

**Rate Controls on the Chemical Weathering of Natural Polymineralic Material II.
Rate-controlling mechanisms and mineral sources and sinks for element release
from four UK mine-sites, and implications for comparison of laboratory and
field scale weathering studies**

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ABSTRACT

Predictions of mine-related water pollution are often based on laboratory assays of mine-site material. However, many of the factors that control the rate of element release from a site, such as pH, water-rock ratio, the presence of secondary minerals, particle size, and the relative roles of surface-kinetic and mineral equilibria processes can exhibit considerable variation between small-scale laboratory experiments and large-scale field sites.

Monthly monitoring of mine effluent and analysis of natural geological material from 4 very different mine sites have been used to determine the factors that control the rate of element release and mineral sources and sinks for major elements and for the contaminant metals Zn, Pb and Cu. The sites are: a coal spoil tip; a limestone-hosted Pb mine, abandoned for the last 200 a; a coal mine; and a slate-hosted Cu mine that was abandoned 150 a ago. Hydrogeological analysis of these sites has been performed to allow field fluxes of elements suitable for comparison with laboratory results to be calculated. Hydrogeological and mineral equilibrium control of element fluxes are common at the field sites, far more so than in laboratory studies. This is attributed to long residence times and low water-rock ratios at the field sites. The high water storativity at many mine sites, and the formation of soluble secondary minerals that can efficiently adsorb metals onto their surfaces provides a large potential source of pollution. This can be released rapidly if conditions change significantly, as in, for example, the case of flooding or disturbance.

1. INTRODUCTION

Mining activities expose large volumes of fresh rock to atmospheric conditions. Subsequent weathering and release of rock constituents, especially via sulphide oxidation, can lead to acidic solutions and elevated concentrations of environmentally undesirable elements in surrounding waterways (Younger, 2000; Banks *et al.*, 1997). This global problem is exacerbated by the lack of an effective framework for determination of legal liability, which means that resources for remediation of contaminated abandoned sites are limited (Younger, 1997). Fortunately, pre-mining environmental assessments are now required in the majority of countries, and for this, as well as for cost-effective remediation, it is necessary to develop the ability to predict the severity and longevity of mining-related contamination on a site-specific basis. An understanding of the processes affecting weathering is also relevant to climatic modelling, where a better knowledge of field-scale mineral dissolution rates is necessary to facilitate assessment of relationships between temperature, precipitation, elevation and weathering rate (e.g. White and Blum, 1995).

Laboratory assessments are the most convenient method of measuring the contamination potential of spoil. Detailed studies of the dissolution of individual mineral phases have determined dissolution 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, 1992; Martello *et al.*, 1994; Peiffer and Stubert, 1999; Holmes and Crundwell, 2000), but it is difficult to use such work to account for interactions between the components of the phases in a polymineralic assemblage. Rudimentary acid-base measurements on polymineralic materials are popular (e.g. Adam *et al.*, 1997), because of the relative ease and rapidity with which they can be undertaken and interpreted. Such methods measure the total potential of a

sample for contamination, but do not provide information on the rate at which contamination is produced, and are thus of limited use (e.g. Jambor, 2000). Batch and column experiments have also been used (van Grinsven and van Riemsdijk, 1992; Stromberg and Banwart, 1999; Banwart *et al.*, 2002), to measure rates and to distinguish rate-controlling mechanisms of mineral dissolution. Column experiments can be more useful than batch experiments because they involve water:rock ratios and hydrological solute transport processes similar to those found in the field. Regardless of method, however, it is difficult to extrapolate laboratory results to field situations. Laboratory-derived mineral dissolution rates are often 2 to 4 orders of magnitude faster than those measured for minerals in the field (e.g. Schnoor, 1990; White *et al.*, 1996).

A number of factors have been proposed to account for this discrepancy. These include differing pH, grain size, temperature, hydrology, cation exchange characteristics, availability of reactants such as O₂, degree of physical and chemical heterogeneity, secondary mineral behaviour, mineral surface characteristics and proximity to chemical saturation with respect to the dissolving minerals, between weathering environments (e.g. Sverdrup and Warfvinge, 1995; Malmstrom *et al.*, 2000; White and Brantley, 2003). Algorithms that quantitatively account for some of these factors have been devised (e.g. Sverdrup and Warfvinge, 1995; Malmstrom *et al.*, 2000). These are based on the premise that each of the different parameters that affect dissolution rates can be considered separately, and a scaling factor calculated for each. The combination of the scaling factors then allows extrapolation of laboratory-based weathering rates to the field. Calculations are based on fundamental relationships between reaction rate and the physical parameter of interest, and so site-specific calibration is not required for most parameters. Thus, the algorithms should prove to be robust and generally applicable. The algorithm of Malmstrom *et al.*

(2000) has been demonstrated to be successful in a study of the weathering of granitoid waste rock from the Aitik Mine, Sweden (Malmstrom *et al.*, 2000).

However, application of this type of algorithm involves the implicit assumption that the same mechanism determines the rate of element release in the laboratory and in the field, and that mineral sources and sinks play the same role in the two environments. This is not necessarily the case. The present study investigates rate-determining mechanisms and mineral sources and sinks at 4 UK mine sites via a year-long mine-water monitoring program and bulk and mineralogical analysis of samples from the sites. Results are related to those produced by laboratory experiments using results of hydrogeological analyses of the sites. Results for one site are then compared to column and batch experiments on material from the site (Evans and Banwart, 2006). The implications of results for prediction and treatment of mine-water related pollution are discussed.

2. FIELD SITES

Locations of all sites are shown in Figure 1. The criteria for field sites were that they should: be hydrologically well-defined with point discharges; have a well-documented mining history; exhibit commonly-observed contaminant characteristics; be representative of the selected type of mining environment; have available data for rainfall, discharge, topology and geology, and have a reasonably simple geological structure.

2.1 Quaking Houses

The spoil tip at Quaking Houses, near Newcastle-upon-Tyne, County Durham, England (Figure 1a), comprises spoil excavated during working of the Morrison Busty pit between 1922 and 1973. The tip overlies sand and clay drift deposits, which

themselves overlie Carboniferous interbedded mudstones, sandstones and coal seams (Pritchard, 1997). The area of the tip is approximately 35 hectares and the height varies from 4.25 to 11m. The spoil material is a heterogeneous mix of shale, ash, coal and coal dust, with scattered cobbles, sandstone boulders, timber and traces of red burnt shale. The vast majority of particles are smaller than 5cm diameter. Recently formed secondary minerals are common in samples from the upper 5m of the tip. Hydrology of the tip is simplified by the underlying clay-rich drift deposits which act as an aquitard, isolating the tip from groundwater flow (Pritchard, 1997). The discharge at Stanley Burn (output G, OS grid ref: 41770 55095) is thought to collect water from approximately 10% of the tip, plus relatively uncontaminated water that flows from a surface drain (Pritchard, 1997).

Significant tip-related pollution was not recorded between closure of the mine in 1974, and 1986, when construction of the A693 Annfield Plain bypass cut through almost the full depth and breadth of the tip. During construction, drains that serviced the tip were incorporated into the road drainage system, the bulk of which discharges into the nearby Stanley Burn. A subsequent decrease in pH and increases in Fe, Al and SO_4^{2-} contents in the Stanley Burn have been attributed to drainage from the tip. There have been a number of previous studies of water quality at the site. Local authority reports (e.g, Markey-Amey, 1995; Newbegin, 1997) have been complemented by two MSc theses (Pritchard, 1997; Srour, 1998) and a Ph.D thesis (Gandy, 2002) with associated publications (Gandy and Evans, 2002; Gandy and Younger, 2003), which have developed groundwater flow and chemical models for the site.

2.2 Grattendale

Limestone hosted Pb/Zn deposits in the valley of Grattendale in the Peak District, Derbyshire, England (Figure 1b), were mined up to the end of the 18th Century. Grattendale is in the White Peak area, which comprises an inlier of Carboniferous limestone surrounded, except to the extreme SW, by younger fluvio-deltaic sandstones (Stevenson *et al.*, 1982). Mississippi Valley Type (MVT) Pb and Zn ores formed when cooling metal-rich fluids passed sub-horizontally through the limestones (Ewbank *et al.*, 1995). Ore minerals include galena, sphalerite, baryte and fluorite. Mineralisation was controlled by lithology and by pre-existing structure, and resulted in a geometry of near vertical or horizontal sheets, known as rakes and flats respectively, and occasional linear pipes (Ford and Rieuwerts, 1970). Mineralised zones rarely penetrate the volcanic horizons, known locally as toadstones, and are thus found mainly within higher levels of the formation (Ford and Rieuwerts, 1970). Grattendale is a steep sided valley with walls of clean, fossiliferous (rugose, fragmented corals and brachiopods) limestone. The Matlock Lower Lava, known locally as the Grattendale Lava, outcrops partway up the valley; where it is around 9m thick and dips to the NE (Oakham, 1979). Surface expression of mineralisation is rare because most outcropping deposits were extensively worked to a depth of 10 to 15 m and then filled with earth.

Mining in the White Peak since Roman times has produced a poorly mapped network of largely interconnected mines and drainage channels, or soughs (Rieuwerts, 1987). The resultant hydrology is complex; however, Grattendale is effectively hydrologically bounded by topography, geology and soughs and so presents a relatively simple system. The discharge (OS grid reference: 42083 36078) is continuous year round, with a flow rate between 0.1 and 2 L s⁻¹. Mining exposed large areas of fresh sulphide surfaces to relatively oxidising conditions. Regional S

oxidation rates higher than those that pertained before mining began are indicated by S isotopes (Bottrell *et al.*, 1999), and analysis of sediments in cave systems shows fine grained sulphides with a relatively high potential for dissolution (Bottrell *et al.*, 2000). However, solubility of mineral phases bearing Pb, Zn and Ba, the principal potentially toxic contaminants in the area, are relatively low under high pH conditions such as those found in limestone-rich areas because formation of sparingly soluble Pb and Zn carbonates and hydroxides effectively removes most of the metals from solution (Benevenuti *et al.*, 2000).

2.3 Ynysarwed.

The Ynysarwed minewater discharge flows from an old adit connected to the lower Ynysarwed workings in the Neath Valley, South Wales (Figure 1c). The regional geology consists of faulted sandstones, mudstones, siltstones and coals of the Upper and Middle Coal Measures (Westphalian), which dip at approximately 6° SW (Barclay *et al.*, 1988). The topography comprises steep sided narrow valleys, separated by larger areas of relatively flat upland. Upper Coal Measures fluvial Pennant sandstones, interspersed with a number of small, largely unworked coal seams, overlie the Rhondda number two seam, which is the principal worked seam in the area. Below the coal lie Lynfi Middle Coal Measures mudstone beds, which show a marked marine influence (Barclay *et al.*, 1988). It is this marine influence which gives the anthracitic Rhondda number 2 coal its high S content (2-4% pyritic S).

The hydrogeology of the area is dominated by the highly conductive mine-workings. The Ynysarwed discharge (OS grid reference: 28094 20186) is fed by recharge through the relatively permeable Pennant Sandstone (approximately 20% of precipitation) and groundwater flows from the Blaenant system to the west (Younger and Adams, 1997). Underlying Lynfi mudstones are relatively impermeable and are

assumed to prevent downward escape of water from the system. Flows from the neighbouring unsaturated Upper Ynysarwed, Crynant and Lwynon workings, which bound the area under consideration to the north, are thought to be minor as all drain to adits well above the groundwater table (C. Rees, per. comm, 1999; Younger and Adams, 1997). Piezometer measurements show that groundwater flow is from NW to SE, that is, from Blaenant (water table approx 75m AOD) to Ynysarwed (water table 20 m AOD). Prior to the cessation of mining, the Blaenant works were pumped, while the lower Ynysarwed workings drained through the discharging adit. Lower Ynysarwed was closed in 1938, and although an occasional ferruginous discharge was noted at the adit this was not of any volumetric significance. The Blaenant mines closed in 1991, the pumps were turned off, and groundwater levels within the workings began to rise. Minewater discharges were expected to begin at or near the River Dulais, the bed of which passes over the Blaenant workings. However, the coal barriers between the Blaenant and Ynysarwed mines (Figure 1c) proved ineffective and a substantial discharge began at the Ynysarwed adit in 1993 (Younger and Adams, 1997). Water discharges from the adit portal at Ynysarwed are up to 36 L s^{-1} . Discharges were initially acidic with a pH as low as 3, but are currently circumneutral. The discharge is reducing, and rich in dissolved Fe and SO_4^{2-} (200 and 1800 mg L^{-1} respectively), although a gradual decline in Fe concentrations since 1993 has been observed (Ranson and Edwards, 1997). Precipitation of ochre from discharging water has adversely affected fish and invertebrate populations in the Neath Canal, which receives the discharge, and the discharge was given 11th priority in a 1993 water quality survey of British minewater discharges. This led to a significant amount of work on both the hydrochemistry and hydrology (e.g. Younger, 1996; Younger and Adams, 1997).

2.4 Church Coombe

The Church Coombe minewater discharge, Cornwall, England flows into a small stream (Figure 1d). The surrounding area is a geometrically complex mix of Upper Devonian Mylor slates (killas), and Late Carboniferous/Early Permian granites which form part of the Cornubian Batholith. These are intruded by NNE-WSW striking coarse granite porphyries (elvens) and dolerites (greenstones) (Dines, 1956).

Mineralisation was associated with circulation of basinal and meteoric fluids driven by heat from the intrusion of the Cornubian batholith (Gleeson *et al.*, 2001). Mines near Church Coombe are located in a trough of slate between the Carnmellis granite to the south, and the Carn Brea granite to the north. The main ore-bearing body dips at around 30°S in this region and follows the granite-slate contact in the area shown on Figure 1d. A number of ENE-trending sub-vertical off-shoots from the main body were also worked in the area (Dines, 1956). Principal ore minerals are chalcopyrite and cassiterite, with a tourmaline/chlorite gangue (peach). The sub-vertical lodes were worked mainly for Cu, although Sn and As were also produced (Dines, 1956). Mining was well established in the area by 1699, and by 1743 the adit was being used to produce water power (Hamilton-Jenkin, 1965). Mining flourished until the 19th Century, but underground activity had effectively ceased by 1919. The dumps were reworked for secondary and accessory minerals in the 1930s (Dines, 1956).

Exploration and mapping of the adit (portal at OS grid reference: 16916 04076) suggest that it drains the Wheal Bassett system, which includes North Bassett and Wheal Bassett (Figure 1d). Flow rates are up to 90 L s⁻¹. The region is classed as a minor aquifer, with permeability controlled largely by the depth of weathering, rather than by the hydrological properties of the slate or the granite. The water is circumneutral and contains 1mg L⁻¹ of Cu all year round, and thus potentially poses

some threat to receiving water courses. However, this is mitigated by subsequent dilution.

3. METHODS

3.1 Element Release Mechanisms

3.1.1. Water Sampling and Analysis

Sites were monitored monthly for a period of at least 12 months between June 1999 and June 2001. Quaking Houses samples were taken from outfall G (Figure 1a), Grattendale samples from Wraithe Sough (Figure 1b), Ynysarwed samples from the marked adit portal (Figure 1c), and Church Coombe samples from the adit portal marked on Figure 1d.

At Quaking Houses, unfiltered acidified (1% HNO₃) and non-acidified samples were analysed by Atomic Absorption Spectroscopy (AAS) and Ion Chromatography (IC) for metals and common anions (F⁻, Cl⁻, NO₂⁻, Br⁻, NO₃⁻, SO₄²⁻) at the Department of Civil Engineering, University of Newcastle. pH, alkalinity, Eh and conductivity were determined in the field using portable meters. At Grattendale, Ynysarwed and Church Coombe, water samples were filtered through 0.2 µm filters (Schleicher and Schuell) into new Nalgene bottles which were rinsed in the discharge before use. Acidified (1% HNO₃) and unacidified samples were collected at each sampling visit. Acidified samples were analysed by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) for major and abundant trace elements at the Assay Office, Sheffield. Unacidified samples were analysed, in most cases, by Ion Chromatography (IC: Dionex) for light alkali metals and alkaline earths (Na⁺, K⁺, Ca²⁺, Mg²⁺), and common anions (F⁻, Cl⁻, NO₃⁻, NO₂⁻, Br⁻, PO₄³⁻, SO₄²⁻). One or two samples from each site were screened using Inductively Coupled Plasma – Mass Spectroscopy (ICP/MS) at the Centre for Analytical Services, University of Sheffield,

to quantify rarer elements such as Cd, U and Th. Significant concentrations of these elements were not found. Iron-rich samples from Ynysarwed were not analysed by IC because Fe forms insoluble compounds inside the ion exchange columns, and, in any case, it was known that SO_4^{2-} is the dominant anion (Younger, 1997). pH, redox potential, conductivity and temperature were measured with a Myron 6P Ultrameter. Alkalinity was measured by titration with 0.035N H_2SO_4 to pH 4.5 using bromocresol green/methyl orange indicator. Flow rate was also measured at each sampling site. At Quaking Houses and Grattendale this was accomplished using a bucket and stopwatch. At Ynysarwed, flow rates were measured electronically with stream gauging by the Environment Agency. These measurements were affected by the construction of a treatment plant for the minewater effluent and thus results from this site are subject to additional sources of uncertainty, discussed below. At Church Coombe, flow rates were calculated from the velocity of flow in a channel of known cross-sectional area.

3.1.2. Interpretation

Relationships between element concentrations (moles L^{-1}), discharge flow rates (L s^{-1}) and element fluxes (mole s^{-1} ; obtained by multiplying concentration and discharge flow rate) were used to determine the rate-controlling mechanism for each element. Rate-controlling mechanisms were split into those that involved principally (a) surface kinetic-, (b) mineral equilibrium-, and (c) transport-related factors.

3.1.2(a) Surface Kinetic (S)

If surface kinetic processes control the rate of mineral dissolution then the flux of elements sourced from the dissolving mineral is constant, so long as other rate-determining factors such as the quantity of source mineral, pH, temperature and the concentration of reactants remain constant (e.g. Wieland *et al.*, 1988). If processes

such as secondary mineral precipitation do not interfere then the flux of the element from the mine should also be constant. Clearly, temperature, pH, and other rate-controlling factors are likely to change in a mine over the course of a year and so some variation in surface kinetic-controlled element fluxes would be expected. An approximately constant element flux was thus used to infer that the principal mineral source or sources for that element were dissolving at a rate controlled by surface-kinetic processes. The definition of constant flux used here was that of a standard deviation of the monthly flux measurements less than 20% of the average value. The value of 20% is arbitrary, but choices of values for the constant flux threshold between 15 and 40% give very similar results. Thresholds for the other categories described below are also arbitrary, and results show a similar weak sensitivity to the choice of value.

3.1.2(b) Equilibrium (E)

If the concentration of an element is controlled by chemical saturation with respect to a mineral then the concentration of that element is fixed by the presence of the mineral, so long as factors such as pH, temperature, the chemical activity of other aqueous species, and the activity of the mineral phase remain constant. A solution may be chemically saturated with respect to a source mineral present in rock prior to weathering or, to some secondary mineral that incorporates the element of interest. Cation exchange surfaces on clay minerals also exert some control on the concentrations of elements in solution, although the systematics of this are more complicated. It is unlikely that factors that affect the equilibrium concentration of an element are likely to remain constant over the course of a year at any of the field sites studied. Thus, an approximately constant concentration of an element was taken to infer equilibrium control. Constant concentration was diagnosed when the standard deviation of the monthly measurements was less than 20% of the average value, and

where a suitable source/sink mineral was observed, and calculated to be in equilibrium with the solution (see below). The second criterion is included because a constant concentration in a mine discharge may also result from constant concentration in some external source.

3.1.2(c) Transport (T)

Transport control of element release occurs when changes in hydrogeological parameters that affect flow rate, such as the rate of recharge, the percentage of water saturation in the unsaturated zone, or water table height, determine the rate of mineral dissolution and element transport. The transport control described here is similar to the transport-limited erosion described by Stallard and Edmond (1987). However, it is slightly different to the process described by these authors because it does not include situations in which mineral equilibrium is approached, although transport-related processes are implicated in the attainment of mineral equilibrium. Mechanisms for transport-controlled element release include: flushing, where an increase in the height of the water table dissolves soluble secondary minerals precipitated in previously hydrologically-unsaturated parts of a hydrogeological system; dilution, where increased water flow decreases element concentrations and may enhance the rate of mineral dissolution; and changes in the ratio of mobile to immobile water in the unsaturated zone (Evans and Banwart, 2006; Banwart *et al.*, 2004), which affect the efficiency of removal of dissolved mineral constituents. Physical processes that accompany transport control are complex (Clow and Drever, 1996) and so the flux-flow characteristics of transport control are variable; however, all are likely to result in a correlation between flow rate and element release that could be positive (flushing) or negative (dilution). Transport control of element release was inferred when the absolute value of the correlation coefficient between flow rate and element concentration was greater than 0.7.

3.1.2 (d) Depletion (D)

It may be that the supply of a mineral may be depleted by dissolution, and that this process is the main control on the flux of constituent elements of that mineral from the system of interest. If this is the case then the flux of this element from the system will decrease with time. Depletion control of an element was inferred when the absolute value of the correlation coefficient between element flux and time was less than -0.7.

3.1.2 (e) General Transport (I)

The categories defined above are end-members in a continuum of system behaviour that is created by the play-off between mineral reactivity, fluid flow rates, and other hydrological parameters. There are a number of situations for which none of the above criteria would be met, which implies that the rate-controlling factor for element release varies over the course of a year. The rate-controlling element release mechanism in these cases cannot be determined by a simple inspection of element flow and flux characteristics and is classed as General Transport (I).

Figures 2-5 illustrate examples of the relationships between element concentrations, fluxes, time, and discharge flow rate. Inferred rate-controlling element release mechanisms are summarised in Table 2.

3.2 Mineralogy

3.2.1 Sample Collection

20 kg of each of the main lithologies was collected from each site. Representative sampling of 20 kg of material from heterogeneous systems containing many tons of material is not remotely achievable. However, the samples can be used to identify source and sink minerals present at the sites.

At Quaking Houses samples were taken from material retrieved during borehole construction; and consisted of two types, black coal waste (QB), and

orange clay-rich material from boulder clay underlying the tip (QO). QB was made by mixing approximately equal proportions of spoil taken at 1m intervals down the tip. Weathering of the top portion of the tip has caused significant mineralogical variation with depth (Evans *et al.*, 2003). Ore-bearing limestone from Grattendale was collected at a spoil tip 5 km from the adit portal, and non-ore bearing limestone was collected from Grattendale itself. All samples were large (1-5 kg), partly weathered limestone boulders. Material from Ynysarwed was collected from a spoil tip that is known to contain material from both Blaenant and Ynysarwed mines (C. Rees, pers. comm.). Samples were almost unweathered because recent landscaping of the area had exposed relatively fresh spoil at the surface. 20kg each of pyrite-bearing mudstone (YM), clean, mature sandstone (YS) and pyrite-bearing coal (YC), in 1-5 kg lumps, were collected, to allow differences in mineral dissolution rates and composition between lithologies to be determined. At Church Coombe only one set of material (CC) was collected from a spoil tip adjacent to the North Basset Mine. Here, 1-3 kg samples of a reddish-brown hornfelsed mudstone, showing evidence of mineralisation, were taken from a freshly turned spoil tip.

3.2.2 Analysis

Samples were jaw-crushed to a median grain-size of 1mm and homogenised in an industrial mixer at the Dept. Civil Engineering, Sheffield. This preparation was necessary for the laboratory experiments (Evans and Banwart, 2006). Major and trace element compositions for each of the 8 lithologies were determined at the British Geological Survey, Keyworth, using X-Ray Fluorescence (XRF) on glass beads and pellets respectively (Table 3). Mineral assemblages and textural relationships were identified using X-Ray Diffraction (XRD) and scanning electron microscopy (SEM) at the Department of Materials Engineering, Sheffield University, and optical

microscope examination of thin sections. Total S was determined by LECO combustion analysis at the Assay Office, Sheffield, and water- and acid-soluble SO_4^{2-} were obtained using standard methods (Czerewko, 1997). Disulphide-S was calculated from the difference between total S and the sum of acid plus water soluble SO_4^{2-} . Organic S was assumed to be negligible (Taylor, 1989). The specific surface area of the crushed samples was measured by BET analysis at the Dept. of Engineering Materials, University of Sheffield.

3.2.3 Mineral Modes

Mineral modes (Table 4) were calculated for the observed mineral assemblage by solving the set of simultaneous equations that relates bulk composition to mineral modes and compositions (c.f. Ferry, 1988). This set consists of i equations of the form

$$N_i = \sum_j n_{i,j} p_j \quad [1]$$

N_i is the number of moles of element i per unit mass, $n_{i,j}$ is the number of moles of element i in mineral j and p_j is the number of moles of mineral j per unit mass.

Mineral compositions are poorly constrained for minerals that exhibit significant compositional variation. This is because the fine-grained nature of the samples made representative mineral compositions difficult to quantify using techniques such as electron microprobe on single grains. For this reason, important mineral composition variables, such as Tschermak's substitution in illite, were accounted for by specifying the exchange component to be an unknown in the set of equations: for example, the anorthite component in albite was specified as $\text{CaAlNa}^{-1}\text{Si}^{-1}$ (notation of Thompson, 1982). The use of exchange components is discussed further by Thompson, (1982). Water-soluble, acid-soluble and disulphide -S were included as compositional constraints. This allowed a maximum of 10 variables, including mineral modes and

composition variables, to be determined. The plausibility of results was checked by a comparison of the mass of the calculated assemblage to measured mass. Ideally, the assemblage calculated from the analysis of 100g of material should weigh 100g, and incorrect choices of assemblage or mineral formulae will result in deviation from this value.

3.2.4 Identification of source and sink minerals

If a solution is saturated with respect to a mineral then the saturation index of that mineral in solution is 0. 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 (e.g. Appelo and Postma, 1993). A positive saturation index indicates that the solution is supersaturated with respect to the mineral phase, a negative value, that the solution is undersaturated, and a value near zero suggests that saturation is reached, and that equilibrium exists between the mineral and the aqueous solution. Mineral saturation indices for minerals observed by XRD, SEM or thin section observation (Table 5) were calculated using PhreeqC for Windows, v1.0 (Parkhurst and Appelo, 1999) utilising the PhreeqC database (Ball and Nordstrom, 1991). This was used to test diagnoses of equilibrium-controlled element release rates (Table 2). Only solutions with a calculated ion balance of $\pm 10\%$ were used to calculate mineral saturation indices.

3.3 Area-normalised element fluxes

Comparison between laboratory and field element release rates requires some methods of conversion between the element fluxes from field sites ($M T^{-1}$), and the

element fluxes per unit area of reacting mineral surface obtained from laboratory experiment ($\text{M L}^{-2} \text{T}^{-1}$). Element fluxes per unit area are related to element fluxes via

$$F_i = \frac{Q_i}{V\rho SSA} \quad [2],$$

where F_i is the flux of element i in units of moles $\text{m}^{-2} \text{s}^{-1}$, Q_i is the flux of element i calculated from field observations (moles s^{-1}), V is the volume of interacting rock in m^3 , ρ is the bulk density in kg m^{-3} , and SSA is the reacting surface area in $\text{m}^2 \text{kg}^{-1}$.

Uncertainties in the values of V and SSA are significant. This is because V is controlled partly by poorly known effects of hydrological focussing such as fracture flow, and because the SSA of samples in the field is less than that of the crushed material for which BET analyses are available. SSA , which is sensitive to both the freshness of the mineral surface and to grain-size, is difficult to quantify, even for laboratory samples.

Here, 3 different approaches are considered. A maximum value for the SSA , and thus a minimum value for the area-normalised flux, is given by the use of BET-derived SSA (SSA_{BET}). This flux is described and tabulated (Table 6, Table 7) as F_B . Alternatively, SSA_{BET} can be scaled using assumptions of particle size variation between laboratory and field. The SSA decreases by an order of magnitude for each order of magnitude increase in particle radius. Flux estimates derived by this method are referred to here as adjusted BET-derived fluxes (F_{ABET}). However, this method does not account for the increase in mineral surface reactivity that is caused by crushing of the samples before BET measurement. A minimum value for the SSA , and thus a maximum area for the area normalised flux, is given by a purely geometric approach to surface area calculation. The simplest method is to assume that the volume of material that interacts with infiltrating fluids is divided into cubic blocks with side length d m. This assumption gives a total reacting surface area of $6V/d$, and a surface area normalised flux of $Q_i d/6V$. The ratio of the maximum flux (F_G) to the

minimum flux (F_B) is then $6/(d \rho SSA_{BET})$. This value is tabulated in Table 6 for d values of 0.01, 0.1 and 1 m.

V values are calculated from geometric and hydrological considerations at each field site (see below). Uncertainties in F_B were propagated assuming that the input parameters, Q_i , V , ρ , and SSA , were uncorrelated. Calculations were made using the standard expression for propagation of the uncertainty on x where $x = f(a, b, c, \dots)$.

$$\sigma_x^2 = \left(\frac{\partial x}{\partial a} \sigma_a\right)^2 + \left(\frac{\partial x}{\partial b} \sigma_b\right)^2 + \left(\frac{\partial x}{\partial c} \sigma_c\right)^2 + \dots \quad [3]$$

Error propagation used a natural log scale because of the large size of the uncertainties involved. Uncertainties on Q_i at Quaking Houses, Grattendale and Church Coombe were set to the standard deviation of the flux measurements. Flux uncertainties at Ynysarwed were set to twice the standard deviation of the measurements to account for the disturbance to flow rates caused by construction of the mine effluent treatment plant. Uncertainties in ρ and SSA were set to 10 and 20% of their respective measured values. Note that this strategy does not include systematic areas that stem from the inappropriate choice of surface area estimation method; results that use the same method for surface area estimation to be compared, but additional uncertainty should be added if those results are to be compared with results that use a different method of surface area estimation. The bulk of the uncertainty was attributed to V via a standard deviation of ± 2 natural log units. Uncertainties on F_G are of a similar order of magnitude for any given value of d .

3.3.1 Masses of Interacting Rock ($V\rho$)

At Quaking Houses the volume of the tip, and the proportion that interacts with the discharge at outfall G were calculated from plans of the site, and from borehole spoil logs (Pritchard, 1997). The interacting proportion was estimated to be 0.1 of the total

volume of the tip (Pritchard, 1997): $1.08 \times 10^5 \text{ m}^3$. The contribution of groundwater from beneath the tip was assumed to be negligible because the underlying clay has a very low permeability. The average density of the material was assumed to be $1.8 \times 10^3 \text{ kg m}^{-3}$ (Pritchard, 1997).

At Grattendale, the recharge area was calculated from output flow rate, rainfall figures and evapotranspiration estimates. For an average output flow rate of 800 ml s^{-1} , rainfall of 111 cm a^{-1} (data for 1999-2000 taken from rainmeter at nearby Birchover) and 50% evapotranspiration, the area of recharge was calculated to be 0.044 km^2 . The average height of the ground above the level of the adit portal was estimated, using contours from the geological map (Stevenson *et al.*, 1982), to be 177m. The interacting rock volume ($7.79 \times 10^6 \text{ m}^3$) is the product of these two parameters. The average density of the material was assumed to be $2.3 \times 10^3 \text{ kg m}^{-3}$. This was calculated assuming 83% carbonate ($\rho = 2.8 \times 10^3 \text{ kg m}^{-3}$) and 17% void, as either porosity or mined area.

At Ynysarwed, rock interacting with percolating fluids was assumed to be collapsed mudstones and coal filling 80% of the previously mined volume of $1.8 \times 10^6 \text{ m}^3$ (Younger *et al.*, 1996; Younger and Adams, 1997). The average density of the material was assumed to be $1.7 \times 10^3 \text{ kg m}^{-3}$. The density is that of spoil (Pritchard, 1997), which has been reduced to reflect the presence of 17% (by weight) of coal with a density of $1.2 \times 10^3 \text{ kg m}^{-3}$.

The catchment area for the Church Coombe discharge was identified using a digital elevation model (DEM) of the region with a 10m horizontal grid spacing. The DEM was used with a runoff algorithm to generate drainage networks (Jenson and Domingue, 1988), and catchments. The catchment area for the adit at Church Coombe is 2.1 km^2 . The base of the interacting rock volume was taken to be at the level of the adit portal (123m OD), and the top was taken to be the ground surface.

The estimated rock volume is $1.4 \times 10^8 \text{ m}^3$. The average density of the material was assumed to be $2.6 \times 10^3 \text{ kg m}^{-3}$, taken from the lower range of estimates of density for crustal rocks (Verhogen et al., 1997).

3.4 Comparison with laboratory work

Rate-controlling mechanisms and area-normalised element fluxes from Ynysarwed are compared with rate-controlling mechanisms and area-normalised element fluxes for batch and column weathering studies performed on the Ynysarwed mudstone (YM) material (Evans and Banwart, 2006).

4. RESULTS

4.1 Water sampling and analysis

Representative element release patterns for concentration versus time (Figure 2), concentration versus flow rate (Figure 3), element flux versus time (Figure 4) and element flux versus flow rate (Figure 5) illustrate the wide range of behaviour observed. Rate-controlling mechanisms are summarised in Table 2. Table 2 shows that, for just over half the elements analysed, the rate-controlling mechanism is general transport. This is reflected by the scatter in many of the plots in Figures 2-5. Equilibrium-controlled element release is common at Grattendale (Mg, Ca, Na, S: Figures 2-5d, Cl and F), Ynysarwed (Mg, Mn: Figures 2-5e, Ca, Na, K, S), and Church Coombe (Si, Fe, Ca, Na, S, Cl). Transport-controlled element release is rarer, and is shown at Quaking Houses (Fe, Mn, S: Figures 2-5b) and Church Coombe (Cu, N: Figures 2-5g, and F: Figures 2-5h). There is no evidence of surface-kinetic controlled release rates. Other noteworthy features include:

- The decline in Fe concentrations with time at Ynysarwed (Figure 2f), which is not accompanied by a significant decrease in Fe flux. This contrasts with the relatively constant Mn concentrations (Figure 2e).
- The contrast between patterns for Cu and N at Church Coombe. Concentration versus time plots (Figures 2g and 2h) and concentration versus flow rate (Figures 3g and 3h) show opposite trends. However, the two elements show identical trends in the element flux versus time (Figure 4g and 4h) and element flux versus flow rate (Figure 5g and 5h).
- The generally positive trend in the element flux-flow rate plots (Figure 5). This reflects, to some extent, the fact that flux is a function of flow rate, and that the axes are not independent. Nevertheless, elements whose release rates are inferred to be equilibrium- or transport-controlled exhibit stronger correlations than those whose are not.

4.2 Mineralogy

Bulk composition, mineral modes and mineral saturation indices are shown in Tables 3, 4 and 5. Mineral saturation indices exhibit limited seasonal variation and so the results in Table 5 indicate the predominant values for saturation index over the year-long study period. Figure 6 combines a graphical representation of mineral modes with a depiction of the elements present in each mineral. The log scale is used to enable small quantities of secondary minerals such as gypsum to be shown. The total masses of the calculated assemblage are close to 100g in the majority of cases (Table 4), validating the approach taken here. However, the mass of the calculated assemblage is significantly less than 100g for QB, YM, and YC. QB and YM are clay-rich and underestimation of the calculated mass in these cases is attributed to the

presence of mixed-layer clays of unknown stoichiometry. The discrepancy for YC is of less concern as it reflects the absence of C from the modal calculations.

Most elements have multiple potential sources and sinks at most sites (Figure 6). For example, Si at Quaking Houses could come from albite, illite, kaolinite, montmorillonite or quartz. Lead at Grattendale could come from either primary galena or from secondary Pb hydroxide, sulphate or carbonate precipitates. Sulphur has multiple sources and sinks at all of the sites except for Church Coombe. No mineral source of Cl or N was identified. Modes of F-bearing minerals such as fluorite and fluor-apatite were not calculated because the atomic number of F was too low for accurate analysis of this element by XRF. However, it is likely that fluorite was present at Grattendale, which is close to the famous Derbyshire Blue John fluorite mines, and that fluor-apatite was present at Church Coombe (apatite identified in thin-section).

The diagnosis of equilibrium-controlled element release from concentration-flow rate characteristics is backed up, in most cases, by calculated chemical saturation of the solution with respect to at least one source or sink mineral identified as present within the rock samples (compare Table 2 and Table 5). A notable exception is Cl at Grattendale and Ynysarwed; this element is likely to have behaved conservatively during fluid-rock interaction within the mine system, and the concentration is probably determined externally to the adit systems. The rate-controlled mechanism is therefore deemed to be general transport (I). Other exceptions are provided by Na at Grattendale, Ynysarwed and Church Coombe, Mg at Ynysarwed, and Ca at Ynysarwed and Church Coombe. These elements are commonly found as part of cation exchange assemblages in clays, and it is likely that cation exchanger surfaces on clay minerals (illite, kaolinite, montmorillonite) buffered the aqueous concentrations of these elements. The equilibrium-controlled element release inferred

for F at Grattendale is likely to result from saturation with respect to fluorite.

Solutions are predicted to be supersaturated with respect to minerals in some cases, for example, chlorite at Ynysarwed. This results partly from slow kinetics of mineral precipitation for some minerals, but may also reflect poorly known thermodynamic data for the minerals, the effects of mineral solid solution on mineral stability, and changes in solution parameters such as pH and Eh when the discharges are exposed to the atmosphere.

A number of minerals that are observed to be present, and that are calculated to be saturated in the discharges from outflow G at Quaking Houses (alunite, jarosite, Fe oxy-hydroxides) do not appear to exert an equilibrium control on the release of their constituent elements (Fe, K, S, Al). It is tempting to attribute this to dilution of the tip discharge by relatively clean rainwater from the road drains. However, if this were the case then the saturation indices of the secondary minerals would drop. This is not observed. It is possible that the secondary minerals change composition to remain in equilibrium with a seasonally changing fluid composition. If this is the case then the assumption of relatively constant values for mineral compositions and fluid parameters such as pH and O_2 is invalid at a site such as Quaking Houses, and mineral equilibrium would be unable to fix the solute concentrations of the constituent elements of the secondary minerals.

4.3 Area-normalised element fluxes

BET surface area-normalised field fluxes of elements (Table 6) range from 10^{-13} to 10^{-20} moles $m^{-2} s^{-1}$. One sigma uncertainties are almost all close to 2 natural log units, which reflects the predominance of the contribution of the uncertainty in V to the total uncertainty. Larger uncertainties, such as Fe at Church Coombe, or Zn at Ynysarwed record scatter in the initial flux data. Fluxes of Na and Cl from Quaking Houses are

high (10^{-13} moles $\text{m}^{-2} \text{s}^{-1}$) and have very similar values. This is likely to be the result of the dissolution of a large uncovered pile of road salt that was stored unprotected at the tip at the time of the monitoring program. Adjusted BET-derived fluxes (F_{ABET} : not tabulated) are 1, 2 or 3 orders of magnitude higher than the F_{BET} values, depending on the estimate of the field grainsize. Geometric surface area-normalised element fluxes (F_G) are 3 to 6 orders of magnitude higher, depending on the assumed value of d .

4.4 Comparison with laboratory work

A systematic variation in element release mechanism as a function of the type of system was observed (Table 7). Equilibrium-controlled element release was most common at field scale; transport-controlled element release was predominant in the column experiments, and surface-kinetic controlled element release was observed in the batch experiments. There was also a systematic variation in the rate of element release (Table 7; Figure 7). Element fluxes from the batch experiments were 1 to 2 orders of magnitude faster than those from the column experiments which were, in turn, 1 to 2 orders of magnitude faster than BET-normalised field fluxes (F_B).

Adjusted BET-normalised fluxes for field grain sizes that were two orders of magnitude higher than those in the columns (~ 0.1 m) were similar to the BET-derived fluxes from the column experiments. GSA-normalised fluxes (F_G) were higher in all cases, but showed the same trend between batch and column results. Field F_G values for d values of 0.1 m were within error of the column F_G values. The other rock types give similar results (work in progress).

5. DISCUSSION

5.1. Rate-controlling element release mechanisms

The most important result of this study is the predominance of equilibrium- and transport-controls on element release rates (Table 2) which is observed at 4 very different UK mine sites. This suggests that direct scaling between laboratory-derived surface-kinetic controlled mineral dissolution rates and equilibrium- or transport-controlled field rates is unlikely to be appropriate. This conclusion is supported by the comparison between rate-controlling mechanisms for the Ynysarwed material (Table 7). Surface-kinetic processes dominate in the batch experiments, transport and cation-exchange processes control element release in the column experiments, and equilibrium control is most important in the field.

The occurrence of equilibrium-controlled element release presents something of a paradox; mineral dissolution processes that result in equilibrium would normally be assumed to have proceeded more rapidly than those which did not, because relatively rapid dissolution is required to produce solute concentrations that are high enough to reach chemical saturation with respect to the minerals of interest. Yet field rates have been shown to be slower than laboratory-derived rates by 2 to 4 orders of magnitude (e.g. Schnoor, 1990; White *et al.*, 1996). Consideration of surface-area-normalised fluxes is not helpful in this case, because of the large uncertainty on the surface-area appropriate for use in field-based calculations. However, the apparent contradiction can be resolved if hydrological factors are considered. Long residence times and low water:rock ratios are typical of field hydrological conditions, and these factors favour equilibrium-controlled mineral dissolution.

The scale of observation is also a controlling factor. At grain scale, solubility equilibrium occurs when diffusion of solutes away from the surface is slow compared to the rate of dissolution. At aquifer scale, equilibrium results when hydrological flushing is sufficiently slow that mineral dissolution proceeds to equilibrium over a time-scale shorter than the residence time of water within the hydrological system. A

number of other scale-dependent factors that influence the rate-controlling mechanism are also very different in laboratory and field (see below).

5.2. Influences on rate-controlling mechanism

An understanding of the parameters that control the rate-controlling mechanism of element release requires consideration of the factors that favour each mechanism. Equilibrium control is favoured by factors or processes that lead to high element concentrations. These can be split into hydrological factors, such as low water:rock ratios, long residence times, and significant evaporation, and mineralogical factors, such as high mineral reactivity and high reactive surface area. Field environments tend to have lower water:rock ratios and longer residence times than laboratory experiments, but lower mineral reactivities, which result from large particle sizes, and a general decrease in reactivity that results from prolonged weathering (e.g. White and Brantley, 2003). The results of this study suggest that the hydrological factors exert a greater influence, at least at the 4 field sites examined here. This analysis suggests that a continuum exists between field sites with low fluid:rock ratios and high residence times that have a high potential for mineral equilibrium and those with the opposite characteristics, that have a lower potential for mineral equilibrium (Figure 8). Spoil tips would in general, be expected to fall at the low potential for equilibrium end of this scale, whereas large mined systems such as Ynysarwed would be expected to fall at the higher end. This conceptual model is supported by the results in Table 2.

Transport-controlled element release is associated with sites that have relatively large variations in hydrological parameters such as flow rate and the height of the water table. Variations in these parameters are more extreme at smaller, hydrogeologically isolated sites with low residence times, and where water storativity is not high enough to buffer changes in recharge rates driven by temporal variation in

rainfall and other precipitation. Quaking Houses is such a site, and exhibits transport-controlled element release for more elements than any of the other sites.

5.3. Mineral Sources and Sinks

The results of this study emphasize the importance of secondary minerals in the control of element fluxes from mine sites. Secondary minerals are present and are calculated to exert some control on element concentrations at each of the 4 sites studied here (Table 5, Figure 6). They have also been shown to be important at a number of other types of environment (e.g. Blowes, 1991; Benevenuti *et al.*, 2000). In such situations it is inappropriate to interpret field fluxes of polluting elements from laboratory kinetic studies of primary minerals. It is instead necessary to identify dissolution/precipitation and adsorption reactions involving secondary minerals, and quantify rates of element release with appropriate mathematical expressions.

5.4. Recognition of rate-controlling mechanism

Recognition of rate-controlling mechanism for element release requires both monitoring of discharge compositions and investigation of the mineralogy of material at a mine site. For example, use of mineralogy and mineral equilibrium calculations alone at Quaking Houses would have concluded that the presence of alunite, Fe oxy-hydroxides, gibbsite, alunite and jarosite controlled the release of Fe, Al, S and K from the site, a result apparently inconsistent with those of the water-quality monitoring study reported here. Similarly, water analyses alone could have led to the conclusion that Cl and N were fixed by the presence of some mineral at Church Coombe, but mineralogical analysis shows that this is not the case and that some other mechanism is required to explain their constant concentrations. Water-quality monitoring should also be long-term (at least a year). This allows recognition of

monotonic temporal trends in element concentrations and/or fluxes, for example, the declining Fe concentrations at Ynysarwed (Younger *et al.*, 1996). More detailed mineralogical analysis than that presented here is necessary if the role of cation exchange is to be understood and quantified at field sites.

5.5. Use of Algorithms

The use of scaling algorithms (Sverdrup and Warfvinge, 1995; Malmstrom *et al.*, 2000) must be undertaken with caution if there is reason to suspect that element release rates are controlled by mineral equilibrium. Application of the algorithms to sites such as the Aitik mine site are likely to be successful (e.g. Malmstrom *et al.*, 2000) because the mine spoil is porous and highly reactive, and water-residence times are low (Eriksson *et al.*, 1997; Stromberg and Banwart, 1999). However, these algorithms would not have been suitable for the majority of the elements at the mine sites monitored for this study, and different methods should be used.

Fortunately, the systematics of element concentrations controlled by mineral equilibrium are relatively simple; concentrations remain approximately constant so long as the mineral assemblage and other factors such as temperature and pH remain unchanged. However, exhaustion of the controlling mineral phase will lead to changes in the concentrations of elements in solution (e.g. Banwart and Malmstrom, 2001), and the potential for such changes must be taken into account in any long term prediction exercise.

5.6. Practical Implications

The practical implications of this work for prediction and remediation of contamination at mining sites are two-fold.

1. An integrated study of mineralogical and water-quality parameters is necessary if the mechanisms that control element release at mine sites are to be understood. The most poorly known parameters involved in the calculations presented here are the volume of rock or spoil that interacts with percolating water, and the effective surface area of this material. More detailed hydrogeological analysis of sites (e.g. Rivett and Allen-King, 2003) can be used to constrain the former parameter. Issues with the effective surface area are more difficult to resolve. The effective surface area is not equal to either the geometric or BET-derived surface area, and, in spite of extensive research (e.g. Fischer and Gaup, 2004; Metz et al, 2005), there is no commonly used method for measurement of this parameter. The strategy recommended here is that effective surface area conventions should be consistent within any study, and that the uncertainties introduced by scaling between different particle sizes and/or mineral reactivities should be incorporated into error propagation calculations.
2. The presence of soluble secondary minerals such as alunite and jarosite could provide a significant source of contamination which can be accessed if site hydrogeology changes significantly. This is enhanced if the minerals incorporate toxic metals (e.g. Winland *et al.*, 1991). One possible example of this is the change in water quality observed at Quaking Houses after the construction of the Annfield Plain by-pass. Options such as dry-capping by landscaping and soil-washing should therefore be considered carefully.

6. CONCLUSIONS

Analysis of element concentration and element fluxes suggest that equilibrium- and transport-controlled element release mechanisms control the concentrations of major

elements and the principal contaminant metals at the 4 UK mine sites studied. No evidence was found for surface-kinetic controlled element release. Mineralogical analysis and mineral equilibrium calculations support this conclusion. However, diagnosis of rate-controlling mechanism from trends in water analyses can be incorrect if there is significant variation in the hydrological characteristics of the site, if there is significant depletion of source minerals, or if the concentrations of conservative elements such as Cl and N are controlled by processes external to the system under consideration. Secondary minerals such as goethite, gibbsite, alunite, jarosite and Pb and Zn hydroxides, sulphates and carbonates play an important role in the control of element concentrations from the sites. Comparison of element fluxes from the mine sites with those from the laboratory requires that the field fluxes should be normalised to surface area. The biggest uncertainties in such calculations are the volume of rock that interacts with percolating solutions and the specific surface area of reacting mineral grains in the field. A comparison of field- and laboratory-derived element fluxes for one of the sites shows that surface kinetic mechanisms control the rate of element release from the the batch experiments, while transport and equilibrium-control dominate in column experiments and in the field. Element fluxes from batch experiments were 1 to 3 orders of magnitude slower than those from column experiments and field measurements. This result presents a paradox, given that surface-kinetic mineral dissolution would be expected to proceed more slowly than that controlled by mineral equilibrium. This apparent contradiction can be resolved by the consideration of hydrological parameters such as water:rock ratio and water residence time. The implications for practical prediction and remediation of contamination at mine sites are that water-quality monitoring should be accompanied by mineralogical analysis, and that the role of secondary minerals should be considered carefully.

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FIGURE CAPTIONS

Figure 1. Locations and details of the 4 field sites.

Grid references are to the Ordnance Survey grid.

Figure 2. Concentration versus time for representative elements from the 4 field sites. (a) Quaking Houses: Al (b) Quaking Houses: SO_4^{2-} ; (c) Grattendale: Zn ;(d) Grattendale: SO_4^{2-} ; (e) Ynysarwedd: Mn; (f) Ynysarwedd: Fe; (g) Church Coombes: Cu; (h) Church Coombe: NO_3^- . Shaded bands indicate the region of $\pm 20\%$ around the average value.

Figure 3. Concentration versus flow rate for representative elements from the 4 field sites. (a) Quaking Houses: Al (b) Quaking Houses: SO_4^{2-} ; (c) Grattendale: Zn ;(d) Grattendale: SO_4^{2-} ; (e) Ynysarwedd: Mn; (f) Ynysarwedd: Fe; (g) Church Coombes: Cu; (h) Church Coombe: NO_3^- .

Figure 4. Flux versus time for representative elements from the 4 field sites. (a) Quaking Houses: Al (b) Quaking Houses: SO_4^{2-} ; (c) Grattendale: Zn ;(d) Grattendale: SO_4^{2-} ; (e) Ynysarwedd: Mn; (f) Ynysarwedd: Fe; (g) Church Coombes: Cu; (h) Church Coombe: NO_3^- . Shaded bands indicate the region of $\pm 20\%$ around the average value.

Figure 5. Flux versus flow rate for representative elements from the four field sites. (a) Quaking Houses: Al (b) Quaking Houses: SO_4^{2-} ; (c) Grattendale: Zn ;(d) Grattendale: SO_4^{2-} ; (e) Ynysarwedd: Mn; (f) Ynysarwedd: Fe; (g) Church Coombe: Cu; (h) Church Coombe: NO_3^- .

Figure 6. Mineral modes (left axis) and the relationship between mineral phases and dissolved elements in solution (right axis).

(a) Quaking Houses. QO: Quaking Houses orange; QB: Quaking Houses black; (b) Grattendale. D: ore-bearing limestone; W: ore-free limestone. (c) Ynysarwedd. YS: sandstone; YM: mudstone; YC: coal. (d) Church Coombe.

Figure 7. Comparison between element fluxes from field and (a) column experiments and (b) batch experiments. Error bars indicate \pm 1 standard deviation.

Figure 8. Schematic illustration of some of the factors that determine the mechanism of element release during weathering.