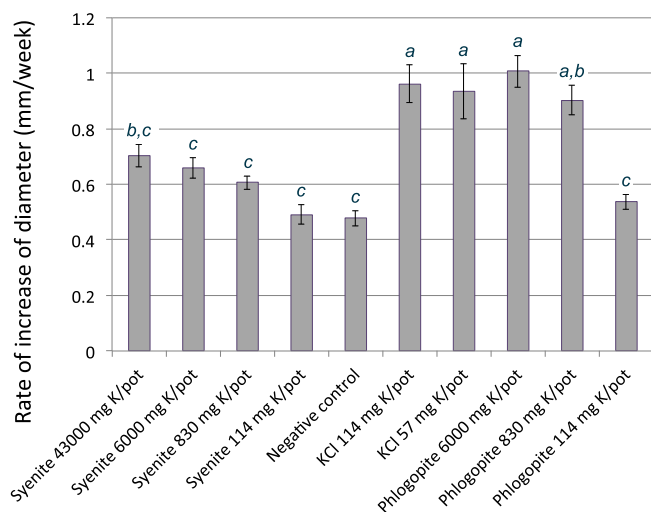


Fig. 2. Effect of crushed rock treatments on rate of diameter increase for leeks over ten weeks. Errors bars represent $1 \times \text{SEM}$; Tukey Pairwise Grouping indicated by a, b, c.

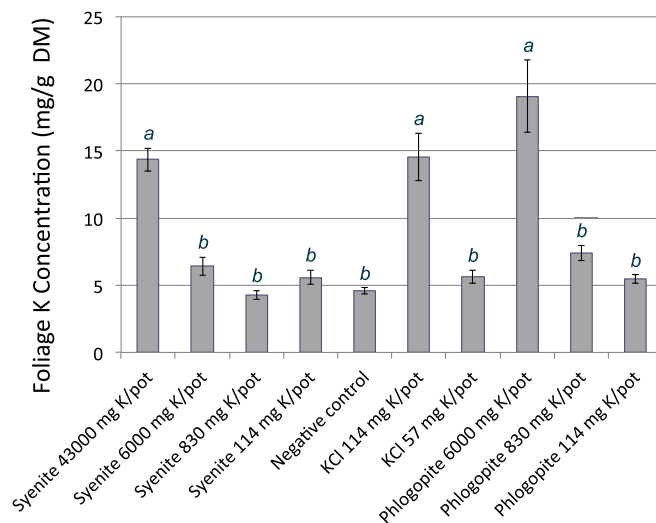


Fig. 3. K concentration in leek plants for different treatments with silicate minerals. Error bars $1 \times \text{SEM}$; Tukey Pairwise Grouping indicated by a, b.

process. Fig. 5 shows SEM images of feldspar surfaces before and after the 10-week growth experiment with 43,000 mg K/pot added as syenite. In these, cleavage steps are clearly visible as are micropores naturally present within the mineral. The feldspar surface is coated with particles $< 1 \mu\text{m}$, and overall there is little visible change in appearance (apart from reduction in the coverage by fine particles), consistent with the short time for reaction. The amount of K removed by plants from the soil as offtake was equivalent to 0.1–0.2% of the added syenite, which is consistent with the observation of little change in grain surface appearance.

The process of release of K from feldspar, the dominant mineral within the syenite, and mica differs. In micas, the crystal structure consists of layers of negatively-charged aluminosilicate sheets with cations, such as K, in the interlayer site. When in soils, the micas weather with the release of K as a consequence of cation exchange reactions (Hinsinger et al., 1993; Singh and Goulding, 1997; Sparks and Huang, 1985). Vermiculite is produced as a consequence of weathering in soils of magnesium-bearing micas. The feldspars have a structure with a 3-dimensional network of Si and Al coordinated tetrahedrally with

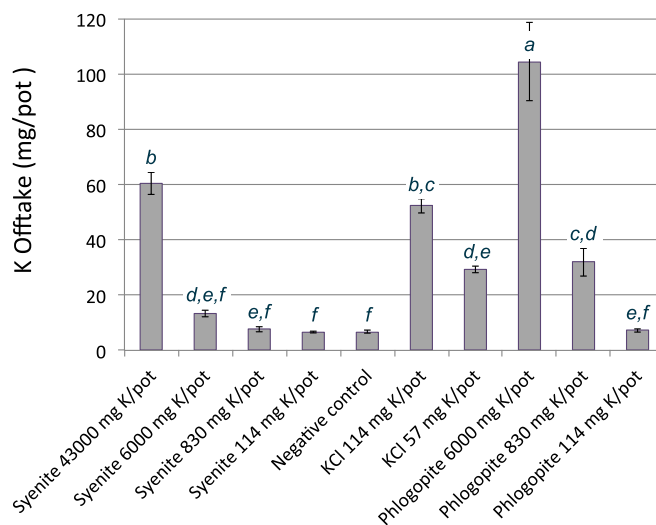


Fig. 4. Amount of K removed from the soil by plant growth (offtake); Tukey Pairwise Grouping indicated by a, b, c, d, e and f.

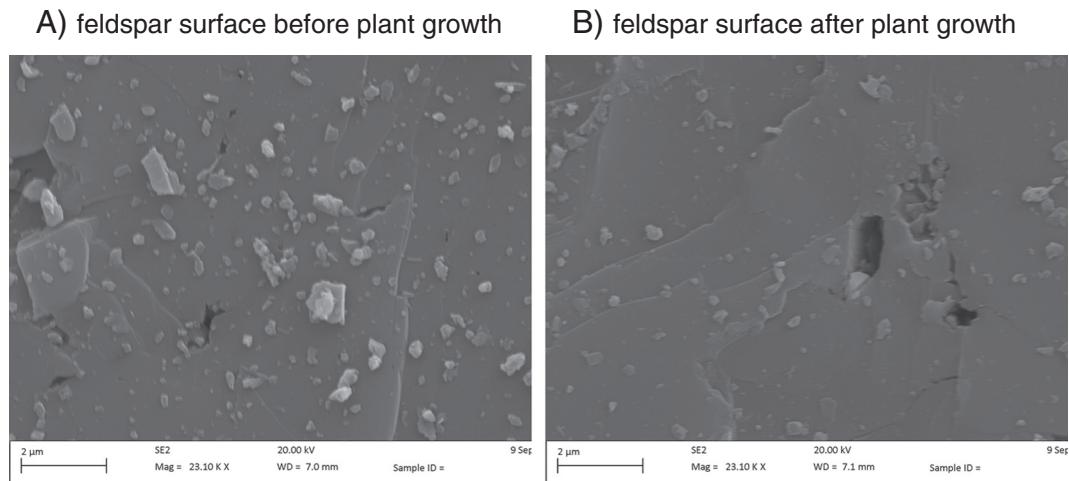


Fig. 5. Surfaces of potassium feldspar grains from leek growth experiments, 10 weeks duration; 43,000 mg K/pot added as syenite. A) feldspar surface before plant growth. B) feldspar surface after plant growth.

oxygen. This structure has to be destroyed to permit release of K to the soil solution.

In comparison with these experiments, on a longer timescale feldspars that have been exposed to soil processes become corroded, as is evident from grains sampled in the field (White and Brantley, 2003; Mol et al., 2003). Such observations confirm the instability of feldspar within the natural soil system, and thus the potential for sustained release of K, which would then become available for uptake by plants.

It is important to bear in mind that the mineral application rates were chosen for the explicit purpose of experimentally testing the availability of K from a silicate-mineral source within a relatively short timescale, and are not intended to lead to recommendations for rates of field application. However, the implications of this research for fertiliser design are significant. We believe that this is the first time that an experiment has been carried out where care was taken to ensure that the soil was free of potassium minerals, or other sources of K, other than what was added as a treatment. Normally, feldspars and potassic clays/micas occur widely within soils developed on a silicate parent rock, especially in temperate climates where physical weathering dominates over chemical weathering.

For silicate minerals to be used as a source of K (and perhaps other nutrients), it is important that the mineralogical composition of the host soil is known, and that this is combined with an understanding of the weathering regime. Addition of a K-feldspar to a temperate soil that already contains K-feldspar, as is common in soils derived from glacial till or developed on granite in northern Eurasia or North America, may not give a response. In contrast, addition of K-feldspar (in syenite or other silicate rocks) to a deeply weathered tropical soil that is dominated by oxy-hydroxides and clays such as kaolinite, is more likely to succeed. In such soils feldspar has already been consumed by weathering. Clearly, experiments of longer duration than 10 weeks and that use appropriate soils and crops would be needed to test this further. Additionally, the response observed in these experiments, which used an artificial sandy soil, suggests that feldspar and mica-bearing rocks may be useful as sources of K in temperate sandy soils that have very low K contents, consistent with results reported by Mohammed et al. (2014).

The research confirms the long-established finding that biotite or phlogopite micas are able to deliver K to plants. Under the conditions and duration of the present experiment, the plant response from phlogopite was approximately 10% of that of treatments with KCl, since for the KCl treatments the offtake was approx. 40% of the total added K, while 4% of the 830 mg K per pot added as phlogopite was taken up into the plant tissue (other phlogopite treatments providing either too little or too much to include in the comparison). This is consistent

with the ability of such micas, as they weather, to influence the K content of the soil solution by cation exchange. Our experiments emphasise how future longer-term experiments must be designed to address the importance of a conceptual model (Sparks and Huang, 1985, Holmqvist et al. 2003) for the availability of K, with fixed K in feldspar, exchangeable K in mica (and vermiculite), and available K in solution (as provided by the dissolution of KCl and other K salts), and to apply this model to deeply weathered tropical soils.

4. Conclusions

Carefully designed pot experiments have been carried out to define the conditions for testing the ability of milled syenite, dominated by the mineral K-feldspar, and milled phlogopite to provide the K needed for plant growth. In these experiments, the only source of K was the treatment. The response of the experimental plant, leek, was proportional to the application rates, both for growth rate and K content of the leaves. These results show that phlogopite is predicted to be a suitable source of K in soils in which K-containing silicates are absent, a condition that holds widely in deeply weathered soils in tropical regions. This may also be the case for syenite and other feldspar-bearing silicate rocks although with a lower initial plant response per g K supplied, however with the expectation that remaining feldspar will continue to release K during a much longer period. In tropical regions with deeply weathered soils, and in temperate soils where K is rapidly removed by through drainage, fertilisers based on silicate minerals should be considered as sources of K.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.09.086>.

References

- Bakken, A.K., Gautneb, H., Myhr, K., 1997. The potential of crushed rocks and mine tailings as slow-releasing J fertilizers assessed by intensive cropping with Italian ryegrass in different soil types. *Nutr. Cycl. Agroecosyst.* 47, 41–48.
- Bakken, A.K., Gautneb, H., Sveistrup, T., Myhr, K., 2000. Crushed rocks and mine tailings applied as K fertilisers on grassland. *Nutr. Cycl. Agroecosyst.* 56, 53–57.
- Bolland, M.D.A., Baker, M.J., 2000. Powdered granite is not an effective fertilizer for clover and wheat in sandy soils from Western Australia. *Nutr. Cycl. Agroecosyst.* 56, 59–68.
- Ciceri, D., Manning, D.A.C., Allamore, A., 2015. Historical and technical developments of potassium resources. *Sci. Total Environ.* 502, 590–601.
- Harley, A., Gilkes, R., 2000. Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview. *Nutr. Cycl. Agroecosyst.* 56, 11–36.
- 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. *Ann. Appl. Biol.* 120, 537–545.
- Hinsinger, P., Elsass, F., Jaillard, B., Robert, M., 1993. Root-induced irreversible transformation of a trioctahedral mica in the rhizosphere of rape. *J. Soil Sci.* 44, 535–545.
- Hinsinger, P., Bolland, M.D.A., Gilkes, R.J., 1996. Silicate rock powder: effect on selected chemical properties of a range of soils from Western Australia and on plant growth as assessed in a glasshouse experiment. *Fertil. Res.* 45, 69–79.
- Holmqvist, J., Øgaard, A.F., Öborn, I., Edwards, A.C., Mattsson, L., Sverdrup, H., 2003. Application of the PROFILE model to estimate potassium release from mineral weathering in northern European agricultural soils. *Eur. J. Agron.* 20, 149–163.
- Jasinski, S.M., 2014. Potash. United States Geological Survey Minerals Yearbook. <http://minerals.usgs.gov/minerals/pubs/commodity/potash>.
- Johnson, C.M., Stout, P.R., Broyer, T.C., Carlton, A.B., 1957. Comparative chlorine requirement of different plant species. *Plant Soil* 8, 337–353.
- 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 fertilisers? *Chem. Geol.* 60, 361–370.
- Manning, D.A.C., 2010a. Mineral sources of potassium for plant nutrition: a review. *Agron. Sustain. Dev.* 30, 281–294.
- Manning, D.A.C., 2010b. Stone meal as a source of plant nutrients, especially potash: a mineralogical approach. In: de Souza Martins, E., Theodoro, S.H. (Eds.), *Anais I Congresso Brasileiro de Rochagem*, Brasília, 21–24 de Setembro de 2009. Embrapa Cerrados Planaltina, DF (322pp).
- Manning, D.A.C., 2015. How minerals will feed the world in 2050. *Proc. Geol. Assoc.* 126, 14–17.
- Mohammed, S.O., Brandt, K., Gray, N.D., White, M.L., Manning, D.A.C., 2014. Comparison of silicate minerals as sources of K for plant nutrition in sandy soil. *Eur. J. Soil Sci.* 65, 653–662.
- Mol, G., Vriend, S.P., van Gaans, P.F.M., 2003. Feldspar weathering as the key to understanding soil acidification monitoring data; a study of acid sandy soils in the Netherlands. *Chem. Geol.* 202, 417–441.
- Rittenhouse, P.A., 1979. Potash and politics. *Econ. Geol.* 74, 353–357.
- Sanz-Scovino, J.I., Rowell, D.L., 1988. The use of feldspars as potassium fertilisers in the savannah of Columbia. *Fertil. Res.* 17, 71–83.
- Sheldrick, W.F., Syers, J.K., Lingard, J., 2002. A conceptual model for conducting nutrient audits at national, regional and global scales. *Nutr. Cycl. Agroecosyst.* 62, 61–67.
- Singh, B., Goulding, K.W.T., 1997. Changes with time in the potassium content and phyllosilicates in the soil of the Broadbalk continuous wheat experiment at Rothamsted. *Eur. J. Soil Sci.* 48, 651–659.
- Sparks, D.L., Huang, P.M., 1985. Release of soil potassium by weathering reactions. In: Minson, R.D. (Ed.), *Potassium in Agriculture*. American Society of Agronomy, Madison WI, pp. 202–276.
- Thorup-Kristensen, K., 1994. An easy pot incubation method for measuring nitrogen mineralization from easily decomposable organic material under well-defined conditions. *Fertil. Res.* 38, 239–247.
- Tsouvaltzi, P., Siomos, A.S., Gerasopoulos, D., Bosabalidis, A.M., 2010. Extension, anatomy and metabolic activity of leaves in minimally processed leek stalks. *Postharvest Biol. Technol.* 57, 149–154.
- White, A.F., Brantley, S.L., 1995. Chemical weathering rates of silicate minerals. *Reviews in Mineralogy* 31. Mineralogical Society of America, Washington, USA.
- White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? *Chem. Geol.* 202, 479–506.