

$^{87}\text{Sr}/^{86}\text{Sr}$ as an indicator of flowpaths and weathering rates in the Plynlimon experimental catchments, Wales, U.K.

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Abstract

A knowledge of the processes involved in streamflow generation are critical to an understanding of solute transport and weathering rates in upland catchments. The determination of specific flow pathways and the formulation of process-based models have proved difficult in such terrains, largely due to the heterogeneous nature of catchments and the necessary limitations of bulked parameter models. Natural geochemical tracers have proved invaluable in developing conceptual models of catchment functioning and for constraining weathering processes and geochemical cycling. Strontium isotopes have been used as a natural tracer to calculate weathering rates for Sr and Ca, and to constrain the dominant flow pathways in two upland forested sub-catchments (Afon Hafren and Afon Hore) of the River Severn at Plynlimon in Central Wales. The dominant source of Sr in the catchments is considered to be from the weathering of silicate minerals. Weathering rates for Sr and Ca in the Afon Hafren, calculated using Sr isotopes, were similar to those derived from mass balance studies. The rates for the Afon Hore were similar for Ca, but significantly different for Sr. The reason for the difference is unclear, but may be due to additional sources (calcite) in the catchment. Strontium isotope ratios for different input sources and compartments within the catchment were characterised and helped to identify potential flow pathways. The data suggest an important role for groundwater inputs in contrast to previous models which indicated a dominant role for soil waters.

Keywords: $^{87}\text{Sr}/^{86}\text{Sr}$; Catchment; Plynlimon; Weathering; Flowpath

1. Introduction

1.1. Background

The processes involved in streamflow generation have received considerable attention over the last few decades, initially in response to concerns about acid deposition and the consequent acidification of streams (Likens et al., 1977 and Mason, 1990). The impacts of acid deposition and other pollutant inputs on water quality and ecosystem balance depend largely on the ability of catchment materials to neutralise or disperse such inputs. The sustainability of aquatic ecosystems is also dependant on the transfer and cycling of nutrients through the catchment. This is particularly true of upland catchments which are often base and nutrient poor and therefore sensitive to both climate and land-use change. Fundamental to modelling the response of catchments to environmental change is a knowledge of the water flowpaths, residence times and the

source and behaviour of solutes in groundwater and through the soil and unsaturated zone.

The majority of upland catchments have traditionally been assumed to be underlain by impermeable bedrock. The source areas and flow pathways in upland catchments are poorly understood and the subject of considerable debate (Bonell, 1998, Kirchner, 2003, McDonnell, 2003 and Shand et al., 2004). However, it is becoming increasingly apparent that many upland catchments in hard rock terrains, previously considered to be underlain by impermeable bedrock, contain groundwater which may play an important role in streamflow generation. (Shand et al., 1997, Neal et al., 1997a, McGlynn et al., 2002 and Soulsby et al., 2005). The contributing sources and flowpaths in upland catchments vary both seasonally and at the event scale depending on rainfall intensity, antecedent conditions and the structure of the soils and bedrock, making solute-transport modelling difficult. This is particularly the case in areas underlain by fractured bedrock which are typically characterised by extreme spatial variability in hydrogeological parameters such as hydraulic conductivity and groundwater flow rate (Cook, 2003).

1.2. Chemical weathering

Chemical weathering is the term used to describe the transformation of minerals formed at particular P–T conditions within the earth into more stable secondary minerals and solute species through interaction with dilute waters close to the earth's surface. Weathering of carbonate minerals is generally rapid in comparison with much slower rates for silicates, and although much less abundant in terms of quantity, provides a disproportionate input into natural waters. The weathering of silicate minerals is important because the release of base cations to solution provides plant nutrients as well as neutralising acidity and generating alkalinity (Drever, 1997). The role of silicate weathering is also considered to be an important control on atmospheric CO₂ and consequently important long-term control on climate change. Unlike carbonate weathering, where CO₂ consumed in dissolution is released during precipitation of calcite in the oceans, silicate weathering and subsequent precipitation results in a net loss of CO₂ from the Earth's surface (Berner et al., 1983). This makes estimates of weathering rates and processes important in predicting the effects of climate change over longer time scales. The soil zone, where weathering is intense, has traditionally been considered as dominating weathering and the export of solutes from catchments. However, the export of solutes may be derived from less intense weathering of large volumes of rock in the sub-surface environment below the soils. It is evident from geochemical studies of soils and groundwater that both are important, but the relative importance of each is not well established.

Chemical weathering results in the production of base cations and alkalinity from reactions between rainfall and soil-derived carbonic acid with solid phases. This supply of base cations is augmented by input from atmospheric deposition, and in order to calculate weathering rates it is necessary to calculate atmospheric deposition. The weathering of silicate minerals is extremely important because silicate weathering reactions are generally non-reversible and therefore act as a long-term sink of H⁺. Ion exchange reactions, on the other hand, are rapid and reversible and may only act as temporary sinks to acidity. Miller et al. (1993) have also attempted to discriminate weathering rates from exchangeable cation loss based on Sr isotopes. The production

of base cations in catchments due to chemical weathering is important because of their role as plant nutrients, in neutralising acidity or generating alkalinity and in the replenishment of the soil ion exchange pool.

1.3. Isotopes in catchment studies

A range of natural isotope tracers have been used to highlight the sources of solutes and elements cycling in catchments (Kendall and McDonnell, 1998). A number of studies over the past few decades using the stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$ which are truly conservative) have emphasised the importance of “pre-event” water in stream flow generation i.e. water which fell on a catchment prior to the hydrograph response of the antecedent rainfall event (Sklash and Farvolden, 1979 and Pearce et al., 1986). However, the implied storage identified in such studies, whether in soils, superficial deposits or the underlying bedrock remains largely unresolved.

Strontium isotopes have proved to be effective as a tracer of weathering and solute transport in catchment studies (see summaries in Bullen and Kendall, 1998, Capo et al., 1998, McNutt, 2000 and Blum and Erel, 2005). These isotope ratios are extremely useful because they are not fractionated by geochemical reactions (e.g. mineral dissolution and precipitation) or biotic processes, and may be used to investigate mineral weathering reactions. Differences in isotope ratios reflect only mixing, thereby providing valuable information on sources, pathways and geochemical processes (Land et al., 2000, Aubert et al., 2002, Hogan and Blum, 2003 and Négrel and Petelet-Giraud, 2005). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in streams and rivers varies widely, from values as low as 0.7046 in young basaltic terrains (Wadleigh et al., 1985) up to 0.7456 in granitic terrains of Proterozoic age (Åberg and Wickman, 1987 and Åberg et al., 1989). The importance of bedrock type and age in controlling the variation in isotope ratios is well established (Wadleigh et al., 1985).

In contrast to the stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), Sr isotopes can change through reaction with minerals and so indicate chemical reactions which have taken place in the catchment. Several other stable isotope tracers (e.g. $\delta^{32}\text{S}$, $\delta^{15}\text{N}$, $\delta^{13}\text{C}$) may also change in response to chemical reactions, but are more complex in that they are often fractionated during chemical reactions in different environments. However, solute tracers provide information primarily about the solute measured and not necessarily the water itself, hence assumptions are often required to relate solute transport to flow pathways. Strontium concentrations in runoff, soils and biomass are primarily a function of mixing between atmospheric inputs and mineral weathering. Differences in solute Sr isotope ratios are controlled by variations in initial inputs, differences in mineralogy along flowpaths, mineral dissolution characteristics and residence time. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in waters will therefore be a function of the “weatherable Sr” and the efficiency of exchange (Åberg et al., 1989). One of the main problems for Sr isotope tracer studies lies in defining the isotope composition of this weathering-derived Sr. Complete rock or soil dissolution does not give a fair representation of the weathering ratio because of the different weathering rates and stabilities of minerals in the weathering environment. The whole rock isotope ratio is, therefore, of little relevance in determining weathering rates because the weathering-derived ratio will be dominated by those mineral phases with the highest dissolution kinetics. A range of leachate and extraction techniques, usually employing organic acids, have therefore been used to determine the weathering component of Sr in soils (Åberg et al., 1989, Wickman and Jacks, 1992 and Miller et al., 1993). The presence

of different mineral phases and different water flowpaths necessitate considering isotope data in conjunction with solute chemistry.

Strontium isotopes have also been used to estimate weathering rates of Sr, and also as a surrogate for the essential alkali earth element Ca (Graustein and Armstrong, 1983, Jacks and Åberg, 1987 and Åberg et al., 1989), based on the assumption that calcium exhibits the same ratio of deposition to weathering as strontium (Jacks et al., 1989). Although Sr generally behaves similarly to Ca, minerals may have significantly different Sr/Ca ratios and, therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios may not necessarily be a precise indicator of Ca sources (Kendall et al., 1995 and Shand et al., 1997). Wickman and Jacks (1992) emphasised that, in order to improve the application of Sr isotopes to weathering studies, a knowledge of Sr isotope signatures is required for different parts of a catchment.

The aim of this study is to assess the use of strontium isotopes in determining flow pathways, weathering rates and the role of groundwater in streamflow generation in the upland catchment of Plynlimon in Central Wales. It specifically sets out to assess whether previous models of streamflow generation dominated by soil water sources are valid. We also compare weathering rates calculated using Sr isotopes with those previously derived from mass balance studies (Durand et al., 1994).

2. The Plynlimon catchments

2.1. Study site

The Plynlimon experimental catchments (Fig. 1), approximately 16 miles northeast of Aberystwyth, have been a focus of catchment research since the early 1970's. Detailed information regarding the catchments have been presented by Kirby et al. (1991) and recently updated (see Neal, 1997 for summary). Much of the early hydrochemical work focussed on the effects of land use change on water quality (Neal et al., 1992), largely based on data monitored at flumes at catchment and sub-catchment outflows. The Afon Hafren and Afon Hore catchments form the two main headwater sub-catchments of the river Severn: they are of similar size, about 340 ha, with elevations of 350–750 m above sea-level. The catchment is largely forested, mainly with Sitka Spruce, although semi-natural moorland is present in the upper parts of the catchment. Mean annual temperature is 7.2 °C and rainfall in the area is around 2500 mm, most (nearly 75%) of which is derived from synoptic westerly air masses.

Lower Palaeozoic mudstones and shales dominate the bedrock geology with minor well-cemented sandstone and grit locally present in the headwaters of the catchment. The upper part of the catchment comprises the Ordovician Fan Shales, a series of blue–grey mudstones and shales which are well exposed forming competent outcrops in the stream channel. The uppermost part of this sequence is the Rhaeder Mudstone, a thick resistant band which forms a waterfall (Blaen Hafren) separating it from the younger Silurian Gwestyn Shales further downstream. The Gwestyn Shales are grey to black shales and mudstones, locally containing abundant pyrite. The mineralogy of the mudstones comprises an iron magnesium chlorite, a dioctahedral mica and quartz, with lesser amounts of feldspar and iron oxides.

The catchment is covered with thin (0.5–1.0 m) acidic soils, mainly podzol on the free draining slopes and peat overlying podzol on the flat upper parts and wider interfluvies (Kirby et al., 1991 and Shand et al., 2005). Soil mineralogy is closely related to the bedrock but with alteration of chlorite and transformation of illite to vermiculite, particularly in the upper soils. The valley bottoms where drainage is sometimes impeded often contain a complex of peat and gleyed mineral soils.

The hydrological response of the streams is typical of upland catchments displaying a rapid, flashy response to rainfall events, with chemistry changing from more alkaline at baseflow to more acidic during storm events. The bedrock in the catchment was traditionally considered to be impermeable and the role of groundwater in streamflow generation was, therefore, considered to be negligible. Models were initially developed whereby the baseflow component was derived from deeper mineral soils and the more acidic stormflow component from organic-rich horizons of the soil and from peat in the upper reaches of the catchment. However, the relatively alkaline nature of stream baseflow was inconsistent with derivation from acidic soils, and recent work (Neal et al., 1997a, Neal et al., 1997b, Neal et al., 1997c, Shand et al., 1997 and Haria and Shand, 2004) has highlighted a potential role for groundwater in streamflow generation. Bedrock exposure in the catchment is very patchy. A combination of field observation and geophysical logging (Shand et al., 2005) has shown that fracturing in the bedrock is spatially heterogeneous. The upper part of the bedrock is typically heavily weathered and fractured (sub-cm to m scale), most likely related to periglaciation during and following the late stages of the last ice age (ca. 10,000 yr BP). Deeper fractures are likely to represent bedding plane fractures with groundwater flow dominated by high horizontal transmissivity and limited vertical transmissivity. Recent hydrochemical studies (Shand et al., 2005) have highlighted the large spatial and temporal variations in soil water complex chemistry, stream chemistry and groundwater chemistry, making the determination of source and pathway using concentration data fraught with difficulties.

2.2. Sampling and analytical techniques

A total of 54 water samples, including rainfall, streams and groundwater from boreholes were collected and analysed during this study, mainly in the Afon Hafren catchment. Three soil profiles (podzol, gley, peat) were also studied (soil porewaters and acid extractions) as well as representative samples of mudstone, greywacke and a vein assemblage from a disused mine in the Afon Hore catchment were analysed for $^{87}\text{Sr}/^{86}\text{Sr}$. Sample locations for the streams and boreholes are shown in Fig. 2 and background hydrochemistry has been previously published by Shand et al. (2005).

Two samples of mudstone (PLR 1,4) and a sample of grit (PLR 2) were collected from the Afon Hafren catchment. The mudstones were composed predominantly of illite with lesser chlorite and minor quartz and altered feldspar. The grit was of variable grain size and composed dominantly of anhedral to subhedral quartz with lesser quantities of plagioclase, K-feldspar and chlorite. Several quartz carbonate veins (PLR 3,5,6) from spoil tips at the Snowbrook mine in the Afon Hore catchment were also collected and whole-rock and acetic acid extractions completed, the latter to dissolve the calcite. The rock samples were jaw-crushed and split, with representative 100–200 g sub-samples finely ground to give – 200 mesh powder for isotope and

geochemical analysis. The vein samples were coarse crushed and the carbonate fraction hand-picked under a microscope. Rb and Sr concentrations and Rb/Sr ratios were determined by X-ray fluorescence spectrometry.

Two soil profiles were sampled from the Hafren Forest and a peat profile from near the source of the Afon Hafren. The first profile was taken from a podzol in a relatively dense part of the forest, and the second from a gleysol excavated approximately 30 m from the Nant Tanllwyth. Sampling of the profiles was based on readily identifiable soil horizons. In order to keep the number of samples to a minimum, both profiles were split into three sections. For the podzol this comprised combining the humus layer with the dark brown organic-rich A horizon, and samples were collected from an underlying brown B horizon and grey C horizon. The humus layer and the A horizon were also combined for the gley which included a narrow band of black peat. The distinction between the B and C horizons was less clear for the gley and the subdivision was somewhat arbitrary. Much of the peat above the forest was eroded into 'hags' and this was sampled where it rose above the adjacent peat soil pit. A B horizon was present beneath a thick Ea horizon. During excavation, the soil pit filled with water rapidly so it was not possible to assess depth to bedrock. Soil solution was displaced from the field-moist samples within 1 day of sampling using the centrifuge drainage method. A Beckman J2-21 refrigerated centrifuge with a 6×250 cm³ JA14 fixed angle rotor was used. Specially made Delrin liners held the soil in the centrifuge rotor. All six liners were used for each horizon and were thoroughly washed in between. Operational settings were: speed, 14,000 rpm (30,000 g); temperature, 4 °C; time, 35 min. Yields varied from 35% at the top of the podzol profile to 43% at the bottom and from 25% at the top of the gley to 52% at the bottom.

A 0.43 M HNO₃ extraction (details in Gooddy et al., 1995) was used to extract cations and those present in readily-soluble oxide phases. The 0.43 M nitric acid extraction was chosen in the present study since it will remove exchangeable as well as sorbed and organically bound Sr (which may be an important potential source of Sr to the soil porewaters). Approximately 10 g of air-dried soil from each horizon was accurately weighed into a pre-weighed 250 cm³ oak ridge polypropylene centrifuge tube to which was added 100 cm³ of 0.43 M HNO₃ (Suprapur grade, Merck). The tubes were shaken on a box shaker in a constant laboratory temperature (23 °C) for 2 h, centrifuged for 10 min at 14,000 rpm, and finally the coloured supernatant solutions were filtered through 0.45 µm filter membranes. Extractions were performed in duplicate and for each horizon these were bulked. Approximately 100 ml of sample was collected for Sr isotope analysis and the remainder used for the determination of cations by ICP-OES and ICP-MS. A procedural blank was also prepared for isotope and cation analyses.

Two rainwater samples were collected from a meteorological station at the headwaters of the Afon Hafren. One-litre polyethylene bottles were used to collect two consecutive weekly rainfall samples between 26 September and 10 October 1995. Stream samples were collected from six sites during December 1994 (stormflow), June 1995 (baseflow) and December 1995 (intermediate flow regime). Borehole samples were collected initially using a whale pump and the boreholes were pumped prior to sample collection and measurement. Only one very shallow borehole (US 1) at the headwater of the catchment was pumped dry. This borehole refilled relatively

quickly and was sampled after being emptied several times. Depth samples were also collected from the deep (VB2, VB3, LS6) and intermediate depth (US3 and IS4) boreholes. The depth samples were all collected during pumping whilst geophysical logging. It was realised that the pumped samples represented a mixed sample from several distinct fractures and that the chemistry was often dominated by more highly mineralised water from the deeper fractures which typically had high upward heads. In order to preferentially sample water from shallowest fractures, waters were also collected using an open-ended bailer. The sample was collected after discarding five or more bailed volumes.

On site analysis included temperature, specific electrical conductance (SEC), pH and dissolved oxygen (DO) by electrode, and total alkalinity (as HCO₃) by titration. Detailed hydrochemistry was presented by Shand et al. (2005). With the exception of rainfall, all samples for laboratory analysis were filtered through 0.45 µm membranes. Samples for Sr isotope analysis were filtered into nalgene bottles but left unacidified in order to keep potential contamination to a minimum.

A suitable volume of each water sample, 10 to 200 ml depending on strontium concentration, was evaporated to dryness and the residue dissolved in 2.5 M hydrochloric acid. Aliquots of North Atlantic seawater were also prepared in the same way. Soil extraction samples were evaporated and the residue treated with 6 M hydrochloric acid. The solutions were then centrifuged and the supernatant liquid carefully decanted into nalgene beakers and evaporated. In some cases this procedure was repeated in order to obtain a clean solution when the residue was dissolved in 2.5 M hydrochloric acid. The whole rock samples were dissolved in a mixture of hydrofluoric and nitric acids (8:2) and, following evaporation, the residue was converted to the chloride form with 6 M hydrochloric acid. Strontium was separated from the water and rock samples by conventional ion exchange techniques using BioRad AG-50W cation-exchange resin. Strontium was loaded onto single tantalum filaments prepared with phosphoric acid, and isotope ratio measurements were made on an automated multi-collector Finnigan-MAT 262 mass spectrometer. Data were collected over a period of two years and during that time the ⁸⁷Sr/⁸⁶Sr ratio for the NBS 987 strontium isotope standard varied from 0.710186 ± 0.000014 ($2\sigma, n = 14$) to 0.710244 ± 0.000011 ($2\sigma, n = 19$). Therefore, in order to be consistent, the measured isotope ratios have been normalised to a standard value of 0.710244.

3. Results

3.1. Bedrock samples

Whole rock ⁸⁷Sr/⁸⁶Sr ratios for the two mudstone samples were radiogenic (Table 1) and similar to Welsh Ordovician/Silurian mudstones reported elsewhere (Evans, 1996). The isotope ratio of the grit was significantly lower than the mudstone reflecting the relatively high plagioclase content. Strontium concentration was also lower reflecting the relative abundance of quartz. The vein sample PLR 3 from the spoil tips of the Snowbrook mine had the lowest whole rock isotope ratio and a low Sr concentration. The vein sample contained some host rock fragments, and an acetic acid extraction was carried out in order to determine the isotope ratio of the calcite. Two further samples were analysed which indicated a narrow range of ⁸⁷Sr/⁸⁶Sr for

the calcite with a mean of 0.711507, significantly less than the whole rock ratios (Table 1).

3.2. Rainfall

The Sr isotope ratios of the two rainfall samples (Table 2) are indistinguishable within error from the values obtained for seawater ($0.70917 \pm 2, 2\sigma, n=13$) and slightly lower than the range (0.7093–0.7104) reported by Bain and Bacon (1994) and Bacon and Bain (1995) from three sites in Scotland. The two samples collected were very different with respect to TDS: samples 1 and 2 had Cl concentrations of 13 and 1 mg l⁻¹ respectively. The long term Sr isotope ratio of precipitation is most likely to be similar to the measured values because of the dominant input into the catchment of a marine derived source for the alkali and alkali earth elements (Neal et al., 1997b).

3.3. Soil samples

The soil porewater and acid-extraction data showed significant depth variations both in isotope ratio and element concentration in the profiles (Table 3 and Table 4). The isotope ratios and concentrations in the upper organic-rich O/A horizons are similar in the soil profiles and, although low, are significantly above rainfall ⁸⁷Sr/⁸⁶Sr. The podzol shows a peak in Sr isotope ratio in the B horizon in contrast to the gley where the ratio increases down the profile (Fig. 3). Strontium concentrations correlate inversely with ⁸⁷Sr/⁸⁶Sr in the gley soil but there is little variation in Sr concentration in the podzol. The Sr isotope ratios in the peat and underlying podzol were relatively low, but increased with depth.

The acid extractable Sr displayed very similar trends to the porewaters but with much higher concentrations and higher ⁸⁷Sr/⁸⁶Sr (Table 4). The exception to this is ⁸⁷Sr/⁸⁶Sr of the O/A horizon in the gleyed soil where the ratio was slightly higher in the pore water. The porewater ⁸⁷Sr/⁸⁶Sr is thus not in isotopic equilibrium with the exchangeable ⁸⁷Sr/⁸⁶Sr, however it displays similar trends through the soil profiles (Fig. 3). The values of log K_d (the log of the solid/liquid partition coefficient between the exchangeable Sr and porewater Sr) in the organic horizons were generally similar to data from acid sandy soils (Goody et al., 1995) but the C-mineral horizons have higher K_d values probably reflecting higher clay contents in the Plynlimon soils.

3.4. Stream waters

The stream water samples showed a significant variation in strontium isotope ratios between sites (Table 5), but relatively little variation during the different flow regimes (Fig. 4). The River Severn sample represents the total outflow from the catchment and was intermediate between the three sub-catchments. There was a significant decrease in Sr and Ca concentration with increased flow, but the magnitude of the decrease was much smaller than the changes in flow which showed a 12–20 fold increase at the four flume sites sampled.

Both the Afon Hafren and Afon Hore sub-catchments showed an increase in Sr isotope ratio downstream from the upper catchment, and the Afon Hore samples had

more radiogenic Sr than the Hafren despite the presence of calcite (with a lower isotope ratio) in the headwaters (Table 3). The Tanllwyth tributary is distinctive in its relatively high isotope ratio and Sr concentration at baseflow and significant decrease in isotope ratio at high flows (Fig. 4). However, the baseflow samples may have been affected by leakage from the adjacent borehole (Neal et al., 1997c).

3.5. Groundwaters

Strontium isotope data for the pumped groundwaters are presented in Table 6 and Table 7. There is a considerable range in isotope ratios varying from values similar to rainfall in the shallow borehole (US 1, 0.709326) at the headwater of the catchment to 0.7149 in the deeper boreholes. The shallow pumped boreholes from the Hafren (LS 1, LS3), Carreg Wen (US 1, US 3) and the intermediate slope (IS 4) showed a wide range in isotope ratios, whereas the Tanllwyth (VB 4) and nearby Met Site (VB 1) boreholes had consistently higher ratios. Depth samples were collected from the three deep (c. 45 m) boreholes (VB 3, VB 2, LS 6) during pumping and these all had relatively high ratios showing little variation with depth (Fig. 5). The bailed groundwater samples from shallow boreholes also displayed a wide range of Sr isotope ratios, displaying an increase in $^{87}\text{Sr}/^{86}\text{Sr}$ with depth of borehole (Fig. 6).

Strontium concentrations showed considerable variation, from values similar to stream water in the shallow boreholes in headwater sites, to greater than $300 \mu\text{g l}^{-1}$ in the deep groundwaters along valley bottoms. Although the groundwaters show a large increase in Sr concentration with depth (Table 6), Sr isotope ratios remained relatively constant and significantly less radiogenic than the dominant host rocks of the catchment.

4. $^{87}\text{Sr}/^{86}\text{Sr}$ as an indicator of weathering phases and weathering rates in the catchment

Several methods have been used to calculate weathering rates in catchments including long-term hydrochemical mass balance (stream flux minus atmospheric flux), the use of laboratory-derived mineral dissolution rates and normalisation to kinetically stable components in soils, all of which have potential problems. A mass balance approach is useful for determining current weathering rates, but requires detailed knowledge of all contributing sources and pathways. Some inputs, e.g. dry deposition, are poorly constrained and such inputs are generally calculated by deduction rather than directly. One of the problems in determining mixing/mass balance calculations in such a complex system as a river catchment is the inability to uniquely characterise the various reservoirs in the system, but the use of isotope ratios may allow the inputs from atmospheric and weathering components to be differentiated. A long-term mass balance approach was presented by Durand et al. (1994) and forms a good comparison for testing the Sr isotope approach.

The value of $^{87}\text{Sr}/^{86}\text{Sr}$ in local stream waters will be strongly influenced by the most easily weathered phase which will generally have a different Sr isotope signature from that of the whole rock. Although it is often assumed that the weathering-derived ratio of $^{87}\text{Sr}/^{86}\text{Sr}$ is constant, this is likely to be the case only in monomineralic terrains. The early stages of weathering in some terrains have been shown to be dominated by dissolution of the most reactive minerals (e.g. biotite, plagioclase) and the

contributions of Sr may therefore vary with the age of the soil (Bullen et al., 1995 and White and Blum, 1995). There are usually discrepancies between laboratory and field based methods of estimating weathering rates, with the former often being an order of magnitude higher. A major factor is the differences between the two methods in the exposure of mineral surfaces to water as a result of variable flow paths and inhomogeneities in soils (Velbel, 1993 and Berner and Berner, 1996).

The shallow groundwaters are variable both in terms of Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ but there is a general increase in Sr with depth in the shallower groundwaters, generally less than c. $45 \mu\text{g l}^{-1}$ Sr. The deeper groundwaters show large increases in Sr concentration (up to $346 \mu\text{g l}^{-1}$) as the waters evolve but with no further increase above a maximum of c. 0.7148 where Sr is higher than ca. $50 \mu\text{g l}^{-1}$ (Fig. 7). This maxima implies control by a single mineral phase. This isotope ratio is significantly higher than calcite sampled from the upper Hore and much lower than the whole rock, the latter dominated by illite and chlorite. The high concentrations of base cations, silica and bicarbonate in the groundwaters in comparison with atmospheric inputs shows that weathering is the dominant source.

The maximum Sr isotope ratio found in the groundwaters is similar to that extant during diagenesis, when the system was homogenised through the smectite–illite transition (Evans, 1996). This implies that the weathering phase is Rb-poor or Rb-free because no further increase in $^{87}\text{Sr}/^{86}\text{Sr}$ has occurred since low-grade metamorphism in the Lower Palaeozoic. The groundwaters and surface waters initially show a positive correlation of Sr with Si, Na/Cl (a measure of excess Na over rainfall) Ca and HCO_3 (Fig. 8), implying that a phase containing these elements is the main control on the weathering of Sr. It is proposed that the controlling phase is likely to be plagioclase feldspar. However, other candidates include apatite or epidote, although these are dominated by either Na or Ca and two phases would then be needed to explain the correlations. The higher Ca concentrations in the Afon Hore have been assumed to be due to calcite dissolution from an old Pb–Zn mine in the headwaters of this stream. This is indicated by relatively high Ca/Sr ratios in the Afon Hore stream waters ($0.4\text{--}0.5 \times 10^3$ compared to typically $0.2\text{--}0.3 \times 10^3$ in the Hafren). However, Sr isotope ratios are higher in the Hore, which is opposite to that expected if calcite dissolution was a major contributor to the Sr. The highest Ca concentrations were found in the Tanllwyth but here Ca/Sr ratios are similar to the Hafren and the Sr is likely to be from a non-carbonate source as indicated by the relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the streams. The very high Sr concentrations in the deeper groundwaters indicate that their contribution to streamflow is not significant, but it has been shown that the shallow bedrock acts as a mixing zone for rainfall and deeper upwelling groundwater, consistent with higher heads in the deep groundwaters (Shand et al., 2005).

The implication that groundwater supplies base cations to streams implies that the weathering of large volumes of bedrock in the groundwater environment is important in terms of catchment output. Weathering rates calculated here are based on total output from streams and may not be truly representative of weathering rates within the catchment: any export of groundwater from the catchment means that calculations based on stream export are likely to be an underestimate. In addition, biomass uptake may also remove large amounts of base cations and if the catchment is not at steady

state, this will further underestimate weathering rates. Long term flux measurements are necessary to average out the latter effects, because small term fluctuations will be averaged out if the system is at steady state. Robson and Neal (1996) have studied long term statistical variations in the Plynlimon catchments and concluded that long term trends are not apparent for most elements, including base cations. A steady state system is, therefore, assumed.

Providing that the end-member compositions are known and that they are of constant composition, mixing is generally a simple calculation if only two components are present. Strontium in the catchments is ultimately derived from two sources: atmospheric inputs and weathering-derived. The atmospheric end-member is taken to have a concentration of $2.1 \mu\text{g l}^{-1}$ (long-term flow weighted average of rainfall; Neal et al., 1992) and an isotope ratio of 0.7092. The weathering end-member is more difficult to estimate. If we assume that the maximum isotope ratio found in the groundwaters represents the weathering value of the groundwater system, then 0.7149 is a reasonable estimate. It is evident, however, that higher ratios are present as Sr bound to the soils in both the podzol and gley (Table 3 and Table 4). The podzol, which is the dominant soil type, has porewaters with a similar Sr isotope ratio and the exchangeable ratio is only slightly higher than this (0.7162). Therefore, the non-fixed weathering-derived strontium is considered to be justified at a ratio close to these values. The concentration of Sr is more difficult to estimate in the groundwater end-member because of the large degree of heterogeneity (Shand et al., 2005). This will be assessed in the next section.

The isotope ratios in runoff are intermediate between the precipitation and weathering derived Sr and it is therefore possible to calculate the fraction of Sr derived from each component. If we assume simple mixing between rainfall and rock weathering derived Sr, this indicates that between 60% and 80% of the Sr in the three streams is derived from weathering with the Tanllwyth containing the most and the Afon Hafren the least. The main Severn, Afon Hafren and Afon Hore show little variation with flow similar to variations noted in other studies (Wickman and Jacks, 1992 and Bain and Bacon, 1994).

The long term flow weighted concentrations and isotope ratios derived in this study can be used to calculate weathering rates for Sr (Wickman and Jacks, 1992):

$$W\% = \frac{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_R - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]}{\left[\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_W - \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_D \right]} \times 100$$

where R, D and W refer to runoff, deposition and weathering respectively.

Strontium isotopes have been used as a surrogate to estimate the behaviour of Ca in many catchment studies (Åberg et al., 1990). This is because the two elements often show similar chemical behaviour in simple ecosystems (Wickman and Jacks, 1992 T.

Wickman and G. Jacks, Strontium isotopes in weathering budget. In: Y.K. Kharaka and A.S. Maest, Editors, Proc. 7th Intern. Sym. on Water–Rock Interaction, A.A. Balkema (1992), pp. 611–614. (Wickman and Jacks, 1992). The application of Sr isotopes to the major cation Ca may be complicated by different behaviour or to sources with different Sr/Ca ratios. Strontium tends to show a slightly greater affinity for adsorption sites on clay minerals, however, such differences are relatively small as both are extremely mobile during weathering in most weathering environments. The similar behaviour of Sr and Ca in the present study is indicated by the good correlation of these elements in the streams and groundwaters (Fig. 8). Weathering rates for Ca have been calculated assuming similar behaviour for Sr and Ca:

where FCa is the long term flow weighted Ca flux. This assumes that the Sr/Ca ratio in the runoff is the same as that of the weathering source. Weathering rates for the Hafren and Hore have been calculated using Sr isotopes and are shown in Table 8, along with calculations based on long-term mass balance studies (Durand et al., 1994). The chemical budgets calculated by Durand et al. (1994) were considered to be an “indicator of the biogeochemical functioning of the catchments, rather than as an exact balance of the elements”. This was suggested because of the problems with estimating solute fluxes in streams due to the lack of continuous monitoring of geochemical compositions which tends to bias calculations to low flow concentrations. The rates for the Afon Hafren are very similar to those obtained by mass balance, particularly for Sr (Table 8). The calculations for the Hore, however, are similar for Ca but not for Sr, which has a much higher estimated weathering rate of Sr using the Sr isotope method. The measured long term fluxes of Sr for the Hore and Hafren are similar (51 and 52 g ha⁻¹ yr⁻¹) but the isotope ratio in the Hore stream is significantly higher.

There are several potential reasons why the weathering rate of Sr does not match more precisely the mass balance calculations in the Hore. Firstly the stream chemistry (necessary to quantify weathering flux) is truly biased toward baseflow and although Sr concentration is higher in baseflow, the fluxes are much greater during stormflow. However, the similarity for the Hafren in both methods implies a different reason. Secondly, it is possible that the Sr concentration and flux in atmospheric input is too high. This may be due for example to the poor precision at the very low concentrations present in rainfall, but again the calculation appears to agree for the Hafren. Thirdly, one of the end-member ratios chosen in the isotope mixing technique may not be correct. This is most likely to be the weathering end-member e.g. if the ratio of 0.7048 chosen from the groundwaters is not representative of the total weathering-derived Sr in runoff. The soils and groundwaters were collected from the Hafren catchment and it may be the case that weathering in the catchments is different e.g. more intense in the Hore. Finally, the Hore is complicated by potential inputs of calcite with a different Sr/Ca ratio. Further data is required to estimate such a three-component mixing model.

Higher Ca concentrations in the Hore catchment have previously been taken as evidence of calcite dissolution from an old Pb–Zn mine in the Upper Hore and the higher weathering rate in the Hore may be due to calcite dissolution, the kinetics of which are much faster than silicate dissolution. Calcite dissolution, however, would lead to lower ⁸⁷Sr/⁸⁶Sr in the Afon Hore catchment, the opposite to what is actually measured in the Afon Hore stream. It is difficult to say at present which if any of the

above processes is important. Nevertheless, it appears that Sr isotopes provide a means of estimating weathering rates, and certainly for the Afon Hafren stream, the rate is comparable to mass balance techniques. A benefit of using Sr isotopes for the determination of weathering rates is that it does not necessitate an accurate knowledge of atmospheric input fluxes, an extremely difficult flux to measure. The amount of dry deposition, for example, is difficult to estimate and normally calculated on the basis of Cl mass balance. However, recycling of Cl or depositional differences between Cl and Sr make this calculation fraught with uncertainties.

5. $^{87}\text{Sr}/^{86}\text{Sr}$ as an indicator of flow paths in the catchment

Since strontium isotopes are not fractionated by low temperature geochemical processes or biological processes, they can yield information about the sources of strontium and the flow and transfer of strontium within an ecosystem. The variations in the concentration of strontium with discharge are difficult to interpret due to the large number of potential sources and geochemical reactions modifying the concentration e.g. atmospheric, weathering, decay of organic matter and ion exchange in the various soil horizons. Isotope ratios provide a means to characterise sources independently of gains to or losses from the system.

Graustein (1988) used Sr isotope data elsewhere to show that much of the Sr in runoff was not derived from soil solution. He considered two possibilities to explain low Sr isotope ratios in soils studied compared with runoff: 1) most of the flow from the soil surface to the aquifer occurred by rapid transport or 2) strontium in the shallow soil solution was totally absorbed in the rooting zone and replaced by weathered strontium below the root zone. These conclusions cause problems for relating flux information and budgets in soil zones to nutrient budgets derived from stream hydrochemical data (Graustein, 1988).

5.1. The soil zone

The soil horizons displayed a wide range in both Sr concentrations and isotope ratios (Fig. 3). In the gley profiles, Sr shows a decrease in concentration with depth in both porewaters and exchangeable Sr, whereas Sr isotope ratios increased. The porewater Sr isotope ratios are intermediate between the exchangeable Sr and that derived from rainfall and are interpreted as mixing between these two components. The porewaters are not in isotopic equilibrium with the exchange pool, demonstrating inefficient exchange during water transport through the soils. This is most likely due to rapid transit rates through the soils or to the unavailability of the exchangeable Sr (because of discrete flowpaths) or to Sr being present on unreactive sites. The high Sr concentration in the exchange complex of the upper organic-rich soils is probably related to nutrient cycling and release from biomass. This Sr is dominantly atmospheric-derived but a small component of weathering-derived Sr is present. This profile is considered to be typical of a simple weathering profile where active weathering is occurring in the deeper parts of the soil zone in the C horizon.

The podzol profile also displays some of the characteristics displayed by the gley, but very high Sr isotope ratios are present in the B horizon, as well as very low Sr concentrations in the exchange pool. This implies weathering of a radiogenic

component of soils, most likely illite or chlorite which swamps the atmospherically-derived Sr. The soils, therefore, show significant vertical heterogeneity, but the deeper weathering horizons of both soils are similar. It is clear that contributions from the organic soil horizons are easily discriminated from the deeper mineral soil horizons and it is likely that mixing between porewaters from the different soil horizons would produce significant variation if they formed a major component of stream waters. In addition, different antecedent conditions would likely impose further variations.

5.2. Surface water and groundwater

Strontium concentrations at individual sites show a typical decrease in concentration with flow but this is small in comparison with the large increases in discharge. In contrast, strontium isotope ratios typically showed a remarkably small change in isotope ratio (except for samples in the Tanllwyth tributary as discussed earlier). This lack of variation implies a well mixed relatively homogeneous source of Sr. Isotope ratios in the Afon Hore and Afon Hafren increase downstream implying a greater proportion of atmospherically-derived Sr in the headwaters, with weathering-derived Sr becoming more important downstream. The high strontium concentrations in groundwater compared to rainfall and soil porewaters show that the dominant source of strontium in these is from weathering of bedrock (probably plagioclase as deduced in Section 4) rather than soils. Groundwaters in the headwaters of the catchment display the least radiogenic strontium isotope ratios with one very shallow groundwater having a ratio only slightly higher than rainfall i.e. they display the same spatial pattern as found in the streams. However, it was not possible to assess the water chemistry of the shallowest fractures because of upward flow in the borehole column (Shand et al., 2005). The bailed samples had much lower strontium concentrations than the pumped samples with both concentrations and isotope ratios being generally similar to the stream waters.

Strontium isotope ratio is plotted against $1000/Sr$ for the Hafren and Tanllwyth sites, where both surface and groundwater data are available, in Fig. 9. Such a plot is useful because the mixing of two components is represented by a straight line between the end-members. This clearly has potential to constrain models for the evolution of stream waters: it will indicate whether two or more end-members are present. Some of the shallow groundwaters lie close to the upper organic soils but most form a tight cluster. It is evident that the stream waters do not lie on a mixing line between the upper and lower soil horizons or between the soils and groundwater. In the case of the Hafren, the stream waters lie on a potential mixing line between the groundwater or deep soil and average rainfall, and in the Tanllwyth, between groundwater and average rainfall. Only in the case of the Tanllwyth, which shows the largest change in concentration with flow, is there a shift away from this line. The Tanllwyth stormflow stream waters, however trend towards the deeper soils and not the shallow organic horizons as expected.

5.3. Flow processes and mixing in the catchment

A plot of $^{87}Sr/^{86}Sr$ vs. $1000/Sr$ is shown for all the data on Fig. 10. Most of the pumped groundwaters form a tight cluster with relatively high strontium concentrations and isotope ratios; this cluster is dominated by groundwater from close to the valley bottoms. Several pumped samples, those in the headwaters and interfluvial

area, lie close to the upper organic soils or on a mixing line between the upper soils and groundwater showing that soil inputs contribute to the shallow groundwater in these areas. The samples which fall below or to the left of this mixing line have most likely been strongly affected by evapotranspiration processes, which affect the concentration, but not the isotope ratio of Sr. The majority of the bailed samples, like the streams, lie on a mixing line between rainfall and the deeper groundwaters implying that the water derived from these shallow fractures is formed by dilution of the more evolved deeper groundwater. The groundwater US1 is from a 1 m borehole beneath peat and appears to have a significant soil-organic component. Taking into account the strontium concentrations and position of samples on the mixing diagram, it appears that the deeper weathering parts of the soils do not form the major input to the groundwater system. The differences between the deep and shallow groundwaters show that mixing is not rapid and probably takes place along discrete fractures connecting the two, but they are likely to be poorly connected.

The stream water data lie dominantly on a mixing line between rainfall and the deeper groundwaters implying that these components form the major inputs to the streams (Fig. 10). Although the C horizon podzol porewaters also lie on this line, the alkalinity is too low to explain the low flow component of the streams. The trend during higher flow conditions is away from the soil porewaters towards lower strontium concentrations; however, dilution of the podzol soil porewaters may occur during storm events and this would generally be towards the rainfall component. It is clear that the source of the dominant input is relatively well buffered for most of the flow conditions and the similarity of shallow groundwaters to the stream may imply that there is a dominant input from the shallow groundwaters. This would indicate that flow routing through bedrock fractures is important for the transfer of rainfall to the stream channel. What is very clear, is that there is no trend towards the upper organic soils, limiting their direct involvement during stormflow conditions.

The fact that there is such a small variation in isotope ratios in the streams is taken as evidence that the stream water cannot be a recent mixture of rainfall and deep groundwater because it is unlikely that this could produce a relatively constant isotope ratio: during large rainfall events the streams would be dominated by rainfall and at baseflow by groundwater, which should result in large temporal variations in the isotope ratios measured in the streams. The evidence indicates that the source is well mixed implying a significant residence time and storage in the shallow bedrock fractures. This is consistent with stable isotope studies of events in the Hafren (Shand et al., 2004) and adjacent Wye catchments (Sklash et al., 1996) which showed that stormflow is dominated by older pre-event groundwater, implying high enough storage to dampen atmospheric inputs, but low enough to remain highly responsive to rainfall events. Simple mixing calculations (Fig. 11) show that the streams are dominated by rainwater (the precise amount depending on end-member Sr concentrations chosen), although as stated above, this occurs in a storage medium within the catchment prior to becoming river discharge.

The rapid response of the streams to rainfall, and the dominance of storm flow by pre-event water are postulated to be due to increased head gradients which displace older water rapidly from the lower parts of the catchment to the streams. There is, therefore, a decoupling between the physical and chemical parameters. The dilution of many

solutes during rainfall events does indicate that dilution from rainfall occurs, but this contribution is likely to be relatively small except under very high flow conditions where the catchment has wetted up. This model explains the apparent buffering capacity of catchments in terms of the damped response of many solutes, but fails to explain the large increase in acidity, aluminium concentrations and stream organic loadings which indicate an important role for the soils in streamflow generation. However, where the water table is shallow, groundwater rises into the soils (Haria and Shand, 2004) causing mobilisation of both Al and DOC which are then transported to the stream channel.

Although the role of flow pathways in the soil is concluded to be of much less importance than previous studies on Plynlimon have indicated, their role in weathering remains important. It is simply postulated that an important pathway exists from the soils to the streams via the groundwater system. The details of flow pathways and how these change with flow and antecedent conditions is not possible with existing data, and requires more intense sampling. Nevertheless, Sr isotopes have proved a useful tool in weathering studies and constraining flow pathways in the catchment.

6. Summary and conclusions

Strontium isotopes have been used as a natural tracer to determine the dominant flowpaths of water through the Plynlimon catchments and to indicate weathering rates and processes. The isotope ratios in soil porewaters and on exchange sites are very variable and the porewaters are not in equilibrium with strontium on the exchangeable sites, most likely as a result of rapid transit times and discrete transport pathways. The extraction of porewater from a range of pore size distributions may, in addition, not be in equilibrium with the “average” of the exchangeable Sr due to local heterogeneity of the exchange complexes. The large variation of isotope ratios within the catchment is due to mixing between weathering- and atmospherically-derived sources.

The strontium in stream waters represents a mixture of strontium from atmospheric and weathering sources. Although there is a regional variation in isotope ratios in streams from different parts of the catchment, the site variations are small over large amounts of stream discharge. This implies that the streams are largely derived from a well-mixed source. The stream waters lie on a mixing line between groundwaters and rainfall suggesting that these form the dominant inputs even at high flow. Shallow groundwaters are similar chemically and isotopically to the streams and it is concluded that flow routing and mixing through the shallow bedrock fracture system is important in streamflow generation. The fact that there is such a small and consistent variation implies that the waters do not represent recent mixing as this would produce significant scatter depending on the antecedent conditions and amount of rainfall. This is consistent with stable isotope studies, which imply that the stream water is dominated by pre-event older water. The model presented in this study, where a major flow path is present through bedrock fractures contrasts with most models for upland catchments which are assumed to be impermeable beneath the bedrock, a model previously assumed for Plynlimon. The model presented here is, however, consistent with fractal studies of Cl input–output signals from a range of catchments, which indicates a large range in residence times (Kirchner, 2001 and Kirchner et al., 2001).

Weathering rates have been calculated assuming mixing between atmospherically-derived and weathering-derived strontium and these generally show good agreement with previously published mass balance studies. Weathering varies considerably in the soils with intensive weathering in the B horizon podzols where sheet silicates are being weathered. This is thought to be relatively small in terms of weathering flux, in comparison with deeper mineral soils where the dominant active weathering occurs. Relatively long residence time waters are present at depth in the bedrock and weathering is thought to be dominated by a single mineral phase e.g. plagioclase feldspar. Dissolution of calcite occurs in the upper parts of the Afon Hore catchment but the isotope signatures imply that there is not a significant effect on strontium concentrations and isotope ratios (although some Ca may be derived from this source). The shallow groundwaters, present in shallow fractured bedrock, are postulated to represent a zone of mixing between rainfall-derived recharge and deeper upwelling groundwaters, although the volumes of deeper groundwater contributed are small.

This study has shown that there is significant flow through fractured bedrock, especially in the shallow system, and that well mixed shallow groundwater may provide much of the stream input, even at times of high flow. These are important factors that should be considered in the resource management of upland catchment systems and in water quality models. It is likely that groundwater plays a much more significant role in streamflow generation in upland catchments than has hitherto been accepted.

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