Rate Controls on the Chemical Weathering of Natural Polymineralic Material I. Dissolution behaviour of polymineralic assemblages determined using batch and unsaturated column experiments.

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Abstract

Chemical weathering rates for a mudstone obtained from a mining environment were

investigated using a combination of batch reactors and hydrologically-unsaturated column

experiments. Results of tracer tests were combined with relationships between solute

concentrations, mass fluxes, flow rates and residence times, and used to calculate element release

rates and infer rate-controlling mechanisms for the two different experimental environments.

Elements that eluted from column experiments exhibited either:

1) concentrations independent of flow rate and column length coupled with mass flux increasing

with flow rate, or

2) an inverse relationship between concentration and flow rate coupled with mass flux increasing

with both column length and flow rate.

The former is attributed to equilibrium-controlled release of particular elements (Si, Al), while

the latter is ascribed to transport-controlled release of others (Mg, Mn, Ca, Na, K, S). Tracer

tests using NaBr solutions revealed that some elements were also affected by ion exchange (Mg,

Mn, Ca, Na), but these effects were temporary and did not mask underlying dissolution rate-

controlling mechanisms. Analysis of characteristic diffusive lengths was used to distinguish

between transport rates limited by the transfer of solutes between immobile and mobile water

within the columns, and rates limited by slow diffusion across partially reacted mineral layers.

The analysis suggests that transfer between immobile and mobile water limited the element

release rates, with diffusion hindered by low diffusion coefficients within the unsaturated

medium, and by low interfacial areas between mobile and immobile fluids. Results of the batch

experiments showed different characteristics. Element concentrations either rose to a plateau or

increased linearly with time. Rate-controlling mechanisms associated with these characteristics

were equilibrium (Fe) and surface kinetic reactions (Si, Mg, Mn, Ca, K, S), respectively. Surface area-normalized element release rates for Mg, Mn, Ca and S are consistently a factor of 4 higher than those from the column experiments. This is a significant difference and cannot be attributed to differences in mineral preparation or to factors influencing individual minerals. It must, therefore, reflect the difference in the rate-controlling mechanism, that is, transport vs. surface-kinetic control.

These results suggest that some proportion of the commonly recorded discrepancy between laboratory and field weathering rates is due to hydrological differences between the two environments, and that hydrological characterization of weathering environments is, therefore, as important as physical-geochemical characterization of reacting solids. An important practical implication of the work is that substantial reservoirs of solutes are held in immobile water in the unsaturated environment, and that these could be released by soil disturbance or flooding.

1. INTRODUCTION

An understanding of chemical weathering mechanisms and rates under non-equilibrium conditions is essential for successful prediction of earth surface processes on global, local and microscopic scales (e.g. White and Blum, 1995; Berner and Kothavala, 2001; Lefebvre *et al*., 2001). Applications for such information include a wide range of natural processes, for example: acid mine drainage production; amelioration of soil acidity by mineral weathering; and the impact of mineral weathering on atmospheric CO_2. Much study has been devoted to the elucidation of rates of mineral weathering processes under laboratory conditions, and studies on individual mineral phases have determined detailed reaction mechanisms and relationships between dissolution rates and pH, temperature, surface and crystallographic characteristics and rate-determining concentrations of reactants that influence kinetic mass action (e.g. Wieland *et al*., 1988; Xie and Walther, 1993; Martello *et al*., 1994; White and Brantley, 1995; Peiffer and Stubert, 1999; Holmes and Crundwell, 2000). However, application of these rates to natural environments can be problematic. A large proportion of weathering takes place in the unsaturated zone where water-rock ratios, fluid flux rates and element concentrations are very different to those found in laboratory experiments. Field studies of weathering rates (e.g. White *et al*., 1996), have found that laboratory weathering rates are up to 5 orders of magnitude faster than those observed in the field (Schnoor, 1990, White *et al*., 1996; White and Brantley, 2003).

Differences in weathering rates are often attributed to differences in rate-determining factors between laboratory and field (White and Brantley, 1995). White and Brantley (2003) have split these rate-determining factors into intrinsic and extrinsic groups. Extrinisic rate-controlling factors are determined external to the immediate weathering environment, and

include permeability, temperature, biology, hydrodynamic factors (e.g. Sjoberg and Rickard, 1983), and infiltrating concentrations of rate-determining solutes (e.g. pH). Intrinsic factors are determined by the weathering minerals, and include pH, temperature, reactive surface area, and the presence or absence of bacterial catalysts (White, 1995).

Differences in dissolution rates as a result of intrinsic or extrinsic factors may result in different rate-limiting steps for element release in the laboratory and the field. For example, low water: rock ratios and slow fluid percolation rates can result in chemical equilibrium between soil solutions and parent or secondary minerals for minerals that exhibit surface-kinetic controlled dissolution rates in the laboratory. Hydrological factors can cause other forms of variation in the release of dissolved mineral constituents. For example, van Grinsven and van Riemsdijk (1992) observed a positive correlation between flow rates and element fluxes measured from column and field experiments on soil material. Similar trends in field weathering experiments from a weathered granite catchment have been ascribed to flushing of concentrated soil solutions during times of increased flow (Clow and Drever, 1996). Unsaturated systems contain freely moving, mobile water and stagnant immobile water which is held in small pores by surface tension. Unsaturated systems often exhibit bimodal or continuous velocity distributions (e.g. Velbel, 1993; Kamra *et al*., 2001) with a resultant complexity in the systematics of transport of dissolved mineral consituents. Factors that relate to the geometry of fluid flow can also influence dissolution rates. Sjoberg and Rickard (1983) showed that vessel shape could alter dissolution rates, even in tightly controlled single mineral laboratory experiments.

It is more difficult to identify the factors that control element release rates when polymineralic materials are considered. Unsaturated column experiments on mining waste rock

(Stromberg and Banwart, 1999a) showed that important elements such as Al and S can be controlled by the precipitation of secondary phases, although kinetic factors can hinder such precipitation (Bertrand *et al*., 1994). Batch experiments that compared distinct particle size fractions of the same material (Strömberg and Banwart., 1999b) demonstrated that intra-particle diffusion mass transfer provides an important rate control. Adsorption has also been shown to control element release in some cases (e.g. Plassard *et al*., 2000).

Previous work has generally focussed on *either* the geochemistry of reacting column material, *or* the physical transport, so that it is difficult to identify aspects of mineral dissolution that result from the synthesis of the two aspects, e.g., the extent to which solution transport processes affect chemical weathering rates. Yet it has been shown that both transport and chemical processes can influence dissolution rate simultaneously; Eriksson *et al*. (1997) requires both secondary mineral precipitation and preferential flow to explain results from unsaturated columns containing Cu-rich mining waste rock. Links and feedbacks between hydrological and chemical influences on mineral dissolution are poorly known. In particular, the impact of unsaturated flow conditions is largely unknown.

In this study results from saturated batch and unsaturated column experiments on a well-characterized mudstone from a mine waste deposit are compared. Principal objectives are to: quantify element release rates from natural polymineralic material reacted under controlled laboratory weathering environments; identify the rate-controlling step for chemical weathering within batch and column experiments on identical materials; assess the degree to which transport-related processes affect chemical weathering in the laboratory environment; and to use the experimental results to make inferences about the type of rate-controlling process that dominate chemical weathering in natural environments.

2. METHODS

2.1 Experiment design strategy

The design of mineral dissolution experiments is critical. Factors that include, but are not limited to, sample pretreatment methods, length of experiment, and sampling strategies have all been shown to systematically affect results (e.g. Hornberger and Brady, 1987; Hodson, 1999). It is therefore necessary to consider the effects of all components of the experimental method, including data analysis, in the light of the specific experimental aims. Experiments on natural polymineralic materials are particularly challenging, because each mineral responds differently to the experimental conditions, and bulk characterization of the material may not provide sufficient information for interpretation of results. Further problems arise when the different constituents of a polymineralic material respond in different ways to pretreatment protocols. For this reason the measurement of dissolution rates and observations of rate-controlling processes is generally carried out on pure minerals (e.g. Peiffer and Stubert, 1999; Holmes and Crundwell, 2000). However, it is also necessary to study polymineralic systems because they behave in ways which cannot be predicted from a combination of pure mineral studies; some features of chemical weathering arise from interactions between the weathering products of different minerals. An example of this is the formation of jarosite, with Fe and S derived from pyrite dissolution, and K produced by weathering of micas or feldspars.

Here, the aim of the experiment is to observe mineral dissolution in polymineralic materials under experimental conditions that mimic the hydrology of soil environments. To preserve the characteristics of, and mineralogical relationships between, naturally occurring

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minerals, sample preparation was reduced to the bare minimum consistent with a workable experimental method. Sample preparation artifacts decrease with time, as experimental systems settle towards steady state, and so the probability of bias arising from sample preparation was minimized by the use of extended experimental timescales of up to several months, and by the use of results derived from two very different experimental methods on identically prepared materials

2.2. Sample Collection and Characterization

20 kg of rock (Ynysarwedd mudstone, denoted YM) was collected from the field site, a coal mine waste deposit in Wales, U.K. (Figure 1, see Evans *et al.* (2006) for description). Samples were air-dried at room temperature to minimize heat-driven dehydration reactions and were then jaw-crushed to a median grain size of approximately 1mm. This treatment was required to reduce the grain size of the material to a size which would allow steady, evenly distributed flow of infiltrating water in the column environment and was carefully chosen to provide the minimum pretreatment capable of producing the required grainsize (~1mm). Jaw crushing creates fresh, highly reactive mineral surfaces which dissolve rapidly. Extended experimental timescales were used to identify and account for any experimental artifacts resulting from this. The material was then homogenized in an industrial rock aggregate mixer for 30 min. Homogenization was performed for the shortest possible time to minimize any further reduction in particle size. Samples were not washed after crushing as this would preferentially remove components of the system that are associated with finer grained or more friable minerals, such as micas. Loss of fine-grained material from the column experiments was prevented by the experimental design (see below).

Particle size curves were measured using a shaker and a series of sieves (Figure 2). Sample homogeneity was tested by multiple analysis of bulk composition and was confirmed for major and most trace elements. The material was not sterilized, as the heat treatment involved would have partially dehydrated mixed-layer clays, changing the structure, ion exchange capacities and dissolution characteristics of these minerals. Major and trace element compositions were obtained at the British Geological Survey, Keyworth, using X-Ray Fluorescence (XRF) on glass beads and pellets respectively (Table 1). Mineral assemblages and textural relationships were identified using X-Ray Diffraction (XRD), scanning electron microscopy (SEM) and optical microscope examination of thin sections. Total S was determined by LECO analysis, and the S contained in water- and acid-soluble SO_4^{2-} (Table 1) was measured using standard methods described by Czerewko, (1997). Sulfur contained within pyrite was calculated from the difference between total and the S in acid- and water-soluble SO_4^{2-} (Table 1). Organic S content was assumed to be negligible (c.f. Taylor, 1989). Density was calculated from triplicate observations of the wet and dry mass of $50cm^3$ of material, packed in a similar way to the packing within the columns. Residual water content was also measured and found to be negligible. Surface area of unreacted and reacted samples was determined using (a) BET analysis, and (b) as geometric surface area assuming a spherical geometry with a diameter of 1mm (Table 1).

2.3. Column Experiments

All experiments took place in a temperature controlled laboratory at $20^{o}C$. Columns of lengths 12.5 and 50 cm were constructed from 10 cm diameter UPVC (Unplasticized PolyVinyl

Chloride) drainpipe (Figure 3). A peristaltic pump was used to pump deionized water at fixed flow rates selected between 0.05 and 0.2 mL min^{-1} onto a glass sintered disc of higher suction than the reacting material, which rested on the material at the top of each column. The influent tube was constructed of 0.5 mm ID (Internal diameter) PTFE (Poly Tetra Fluoro Ethylene) and input was via a slow steady drip onto the sinter. The sinter could not transmit water into the material until fully saturated. Once saturated, water was transmitted evenly into the mudstone in contact with the disc. This ensured that all the mudstone received an equal quantity of influent at the upper boundary of the column reactor. This was tested by dripping a fluorescent dye, fluorescein, onto a test column containing pale sandstone; the sinter saturated with the dye before any solution was transmitted to the test sandstone, and the sandstone exhibited 100% coverage of the dye, from which uniform distribution was inferred. A cover was placed over the sinter to minimize evaporation of the influent fluid. The proportion of influent which evaporated was calculated from comparisons of influent and effluent flow rate and was found to be less than 2%. The sinter diameter was 90mm, and it was positioned to leave a ring of mudstone at its perimeter. Under these circumstances, air within the mudstone is free to exchange with the atmosphere, and the gas composition in the pores of the mudstone is determined by the relative rates of gas exchange with the atmosphere and mineral reaction.

Column bases were constructed of UPVC in 3 sections. Sampled material rested directly on a lower 90 mm diameter glass sinter which was sealed into a supporting recessed UPVC disc using laboratory-grade silicon sealant. This upper disc overlay a supporting perforated section and lower shallow conical reservoir (volume less than 1cm^3). Effluents drained from the column via a 1.59mm diameter PEEK (Poly Ether Ether Ketone) pipe through a succession of 3 PVDF (Poly Vinyli Dene Fluoride) flow cells that contained permanently located pH, redox and

dissolved oxygen probes. Galvanic dissolved O_2 probes were supplied by InteliSys Ltd. Redox and flat-bottomed pH probes were supplied by BDH. Probes were calibrated using standard solutions at the beginning and end of each run. Probe output was amplified using purpose built amplifiers (InteliSys Ltd) and measured daily on a PC via an A/D board using Dasylab (1996) software. Continuous monitoring was possible but daily readings were found to track changes in output parameters adequately. Effluent drained under gravity into conical flasks. The point of drainage was at the same height as the base of the column of mudstone. This maintained hydrological saturation at the base of the column and minimized the risk of air bubbles becoming entrained in the effluent, which reduced the probability of preferential or unsteady flow. Samples were taken from the conical flasks on every weekday, filtered with a 0.2µm filter and split into acidified (with 1% HNO_3) and non-acidified portions. Acidified samples were analyzed by ICP-AES (Tables A1,A2) for dissolved cations. Most of the unacidified samples were analyzed by ion chromatography (IC) for anions (SO_4^{2-}, NO_3^-, Br^- and Cl^-). Iron- and Al-rich samples were excluded from IC analysis as these metals form insoluble compounds within ion exchange columns and damage them. Quality Control (QC) samples were run on the IC every 10 samples. The standard deviation for all QC samples run during the column run was better than 5% relative, except for PO_4^{3-} (7.5%) and Na (5.9%). QC samples of a mine-water from Derbyshire, U.K. were run on the ICP-AES every 20 samples. Accuracy on the ICP-AES over the course of the experiment was better than 7% relative for concentrations greater than 1 mg L^{-1}, and better than 10% relative for concentrations between 0.1 and 1 mg L^{-1}, except for P, which was not recorded. The detection limit for the IC was taken as 1 mg L^{-1}, and for the ICP-AES as 0.1 mg L^{-1}.

pH was also determined in some effluent samples after they had flowed out of the system because oxide and/or bacterial coatings built up on probes within flow cells during some runs and impaired their performance. Alkalinity was measured by titration with HCl to a pH of 4.5 in neutral and alkaline samples. This parameter was not measured in samples with a pH of less than 4.5 because the increase in pH with alkalimetric titration caused precipitation of Fe oxides so that the original acidity could not be calculated.

Blank experiments on the column apparatus were performed using (a) dilute HCl and (b) de-ionized water. These demonstrated that there was no element flux from the reactor materials. The mudstone material was then loaded into the columns. Loading took place in 5-8 increments and each increment was lightly packed before the next one was placed on top. The material was run for 10 weeks. Each run consisted of initial water addition and water content assessment, followed by periods spent at each of 3 influent flow rates (see Table 2 for details). Flow conditions were monitored by measurement of effluent flow rates and comparison of these with influent rates. Steady state flow conditions were judged to have been reached when influent and effluent flow rates were equal. Steady flow conditions were generally approached within a few hours of flow rate changes. A final return to an intermediate flow rate was followed by the construction of a soil-water retention curve by the method described by Fetter, (1993) for the 12.5 cm column. This measurement characterizes the ability of a porous material to draw fluids into its pores by capillary forces when the pores are only partially filled with water. A curve was not completed for the longer column because air bubbles introduced during the desaturation stage of the curve prevented further hydrological equilibration. An attempt at suppression of bacterial activity during a test run was made using chemical sterilization with $HgCl_2$. Acidity output from the material decreased by a third, but the Hg was not recovered from the effluent.

This suggests that surface adsorption of the Hg occurred. Surface adsorption of the Hg would (a) have affected the cation exchange and adsorption characteristics of clay minerals and hence the surface kinetic reactivity of dissolving minerals, (b) have led to a long-term, low Hg concentration effluent with significant Health and Safety implications. The procedure was therefore not repeated. Other methods for suppression of bacterial activity, such as heat treatment or the use of surfactants, were rejected as they would change the surface chemistry of the dissolving material and hence influence results. It is therefore likely that bacterial activity occurred, and consequent effects on the mineral dissolution processes in both column and batch experiments cannot be ruled out. Tracer tests were performed on each column at one or two of the different flow rates by replacing the influent with a dilute NaBr solution (500 to 2000 mg L^{-1}) for a period of several hours. Effluent samples were then taken every 1.5 h over a period of 2 to 3 weeks by diverting effluent into an automated sample collector. These solutions were analyzed for anions and selected cations by ion chromatography (IC).

When the runs were complete the influent was shut off and the columns were immediately (<5 mins) dismantled. The reacted mudstone from the columns was rapidly split into approximately equal segments. The segments were weighed before drying in an oven at $60^{o}C$ for 3 days, then reweighed. Drying for times longer than this showed that no further mass was lost after 3 days. The mass lost was used to calculate the water content of each section of the column, and so to assess the variation of water content with height in the column (Figure 4). The saturated porosity was calculated from the water content of the bottom column section. The average water content, weighted for the size of the section measured was also calculated. This was used to calculate the average percentage of hydrological saturation, where 0% would indicate a dry column, and 100% would indicate that all pores were completely filled with water.

Acid and water soluble SO_4^{2-} contents, plus surface area by BET analysis, were determined on the post-run material (Table 1). Selected post-run samples were examined using SEM to discern mineralogical changes occurring as a result of the run. Post-run XRD and XRF were not performed as previous work (unpublished) has shown that significant bulk changes do not occur on the 2 to 3 month timescale of the runs. This is supported by estimates of total mass loss calculated by integrating element fluxes with respect to time. Values obtained by this method do not represent a significant proportion of the major element budget of the samples. Replicates of the mudstone-bearing column experiments were not performed, but repeats of column runs with other materials (unpub. results) showed that identical columns produced element fluxes that were identical within the uncertainty of the measurements.

2.4. Batch Experiments

A batch experiment was performed using the methods described by Banwart *et al*. (2002) with minor modifications. The experiments was performed in a temperature-controlled laboratory at $20^{\circ}C$. Sample material was prepared identically to that used in the column experiments. Approximately 8g of sample in 200 mL of 0.1M NaCl was placed in QuikFit (Merck/BDH, Poole) reaction vessels. During the run the reactor was stirred continuously, and equilibrium with atmospheric O_2 was maintained by bubbling water-saturated air through the samples. Two mL samples were taken at regular intervals. These were filtered using a 0.2 µm filter and split into a diluted, acidified portion for ICP-AES analysis of cations and a non-acidified sample for anion analysis by IC as described above. Seventeen samples were taken from the reactor over the 70 day duration of the experiment. Evaporation occurred in some experiments, which were

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maintained at 200mL using UHQ additions. Volumes of UHQ added were measured and results were corrected for this and for mass removal by sampling. A replicate of the batch experiment was not performed.

2.5. Assessment of Column Flow and Transport Processes

Physical transport processes (Table 2) were assessed by calculating the first 2 temporal moments for each tracer test using the methods of Eriksson *et al*., (1997). The zeroth temporal moment measures mass recovery for the test ($\underline{M}$) as a proportion of input mass. The first temporal moment is the time at which the centre of mass arrives at the measuring point (τ). The zeroth and first temporal moments were combined to derive a preliminary estimate of flow porosity within the column. The flow porosity is a measure of the porosity in which fluid flow occurs. This is different from the total porosity in unsaturated soils because some of the porosity is filled with air, while other portions of the porosity may contain immobile solution that does not participate in the fluid flow. If solute exchange occurs between mobile and immobile water so that solutes are stored in immobile water that is not accounted for by the flow porosity then the flow porosity will be overestimated. Here it provides an initial estimate.

3. RESULTS

3.1. Material Characteristics

YM is a soft, heavily weathered, dark-grey, fine grained (<0.5mm) mudstone. Some surfaces show sulfurous yellow deposits, indicative of the formation of soluble sulfate mineral weathering products such as alunite. Orange ochreous crusts are also seen. SEM work identified these as Fe

oxyhydroxides. The mudstones split easily along bedding planes and often contain small plant

fossils. A bedding parallel cleavage, and an incipient cleavage at an angle to bedding can be

seen in some samples. This suggests that metamorphic grades were high enough to transform

mixed layer clays (smectites) to illite/chlorite. Millimetre-scale variations in C content, the

proportion of pelitic minerals, and grain size were observed perpendicular to the bedding planes.

Samples were homogeneous parallel to bedding on the length-scale of observation (dm).

Individual grains are mostly too small to be distinguished in handspecimen, although angular

white mica grains aligned with the bed-parallel cleavage were observed in some samples. The

preferential alignment and angular shape of this mica suggests that it is diagenetic or

metamorphic rather than detrital. Small (<1mm) gold-colored cubes are also found in

approximately 30% of samples. These were identified as pyrite by XRD. No evidence of

framboidal pyrite was found.

Investigations by XRD/thin section/SEM reveal that the rock is composed of quartz,

muscovite/illite, pyrite and siderite with accessory apatite. EDX analysis of the μm-sized flakes

of clay minerals show that they contain Mg but negligible Fe, confirming that the Fe in these

rocks is contained within siderite and pyrite. Particle size curves (Figure 2) show a median grain

size just under a mm, and that particle sizes were not affected by the column experiments. Post-

run SEM results showed that significant bulk changes did not occur on the 2 to 3 month

timescale of the runs. However, only a very small fraction of the reacted material could be

examined by SEM so quantification of changes in secondary mineral modes was not possible by

this method. In addition, phases not observed were not necessarily absent. The S content of the

post-run sample is slightly higher than that obtained from pre-run analysis. This is attributed to

incomplete homogenization of the samples for elements occurring in dense, low abundance

minerals such as pyrite. Sulfur mineral speciation investigations (Table 1) show that pyrite-hosted S forms over 60% of the total, and that the proportion of water soluble SO_4^{2-} decreases from 14% to <2% during the experiment.

3.2. Column Hydrology

Columns exhibited unsaturated flow at a hydrological steady state over the entire experimental period, with the exception of a few hours (<6) subsequent to each flow rate change. The 12.5 cm column (YM) ran close to hydrological saturation (90%), while final water content measurements show that the 50cm column (2YM) ran at 60-70% of hydrological saturation. The hydrological saturation is the percentage of pores that are filled with mobile or immobile water. Comparison of input and output volumes showed that water content did not change as a function of flow rate. This suggests that the mobile/immobile water mass ratio changed in response to changes in flow velocity, rather than the saturation state.

Tracer concentrations (Figures 5 and 6) rose rapidly to a peak (<30 h, 12.5 cm column, ~120 h, 50 cm column) then declined slowly, with zero concentrations of Br reached after > 150 h for the 12.5 cm column, and > 400 h for the 50 cm column. The asymmetric Br^- tracer peak and the gradual decline of tracer concentrations indicate that solute exchange between mobile and immobile water retarded the tracer. Spreading of the Br^- tracer peak by dispersion alone would have resulted in symmetrical tracer peaks, rather than the long-tailed asymmetric peaks that were observed. This conclusion is supported by advection-dispersion models using porosity and dispersion coefficient values obtained from temporal moment analysis (Eriksson *et al*, 1997). Results of such models demonstrate that asymmetric peaks, such as those seen in Figures 5 and 6 are a result of solute exchange between mobile and immobile water .

This interpretation is also supported by the ability of dual porosity advective-dispersive computer codes that consider mass transfer between immobile and mobile water to successfully replicate tracer breakthrough results from similar column experiments in this series (Banwart *et al*. 2004). In those model simulations, observed asymmetric Br profiles could not be reproduced unless immobile water was included in the model. Spikes in the concentration of cations other than Na (Figures 5C, F), and retardation of Na relative to Br (Figures 5A,B and 6A,B) suggest that clays in the column acted as ion-exchangers. Rapid reattainment of steady state concentrations for these cations suggest that equilibrium with the ion exchange surfaces was achieved within 10-20 hours. After 400 h Br contents from the tracer test for the long column (2YM) were still significant and the test had to be curtailed before mass recovery of the tracer was complete, invalidating the use of temporal moment analysis. Temporal moment analysis of results from the shorter column suggested a residence time of 45 h. The calculated mobile water contents were higher than the measured porosity. This suggests that exchange of solutes between mobile and immobile water was significant.

3.3 Column Element Release Characteristics

Full results are given in Appendix 1; selected results are shown and discussed here. Figure 7 shows plots of concentration and pH against time for the selected elements eluting from the 50cm column (2YM). All elements exhibit an early high concentration flush (Figures 7A-F) in the first few days of the experiment, followed by an approach to a quasi-steady state. Results from the preliminary flushing period (times up to 28 days) record dissolution and removal of rapidly soluble mineral salts, attainment of ion-exchange equilibria with mineral surfaces and the rapid dissolution of very fine-grained particles produced during the crushing process. These

results are omitted from subsequent figures and are not considered further. Dissolved O_2 (DO, Figure 7G) and pH (Figure 7H) are also affected by the preliminary flushing. pH values are initially low but rise to an approximate steady state after ~30 days. DO values are also initially low, rise to around 1.5 % and then decrease to close to zero over the remainder of the experiment.. Low effluent O_2 levels suggest that O_2 consumption was significant and that columns were acting as partially closed systems with respect to gases. The implications of this for results are discussed below. Changing concentrations with time at constant flow rate indicate that true steady state was not strictly reached on the 80 day timescale of the test. However, concentrations fall exponentially towards a steady state; small changes after 1 month suggest that constant concentrations were approached sufficiently closely to allow interpretation at steady-state. Increases in the concentrations of Si, Ca and Mg when flow rate is decreased demonstrate that the signal of the early flushing is negligible during the latter part of the experiment.

Figure 8 shows concentration versus flow rate for the parameters shown in Figure 7. Al (Figure 8A) and Si (Figure 8B) concentrations, and pH (Figure 8H), are independent of flow rate, while Mg (Figure 8C), Ca (Figure 8D), K (Figure 8E) and Fe (Figure 8F), exhibit a negative correlation. All correlations were tested statistically and are significant at the 90% level or better. Oxygen saturation (Figure 8G) exhibits a weak positive correlation which is not statistically significant. The working assumption of steady state is supported by the clustered concentrations observed at a flow rate of 0.1 mL min^{-1} flow, which correspond to sets of samples taken at 2 different periods during the experiment (30-50 days and 75-80 days). Under these circumstances changes in element concentrations caused by variations in influent flow rate are larger than those caused by any possible remnants of the preliminary flushing, and useful information on rate-controlling processes can be inferred. Element fluxes, which record the

total rate of mass removal from the column for each element were then calculated from the product of concentration and flow rate for each data point. Figure 9 shows comparisons between the long and short columns for Si and Mg, two elements which behave differently. Dissolved Si concentrations and fluxes are almost independent of column length (Figures 9C and D), while those for Mg (Figures 9A and B) are approximately 4 times higher for the longer column. Both Si and Mg fluxes show a positive correlation with flow rate, this aspect is important, and is discussed further below.

Relationships between concentration, flow rate and element flux can be split into a small number of different types. The characteristics of these types are described here. These characteristics can be used to infer the process which controls dissolution rates, as discussed below.

Type 1 characteristics are shown by Si. Concentrations are essentially constant once the first flush is completed (time > 10 days, Figure 7B) and are independent of flow rate (Figure 8B) and show a weak dependence on column length (Figure 9C). Fluxes (Figure 9D) also show a correlation with flow rate, which is significant at the 90% level. Aluminium (Figures 7A and 8A) also shows characteristics of this type but concentrations were often close to, or below, the lower detection limit of the ICP-AES.

Type 2 characteristics are shown by K. Concentrations show a negative correlation with flow rate (Figure 8E), longer columns elute higher concentrations (not shown), and there is a positive correlation between element flux and flow rate. Element concentrations are relatively unaffected by input of NaBr (Figures 5E,6E).

Type 3 characteristics are shown by Mg. Concentrations show a negative correlation with flow rate (Figure 8C) and longer columns elute higher concentrations (Figure 9A). Input of

NaBr during tracer tests causes a spike in output Mg concentrations (Figure 5F), and element fluxes show a positive correlation with flow rate (Figure 9B). Calcium (Figures 5C, 7D and 8D) also shows characteristics of this type.

Type 4 characteristics are shown by Fe (Figures 7F, 8F). This is identical to that shown by K, except for a lack of any significant relationship between element flux and flow rate.

Average element fluxes and standard deviations, normalized to the measured BET surface area, are shown in Table 3 for elements showing the characteristics of types 2, 3 and 4 (Table 3). Fluxes for type 1 are not tabulated because they are not controlled by kinetic factors, see discussion below. Average values were used because the variability between flow rates was low in comparison to overall variation in solute fluxes. Surface area-normalised release rates obtained from column experiments with material of the same lithology were reproducible to within 20%.

3.4. Batch Results

Results from batch experiments on the mudstone are shown in Figure 10. Results shown are for the raw results; that is, the concentrations are not corrected for dilution by replacement of sample volumes or for the small evaporative losses which were compensated for weekly over the course of the experiment. These plots reflect the actual changes in concentration rather than plots of the corrected concentrations that are used to draw conclusions on rates of element release from dissolving mineral phases. Trends and determined element release characteristics for corrected and uncorrected data are identical although absolute values of concentrations and calculated release rates differ. As for the columns, there are distinct types of element release patterns which can be used to infer the rate-controlling step for dissolution.

Type 5 characteristics are shown by the bulk of elements from this experiment. An approximately linear increase in concentration with time is observed. More detailed observation reveals an initial period of rapid release followed by a decrease in rate. Examples of these characteristics are shown in Figures 10A-D.

Type 6 results show an initial rise in concentration followed by either a plateau, or a drop followed by a plateau; e.g. Fe, shown in Figure 10F.

Neither of the patterns are systematically affected by the fluctuation in pH ($4 < $ pH $ < 6$: Figure 10H). Potassium and Mn (Figs 10E and G, respectively) show a decrease in release rate as the experiment progresses, but the data still fit a straight line with a positive slope and so these elements are judged to show type 5 characteristics.

Average element fluxes and standard deviations were calculated from the slope and slope uncertainty, respectively, of corrected concentration vs. time plots, and were then normalized to unit surface area (Table 3). Rates were not calculated for Fe because the constant concentrations are interpreted to record chemical equilibrium between the solution and Fe-bearing minerals, as discussed below.

3.5. Batch/Column Ratios

Ratios between element release fluxes for the batch/column experiments were also calculated and are shown in Table 3. These results are independent of assumptions regarding the mineral hosts for the elements, and, because of the identical sample preparation methods for the two experiments, reflect only the different processes acting within the two types of reactors. Magnesium, Mn, Ca and S show remarkably similar ratios, between 3 and 4. These ratios are

consistently outside the error bars calculated for the different experiments, and this, and the

similarity between them, suggest that they record a real difference between the two experimental

setups. The similar ratios for elements hosted by very different minerals suggests that the factor

causing the difference is independent of the individual mineral surfaces or the stoichiometry of

mineral dissolution reactions. This independence indicates, for example, that rate differences are

not caused by stirring-induced high surface areas in the batch experiments, as such abrasion

would affect different minerals to different extents. This view is supported by the results of

visual inspection of the post-run material, which do not reveal any large change in particle size.

The batch/column ratio for K is much higher, at 73, suggesting that a difference in rate-

controlling factors in addition to that/those observed for the other elements was in operation.

The magnitude of the difference for all elements is consistent with results from previous workers

(e.g. Stromberg and Banwart, 1999b)

4. DISCUSSION

4.1. Rate-Controlling Step

The different types of element release shown by batch and column experiments can be used to

make inferences about rate-controlling mechanisms for the release of the elements. To make this

inference it is necessary to consider the characteristics of potential controls on element release in

column and batch environments.

4.2. Equilibrium Dissolution (Types 1 and 6)

The dissolution of minerals can increase the concentration of solutes such that the solution may approach chemical saturation with respect to primary (parent) or secondary minerals which incorporate the elements considered. This type of dissolution, described here as equilibrium dissolution, is facilitated by low water: rock ratios, low mineral solubilities, high dissolution rates, and, in the case of the column experiments, by low flow rates. The characteristics of equilibrium dissolution are that element concentrations reach a constant value, and, in the case of the columns, that the overall rate of element mass removal (flux) from the reacting column is controlled by eluent flow rate.   Element concentrations in column effluents would therefore be independent of flow rate (e.g. Figure 8A, time>20 days, Figure 8B, time>30 days) and, in the batch experiments, concentrations would become independent of time once saturation was reached (Type 6: e.g. Figure 10F, time>10 days). Element fluxes for types 1 and 6 are not recorded because the rate information they provide is system dependent.

4.3. Transport-controlled Dissolution (Type 2).

If the rate at which a dissolved element is released from a mineral surface is faster than the rate at which the element can be transferred to the bulk solution, then a zone develops adjacent to the mineral surfaces in which solute concentrations are higher than those found in the bulk solution. If solute concentrations in this zone increase sufficiently to inhibit dissolution rates then the overall mineral dissolution rate is controlled by the transfer of dissolved elements away from the mineral surface, i.e. dissolution is transport-controlled. Under undersaturated flow conditions such a zone may be created by slow transfer of elements between the immobile water held by surface tension forces close to mineral surfaces and the mobile water which moves through larger pores, or by slow diffusion through partially reacted mineral layers at the grain surface

(e.g. Schnoor, 1990). Both types of transport-controlled dissolution are more likely to occur in a column environment than a batch experiment, because rapid stirring and particle-particle contact in the batch experiments minimizes the volume of immobile water at the grain surface and reduces the probability of a build-up of partially reacted layers. The characteristics of transport-controlled dissolution are: a negative correlation between flow rate and element concentration; a positive correlation between flow rate and element flux; and a proportionality between element concentrations and column length. The latter occurs because element fluxes are proportional to the total area of the mass transfer surface, whether this is the mobile-immobile water interface or the surfaces of the partially-reacted mineral grains. These are the characteristics of type 2 dissolution.

The characteristic diffusive lengths of each process can be used to distinguish between the two types of transport-controlled dissolution outlined above. Lengths for mobile-immobile transfer are expected to be on a sub-mm to mm scale, while those for intraparticle diffusion in relatively fresh grains would be significantly smaller (μm to sub-mm). Preliminary information on diffusive lengths is obtained by considering the relationship between element release rate, concentration and flow rate. Fick's first law, Eqn. 1, describes steady state diffusive release.

$$F = D_l \frac{(C_{im} - C_m)}{\Delta y} \qquad (1)$$

F is the flux of element per unit area of the mobile/immobile water interface ($ML^{-2}T^{-1}$), D_l is the effective diffusion coefficient (L^2T^{-1}), C_{im} and C_m are concentrations of the element considered at either side of the diffusive barrier (ML^{-3}), and Δy (L) is the diffusive path length. Eqn. 2 relates element flux per reacting unit area to measured concentrations in the bulk fluid, and to flow rate;.

$$F = \frac{C_m f}{A} \qquad (2)$$

where f is the flow rate (m^3 min^{-1}) and A is the total area of the transfer interface active for the mineral of interest (L^2). Combining Eqns. 1 and 2 and rearranging gives

$$\Delta y = D_l A \frac{(C_{im} - C_m)}{C_m f} \qquad (3),$$

which Δy to be estimated. D_l varies widely in unsaturated soils (e.g. Lim *et al.*, 1998, Mehta *et al.*, 1995) and a range for D_l of 10^{-7} to 10^{-11} m^2 s^{-1} is considered here. A varies with mineral mode as well as with mineral surface area so a range of 0.1 to 100 m^2 was considered, based on the observed range of specific surface area and reacting rock mass. For typical C_{im} and C_m values of 50 and 20 mg L^{-1} respectively, and a flow rate of 0.1 mL min^{-1}, the diffusion length calculated from the column experiments lies somewhere between a maximum of 10^4 m and a minimum of 10^{-3} m. The uppermost of these values is physically unreasonable but the lower value puts a lower limit on the length scale of the diffusion might be expected to produce the observed results. This is consistent with mm-scale mobile-immobile transfer associated with low diffusion coefficients and small mobile-immobile interfacial areas, rather than with sub-mm to µm scale intraparticle diffusion. Further support for this conclusion is provided by:

- the fact that transport control affects all elements equally; if intraparticle diffusion were operating some dependence of release characteristics on mineralogy would be expected;

- extended times required to achieve chemical steady-state after flow rate changes. These are several times higher than the time required to attain hydrological steady-state or equilibrium with ion-exchangers. This suggests that a mass transfer step slower than either simple advective transport or readjustment of mineral surface speciation to changes in the ambient fluid composition is involved in the approach to chemical steady state.

- the sensitivity of element flux to flow rate changes. This would be expected to be relatively minor for intraparticle diffusion because changes in flow rate could not directly affect particles behind the partially reacted layer. In contrast, changes in flow rate which alter the proportion of mobile to immobile water would affect element release controlled by exchange between these 2 reservoirs. Under these circumstances, an increase in flow rate would lead to an increased fraction of mobile water. This change affects the transfer between the two reservoirs of solution (mobile and immobile) via the changed area of the interface between the two solutions. Increased flow rate would result in increased element flux, as seen, as diffusion from the immobile zones becomes more effective, but with a possible decrease in concentration, as solutions become more dilute.

Transport-controlled dissolution is more likely to dominate in hydrologically unsaturated conditions than for hydrologically saturated. This is because diffusion coefficients and the area of the mobile-immobile water interface are likely to be much higher in saturated materials, and increases in both factors enhance the efficiency of transport. Diffusion coefficients in unsaturated systems decrease by up to several orders of magnitude due to the increased tortuosity of a partially connected water network, the electrostatic effects of charged mineral surfaces, and the effects of air bubbles (Mehta *et al*., 1995, Olesen *et al*., 2001). Additionally, the area of the mobile-immobile interface in an unsaturated system is likely to be small compared to the area of the reacting mineral surface-immobile water interface. It is probable that decreases in diffusion rates were relatively minor at the column water-saturation levels of 60-90%, but a reduced mobile-immobile interfacial could have led to a substantial reduction in diffusive transfer rates. The proposal that mobile-immobile transfer controlled dissolution rates is also supported by the

calculations of diffusion length, which show that element release rates are consistent with a diffusive transport mechanism.

4.4. Ion-exchange influences (Type 3).

The presence of clay minerals within a mudstone provide it with an ion exchange capacity. Ion exchange between clay mineral surfaces and adjacent fluids exerts an influence on the composition of the fluid. Additional complexity is introduced by the possibility that the composition of ion exchange assemblages may vary down the length of the column. This will occur if ratios of exchanging ions vary in response to the attainment of chemical equilibrium for certain elements. The influence of ion exchangers on fluid composition is temporary because the solutions are unaffected once ion-exchange equilibrium has been reached. The influence of cation exchange on column effluents is recognized using the tracer test characteristics. In cases where the tracer elicits a spike in elements other than Na and Br, those elements are judged to have been displaced from ion exchange sites (e.g. Figures 5C,5F). Tracer plots indicate that this influence is of relatively short duration (10s of hours), so most of the results should be unaffected by this process, and it should be possible to recognize underlying rate-control mechanisms.

4.5. Surface-kinetic controlled dissolution (Type 5).

Mineral dissolution, according to transition state theory, (e.g. Furrer and Stumm, 1986; Lasaga, 1995), requires that unstable activated complexes form at the mineral surface, and subsequently

decompose, transferring metal ions to the surrounding solution. If this is the slowest part of the overall process leading to element removal from the column then a constant flux away from the mineral surface would be expected, so long as other rate-determining parameters such as ambient pH, redox and the concentrations of potentially dissolution-inhibiting elements remain constant. Such a constant flux would lead to a negative correlation between flow rate and the concentration of dissolution reaction products. A constant flux would not be expected if values of rate-controlling parameters such as pH or O_2 concentration varied significantly as a result of flow rate changes. This is because dissolution rate changes as a result of the changes in pH or D.O. would lead to changes in element fluxes even when dissolution is surface-controlled. In this case, increases or decreases in surface reaction rates could occur, depending on the parameter affected. If flux increased with flow rate then it would be very difficult to distinguish between surface- and transport-control of dissolution rates, so it is necessary to consider the relative magnitude of such effects.

pH and O_2 concentrations are the principal parameters capable of affecting mineral dissolution rates. Variations in pH are minor (0.4 pH units for 2YM) and could not have caused the observed variation in dissolution rate. Variations in O_2 content in the short column, on the other hand, were significant (30 – 50 % saturation over the course of the experiment), and may have been large enough to influence dissolution rates. The data suggest that this is unlikely for two reasons. First, if O_2 depletion were an important control on dissolution rates of minerals such as pyrite (c.f. Williamson and Rimstidt, 1994), then the longer column, which experienced greater O_2 depletion, would produce solutions with a higher pH. This was not the case. Second, following similar logic, a negative correlation between pH and DO would be expected for the shorter column. Again, this was not the case. This evidence is supported by calculations on the

potential effects of O_2 depletion which were performed using the algorithm presented in Malmstrom *et al*. (2000). These calculations showed that the observed O_2 depletion could not have affected dissolution rates by more than a factor of two. Thus it is improbable that oxygen depletion in the columns could have led to anything other than a constant flux for surface-kinetic controlled mineral dissolution. This type of behaviour was not observed.

Surface-kinetic control in the batch experiments would be expected to manifest as a linear increase in concentration with time (e.g. Figures 10A-E and 10G). This is characteristic of release type 6.

4.6. Classification

The criteria developed above were incorporated into a sequence of statistical tests which were used to classify element release patterns for batch and column experiments into the different types of element release described above (Table 3). The hypothesis that any given data lay on a straight line was tested by calculation of the probability associated with the value of chi-squared for the fit. Cases in which rate-controlling mechanisms may have varied because of down-column variations in rate-determining solutes such as protons and dissolved O_2, were avoided by the exclusion of element release patterns that exhibited non-linear relationships between flow rate and concentration. Independent checks on diagnoses of equilibrium dissolution were made by calculation of saturation indices (Table 4) for primary and secondary minerals using PhreeqC for Windows, v1.0 (Parkhurst and Appelo, 1999) and the Wateq4f database (Ball and Nordstrom, 1991). The saturation index is the base 10 logarithm, of the observed Ion Activity Product of the stoichiometric mineral dissolution reaction of interest divided by the conditional thermodynamic

constant for the corresponding stoichiometric reaction for mineral solubility. A positive saturation index indicates that the solution is supersaturated with respect to the mineral phases, a negative value, that the solution is undersaturated, and a value near zero suggests that saturation is reached, and that apparent equilibrium between the mineral of interest and the aqueous solution is maintained. Saturation indices (Table 4) close to zero are calculated for minerals that contain elements inferred to be controlled by mineral equilibrium (Table 3).

The rate-controlling mechanism of chemical weathering is linked in a predictable way to mineralogical composition (Table 3). The mudstone is clay-rich and so shows element release affected by ion exchange for several elements (Mg, Mn, Ca, Na, K). The relatively low pH, which is caused by the dissolution of pyrite, inhibits solubility equilibrium with secondary oxide and hydroxide minerals; this allows signatures for element release due to irreversible dissolution of parent minerals to be observed more clearly. Several elements show a positive correlation between flow rate and element flux; this is indicative of transport control which is attributed to slow rates of immobile-mobile solute mass transfer. Batch experiments exhibit surface-controlled kinetic release for a number of elements. Kinetic controls in batch experiments are favored by a combination of the high water: rock ratios, which prevent solution saturation with respect to primary or secondary minerals, and the stirring, which accelerates mass transfer processes and prevents transport-kinetic control of dissolution reactions.

4.7. Implications of Rate-Control Differences

It is proposed that the reason for the method-dependent (column vs. batch reactor experiments) differences between element fluxes from identical materials, prepared in an identical way, (Table 3), is the difference in rate-controlling mechanism. Element release is largely controlled by

mobile-immobile transfer in the columns, but by surface-kinetic control in the batch experiments. If mobile-immobile transfer is the rate-controlling step then the combination of physical transport and chemical kinetic control, and the potential for switching between the two with changing water: rock ratio and associated changes in hydraulic saturation, has important implications for interpretation of field weathering rates studies and comparisons between rates in laboratory and field systems. The results suggest that hydrological characterization is as important as chemical characterization in the understanding of unsaturated zone chemical weathering processes. They also suggest that substantial reservoirs of concentrated solutions could exist as immobile water in the unsaturated zone which could be released if material were disturbed or if water flow paths changed. This point is particularly pertinent to the treatment of mining waste material, because concentrated immobile solutions in these cases could be highly toxic. Strictly speaking, the results can only be applied to field situations with similar grain size and hydrological parameters to those found in the columns, i.e. mm grain size, loosely compacted sediments close to water saturation. This type of environment can be found on many mine waste and drained tailings deposits, and within poorly sorted soil profiles. The full range of depth for which the results are relevant cannot be specified because only a limited range of water contents was examined, but it may extend across a significant proportion of the unsaturated zone. The probability of diffusion control by mobile-immobile transfer is likely to decrease as the saturated zone is approached, because diffusion coefficients for all solute species increase with increasing water content.

5. CONCLUSIONS

Results show that the unsaturated column apparatus described here can be used to assess the systematics of chemical weathering and to measure rates of element release for unsaturated flow conditions similar to those found in natural weathering environments. Relationships between effluent concentration, flow rate and element fluxes, in the case of column experiments, and between concentration and time, in the case of batch experiments, allow the processes that control the release of elements to be identified in the majority of cases. Solubility and ion-exchange equilibria, surface-controlled kinetics and transport controlled kinetics could all be distinguished in this way. Results can be classified in this way if relatively steady conditions have developed and if the data reflects the dominant processes and rate controls. Dominant processes are determined to some extent by the system observed; batch experiments favor surface-controlled kinetic release, while column experiments create conditions under which mobile-immobile transport control of element release can become significant.

Column experiments produced element fluxes for Mg, Mn, Ca and S which were consistently a factor of 3-4 less than batch experiments. This is a significant difference given the similar scale of observation and identical mineral preparation for the two types of experiment and is attributed to rate control by diffusion between mobile and immobile water. The differences between laboratory and much larger field systems may be considerably greater. This observation has important implications for field scale weathering studies; prediction of weathering rates in unsaturated materials may be controlled by complex interactions between the hydrological properties and surface chemical characteristics of the material. Thus studies that ascribe rate control a priori to one or the other sets of parameters at any given field site may fail to recognise features produced by interactions between hydrological and chemical factors.

Further work is needed to identify field conditions that correspond to situations where hydrologic and chemical controls, respectively, determine weathering rates.

Appendix 1

Results of the column, batch and tracer experiments are shown in Tables A1 to A4.

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Figure Captions.

Figure 1. Location of the field site.

Figure 2. Particle grainsize curves for pre and post-run material. No change in grainsize is observed as a result of the experiment.

Figure 3. Schematic diagram showing the experimental apparatus.

Figure 4. Variation of water saturation with height in the columns. Increase close to top probably related to the presence of the saturated sinter.

Figure 5. Tracer results from YM (12.5 cm column). A. Na; B: Br; C: Ca; D: SO_4^{2-}; E: K; F: Mg. Peaks for ions other than Na and Br record ion exchange.

Figure 6. Tracer results from 2YM (50cm column). Delayed peak for Na records cation exchange. A. Na; B: Br; C: Ca; D: SO_4^{2-}; E: K; F: Mg. The long tail at the right hand side of the Br peak (B) records mobile-immobile water exchange.

Figure 7. Plots of concentration against time for elements eluting from column 2YM. Early high values record flushing of water soluble reaction products. Vertical lines indicate times of flow rate changes, value of flow rates, in mL min^{-1}, are shown at the top of Figure 7A.

Figure 8. Plots of concentration against flow rate for elements eluting from column 2YM. Constant concentration indicates dissolution at or close to mineral equilibrium. Negative correlations indicate that kinetic factors controlled dissolution.

Figure 9. Comparing concentrations and element fluxes from the long and short columns for Mg (A and B) and Si (C and D). Mg shows an approximate factor of 4 difference between concentration and flux for the two columns while Si shows concentrations and fluxes that show a much weaker correlation with column length.

Figure 10. Concentrations from the batch experiments, uncorrected for sampling and

evaporation. Corrected plots show identical trends.

Tables

Table 1. Results of sample characterization.

Major elements (wt %)	*YM*	*YM post run*
SiO_2	44.89	44.25
TiO_2	0.85	0.87
Al_2O_3	22.17	22.13
Fe_2O_3	4.61	5.00
MnO	0.11	0..08
MgO	0.95	0.84
CaO	0.43	0.36
Na_2O	0.47	0.39
K_2O	3.65	3.49
P_2O_5	0.29	0.3
SO_3	<0.1	<0.01
Cr_2O_3	0.02	
SrO	0.02	
ZrO_2	0.02	
BaO	0.08	
NiO	0.01	
CuO	0.01	
ZnO	<0.01	
PbO	<0.01	
LOI	21.05	
Total	99.63	
Trace Elements (ppm)		
Ni	52	
Cu	125	
Zn	62	
As	13	
Sr	nd	
Ba	nd	
Pb	36	
WSS (% S_{tot})	24	14
ASS (% S_{tot})	20	2
Pyrite (% S_{tot})	56	84
Total S (wt %)	0.18	0.48
BET ($m^2 g^{-1}$)	1.05	1.37
Geometric S.A. ($m^2 g^{-1}$)	1.89×10^{-3}	

WSS: Water soluble sulphur; ASS: Acid soluble sulphur.

Table 2. Details of column experiment

Date	Day	Action
25/01/2001	1	Start experiment at 0.15 mL min^{-1}
29/01/2001	5	Begin sampling
1/02/2001	8	Change to 0.1 mL min^{-1}
3/02/2001	10	Change to 0.05 mL min^{-1}
5/02/2001	12	Soil water retention curve
7/02/2001	14	Return to 0.05 mL min^{-1}
9/02/2001	16	Change to 0.15 mL min^{-1}
13/02/2001	20	Begin tracer test
23/02/2001	30	Complete tracer test, change to 0.1 mL min^{-1}
16/03/2001	51	Change to 0.05 mL min^{-1}
10/04/2001	76	Change to 0.1 mL min^{-1}
12/04/2001	78	Dismantle columns

Column prefix	**YM**	**2YM**
Column length (cm)	12.5	50
Column volume (cm^3)	981	3925
Mass of rock (g)	1508	6331
Water filled porosity (wt%)	18	15
Total porosity (wt%)	20	24
Tracer test prefix	**YMT**	**2YMT**
Recovery (M/M$_o$) %	89	<50
Average residence time (hrs)	45.3	165

Table 3 Element fluxes from batch and column experiments

	moles m^{-2} s^{-1} x 10^{13}		Column RC	moles m^{-2} s^{-1} x 10^{13}	Batch RC	Batch/Column Ratio
	YM	2YM				
Si			E	13.6 +/- 1.1	S	
Al			E		X	
Fe	0.133 +/- 0.297	0.435 +/- 0.128	X		E	
Mg	1.581 +/- 0.351	2.38 +/- 1.13	I,T	6.8 +/- 0.8	S	3.4
Mn	0.41 +/- 0.09	0.57 +/- 0.03	I,T	2.1 +/- 0.2	S	4.3
Ca	1.39 +/- 0.3	2.26 +/- 1.14	I,T	7.6 +/- 1.7	S	4.2
Na	1.83 +/- 1.32	0.48 +/- 0.19	I,T			
K	1.38 +/- 0.374	0.702 +/- 0.277	I	76.1 +/- 9.2	S	73
S	5.67 +/- 1.43	7.31 +/- 3.2	T	20.2 +/- 3.2	S	3.1
pH	4	5.6		4.6-5		

Abbreviations: RC: rate controlling mechanism; E: equilibrium; X: indeterminate; I: ion exchange; T: transport; S: surface kinetic. Fluxes from batch experiment are corrected for sampling and dilution. Uncertainties are combination of $\pm$ 1 s.d. on the group of measurements (n=25) propagated uncertainty in BET surface area.

Table 4. Saturation indices for observed primary and potential secondary minerals in batch and column experiments.

	YM	2YM
Albite	-11.3	-5.3
Illite	-12.3	-1.2
Kaolinite	-4.7	3.0
Montmorillonite	-9.7	0.2
Pyrite	-80	-4.5
Quartz	-0.4	-0.1
Alunite	-2.7[1]	4.5
Fe(OH)3	-4.8	-5.1
Gibbsite	-5	-1.5
Gypsum	-1.8	-0.8
Jarosite	-12.4	-16.9
Calcite	-5[2]	-2.8
Dolomite	-9[2]	-5.5
Siderite	-5[2]	-1.0

[1] Decreased over the course of the experiment
[2.] Average of first 3 weeks. After this alkalinity declined below zero and the concentration of carbonate could not be measured.

Table A1. Column results for 12.5 cm column (YM)

						ICP-AES Results (mg L^{-1})								
Day	Flow rate (mL min^{-1})	Flowcell pH	Redox (mV)	DO (% Sat)	Alk (mg l^{-1})	Al	Ca	Fe	K	Mg	Mn	Na	S	Si
4		4.3	180	16		10.7	322.2	54.8	111.8		139.6	35.8	1117.3	12.2
5	0.15	4.5	166	11		0.7	86.3	16.6	92.2	70.8	27.6	8.9	237.3	5.0
6	0.17	4.5	166	7		0.2	48.6	11.9	65.9	39.4	15.4	5.5	134.7	3.8
7	0.16	4.7	151	5		0.1	36.8	11.1	51.7	30.4	11.8	3.9	103.4	3.3
8	0.12	4.7	146	4		0.1	36.1	12.0	50.3	30.0	11.8	3.1	102.8	3.0
11	0.06	4.9	110	3	7	0.1	42.2	15.9	55.3	34.0	13.7	3.5	118.4	3.0
13		4.6	229	15										
14	0.11	4.1	337	22	10	0.1	30.1	2.6	49.6	23.8	10.1	2.1	79.3	3.1
15		3.9	356	13		0.3	51.0	0.8	41.8	38.5	16.9	3.5	129.9	3.7
18	0.17	4.5	269	2		0.1	29.2	0.7	17.6	22.3	9.9	1.8	75.1	2.2
33	0.11	5.5	17	b.d.	12.4	b.d.	23.1	10.7	19.2	15.5	8.7	33.7	86.5	2.4
34	0.11	5.6	24	b.d.	14	b.d.	19.3	7.7	19.5	13.1	7.3	31.1	74.6	2.4
35	0.10	5.4	56	1	14	b.d.	17.8	5.5	19.3	12.0	6.8	29.2	69.5	2.4
36					12	b.d.	14.7	4.2	18.1	9.9	5.7	25.9	58.5	2.7
40		4.3	440	39	5	b.d.	27.5	0.3	21.0	19.4	11.4	8.1	80.6	2.1
41						0.1	13.8	0.1	18.7	9.6	5.5	22.6	54.4	2.6
42	0.12	4.4	390	42	10	0.1	14.2	0.0	18.8	9.9	5.8	18.6	53.3	2.4
43	0.11	4.4	420	44	6	0.1	15.5	0.0	18.4	10.8	6.4	18.2	55.5	2.3
46	0.11	4.7	410	54	6	0.1	16.3	0.0	17.8	11.4	6.7	16.5	56.8	2.2
47	0.11	4.5	420	51	4	0.1	16.3	0.0	18.0	11.4	6.8	14.8	56.1	2.1
48	0.11	4.4	380	41		0.2	16.6	20.9	18.5	11.6	7.0	14.4	55.4	2.3
49	0.11	4.5	420	40		0.1	17.9	8.6	18.9	12.3	7.4	13.9	58.0	2.3
50	0.11	4.5	380	36		0.1	18.3	4.0	18.5	12.8	7.7	13.3	59.5	2.2
53	0.06	4.1	400	36		0.1	20.9	2.8	23.2	14.6	8.9	12.8	64.7	2.2
54	0.06	4.1	380	37		0.1	23.6	2.2	23.7	16.5	10.1	12.6	72.6	2.4
55	0.06	4.1	410	36		0.1	24.7	0.2	24.3	16.6	9.6	12.4	76.3	2.2
56	0.06	4.0	290	38		0.1	24.2	0.4	22.9	16.2	9.4	11.8	72.6	2.1
57	0.06	4.0	410	36		0.1	25.2	0.1	23.1	17.0	9.8	11.9	76.8	2.2
60	0.06	3.9	360	37		0.1	26.1	0.2	22.6	17.8	10.4	11.6	79.9	2.2
61	0.06	3.9	420	38		0.1	27.8	0.2	22.3	18.7	10.9	11.3	81.8	2.2
62	0.06	3.9	360	34		0.1	27.5	0.2	22.3	18.7	10.9	10.9	81.4	2.1
63	0.06	3.9	420	32		0.1	27.1	0.1	22.6	18.8	10.9	10.7	81.0	2.1
64	0.06	4.0	360	34		0.1	27.0	b.d.	21.0	18.7	10.9	10.2	79.8	2.2
67	0.06	3.9	430	36		0.1	28.6	b.d.	21.9	19.9	11.6	9.9	84.8	2.2
68	0.06	3.9	370	35		0.1	26.9	b.d.	22.1	18.9	11.0	8.8	80.4	2.2
69	0.06	3.9	420	35		0.1	27.6	b.d.	21.6	19.4	11.4	8.8	82.2	2.2
70	0.05	3.9	380	37		b.d.	28.1	b.d.	20.3	19.6	11.5	8.3	81.6	2.2
74	0.06	3.9	390	33		b.d.	24.3	b.d.	17.2	17.5	10.1	6.4	74.0	2.0

ICP-AES: Inductively Coupled Plasma Atomic Emission Spectrometry; IC: Ion Chromatography. No data indicates no analysis. Alk: Alkalinity

Table A2: Results for 50 cm column (2YM)

					ICP-AES Results in mg L^{-1}								
Day	Flow rate (mL min^{-1})	Flowcell pH	Redox (mV)	Alk (mg l^{-1})	DO (% Sat)	Al	Ca	Fe	K	Mg	Mn	Na	S	Si
4		3.9	240		80									
5		4.0	251		48	22.2	444.6	79.8	128.1		285.4	75.3	2058.3	20.6
6	0.17	4.2	247		29	14.4	425.4	70.8	118.6		253.5	64.0	1858.9	16.7
7	0.16	4.3	237	14	22	9.0	428.8	77.2	103.8		216.9	53.9	1639.7	14.1
8	0.12	4.3	242	12	17	5.0	400.3	87.7	109.5		184.8	45.8	1430.2	11.7
11	0.07	3.8	310	<0	b.d.	1.7	335.5	87.3	122.3		137.0	31.8	1090.9	8.7
12	0.05	3.7	320	<0	b.d.	1.7	346.8	96.1	136.2		134.6	28.6	1073.0	8.2
13	0.06	3.8	300		b.d.	1.3	332.3	92.7	117.5		121.0	25.1	996.1	7.8
14	0.06	4.0	286		b.d.	0.5	291.2	81.6	101.8		98.7	20.2	832.0	7.0
15		4.2	264		b.d.	0.2	274.7	71.9	103.0		88.8	19.3	754.6	6.5
18	0.16	5.3	139	11	1	0.1	166.1	24.1	40.5		48.6	10.9	412.0	5.0
19	0.17	5.3	117	10	1	0.1	152.4	24.5	37.0	95.7	48.8	10.6	375.1	5.4
20	0.17	5.4	100	17	1	0.1	136.4	20.5	35.7	84.8	43.2	9.5	331.4	5.1
22	0.18	5.5	59	11	1	0.1	116.3	16.7	32.4	72.9	37.6	7.9	281.7	4.6
23	0.17	5.5	44	14	1									
26	0.16	5.6	42	22	1	0.1	101.1	14.1	29.5	61.3	32.6	6.3	237.9	4.3
27	0.17	5.6	39	20	1	0.1	92.4	11.7	26.8	56.2	30.4	5.6	217.4	4.0
28	0.17	5.6	34	20	1	0.1	91.0	9.0	27.7	55.1	30.1	5.4	210.6	3.9
29	0.17	5.6	29	19	1	0.1	89.6	9.4	27.9	55.3	29.8	5.1	211.9	3.9
42		5.6	-20		1	b.d.	102.3	44.7	35.0	71.6	37.9	21.6	310.8	3.9
50		5.6	-40		b.d.	0.1	104.7	32.9	33.4	68.4	39.9	14.8	274.5	3.9
53	0.13	5.7	-40		b.d.	0.1	96.4	43.1	27.4	62.7	36.8	18.1	253.6	3.6
54	0.06	5.6	-40		b.d.	0.1	112.9	52.0	38.7	73.8	43.2	18.0	306.8	4.4
55	0.06	5.6	-40		1	b.d.	97.9	44.6	35.2	68.0	35.2	15.1	295.8	3.8
57	0.06	5.7	-40		b.d.	b.d.	109.3	47.7	38.2	72.8	38.5	15.6	305.5	4.1
60	0.06	5.6	-50		b.d.	b.d.	108.5	47.2	39.5	72.6	38.4	14.8	304.7	4.2
61	0.06	5.7	-50		b.d.	0.5	117.6	56.6	40.1	75.5	40.2	15.8	316.9	4.4
62	0.06	5.7	-50		b.d.	b.d.	112.9	52.2	38.3	75.8	40.3	15.9	315.4	4.2
63	0.06	5.7	-50		b.d.	b.d.	113.8	52.5	39.7	76.7	40.7	17.0	319.5	4.2
64	0.06	5.7	-50		b.d.	b.d.	114.5	47.9	38.7	77.3	41.2	18.3	323.2	4.3
67	0.06	5.6	-40		b.d.	b.d.	117.0	50.9	39.3	80.1	42.3	20.5	342.7	4.4
68	0.06	5.7	-50		b.d.	b.d.	119.5	47.5	40.5	80.6	43.4	23.5	338.9	4.3
69	0.06	5.7	-50		b.d.	b.d.	120.0	56.2	41.4	81.8	43.8	24.6	344.4	4.8
70	0.06	5.7	-50		b.d.	0.2	120.4	51.9	41.0	81.2	43.6	25.2	340.4	4.7
74	0.06	5.7	-50		b.d.	b.d.	123.4	46.1	42.5	84.2	45.1	27.1	355.3	4.5
76	0.10	5.7	-50		b.d.	b.d.	115.1	39.7	31.7	69.8	42.9	23.6	300.9	4.0
77	0.11	5.8	-50		b.d.	b.d.	121.1	29.0	33.4	73.4	44.7	24.4	321.2	3.8

Table A3: Results of batch experiment

ICP-AES in mg L^{-1}

Day	Ca	Fe	K	Mg	Mn	S	Si
0	11.7	2.2	5.4	6.8	2.2	15.0	0.4
1	16.8	2.9	29.4	10.2	3.7	19.4	0.7
4	14.8	3.6	28.3	11.8	4.9	20.9	1.0
5	16.4	3.6	54.3	11.9	5.1	22.2	1.1
7	17.4	2.7	53.1	12.3	5.5	22.4	1.2
8	16.3	2.2	66.1	11.8	5.3	21.4	1.2
11	15.0	0.3	60.8	11.0	5.4	18.8	2.4
13	20.3	0.2	77.5	14.2	6.9	24.7	3.3
15	20.2	0.2	77.4	14.3	7.0	25.2	4.1
20	36.7	0.4	161.0	25.6	13.2	44.9	6.5
27	23.8	2.3	104.2	16.7	8.6	31.1	5.5
34	28.0	0.4	118.8	20.0	10.8	38.8	7.9
41	41.4	0.5	169.8	29.4	16.3	61.3	17.6
48	46.0	0.6	186.2	33.4	18.5	73.2	26.3
55	26.9	0.9	99.9	18.7	10.8	43.5	17.0
61	33.8	17.2	112.2	22.2	11.7	134.2	25.6
66	29.7	1.4	113.6	21.5	12.4	57.0	28.6

Table A4: Tracer test results for 12.5 cm column.

				Ion Chromatography. Results in mg L^{-1}.						
Sample	Number	Time (hr)	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Cl$^-$	Br$^-$	NO$_3^-$	SO$_4^{2-}$
YMT2	2	9	4.7	59.2	28.1	34.3	40.7	52.4	17.8	179.4
YMT3	3	13.5	82.1	25.7	83.4	95.0	9.0	1291.1	20.1	103.9
YMT4	4	18	243.2	28.7	129.9	150.7	7.2	2868.7	22.3	85.1
YMT5	5	22.5	309.5	29.2	127.8	148.3	7.9	3149.7	23.6	88.0
YMT6	6	27	252.7	25.8	111.4	128.9	7.9	2576.0	22.2	95.9
YMT8	8	36	167.8	44.2	93.1	108.6	25.5	1757.4	21.5	142.2
YMT9	9	40.5	129.0	32.2	72.5	85.0	17.5	1184.3	20.8	168.3
YMT10	10	45	101.2	27.5	53.4	64.1	15.0	728.6	20.8	190.7
YMT11	11	49.5	82.8	24.9	40.2	48.7	13.2	468.9	19.5	202.9
YMT12	12	54	71.3	25.8	34.5	42.3	14.6	327.2	19.4	199.9
YMT13	13	58.5	62.6	25.6	29.9	37.0	14.2	252.9	18.2	191.3
YMT14	14	63	56.0	22.4	26.9	33.5	11.8	203.6	18.8	186.0
YMT15	15	67.5	51.2	20.0	24.2	30.3	9.9	171.1	17.6	183.3
YMT16	16	72	48.0	18.0	23.0	29.1	8.6	145.4	17.2	181.5
YMT17	17	76.5	44.8	19.2	21.5	27.8	10.3	124.7	17.4	176.7
YMT18	18	81	41.6	19.8	20.8	26.3	10.5	108.6	17.8	169.9
YMT19	19	85.5	44.7	19.8	20.5	26.6	10.1	109.9	17.2	182.5
YMT20	20	90	44.4	20.5	22.6	28.6	9.8	113.5	17.2	194.4
YMT21	21	94.5	44.0	18.2	23.4	29.4	8.5	104.8	17.3	196.2
YMT22	22	99	42.2	17.7	22.7	28.5	8.0	95.1	17.7	196.6
YMT25	25	112.5	39.7	19.3	22.3	28.2	9.1	78.0	17.7	197.8
YMT28	28	126	37.0	17.1	21.7	27.2	7.7	64.2	17.9	197.0
YMT31	31	139.5	33.6	17.1	20.4	26.1	7.9	51.8	17.8	187.5
YMT34	34	153	31.5	16.2	19.9	25.8	7.4	44.3	17.9	183.2
YMT37	37	166.5	29.3	15.6	17.5	23.4	6.9	36.6	17.4	177.6
YMT42	42	189	28.6	15.9	19.1	24.7	6.8	30.9	8.3	188.9
YMT45	45	202.5	27.8	15.3	18.2	23.1	6.2	26.0	8.2	187.3
YMT48	48	216	27.8	16.7	19.5	25.2	6.9	24.2	8.5	199.9
YMT51	51	229.5	27.0	19.0	19.3	24.3	8.7	21.0	7.8	198.2

Input concentration was 7600 mg L^{-1} Br$^-$