

Evaluation of batch and column techniques to measure weathering rates in soils

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ABSTRACT

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Six batch and column techniques were evaluated with respect to their potential to measure realistic weathering rates in soil. Soil samples were taken from a C-horizon of a Dystrochrept. Rates observed in the laboratory were one to three orders of magnitude higher than those inferred from field studies. Batch techniques that involve stirring or shaking, generally gave the highest weathering rates, probably due to abrasion of mineral particles. Column techniques are to be preferred, but in a classical column leaching experiment chemical conditions in the pore water may vary considerably within the column and over the duration of the experiment. To reduce variation of chemical conditions in a column titration experiment, a new technique was used, in which the influx of protons was automatically adjusted proportionally to the overall buffering rate.

Results of the column techniques show that dissolution rates for base cations and aluminum strongly decrease with the extent of reaction. Experimental evidence was found that an increase of the column percolation rate will increase the weathering rate. Although the underlying mechanism for a relationship between percolation rate and weathering rate is not yet clear, this relationship may explain an important part of the discrepancy between weathering rates of base cations from column studies and rates that are observed in the field.

INTRODUCTION

Large areas covered by forest, both in temperate and tropical regions, are increasingly affected by human action. Intensified timber-felling, shifting cultivation and acid rain cause global deforestation, and increase erosion and leaching losses of base cations (K, Ca, Mg) from the soil. Estimates of long-term mineral weathering rates are needed to assess the vulnerability of forest ecosystems. The best estimates available come from budget studies of soils or

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hydrological catchments (Paces, 1983, 1985, 1986; Velbel, 1985; Van Bree-men et al., 1986; Mulder et al., 1989). However, these estimates may be inaccurate due to difficulties in measuring leaching, atmospheric inputs and cation exchange. Alternative estimates of mineral weathering rates can be obtained from dissolution experiments in the laboratory. Interpretation of short-term soil dissolution studies in an uncontrolled chemical environment is arduous, because the change in solution composition will be the sum of salt displacement, cation exchange and mineral weathering. Adequate pretreatment may eliminate these interfering cation sources, but likely will change the mineral surfaces and thus influence weathering kinetics. Weathering kinetics may also be influenced by the conditions during the experiment.

Most weathering experiments use pure minerals, obtained from standard rock samples (Chou and Wollast, 1984; Holdren and Speyer, 1985a) or picked from soil samples (Berner and Holdren, 1979). Mineral samples are generally conditioned to obtain a well-defined starting material. Common pretreatments are crushing, grinding, sonic cleaning, sieving, washing and drying. Experimental conditions rarely resemble natural conditions with respect to ionic strength and temperature. It is commonly accepted that the initial observations in dissolution experiments are mainly artifacts of the sample pretreatments. Crushing and grinding create fine particles and fresh mineral surfaces causing initial non-linear dissolution behaviour (Holdren and Berner, 1979; Holdren and Speyer, 1985b). Observed laboratory dissolution rates are commonly much higher than those concluded from catchment studies (Paces, 1983; Velbel, 1986). Discrepancies may be caused by different characteristics of the mineral surfaces in the laboratory as compared to nature, overestimates of the contact area between minerals and percolating solution in nature, and a higher degree of undersaturation in short-term dilute laboratory experiments (Velbel, 1986).

Laboratory experiments have generated several weathering theories. Until the mid-seventies the weathering rate was believed to be limited by the transport rate of reactants to and from the reacting surface (Correns and von Engelhardt, 1938; Helgeson, 1971; Paces, 1973; Busenberg and Clemency, 1976). Transport-controlled weathering kinetics appeared less likely after X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) did not confirm the existence of a hypothetical diffusion limiting layer of leached material or secondary products covering the mineral surfaces (Wilson, 1975; Berner and Holdren, 1979). Earlier Berner (1978) had stated that dissolution rates predicted by diffusion control were much higher than actual rates observed in laboratory experiments. At present the prevailing theory is that the rate of the surface reaction determines the overall dissolution rate (Berner, 1978; Aagaard and Helgeson, 1982; Lasaga, 1984; Blum and Lasaga, 1986).

Two possible rate limiting surface reactions are surface protonation and

detachment of the surface complex (Aagaard and Helgeson, 1982; Stumm et al., 1985). Simultaneous with the rejection of diffusion control it became clear that surface reactions were confined to specific sites on the mineral surface, resulting in the appearance of etch pits (Wilson, 1975; Berner and Holdren, 1979). If mineral dissolution is indeed a highly local phenomenon, the specific surface area and the chemical composition of the surface of the bulk mineral, emphasized in earlier studies, become rather meaningless (Holdren and Speyer, 1987). At the same time, however, the diffusion control hypothesis was rejected on the basis of either calculation of the maximum diffusion flux from the magnitude of the reactive surface area (Berner, 1978) or on XPS observations of macroscopic portions of the mineral surface (Berner and Holdren, 1979).

At present there is no clear overview of the usefulness of laboratory methods for measuring field weathering rates. In this paper the effect of experimental conditions on observed dissolution kinetics is evaluated by comparing dissolution data from various batch type and column type experiments, exposing one type of soil material to solutions of variable composition. Data were collected from diverse studies during four years. Observed dissolution rates are compared with estimated weathering rates from field mass balance studies.

MATERIAL AND METHODS

Soil material and chemical analysis

The soil material (Table 1) was sampled from a C-horizon of a sandy, mixed, acid, mesic Umbric Dystrochrept, in a woodland in the Netherlands (Van Breemen et al., 1986). The average pH of field soil solutions was 4. Soil was sampled from a soil pit, sieved (1 mm mesh) to remove stones and roots, freeze dried and mixed. Freeze-drying was preferred over air drying to prevent formation of soil lumps requiring subsequent grinding to obtain a homogeneous sample. The elemental composition of the soil was determined by X-ray fluorescence spectrometry. The composition of the cation exchange complex was determined by an unbuffered BaCl_2 extraction (Bascomb, 1964). The concentrations of field soil solutions are flux-weighted means based on a three-year period of monthly sampling. For methods reference is made to Van Breemen et al. (1986, 1987). The mineral composition was determined by counting using the optical microscope. All experiments were carried out at a temperature of 10°C and in duplicate unless stated otherwise. In the solutions of the experiments Ca and Mg were analyzed by atomic absorption spectrometry, K and Na by atomic emission spectrometry. Si and Al were analyzed by inductively coupled plasma spectrometry and H potentiometrically. Samples were passed through a 0.45 μm filter before analysis.

TABLE 1

Texture, chemical and selected mineralogical characteristics of the soil material, and chemical composition of average field soil solution, batch solutions and column percolates

	<2	2–50	50–150	150–300	> 300	(μm)					
	----- (mass fraction %) -----										
Texture	3.9	4.7	39.0	47.8	8.5						
	K ₂ O	Na ₂ O	CaO	MgO	Al ₂ O ₃	SiO ₂					
	----- (mass fraction %) -----										
Elemental composition	1.10	0.55	0.10	0.10	3.08	94.5					
	K	Na	Ca	Mg	Al	H					
	----- (mmol _c /kg) -----										
Exchangeable	<0.1	<0.1	0.1	0.1	3.9	5.1					
	K	Na	Ca	Mg	Al	Si	H	Cl	SO ₄	NO ₃	
Solutions	----- (mmol _c /m ³) -----										
Average field	100	250	350	220	1850		100	410	1450	960	
Experiments:											
C2 (saturated), A5	7	60	8	10	2	0	1010	1035	65	0	
C2 (unsaturated)	120	250	390	240	2370	0	775	4145	0	0	
Mineralogical composition [mass fraction (%) < 1 mm]											
“free” Al-oxides			0.12								
K-feldspar			14								
Plagioclase			5								
Micas (muscovite)			3								
Heavy minerals			0.8								
of which:											
pure alumino-silicates			0.1								
pyriboles			0.2								

Batch experiments

Figure 1 gives a diagrammatic overview of the batch and column techniques used in this study and of some related techniques. Selection of techniques for this study was aimed at minimizing disturbance of the soil material and at controlling the composition of the solution during the experiment.

For the A3-type experiments (Fig. 1) 10 g of soil were mixed with 30 ml of 1 mmol/l HCl (pH is 3) in 50 ml centrifuge tubes. Separate batches were analyzed after 1, 2, 5, 15, 29, 90, 240 and 720 h. The soil material was perwashed 7 times for 1 h with 30 ml 1 mmol/l HCl.

In the unstirred type-A4 experiments, about 30 g of soil were added to 150

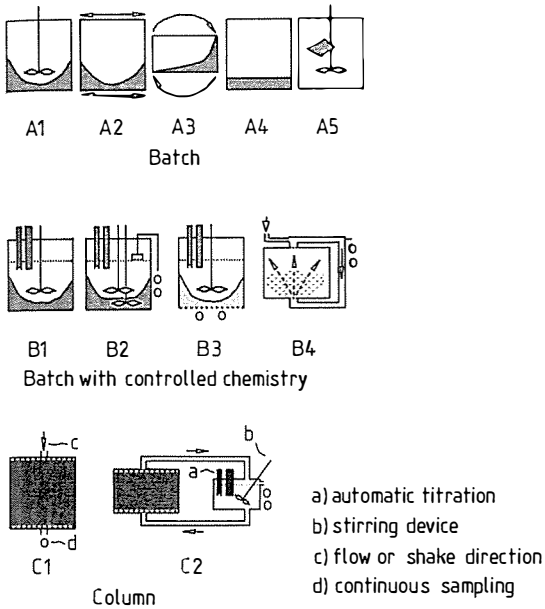


Fig. 1. Main features of methods to measure mineral weathering rates.

(A) Batch-type; uncontrolled chemistry: (1) Stirred; (2) Reciprocal shaker; (3) End-over-end; (4) Unstirred; (5) Sediment in dialysis bag.

(B) Batch-type; controlled chemistry: (1) Stationary pH by automatic titration with concentrated acid using one fast stirring device; (2) Two stirring devices; a slow one for the sediment and a fast one for the solution: Optional titration with dilute acid and continuous extraction of solution samples to maintain a constant ionic strength and reaction volume; (3) Flow cell: One stirring device and constant addition of reactants and extraction of solution through a porous bottom; and (4) Fluidized bed reactor: homogenization by fast upward flow.

(C) Column-type: (1) Fixed flow rate and variable outflow pH, or adjustment of flow rate proportional to buffer rate to control outflow pH; (2) Titration of solution in a separate vessel, which is continuously sampled and recirculated. Additional options: (a) Upward or downward flow direction, (b) disturbed or undisturbed soil material, (c) saturated or unsaturated hydrologic conditions, (d) zero or finite input concentrations.

ml of solution in a plastic container with a diameter of 10 cm. The soil material was leached beforehand for two days with 1 mmol/l HCl. The initial concentrations of all ions except H and Cl were equal to concentrations determined previously by recirculation of demineralized water through a prewashed soil column for two days (C2-saturated, Table 1). The batch solutions were acidified to pH 3 with HCl. When pH had increased by more than 0.1 unit, 100 ml of the solution was sampled and replaced by a fresh solution. Experiments were continued for 90 days. The equation for steady-state diffusion was used to verify the effectiveness of diffusion to homogenize the 2 cm thick supernatant, assuming the dissolution rates from the stirred experiments to be valid. Diffusion transport proved to be adequate except for Al dissolution.

In the stirred type-B2 experiment a batch of 20 g of soil in 120 ml was maintained at pH 3 by automatic titration with 0.1 mol/l HCl. A fast (400 rpm) and a slowly (4 rpm) revolving magnetic stirring bar were used to mix solution and sediment, respectively. The experiment lasted for 10 days. Only the final composition of the batch was analyzed.

Column experiments

Percolation experiments were carried out while soil cores were either completely (saturated conditions) or partly (unsaturated conditions) saturated with water.

Soil columns were percolated under unsaturated conditions at a flow rate of 45 ml/day (23 mm/day, diameter 5 cm) (C1a). Both packed columns, with soil pretreated as described earlier, and undisturbed soil columns, excavated at the field site, were leached with a 3 mmol/l HCl solution. The soil cores were 5 cm high and 5 cm in diameter, weighed about 120 g and were enclosed between 2 cm thick layers of quartz sand to obtain homogeneous throughflow. For the chosen percolation rate about one pore volume is replaced per day. The percolate was sampled daily over a period of 200 days.

In similar experiments the flow was adjusted manually to maintain an output pH ranging between 3.2 and 3.3. (C1b). Flow was lowered from 100 ml/day to 10 ml/day in the course of the experiment. In the experiments columns were packed with a mixture of 20 g of soil and 20 g of quartz sand to increase the hydraulic conductivity. The composition of the input solution was equal to that observed in the field (Table 1) but acidified to pH 3.1. Experiments lasted for 75 days.

Cores of 20 g of soil mixed with quartz sand were also percolated under saturated conditions for 10 d (C1c). The flow rate was automatically adjusted to maintain a constant pH in the outflow (C3). Input concentrations were equal to those used for the unstirred batch experiments (Table 1).

RESULTS

Column experiments with constant flow; packed columns versus undisturbed cores

The rates of dissolution of aluminum from packed columns and the undisturbed cores were similar but decreased markedly in time (Fig. 2). Since there is no input of aluminum to the column, the leaching rate can be taken as the dissolution rate of aluminum. During the first 20 (undisturbed) to 40 days (packed) the dissolution rate of Al is constant at about $1.1 \mu\text{mol}_c \text{ g}^{-1} \text{ day}^{-1}$, and proton buffering is nearly (97%) complete. In this stage percolates are

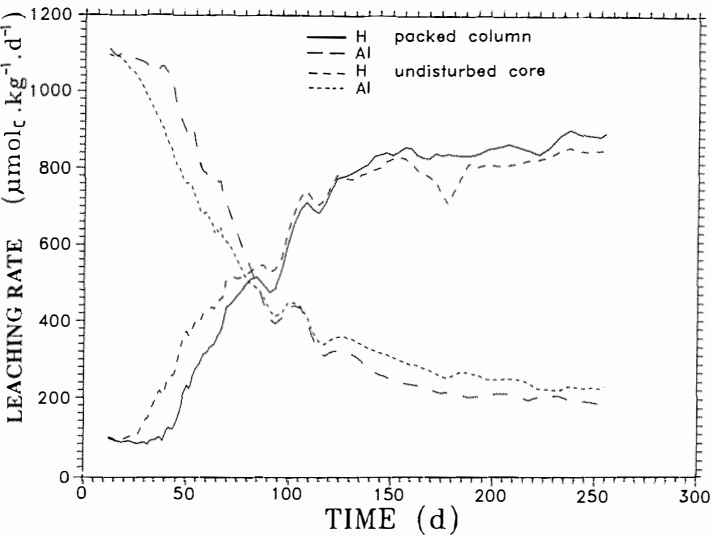


Fig. 2. Rates of Al release and H consumption during percolation of packed and undisturbed soil cores with 3 mmol/l HCl.

slightly undersaturated [$\log(Q_{so})=8$] with respect to dissolution of natural $\text{Al}(\text{OH})_3$ [$\log(K_{so})=8.8$; Driscoll and Bisogni, 1984]:



After this initial stage the dissolution rate of Al decreases rapidly while proton concentrations in the pore water increase. The observed decrease of the Al dissolution rate is the net effect of accelerated dissolution of aluminum hydroxide (Stumm and Furrer, 1986) by the decrease of pH and decelerated dissolution by depletion of most reactive Al sources. Apparently the depletion effect is dominant.

The small difference between results from undisturbed and packed columns is more clear when the ratio of the Al release for packed columns and undisturbed cores is plotted (Fig. 3). The initially higher rate for the packed column may be explained by exposure of reactive aluminum sites created by mechanical disturbance during sample pretreatment. Because the total pool of reactive Al is fixed, higher dissolution rates of Al cause faster depletion of this pool, eventually leading to lower dissolution rates of Al in the packed columns than in the undisturbed soil cores. At the end of the experiments 40 mmol Al per kg soil has been dissolved, which is approximately 50% of the initial pool of sodium-dithionite extractable Al (free oxides).

Less than 5% of the buffering is caused by release of alkali cations. No difference is observed in the behaviour of these ions in the two column types. The average rates of release are shown in Table 2.

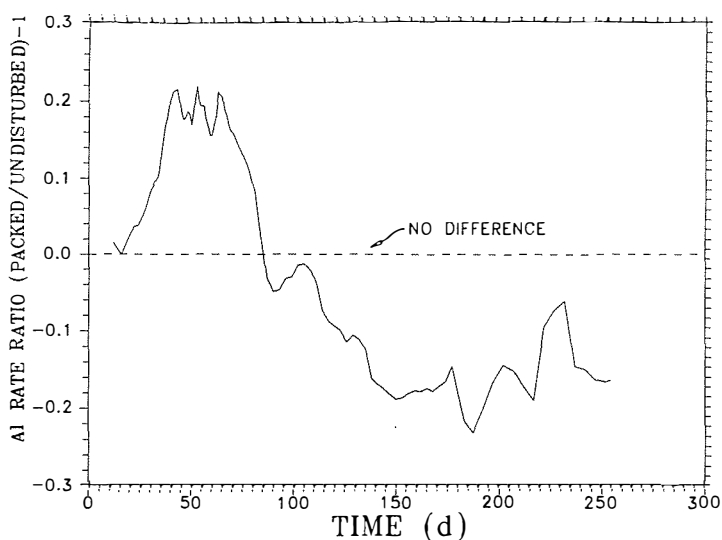


Fig. 3. The ratio of the rates of Al release from packed soil cores and undisturbed soil cores during percolation with 3 mmol/l HCl.

TABLE 2

Mean rates of release of cations and Si (kg^{-1} soil) from duplicate (1 and 2) disturbed and packed soil columns percolating with 42 ml/d 3 mmol/l HCl for 260 d

		K		Na		Ca		Mg		Si	
		-----($\mu\text{mol}_c \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$)-----									
		Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
Disturbed	1	3.7	0.3	6.0	1.2	2.8	0.6	5.5	0.7	75.8	16.4
	2	3.5	0.4	6.0	0.5	3.1	0.6	5.8	0.8	98.8	29.5
Undisturbed	1	3.9	0.4	6.7	0.6	3.4	0.8	5.9	0.7	104.6	18.8
	2	3.5	0.5	5.9	0.5	2.8	0.5	3.8	0.6	90.8	17.6

Weathering experiments at constant pH

When the solution pH is kept constant, there is a dramatic difference between the column experiment on the one hand (C1b, C1c) and the stirred batch experiments (B1) on the other hand (Fig. 4). In the stirred batch experiment the buffering rate initially decreases sharply with reaction progress, but then remains at a high and nearly constant level, almost independent of reaction progress. In the column experiments buffering rates continue to decrease, and there is no indication that buffering rates will become constant with further progress of the reaction. In total the buffering rates in the column

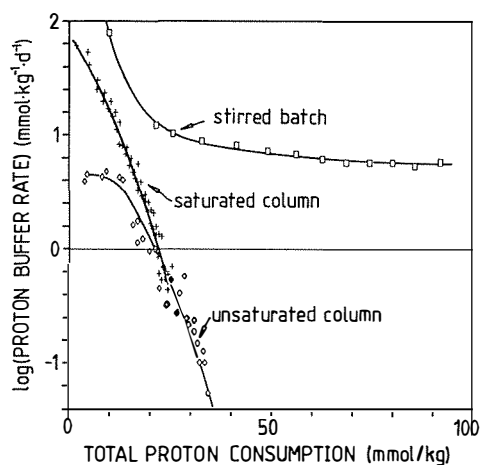


Fig. 4. Comparison of the proton buffer rates with reaction progress, at pH 3 during a stirred batch titration and two column experiments under saturated and unsaturated flow conditions, with low ($10 \text{ mmol} \cdot \text{m}^{-3}$) and high ($240 \text{ mmol} \cdot \text{m}^{-3}$) input concentrations of Al.

experiments decrease by almost three orders of magnitude and, after consumption of 30 mmol/kg of protons, they are two orders of magnitude lower than in the stirred batch experiment.

Buffering rates of saturated and partially saturated column experiments are quite comparable apart from the initial stage. The relatively low initial buffering rate in the unsaturated column experiment is due to the fact that the highest possible gravitational flow rate was too low to maintain a pH value of 3.2 in the leachate during the initial rapid dissolution of Al. After 25 mmol/kg of H^+ has been consumed the buffer rate curves for the saturated and unsaturated column merge, suggesting that differences in water content (approximately 100% versus 50% saturation) and mineral saturation with respect to $\text{Al}(\text{OH})_3$ ($10^{5.1}$ in C1b versus $10^{6.5}$ in C1c) do not influence rates of Al release.

The batch experiment and the saturated column experiment lasted 10 days, whereas the unsaturated column experiment lasted 75 days.

Differences between the column and the batch experiments cannot be attributed to pH differences (Stumm et al., 1985; Stumm and Furrer, 1986) or to differences in the degree of saturation with $\text{Al}(\text{OH})_3$. The pH in all experiments was controlled at a value near 3. Differences in degree of saturation with $\text{Al}(\text{OH})_3$ were small: $\text{Al}(\text{OH})_3$ activity products [eq. (1)] in the column experiments were $10^{5.1}$ (C1b) and $10^{6.5}$ (C1c), respectively, while they reached $10^{6.5}$ towards the end of the batch experiment. The most likely cause for the much higher and more slowly decreasing buffer rates in the batch experiment seems to be mechanical disturbance of the surfaces. Stirring may continuously create reactive surface area. Continuous stirring of the sediment

(Fig. 1) may have stronger effects than sample pretreatment or end-over-end shaking. Amorphous hydrous oxides of Al, such as the Al extracted by oxalate-dithionite extraction, are the most likely source of Al. Mechanical disturbance of these secondary oxides is feasible: SEM photomicrographs (Berner and Holdren, 1979) suggest that secondary Al is present as small particles, often weakly adhering to surfaces of primary minerals.

Comparison of weathering kinetics of base cations using various experimental techniques

Observed rates of release of Na, K, Mg and Si were also markedly higher in the stirred pH-stat experiments (B2) than in all other experiments (Table 3). The rates were corrected for initial salt displacement and cation exchange. Apparently, continuous stirring of the sediment also affects surfaces of silicate minerals. The second highest rates of release for K, Mg and Si were found in the end-over-end experiment. Rates in the unstirred batch experiment and the column experiments were very similar, which may have been expected because during both types of experiments solids were not mechanically disturbed and solutions were stagnant or nearly stagnant. The duration and the total proton consumption of the experiments varied over a wide range; duration from 10 to 150 days and proton consumption from 3 to 110 $\mu\text{mol/g}$. Depletion effects after the initial salt displacement and exchange phase were considered unimportant; relative to total pools of silicate minerals, depletion over the duration of the experiments was negligible.

TABLE 3

Rates of release of Na, K, Mg and Si observed in six different types of dissolution experiments at pH 3

Type	pH	Na ($\mu\text{mol}_c \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$)	K	Mg	Si	Flow, volume (ml/day, ml)	Soil weight (g)	Duration (day)
Batch	3-4	4	33	86	110	30	10	30
Head-over-end	3.0	3	2	8	33	150	16	50
Unstirred	3.0	230	-	370	1350	120	20	10
Stirred titration								
Column								
Fixed flow	2.6-3.3	6	4	6	88	45	120	150
Variable gravit. flow	3.1	20	10	-	20	30	20	60
Variable forced flow	3.0	20	4	2	50	70	20	14

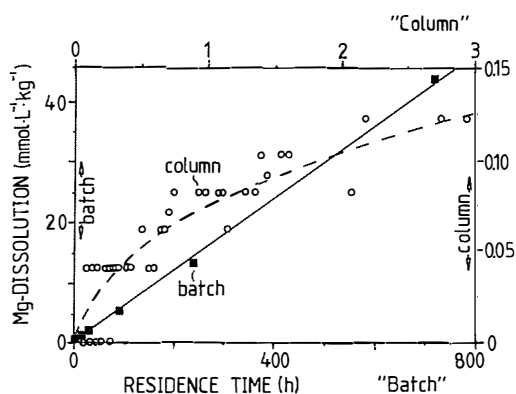


Fig. 5. The dissolution of Mg in a batch and a column experiment with increasing residence time.

The effect of percolation rate on weathering rate

In batch experiments, rates of silicate dissolution tend to become constant with time (Busenberg and Clemency, 1976). A constant dissolution rate results in a linear increase of the dissolved concentration with residence time, as was indeed observed in our batch experiment (end-over-end, A3) at pH 3 for Mg (Fig. 5), K, Na, Mn and Si. Results for a column experiment (forced variable flow, C1c) show that the dissolved concentration of Mg appears to increase less than linearly with residence time. Residence time is calculated as the ratio of pore volume and percolation rate. The observed non-linear dissolution behaviour implies an increase of the dissolution rate with percolation rate. Note the quite different scales both on the horizontal and vertical axis for the two experiments. It might be argued that the two lines are part of the same scale. However, the slope of the curve at the end of the column experiment is about one fourth of that for the batch experiment. The variation of residence time in the column experiment is caused by the decrease of flow rate, which was necessary to maintain a constant pH in the leachate. The increase of residence time goes along with the progress of the reaction for both experiments and therefore unlikely explains the non-linear behaviour in the column experiment. An increase of dissolution rates with percolation rate was observed for K, Na, Mn and Si.

DISCUSSION

The effect of percolation rate

The essential difference between the batch and column experiment is that hydrodynamic conditions in batch experiments are independent of residence

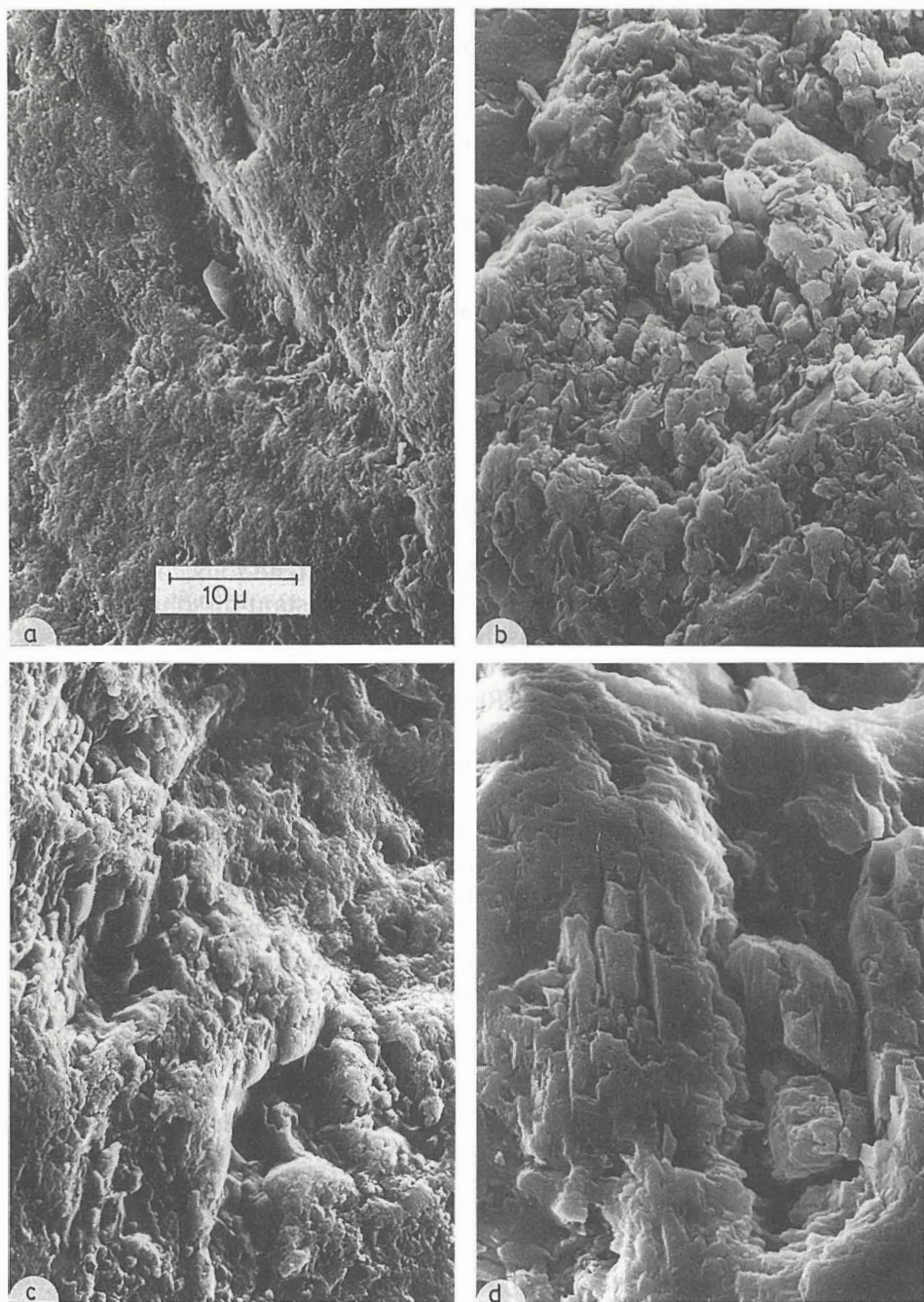


Fig. 6. Scanning electron micrographs of K-feldspars in a C-horizon of an Umbric Dystrochrept with increasing etch pit depths and degree of surface roughness.

time, while in column experiments residence time is inversely proportional to percolation rate. If reaction rates depend on percolation rate, the question is to explain this observed effect in a quantitative fashion. It might be assumed that kinetics are determined by transport through a stagnant water film between the reactive surface and the inter-particle pores which conduct the majority of the water and reactants. The etch pit concept implies that the reactive surface area may be much smaller than the total surface area. SEM photomicrographs (Fig. 6) of K-feldspars in our soil material give an impression of the roughness and heterogeneity of the mineral surfaces and the dimension of the etch pits. If the dissolution rate in the column is equal to the steady state diffusion flux between reactive surface and inter-particle pores, diffusion lengths may range from 5 (etch pit depth) to 50 μm (pore diameter of soil matrix). Applying the equation for steady state diffusion, assuming that proton diffusion is rate limiting, this implies that the reactive surface area is a factor 10^{-7} to 10^{-8} less than the total surface area ($1 \text{ m}^2/\text{g}$).

Another explanation might be that there is a physical impact of flow on the mineral surface, which influences the weathering kinetics. The possibility that the non-linear behavior for the column experiment is not the result of variation of flow but of reaction progress, was already discussed.

Discrepancies between weathering rates obtained in the laboratory and those inferred from field studies

Any comparison of weathering rates measured in the laboratory and rates from field studies can be questioned. In general, laboratory rates apply to much smaller time scales and much smaller soil bodies than field rates. Moreover, field rates are often cumulative values, which may be limited by the supply of reactants. For example the supply of protons is clearly limiting annual weathering of amorphous aluminum oxides in Dutch sandy soil (Mulder et al., 1989), which makes quantitative comparison of field rates and laboratory rates senseless.

Differences in results from the stirred batch experiment and the controlled column experiments show experimental artifacts that may easily enhance weathering rates by two orders of magnitude. In order to be able to estimate the evolution of weathering reactions in the field as a function of time and acid input, a detailed quantitative knowledge is required of the parameters affecting the weathering kinetics.

Since only very small fractions of the minerals containing base cations are dissolved it is to be expected that the weathering rates of such minerals are much less dependent than Al minerals on the extent of the reaction. As has been shown, base cation weathering depends also very much on the experimental technique. The lowest weathering rates for K and Mg and Si observed in the laboratory experiments were 0.002, 0.002 and 0.02 $\mu\text{mol}_\text{c}\cdot\text{g}^{-1} \text{ day}^{-1}$

respectively (Table 3). Extrapolated to field weathering rates for a 1 m soil profile we find 7.3, 7.3 and 73 $\text{kmol}_c \text{ ha}^{-1} \text{ yr}^{-1}$, respectively. Budget studies based on three years of field monitoring revealed weathering values in the order of 0.5 for K and Mg and 1 $\text{kmol}_c \text{ ha}^{-1} \text{ yr}^{-1}$ for Si, for a 0.9 m soil profile (Van Breemen et al., 1986). Weathering rates for the C-horizon may be somewhat higher than the profile average, because silicate weathering rates in the leached A- and B-horizon may be expected to be lower than in the C-horizon. The discrepancy for Si may be attributed in part to reprecipitation of dissolved Si deeper in the soil profile, but it is clear that weathering rates for K and Mg are overestimated in the laboratory by at least one order of magnitude. As shown previously, enhanced weathering due to mechanical disturbance played no role in the column experiments and in the unstirred batch experiments. Moreover, the experiments were continued long enough to exclude the effects of salt displacement and cation exchange. Depression of weathering rates in the field due to chemical saturation effects with respect to K- and Mg-bearing silicates is unlikely at ambient values of pH in soil solution below 4. Other explanations may have to be sought either in respect of pH, using the concept of surface protonation (Stumm et al., 1985), or in respect of hydrodynamic conditions, e.g. through imperfect contact between solids and percolating solution (Velbel, 1986). In general a power relationship is found between silicate dissolution rates and hydrogen activity in solution, where the exponent varies between 0.33 and 0.8 (Stumm and Furrer, 1986). Assuming an increase of the weathering rate with the square root of the hydrogen activity, the pH difference between field (pH 4) and experiments (pH 3) would imply a three times lower weathering rate in the field than in the laboratory.

If it is assumed that the non-linear behaviour for the column experiment is caused by the variation of the percolation rate, discrepancies between laboratory and field weathering rates may also be attributed to differences of percolation rate. As the outflow concentrations in the column experiments could be described as a function of the square root of residence time, the weathering rate increases with the square root of the percolation rate. The lowest flow applied in the column experiments is about 70 ml/day, which is equivalent to $4 \text{ cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$. By comparison, the average flow rate in the field ranges from 0.05 to 0.15 $\text{cm}^3 \text{ cm}^{-2} \text{ day}^{-1}$ (Van Breemen et al., 1986). Assuming a square root relationship between weathering rate and percolation rate, the lowest dissolution rate observed in the column experiment should be 5 to 9 times higher than field rates, which accounts for the larger part of the observed discrepancy of a factor of 15 for K and Mg.

Although the mechanism of the effect of percolation rate cannot be further tested, the observed square root relationship between percolation rate and reaction rate may be used as an empirical method to extrapolate the observed

weathering rates of base cations to rates occurring under flow conditions prevailing in the field.

CONCLUSIONS

This study shows that there are large discrepancies between weathering rates obtained from various laboratory methods and also between rates inferred from the laboratory and the field. These discrepancies can be partly explained. Continuous abrasion of mineral particles in stirred or shaken experiments strongly accelerates weathering. Mild pretreatments like sieving and packing hardly influence weathering rates. The degree of water saturation in column experiments also has little effect on weathering rates. Determination of the dissolution rate of aluminum is complicated by its strong decrease with reaction progress. The effect of reaction progress on the rates of release of base cations appears to be minor for the duration of the experiments. There is some evidence that the percolation rate may affect the weathering rate. The mechanism is unclear. Empirical extrapolation of weathering rates observed in the laboratory to percolation rates realistic in the field, leads to weathering rates that are comparable to those inferred from field mass balance studies. However, this extrapolation is still at least as inaccurate as indirect estimation of weathering rates from field mass balance studies.

Column experiments with adjustment of the addition rate of reactants proportional to the reaction rate and stagnant batch experiments with solution replacement are useful techniques to measure slow weathering reactions, as both have nearly constant chemical conditions, and a minimal disturbance of the solid phase.

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