

Dissolution of milled-silicate rock fertilisers in the soil

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Abstract. Dissolution of dry-milled basalt, dolerite, gneiss, and K-feldspar added to 23 soils has been related to milling time and soil properties. The rocks milled for 10, 60, and 120 min were mixed with 23 type of soils from south-western Australia at a rock/soil ratio of 1/100 (≈ 10 t/ha), wetted to 110% field capacity, then incubated at 20°C for 2 and 10 months. Measurements of cations extractable by 1 M $\text{CH}_3\text{COONH}_4$ at pH 7 indicate that substantial dissolution occurred in the soil and that milling increased dissolution. After 10 months of incubation, about 18% of Ca and Mg had dissolved from basalt and dolerite milled for 120 min and 40% of Na and K from gneiss and K-feldspar milled for 120 min. Some dissolution occurred with 1 h extraction of non-incubated rock–soil mixtures and these released elements are considered to be readily available plant nutrients. The silicate rocks had minor effects on soil pH and EC of soil-rock mixtures (i.e. increased pH by ≤ 0.5 unit and EC by ≤ 127 $\mu\text{S}/\text{cm}$ in 1:5 water extracts). The large increases in silicate rock dissolution in soils due to milling indicate that milled basalt and dolerite may be used as Ca and Mg fertilisers, and K-feldspar as a K fertiliser. Further research is needed to identify soils and plants for which the application of the silicate rock fertilisers will be most beneficial.

Additional keywords: mafic rocks, felsic rocks, agglomeration.

Introduction

There is an increasing interest in the use of silicate and other rock fertilisers as replacements for chemical fertilisers, particularly in organic agriculture (Leonardos *et al.* 1987; Bockman *et al.* 1990). However, the use of silicate rock fertilisers (SRF) in agriculture is limited mainly due to the generally slow release of nutrients from SRF into soil solution, and consequently, impractically high rates need to be applied (Hinsinger and Gilkes 1995). Efforts could, therefore, be made to identify appropriate methods for accelerating the release of nutrients, as well as factors determining the suitability of particular soils and plants for fertilisation with SRF.

Particle size was shown to be a major determinant of the effects of basalt on soil properties and plant growth (Gillman *et al.* 2001) and of the effectiveness of crushed basalt (Minplus^{MT}) as a soil ameliorant in general (Coventry *et al.* 2001). Milling methods that produce super-fine particles of minerals with enhanced chemical reactivity have been evaluated by many workers, including Gasalla *et al.* (1987), Suraj *et al.* (1997), and Sugiyama *et al.* (1994). These methods also had been employed to improve the fertiliser effectiveness of several silicate minerals (Harley 2002) and rock phosphates (Lim *et al.* 2003) as fertilisers. Milling increased exchangeable alkali cations of mafic and felsic

rocks for use as fertilisers, with greater increases being due to dry milling than to wet milling (Priyono *et al.* 2002). It is unclear whether milling will produce a similar increase in dissolution of SRF in the soil environment. It is also not known in which soils the application of SRF will be most advantageous.

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

Materials and methods

Silicate rocks and soil samples

Silicate rocks used in this experiment were basalt, dolerite, gneiss, and K-feldspar from Bunbury, Jarrahdale, Northam, and Fort Hedland, Western Australia (WA), respectively. The first 3 rocks were initially ground to $\phi < 250$ μm , whereas K-feldspar ($\phi < 150$ μm) was supplied by Commercial Mineral Co. Ltd, Perth. The rocks were further milled under dry condition with a ball mill (Spex-8000) for 10 (T0), 60 (T60), and 120 (T120) min. Properties of the rocks relevant to the present research are listed in Table 1.

The virgin soils (under bush vegetation) were from 23 sites in south-western Australia (McArthur 1991). The top 15 cm, excluding the organic matter layer, was sampled, air-dried, and sieved to pass a 2-mm sieve. Selection of the soils was based on previous research by

Table 1. Properties of the silicate rocks milled under dry condition using a ball mill (Spex-8000)

Rock type	Milling (min)	D_{50}^A (μm)	SA^B (m^2/g)	AC^C (%)	Cation contents ^D				Mineralogical composition ^E
					Ca	Mg	K	Na	
					(cmol _c /kg)				
Basalt	Initial	45.3	16.2	1.8	397	304	3.8	68	Hrb, Plg, Aug, Alb, Ant, Bi, Plg
	10	2.8	14.7	4.1					
	60	1.9	7.4	9.2					
	120	1.7	8.6	14.2					
Dolerite	Initial	14.5	1.4	1.2	406	316	7.9	39	Hrb, Plg, Aug, Alb, Ant, Bi, Dio
	10	2.2	5.5	5.5					
	60	2.4	5.5	15.1					
	120	2.2	8.0	20.9					
Gneiss	Initial	32.1	1.3	0.4	72	37	23	131	Qz, Alb, Bi, Chl
	10	3.0	6.2	2.7					
	60	2.5	6.0	8.4					
	120	2.5	6.0	8.8					
K-feldspar	Initial	22.2	0.5	0.2	—	—	246	84	Mc, Alb, Ant
	10	2.9	6.8	1.5					
	60	6.3	9.9	3.7					
	120	6.3	8.7	3.7					

^AMedian particle size, measured using a Malvern Mastersizer.^BEffective surface area, measured by the BET method with N₂ gas.^CQuantity of amorphous constituents, estimated from quantity of oxalate-extractable (Fe + Al + Si).^DMeasured using XRF after fusing the rocks with La-metaborate.^EIdentified using XRD, minerals listed in order of decreasing abundance: Hrb, hornblende; Plg, phlogopite; Aug, augite; Alb, albite; Ant, anorthite; Bi, biotite; Dio, diopside; Qz, quartz; Chl, chlorite; Mc, microcline.

Hughes and Gilkes (1994), who found that these soils were capable of dissolving >40% of added rock phosphate. We postulated that these soils would also dissolve silicate rocks. The sites for field sampling and profile data for the soils are available in McArthur (1991). Soil properties used for identification of relationships between soil properties and dissolution rate are presented in Table 2. The methods used for measurement of soil + rock properties were as follows:

- (1) pH(H₂O) and pH(CaCl₂) at a soil:solution (H₂O and 0.005 M CaCl₂) ratio of 1:5 measured with pH and EC meters (Cyberscan 2000).
- (2) $\Delta\text{pH} = \text{pH}(\text{CaCl}_2) - \text{pH}(\text{H}_2\text{O})$.
- (3) Organic carbon determined by wet oxidation with K₂Cr₂O₇ (Walkley and Black 1934).
- (4) Cation exchangeable capacity (CEC) determined using 1 M ammonium acetate (CH₃COONH₄), pH 7, as an extracting solution (Thomas 1992) with 3 extractions of the same soil sample. Filtrates were collected and used for measurement of exchangeable cations, i.e. Ca and Mg (by AAS) and K and Na (by flame emission). The NH₄⁺ retained by soil was displaced using 1 M KCl. The excess of KCl in the soil was removed using ethanol, and the remaining K⁺ on the exchange sites of soil was displaced using 0.5 M CaCl₂, and the filtrate was collected. The concentration of K⁺ in the filtrate was determined by flame emission, and the quantity of K⁺ was considered to represent the value of the cation exchange capacity (CEC, cmol_c/kg).
- (5) Base saturation (BS) calculated as the sum of exchangeable base cations as % of CEC.
- (6) Total exchange acidity extracted with 1 M KCl and determined by titration using 0.01 M NaOH (Thomas 1992).
- (7) Percentages of sand, silt, and clay determined by the pipette method (Gee and Bauder 1986).
- (8) Fe, Al, and Si extracted with 0.2 M ammonium oxalate ((COONH₄)₂·H₂O) buffered to pH 3.0 determined using the

method described by Rayment and Higginson (1992). The % (Fe + Al + Si) from this measurement was used as an estimate of the quantity of amorphous constituents in the rocks and soils.

Incubation experiment

Each silicate rock milled for each time (0, 10, 60, and 120 min) was mixed with each of the 23 soils at the rate of 1 g rock per 100 g soil (≈ 10 t/ha) in sealed plastic bags, giving a total of 368 treated soils. The soil-rock mixtures were wetted with Milli-Q water to 110% of field capacity and 1 mL toluene was added for microbial suppression. The soil-rock mixtures were then stored in a dark, constant temperature room at 20°C. A set of control soils (23 soils without added rock) was prepared in the same manner. To determine the dissolution of the rocks in the extractant, 25 g of each soil was mixed with 0.25 g rock without adding water and toluene, then 3 subsamples were immediately taken from these mixtures and from control soils for analysis of extractable cations as described below. The value of extractable element (Ca, Mg, K, Na) for soils with added rock minus the value for the control soil was considered to be the rapidly dissolved amount and is designated as ΔE_{0M} .

After incubation for 2 months, 3 subsamples were taken from each treated and untreated (control) soil for measurements of extractable Ca, Mg, K, and Na. An additional subsample was taken for measurements of soil pH and EC. The remaining samples were retained for further incubation up to 10 months. After incubation for 10 months, these measurements were made on 10 soils (see Table 2), where rocks had dissolved extensively during incubation for 2 months.

The quantities of extractable Ca, Mg, K, and Na in the soils were determined using 1 M CH₃COONH₄ buffered at pH 7. Soil (5 g) was added to 25 mL solvent in a 50-mL plastic tube, shaken for 1 h on an end-over-end shaker, and filtered. The concentrations of Ca and Mg in the filtrates were measured by AAS, whereas K and Na were measured by flame emission. For soils treated with K-feldspar, only extractable K

Table 2. Properties of soil samples used in this experiment

No.	Sample code	pH(H ₂ O) (1:5)	pH(CaCl ₂) (1:5)	Δ pH	EC (1:5) (μ S/cm)	C-org (%)	CEC (cmol _c /kg)	Ex. acidity	Sand	Clay (%)	Amor.	Exchangeable base cations				
												Ca	Mg	K	Na	Total
1	ALB-1 ^A	4.73	3.75	−0.98	76	4.4	26.4	1.416	94.0	0.8	0.11	2.13	1.24	1.10	0.26	4.73
2	ALB-5	5.62	5.00	−0.62	273	5.9	36.9	0.093	81.7	8.1	0.22	8.37	3.86	0.98	0.84	14.05
3	DEN-2	5.73	4.84	−0.89	99	4.0	27.2	0.092	77.8	16.0	0.42	6.28	2.92	1.76	0.25	11.20
4	DEN-4	5.60	4.59	−1.01	89	7.0	41.3	0.300	63.6	29.5	0.64	6.32	3.56	1.59	0.18	11.65
5	DEN-7	6.05	5.28	−0.77	71	3.8	26.7	0.068	83.8	6.6	0.68	4.78	2.20	2.17	0.25	9.41
6	KTG-5	5.95	5.70	−0.25	793	1.9	35.7	0.080	34.9	45.6	0.17	5.27	9.77	2.34	4.62	22.00
7	WP-6 ^A	5.03	3.75	−1.28	71	2.8	17.0	0.681	93.0	4.4	0.06	0.55	0.61	2.14	0.18	3.48
8	MR-5 ^A	5.60	4.25	−1.35	65	4.3	19.0	0.878	79.3	8.2	0.52	2.57	0.57	2.15	0.15	3.44
9	SCP-3	6.22	5.62	−0.60	162	5.3	27.2	0.033	76.2	12.4	0.27	7.52	3.54	2.24	0.42	13.73
10	SCP-4	6.43	6.11	−0.32	240	8.1	50.3	0.130	53.6	28.3	1.39	22.85	4.09	2.06	0.32	29.32
11	SCP-5	5.91	5.04	−0.87	52	3.5	40.1	0.076	53.9	32.1	0.54	4.97	6.29	2.77	0.16	14.19
12	SCP-6	6.06	5.38	−0.68	79	3.8	23.2	0.071	79.3	15.8	0.36	4.34	2.97	1.79	0.09	9.18
13	SCP-11 ^A	6.14	4.98	−1.16	21	1.9	14.2	0.071	96.4	1.6	0.02	3.84	0.71	1.08	<0.01	5.64
14	PTN-3	5.87	4.70	−1.17	159	4.0	19.4	0.206	77.1	0.8	0.57	2.40	1.18	1.01	0.42	5.01
15	PTN-4 ^A	5.50	4.13	−1.37	45	4.1	11.1	0.256	79.9	4.4	0.11	1.08	0.35	1.11	0.04	2.58
16	PTN-5 ^A	5.24	4.02	−1.22	66	3.2	15.1	0.582	84.6	3.5	0.10	1.57	0.65	0.66	0.10	2.98
17	BSN-1 ^A	5.70	4.79	−0.91	57	1.5	10.5	0.145	86.8	9.2	0.22	1.27	0.75	0.78	0.09	2.89
18	BSN-4 ^A	5.31	4.38	−0.93	53	1.8	13.7	0.518	70.0	16.9	0.37	0.75	0.52	1.30	0.18	2.75
19	DP-1 ^A	5.83	4.82	−1.01	36	3.3	13.6	0.157	77.1	10.7	0.34	3.32	1.15	1.04	0.08	5.60
20	DP-6 ^A	5.91	4.92	−0.99	42	2.8	15.7	0.091	85.0	5.5	0.17	2.69	0.84	0.82	0.04	4.39
21	BTN-2	5.98	4.86	−1.12	54	4.0	23.2	0.133	89.6	4.8	0.33	4.83	1.65	0.52	0.17	7.17
22	BTN-3a	5.67	4.52	−1.15	58	3.7	27.9	0.479	77.5	13.7	0.56	5.61	2.28	1.34	0.16	9.38
23	BTN-3b	5.61	5.17	−0.44	406	4.7	41.9	0.468	65.3	22.6	1.41	5.89	6.90	1.05	2.02	15.85
Minimum		4.73	3.75	−1.37	21	1.5	10.5	0.033	34.9	0.8	0.02	0.55	0.35	0.52	<0.01	2.58
Maximum		6.43	6.11	−0.25	793	8.1	50.3	1.416	96.4	45.6	1.41	22.85	9.77	2.77	4.62	29.32
Mean		5.73	4.81	−0.92	133	3.9	25.1	0.310	76.5	13.1	0.42	4.66	2.55	1.47	0.48	9.16

^ASoils that were incubated for 10 months.

and Na were measured. The cumulative amounts of each element dissolved from the rocks incubated for 2 and 10 months (respectively designated as E_{2M} and E_{10M}) were calculated from the values for treated soil minus the value for the control. The amounts of element dissolved during the first 2 months (ΔE_{0-2M}) and between the 2- and 10-month incubations (ΔE_{2-10M}), respectively, were calculated from ($E_{2M} - E_0$) and ($E_{10M} - E_{2M}$).

For the measurements of soil pH and EC, 2.5 g soil was added to 12.5 mL H₂O in a 30-mL plastic tube, then shaken on an end-over-end shaker for 1 h. The EC and pH of the clear suspension were measured sequentially with EC and pH meters (Cyberscan 2000).

Statistical analyses

Analysis of variance was employed to evaluate the effect of milling time on the dissolution of elements from SRF (E_0 , E_{2M} , E_{10M}) in which soil type was considered as the block. The relationships of the amount of dissolved elements (E_0 , E_{2M} , and E_{10M} , E_{0-2M} , and E_{2-10M}) from SRF v. the soil properties listed in Table 2, and relationships of E_0 , E_{2M} , and E_{10M} , E_{0-2M} , and E_{2-10M} v. the properties of milled rocks (D_{50} , SA, AC, Table 1), were identified using simple and stepwise multiple regression analyses. The dissolved elements used in these analyses were (Ca + Mg) for basalt and dolerite and (K + Na) for gneiss and K-feldspar. Values of dependent (the amount of dissolved elements) and independent (soil and rock properties) variables were also incorporated as log- and square-root-transformed values to test for non-linear relationships.

Results and discussion

Properties of the silicate rocks and soils

The physical and chemical properties of silicate rocks after high-energy milling are discussed in Priyono *et al.* (2002). For the rocks used in the present research, milling reduced particle size and increased specific surface area (except for basalt) and also greatly increased the content of amorphous constituents, as indicated by amount of oxalate-extractable (Fe + Al + Si) (Table 1). Basalt and dolerite have similar compositions with much Ca and Mg, a moderate amount of Na, and little K. Gneiss contains greater amounts of Na and K, with lesser Ca and Mg. K-feldspar contains K and Na but essentially no Ca or Mg.

As shown in Table 2, the soils used in this experiment have a wide range of properties. The soil texture ranged from sand (0.8% clay) to clay (45.6% clay), and most soils were slightly acid (pH(H₂O) 5.0–6.0) and non to slightly saline (EC(H₂O) 1:5 = 21–793 μ S/cm). The range of oxidisable-organic C was from 1.5 to 8.1%, CEC ranged from 10.5 to 50.6 cmol_c/kg. The quantities of individual exchangeable base cations (Na, K, Ca, Mg) varied widely, with the total of exchangeable base cations ranging from

2.58 to 29.32 cmol_c/kg, which represented 18–62% of the CEC. The relatively low base saturation was partly due to the pH-dependent nature of the charge on the soils; thus, measurement of CEC using CH₃COONH₄ buffered at pH 7.0 (1–2 units higher than original pH of soils) resulted in an overestimate of the CEC of the soils. Total exchange acidity ranged from 0.3 to 1.4 cmol_c/kg.

Effects of milling time

The focus of the following discussion will be on the dissolution of Ca and Mg for basalt and dolerite, and K and Na for gneiss and K-feldspar, as those are the plant nutrient elements that are most abundantly provided by these SRF. The relationships of Ca dissolved v. milling time were similar to those for Mg v. milling time, and those for K were similar to those for Na. To simplify discussion of these data the percentage dissolution values for elements were combined, i.e. (Ca + Mg) for basalt and dolerite and (K + Na) for gneiss and K-feldspar, and are plotted against milling time (Fig. 1).

Dissolution of major plant nutrient elements

Average values of dissolution for the 10 soils plotted against milling time are shown in Fig. 1, which enables comparison

of dissolution values for different incubation and milling times. Considerable dissolution of non-incubated rocks occurred during the extraction (i.e. E₀ values are substantial); relatively minor dissolution occurred for unmilled rocks; and milling greatly increased the percentages of elements dissolved for the silicate rocks for all 3 incubation periods. The dissolution plots for mafic rocks (basalt and dolerite) followed parabolic relationships, indicating that milling for longer than 60 min had not substantially increased dissolution. For felsic rocks (gneiss and K-feldspar) dissolution increased linearly with milling time up to 120 min of milling for each period of rock-soil incubation.

Basalt and dolerite have similar chemical and mineralogical compositions (see Table 1) and dissolution of (Ca + Mg) followed similar trends with respect to milling and incubation time for these 2 silicate rocks. The proportion of these elements that rapidly dissolved (E₀) for both rocks was about 2% (for initial milling, T₀) and increased to 6–8% (for T₁₂₀). After incubation for 2 months (E_{2M}) dissolution increased 2–3-fold for all grinding times with a relative minor additional increase for incubation for 10 months ($\Delta E_{2-10M} = 1-4\%$). The value of

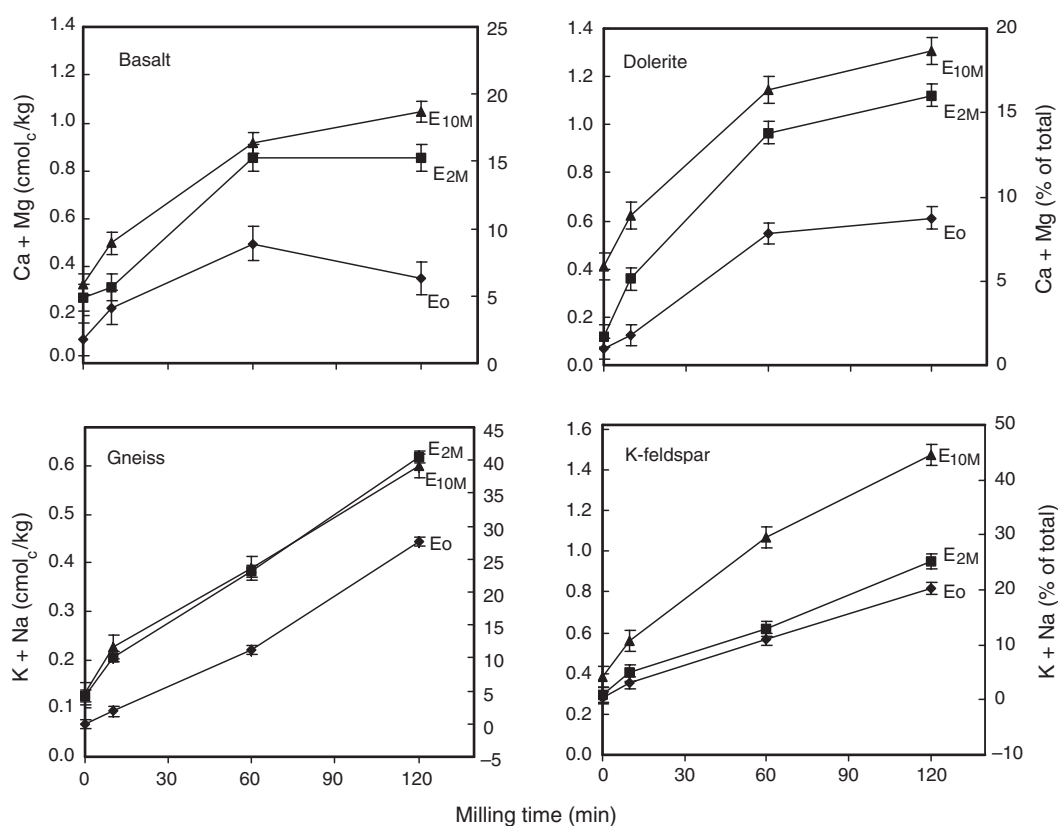


Fig. 1. Mean dissolutions of alkali elements from the silicate rocks in 10 soils incubated for 0, 2, and 10 months (E₀, E_{2M}, and E_{10M}) as a function of milling time. Error bars are standard error of mean.

E_{10M} was about 18% of the total content of (Ca + Mg) for basalt and dolerite milled for 120 min. For basalt, milling for 120 min reduced the values of E_0 and E_{2M} , possibly due to agglomeration of particles occurring between 60 and 120 min of milling (Priyono *et al.* 2002). However, this explanation is not supported by surface area or particle size data.

The % (K + Na) that dissolved rapidly (E_0) for gneiss was approximately 0% (for T0) increasing to about 27% (for T120). An additional 10% (K + Na) dissolved after incubation for 2 months for all milling time, but no further dissolution occurred for incubation up to 10 months ($\Delta E_{2-10M} \approx 0$). For K-feldspar, the rapidly dissolved (K + Na) (E_0) was about 0% (for T0), and increased by milling to about 20% for T120. There was little extra dissolution during the first 2 months of incubation ($\Delta E_{0-2M} = 0-5\%$) for any milling time, but a considerably larger proportion of (K + Na) had dissolved after incubation for 10 months ($\Delta E_{2-10M} = 5-20\%$), reaching a value of about 45% for E_{10M} . It should be noted that for K-feldspar the % Na dissolved during incubation of 2–10 months was much larger (i.e. 60%) than % K dissolved (i.e. 10%), and the values of E_{10M} for Na and K, respectively, were about 80 and 35%. This difference in behaviour presumably relates to the existence of Na- and K-rich feldspar species as lamellae in the material, i.e. microcline ($KAlSi_3O_8$) and albite ($(Na,K)AlSi_3O_5$) determined by Commercial Mineral Co. Ltd (1987) at about 65.6 and 31.2%, respectively.

Clearly, milling increased the proportion of alkali elements dissolved for the silicate rocks. After incubation for 10 months, about 18% of (Ca + Mg) had dissolved from highly milled basalt and dolerite, and about 40% of (K + Na) had dissolved from gneiss and K-feldspar. Between one- and two-thirds of the 10-month dissolution occurred for the initial incubation period ($= E_{0M}$) and thus reflects dissolution of the rocks in the soil–rock mixtures during the extraction process. This rapid dissolution may approximate the

dissolution that occurs in soils in the first days or weeks after application of silicate rock fertilisers.

The quantities of dissolved elements from the rocks released to soil solution were small (i.e. about 1.3 cmol_c (Ca + Mg)/kg soil from basalt and dolerite, 0.55 and 1.5 cmol_c (K + Na)/kg soil, respectively, from gneiss and K-feldspar relative to the amounts of corresponding elements already present in the soils (Table 2) and might not have a substantial agronomic effect. The present research may, however, underestimate dissolution because chemical modification by plant roots (Hinsinger and Gilkes 1995) and the activities of microorganisms in the rhizosphere (Liermann *et al.* 2000; Dong *et al.* 2000; Lee and Fein 2000) enhance dissolution of silicates. Furthermore, highly acid soils in the tropics and elsewhere have extremely low values of base saturation and the amounts of alkali ions released by dissolution of silicate rocks will contribute substantially to the stock of plant-available alkali elements.

Soil pH and EC

Addition of silicate rocks increased pH and EC of soil–rock mixtures, and these effects were increased by prolonged milling. Mean increases in the pH and EC after incubation for 10 months as functions of milling time are presented in Fig. 2. The mean increase in pH (the positive liming effect after 10-month incubation) for basalt was about 0.2 (T0) to 0.4 (T120) units, for dolerite 0.02–0.3 units, for gneiss 0.2–0.5 units, and K-feldspar 0.1–0.5 units. All silicate rocks, therefore, had a positive liming effect that would be beneficial to some plants on these acid soils. Basalt and dolerite increased the EC of soil–rock mixtures by about 5 (T0) to about 25 (T120) $\mu\text{S}/\text{cm}$. Gneiss and feldspar had smaller effects, but in every case these increases in EC (salinity) were negligible from an agricultural perspective (Hunt and Gilkes 1992). Thus, use of silicate rock fertilisers at a rate of about 10 t/ha (equivalent to about 1% in topsoil) may provide a liming benefit without adversely affecting soil salinity.

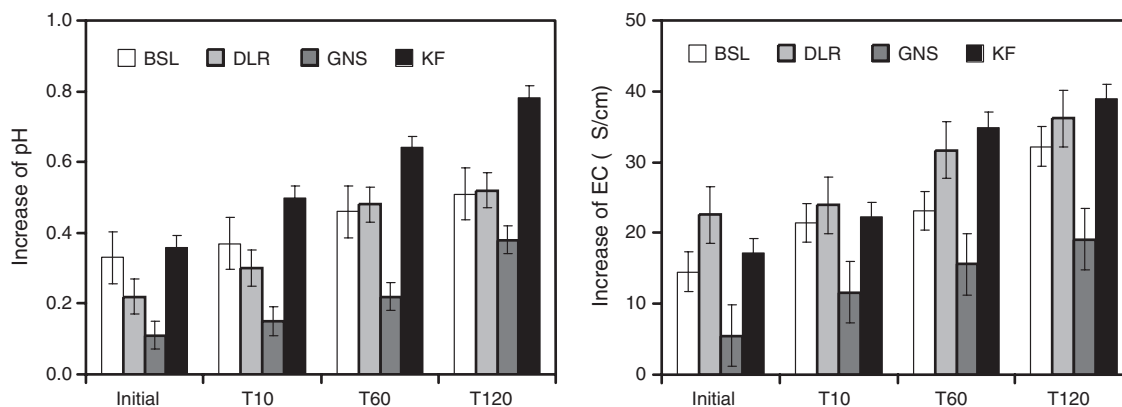


Fig. 2. Mean increases of pH and EC of 10 soils mixed with basalt (BSL), dolerite (DLR), gneiss (GNS), and K-feldspar (KF) after incubation for 10 months as a function of milling time. Error bars are standard error of mean.

The increases in pH and EC for soil with added silicate rocks were essentially due to consumption of hydrogen ions during dissolution of the rocks and the consequent release of alkali cations from the rocks. Consequently plots of mean increases in pH and EC *v.* increases in EAC ($\text{CH}_3\text{COONH}_4$ -extractable alkali cations) show that close relationships exist. The relationships are quite different for each silicate rock as the rocks have different liming values. Positive liming effects of SRF applications, and increased liming effects with increasing fineness, have been shown by earlier workers (Coventry *et al.* 2001; Gillman *et al.* 2001; Harley 2002).

Dissolution of SRF *v.* soil properties

Results of simple linear regression indicate that soil properties which are significantly correlated to dissolution of alkali cations in soil are commonly different for each rock, milling time, and incubation period, with correlation coefficients being mostly smaller in magnitude than 0.70 (Table 3). Thus, single soil properties mostly determine <50% of the variation in dissolution of alkali elements from silicate fertilisers in the soils. No single soil property was highly predictive of dissolution in the soils for any rock, incubation time, or milling time.

Table 3. Soil properties linearly correlated ($P < 0.05$) with dissolution of alkali cations from the silicate rocks in the soils for each milling time
Correlation coefficient (r) is indicated

Rock type (cations)	Dissolution (% of total)	Soil properties (coefficient correlation)
Basalt (Ca + Mg)	E ₀	%Org. C (–0.45) only for T0
	E _{2M}	%Sand (–0.48 to –0.67), %clay (+0.44 to +0.62)
	ΔE_{0-2M}	EC (+0.40 to +0.62), CEC (+0.43 to +0.48), %sand (–0.45 to –0.59), % clay (+0.43 to +0.64)
	ΔE_{2-10M}	%Sand (–0.63), % clay (+0.65) only for T60
Dolerite (Ca + Mg)	ΔE_{0-2M}	%Sand (–0.41 to –0.53), %clay (+0.48 to +0.52)
Gneiss (K + Na)	E ₀	%Sand (–0.41 to –0.53), %clay (+0.48 to +0.52)
	E _{2M}	EC (+0.70 to +0.86), CEC (+0.45 to +0.57), %sand (–0.52 to –0.59), % clay (+0.43 to +0.62)
	ΔE_{0-2M}	EC (+0.79 to +0.85), %sand (–0.50 to –0.71), %clay (+0.57 to +0.75)
K-feldspar (K + Na)	E ₀	Org C (+0.47 for T10 and +0.44 for T60)
	E _{2M}	pH(H ₂ O) (–0.46 for T60 and –0.52 for T120), org C (+0.43 for T0 and T10)
	E _{10M}	pH(H ₂ O) (–0.62 to –0.82), EC (+0.70 to +0.83), CEC (+0.65 to +0.80), exch. acidity (+0.69 to +0.93), CEC (+0.65 to +0.80), exch. acidity (+0.69 to +0.93)
	ΔE_{0-2M}	pH(H ₂ O) (–0.44 only for T60)
	ΔE_{2-10M}	CEC (+0.83) for T10, CEC (+0.91), exch. acidity (+0.93) for T60

Table 4. Multivariate linear equations for dissolution of alkali elements *v.* soil properties with determination coefficient (R^2) > 0.50

Rock type (element)	Milling (min)	Equation	R^2
Basalt (Ca + Mg)	60	$\text{E}_{2M} (\%) = 291 - 178 [\log (\text{pH}(\text{H}_2\text{O}))] - 16 [\log (\text{exch. acidity, cmol}_\text{c}/\text{kg})] - 69 [\log (\text{sand, } \%)]$	0.55
	120	$\log \text{E}_0 (\%) = 3.9 - 0.67 [\log (\text{exch. Na, cmol}_\text{c}/\text{kg})] - 2 [\log (\text{sand, } \%)]$	0.52
		$\text{E}_{2M} (\%) = 158 - 76 [\log (\text{sand, } \%)] - 7 [\log (\text{oxl. ext.} - (\text{Fe} + \text{Al} + \text{Si}), \%)]$	0.53
		$\Delta\text{E}_{0-2M} (\%) = 222 - 72 [\log (\text{sand, } \%)] - 93 [\log (\text{pH}(\text{H}_2\text{O}))]$	0.71
Dolerite (Ca + Mg)	Initial	$\Delta\text{E}_{0-2M} (\%) = 81 - 40 [\log (\text{sand, } \%)] - 7 [\text{org.C, } \%]$	0.53
	10	$\Delta\text{E}_{0-2M} (\%) = 68 - 30 [\log (\text{sand, } \%)] - 1.3 [\text{org.C, } \%]$	0.52
		$\log [\Delta\text{E}_{2-10M} (\%)] = 1.1 - 0.01 [\text{EC, } \mu\text{S}/\text{cm}]$	0.60
Gneiss (K + Na)	Initial	$\Delta\text{E}_{0-2M} (\%) = 86 - 51 [\log (\text{sand, } \%)] + 10 [\log (\text{org.C, } \%)]$	0.61
	10	$\Delta\text{E}_{0-2M} (\%) = 148 - 73 [\log (\text{sand, } \%)]$	0.59
K-feldspar (K + Na)	10	$\text{E}_{10M} (\%) = 76 - 9 [\text{pH}(\text{H}_2\text{O})] - 4 [\text{CEC, cmol}_\text{c}/\text{kg}]$	0.54
		$\Delta\text{E}_{2-10M} (\%) = -0.5 + 0.5 \log [\text{CEC, cmol}_\text{c}/\text{kg}]$	0.78
	60	$\text{E}_0 (\%) = 50 + 26 [\log (\text{CEC, cmol}_\text{c}/\text{kg})] - 12 [\text{pH}(\text{H}_2\text{O})]$	0.52
		$\Delta\text{E}_{2-10M} (\%) = -0.1 + 0.3 [\text{exch. acidity, cmol}_\text{c}/\text{kg}]$	0.83
	120	$\text{E}_0 (\%) = 67 + 22 [\log (\text{CEC, cmol}_\text{c}/\text{kg})] - 12 [\text{pH}(\text{H}_2\text{O})]$	0.54
		$\text{E}_{10M} (\%) = 44 + 0.3 [\text{EC, } \mu\text{S}/\text{cm}] - 0.8 [\text{CEC, cmol}_\text{c}/\text{kg}]$	0.78
		$\Delta\text{E}_{2-10M} (\%) = 117 - 88 [\Delta\text{pH}] + 21 [\text{exch. acidity, cmol}_\text{c}/\text{kg}]$	0.82
		$\log [\Delta\text{E}_{2-10M} (\%)] = 2.9 + 1.76 [\Delta\text{pH}] + 0.13 [\text{exch. acidity, cmol}_\text{c}/\text{kg}]$	0.75

Table 5. Distribution of the values of correlation coefficient (r) for linear relationships of median particle size (D_{50}), effective surface area (SA), and amorphous constituents (AC) of milled rocks with dissolution (E_{2M} and ΔE_{0-2M}) of alkali elements for the rocks incubated in soils for 2 months ($n = 23$)
For basalt and dolerite dissolution is of (Ca + Mg) and for gneiss and K-feldspar is (K + Na)

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

^A E_{2M} and ΔE_{0-2M} respectively are amount of elements dissolved from the rocks within 2-month incubation and that dissolved between 0- and 2-month incubations ($\Delta E_{0-2M} = E_{2M} - E_0$, where E_0 is amount of rapidly dissolved element).

^BCalculated from absolute values.

^CNumbers of significant relationships at $P = 0.05$.

Examples of results from multivariate regression analysis for predictive equations with coefficients of determination (R^2) > 0.50 are presented in Table 4. In general there was no substantial improvement in the prediction of dissolution by relationships generated by multiple regression compared to the results for simple bivariate regression analysis, but some quite predictive equations were generated. The variables % sand (negative) and % clay (positive) appeared several times in both the bivariate and multivariate relationships. It appears that dissolution will be greater in clay-rich soils. Both CEC and exchange acidity were positively related to the extent of dissolution of alkali elements from K-feldspar in soils. Hughes and Gilkes (1994) found only poorly predictive bivariate relationships between percentage dissolution of rock phosphate in soil and single soil properties for 228 soils from south-western Australia; multiple regression analysis indicated a combination of titratable acidity (positive) and % sand (negative) explained about 61% of total variation in percentage dissolution of rock phosphate in soil. In the present work, log % sand (negative) and exchange acidity

(positive) in combination with ΔpH (positive) or $\text{pH}(\text{H}_2\text{O})$ also appear in several of the multivariate equations which respectively explain about 50–70% and 70–90% of total variation in percentage dissolution of SRF, mainly for felsic rocks (gneiss and K-feldspar).

Percentage dissolution v. rocks properties

There was no simple relationship between dissolution of SRF (E_{2M} and ΔE_{0-2M}) in each of the 23 soils and the properties of milled rocks (D_{50} , SA, AC) (Table 5). The values of the correlation coefficient for these relationships varied widely between different soils, and were mostly not significant ($P > 0.05$). Thus, these properties of silicate rocks were not sufficiently predictive of dissolution of alkali elements in soil to provide the basis of a SRF testing procedure.

Conclusion

Milling increased dissolution of alkali elements from SRF in the soil, and this dissolution increased the pH and the EC of the soils. The proportion of dissolved (Ca + Mg) for basalt

and dolerite (T120) in soil for a 10-month incubation reached 18%, and (K + Na) dissolution for gneiss and K-feldspar (T120) was about 40%. Rock and soil properties were not adequately predictive of the dissolution of alkali elements from the SRF in soil.

It is evident that milling can substantially increase the availability to plants of alkali elements in SRF. This procedure may provide a basis for the manufacture of low cost fertilisers. Fine-milled basalt and dolerite may be effective Ca and Mg fertilisers, and K-feldspar can be used as a K fertiliser, whereas gneiss may be less effective as a K fertiliser due to its low content of K. This work should be extended to the development of soil and fertiliser measurements on diverse soils and with diverse plant species that will enable the prediction of the agronomic effectiveness of SRF.

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