Crushed rocks, minerals and mine tailings as sources of potassium in agriculture

HÅVARD GAUTNEB & ANNE KJERSTI BAKKEN

Håvard Gautneb[1] & Anne Kjersti Bakken[2]
1) Geological Survey of Norway, Post Box 3006-Lade , N-7002 Trondheim, Norway.
2) Kvithamar Research Station, N-7500 Stjørdal, Norway.

Introduction

Potassium (K) constitutes about 1 % of the dry matter of plants. In modern agricultural practice it is supplied to the crop in amounts of 100-200 kg per hectare, the main source being water-soluble K-salts in commercial compound fertilizers. In organic farming the use of these highly soluble mineral-salts is banned. There is also some interest among conventional farmers for slow releasing sources of K. Rocks and minerals rich in K might therefore be of increasing importance in the future. Such rocks include those which contain K-feldspar, mica and feltspathoids (leucite and nepheline) as their main minerals. Previous studies have shown that plants are able to utilise K from K-feldspar and micas, such as phlogopite and biotite (Berthelin & Leyval 1982, Hinsinger & Jaillard 1993, Hinsinger et al. 1992, 1993, Sanz Scovino & Rowell 1988, Riggs et al. 1993). In Norway, experiments with crushed rocks as potassium sources in agriculture were carried out already in 1922 by the State Raw Material Laboratory under the direction of V. M. Goldschmidt (Goldschmidt & Johnsson 1922, Cranner 1922, Solberg 1928, Retvedt 1938).

In this contribution we present the results from recent growth experiments with barley using fresh rocks, fresh minerals and mine tailings as K sources and discuss the results in relation to mineralogical and chemical composition as well as grain-size distribution of the used material.

Materials and Methods

Samples

A variety of different rocks and minerals were used (Table 1). Special emphasis was put on material from the Lillebukt Alkaline Complex on Stjernøy due to its relatively high K content and favourable mineralogy (Mjelde 1983, Skogen 1981). Of special interest are the tailings from the nephelinesyenite production at Stjernøy. Approximately 120,000 tons of tailings are dumped each year. It would be of interest from both an economical and an environmental point of view to find viable uses for this material. Other materials are included for comparison. The K-feldspar concentrate from Lillesand and Adularia illustrate the fertilizing potential of K-feldspar. The carbonatites illustrate the potential of nepheline- and biotite-bearing rocks used as fertilizer. The tailings from the De-duster and Filter II represent nepheline and K-feldspar rich material. The biotite concentrate and the Lurgi tailings represent biotite-bearing samples.

The content of K_2O varies from 2.63 % in chlorite schist up to 12.20 % in K-feldspar concentrate (Table 2). There is a great variation in the content of acid soluble K_2O, the extremes being the figures for the carbonatites where nearly all the K is acid soluble and those for K-feldspar where only about two percent of the total K_2O is acid soluble (Table 2).

The rocks were crushed in a jaw crusher and ball

Table 1. Mineralogical composition of the sample material.

Sample name	Q	Pl	Ksp	Ne	Hbl	Bt	Chl	Cc	Ep	Ap	Opaque	Others
						Main minerals (volume %)						
Chlorite schist (1)	30	20			27	8	5	8	1			
K-feldspar concentrate (2)	1		99									
Biotite concentrate (2)						98						2
Carbonatite with Hbl (3)			25	30	17	2		23	1	1		1
Carbonatite, Saravann (4)			2	5	1	44		41	1	3		3
Tailings, De-duster (5)			58	28	6	4		3				1
Tailings, Filter II (5)			58	28	6	4		2				1
Tailings, Lurgi (5)			20	13	34	29		3				1
Adularia, Scotland (6)	6		46			2		39			6	1

Mineral abbreviations after Kretz (1983) (1) Chlorite schist from a quarry at Skjemstadaunet, Inderøy. (2) From North Cape Minerals' feldspar and biotite production at Lillesand. (3) From Lillebukt Alkaline Complex, Stjernøy, Finnmark (Strand 1981), a carbonatite variety with hornblende as the main mafic mineral. (4) From Lillebukt Alkaline Complex, near Saravann, a carbonatite variety with biotite as the main mafic mineral. (5) Tailings from the nepheline production of North Cape Minerals. De-duster are tailings from the primary crusher. Filter II are tailings from the low-intensity magnetic separators. Lurgi are tailings from the high- intensity magnetic separators. (6) Adularia is the commercial name for crushed rocks of the Fucoid beds near Ullapool, Scotland. Mineralogical information about Adularia is according to Gallagher (1964).

Table 2. Chemical composition and grain size of the sample material.

Sample	Chlorite schist	K-feld- spar	Biotite	Carbonatite w/hbl	Carbonatite Saravann	Tailings De-duster	Tailings Filter II	Tailings Lurgi	Adularia	KCl
SiO_2	60.59	66.00	41.00	28.55	16.80	52.38	51.35	47.59	43.51	
Al_2O_3	14.31	18.50	21.00	17.29	6.09	23.38	22.38	18.60	11.20	
Fe_2O_3	0.40	0.08	6.29	0.91	2.44	0.41	0.60	3.74	1.03	
FeO	4.45	0.00	13.65	5.65	9.02	0.93	1.25	4.14	2.42	
TiO_2	0.06		1.50	1.32	2.52	0.47	0.78	2.00	0.44	
MgO	3.24		3.90	2.68	4.34	0.32	0.54	2.39	6.33	
CaO	5.02	0.40	0.17	15.81	28.32	3.02	4.33	7.27	9.62	
Na_2O	2.67	2.90	0.50	6.09	0.77	7.97	7.36	5.90	0.10	
K_2O	2.63	12.20	7.70	4.26	3.43	7.82	7.62	5.45	7.69	59.03[1]
MnO	0.08			0.19	0.19	0.05	0.08	0.26	0.09	
P_2O_5	0.13			0.90	5.87	0.15	0.17	0.19	0.36	
LOI	4.65	0.15	2.50	15.83	19.04	1.68	2.30	0.99	16.44	
Sum	98.23	100.23	98.21	99.48	98.83	98.58	98.76	98.52	99.23	
Acid soluble K_2O	0.67	0.28	4.18	4.00	3.42	2.20	1.94	1.70	0.68	59.03
Sol. K_2O/XRF K_2O (%)	25.47	2.30	54.98	93.89	99.71	28.13	25.46	31.19	8.84	100
Grain size (mm)	<0.59	<0.074[2]	<0.59	<0.59	<0.59	0,038[3]	0,045[3]	0,225[3]	<0.59	

The analysis are whole rock data from XRF analysis, with the exception of acid-soluble K_2O which were done by ICP after digestion of the sample in 7 N HNO_3.
1) Recalculated from content of K to content of K_2O
2) The grain-size data from the K-feldspar are given by North Cape minerals A/S. 100 % is < 74 microns and 50% is < 10 microns.
3) The grain-size of the tailings is as delivered from the nepheline plant and is determined by sedigraph. The given figures are median values.

mill. Crushed material was sieved through 0.59 mm. The biotite and K-feldspar concentrate and the three tailings were supplied by North Cape Minerals A/S from Lillesand and Stjernøy, respectively. The latter samples were not crushed.There was a problem in obtaining a uniform grain size of all our sample material. Because of this the mineral concentrates and the tailings have a grain size distribution that deviates from that of the rock samples.

Growth experiments
Barley (*Hordeum vulgare*, cultivar Bamse) germinated on wetted filter paper was planted in 7.5 l Kick-Brauckmann pots (20 plants per pot) with peat moss fertilized with 15 g $Ca(NO_3)_2$ x $4H_2O$, 3g $MgSO_4$ x 7 H_2O, 11 g Superfosfat P9 (Hydro Landbruk Norway) and 2 g Fritted Trace Elements 36 (Roll Hansen 1970). On the basis of the total K_2O content as analysed by XRF, potassium (3 g per pot) was supplied from KCl and 9 different rocks/minerals (Tables 1 and 2). To prevent differences in pH in the growth medium due to different contents of CaO in the rocks and minerals, $CaCO_3$ was added in the following amounts:15 g $CaCO_3$ to the pots with tailings and carbonatites, 18 g to the pots with chlorite schist and Adularia, 21 g to the pots with KCl, K-feldspar and biotite and 24 g to the pots with no K fertilizer (control treatment). The plants were grown in an acrylic house for 8 weeks from November until January. The day length was 18 h (200 μmolm^{-2}s^{-1} from high-pressure sodium lamps + natural daylight). Day and night temperatures were 11° and 9° C during the first 3 weeks and 13° and 11° C for the rest of the growth period. The plants were watered with tap water with only traces of diverse elements. At harvest they were cut at soil

level and dried at 60° C. The dry weights were recorded and the content of K in the dry matter analysed. Samples of the growth medium were analysed for exchangeable K according to standard methods (Krogstad 1992).

After the harvest of the first set of plants, 15 g $Ca(NO_3)_2$ x 7 H_2O was added to each pot together with $CaCO_3$ in the following amounts: 15 g to pots with K-feldspar, biotite, tailings, Adularia, no K, KCl and chlorite schists, 9 g to pots with carbonatite with Hbl and 6 g to pots with Saravann carbonatite. Sets of twenty pre-germinated barley plants were then planted per pot and grown for 7 weeks as described above, harvested and analysed for K. The day length was 16 h during this growth period.

There were three replicates of the 11 treatments. The data for yield, pH and K content were subjected to two-way ANOVA, with K source and replicate as class variables.

Results
The dry matter production was significantly enhanced in the treatments with chlorite schist, carbonatites and the different tailings relative to the treatment with no K supply (Fig. 1). The production was, however, not as high as in the treatment with KCl as the K source. Plant growth was positively correlated with total uptake of K (Figs. 1 and 2). During the first growth period the uptake from pots with KCl was more than twice as high as the uptake from pots with Saravann carbonatite - the rock supplying most K to the plants (Fig. 2). The barley plants were not able to mobilise significant amounts of K from the pots with biotite concentrate, K-feldspar concentrate and Adularia. After the second growth period, more than 80 % of the K added as KCl was

taken up by the plants, whereas more than half of the added 3 g K was left in the pots with rocks, tailings and mineral concentrates (Fig. 2).

In all treatments there was a decrease in the content of soluble K in the growth medium from the first to the second harvest (Table 3). Of the treatments with rocks/minerals the content of soluble K was highest in the growth medium with Saravann carbonatite (Table 3).

Discussion

Of the minerals in the present study, only biotite and nepheline seem to have supplied significant amounts of K to the plants. The K in K-feldspar seemed to be almost completely unavailable during the two growth periods, as plants grown on Adularia and K-feldspar concentrate were not able to take up more K than plants from the treatment with no K supply. K in biotite seems to be available to the plant, as the only rock rich in biotite - Saravann carbonatite - supplied far more K to the plants than tailings and carbonatite with Hbl. The K taken up from the tailings Filter II and De-duster and from carbonatite with Hbl probably originated from nepheline. The biotite concentrate did not supply any K at all. This fact does not support the statements above that K in biotite is easily available for plants. The grain-size distribution of this biotite concentrate however, was different from the grain-size distribution of the carbonatites and tailings, with a very

Fig. 2. Total yield of K from two successive growth experiments with barley fertilized with K from different sources. The data shown are the means for 3 pots per treatment.

small portion of finer particles in the biotite concentrate. Also the weathering of K from the concentrate might have been inhibited by residues of flotation chemicals on the surface of the particles.

Most of the K in the two carbonatites is soluble in 7 N HNO_3, whereas the acid-soluble fraction K in the rest of the samples was less than 55 % of the total K (Table 2). Although acid-soluble K gives an indication of plant availability, the relationship is not simple because plants grew much better and released more K from the Saravann carbonatite than from carbonatite with Hbl. Some of the acid-soluble K in carbonatite with Hbl must come from K-feldspar, since more than half of the K in this rock is bound in this mineral (Table 1). All biotite-bound K and all nepheline-bound K is acid soluble; in Adularia only a small part of the K-feldspar K is acid soluble, although the grain size is small.

Apart from lack of growth from the biotite concentrate, our results are in agreement with what would be expected from the studies of the solubility of rocks and minerals (Graff & Røste 1985, 1986), water-rock interaction (Lasaga 1984) and studies of chemical weathering processes (Loughnan 1969). Under natural conditions, feltspathoids are found to disintegrate several orders of magnitude faster than K-feldspars (Loughnan 1969, p. 101, Lasaga 1984, Schumann 1993). Micas show a more diverse weathering behaviour. Differences in the orientation of the O-H bonds in the crystal lattice of dioctahedral (muscovite) and trioctahedral (biotite) micas, make the K^+ ions more strongly connected in the
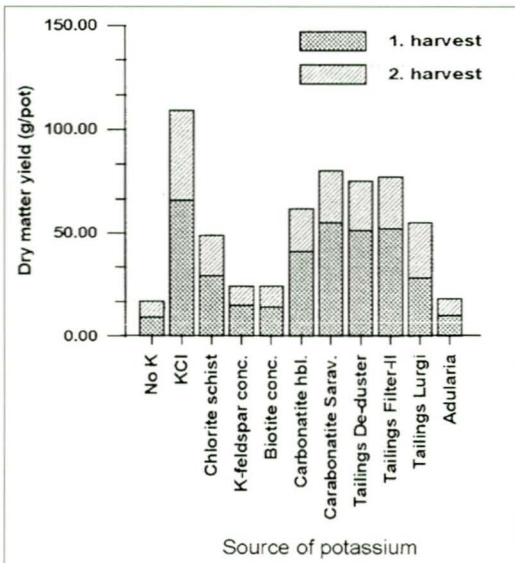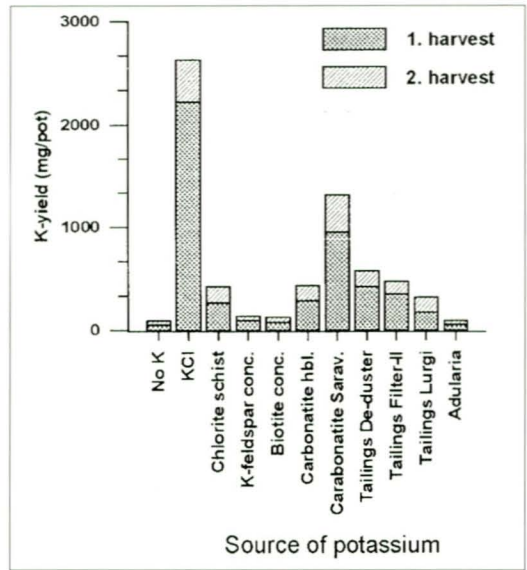
Fig. 1. Total dry matter yield from two successive growth experiments with barley, fertilized with K from different sources. The data shown are the means for 3 pots per treatment. The Least significant difference (5%) was between trestments 7.8 for the 1st harvest and 8.0 for the 2nd harvest.

crystal structure of the former. This again results in greater sensitivity to weathering in the latter (Eggleton 1986, Nahon 1990).

Dissolution of minerals can in a simplified form be written as:

$$mineral + nH^+ \rightarrow silica \pm alumina + cations$$

The reaction rate normally depends on the concentration of H^+ ions, but this is complicated by the amphoteric nature of the alumina (Lasaga 1984). It may be emphasized that the growth medium in the present experiment (peat) differs from natural soils. The low pH-levels in peat probably promote weathering of minerals and thus the release of K to a greater extent than in the higher pH-levels in mineral soils (Sparks & Huang 1985). Further, in soils rich in clay minerals, relatively complex equilibria between fixed and soluble K might be established (Sparks & Huang 1985). There are also considerable differences in grain-size distribution between some of the samples. When comparing industrial waste with natural crushed rocks it is technically difficult to get an uniform grain-size distribution in all the samples. To what degree this grain size difference affects our results is not known. However our results are what would be expected as the consequence of the different chemical and physical properties of the rocks and minerals used in our experiments.

Conclusion

Rocks with K-feldspar as their main K-bearing phase did not supply significant amounts of K to the barley plants, whereas rocks with biotite and nepheline as their main K-bearing phase supplied appreciable amounts to the barley plants. On this basis the rocks and tailings from the Lillebukt Alkaline Complex, particularly the Saravann carbonatite are promising as sources of K in agriculture.

Table 3. Content of exchangeable K (analysed according to Krogstad 1992) in the growth medium after the first and second plant harvests.

K-source	Soluble K in the growth medium (mg/100 g DW)	
	After 1st harvest	After 2nd harvest
No K	12	8
KCl	40	29
Chlorite schist	22	18
K-feldspar concentrate	12	8
Biotite concentrate	12	7
Carbonatite with Hbl.	26	19
Carbonatite, Saravann	34	21
Tailings, De-duster	28	18
Tailings, Filter II	26	12
Tailings, Lurgi	27	12
Adularia	13	8
	LSD(5%)=7.9	LSD(5%)=5.7

LSD = Least significant difference

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