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$^{87}Sr/^{86}Sr$ 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: $^{87}Sr/^{86}Sr$; 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; Mason, 1990). The impacts of acid deposition and other pollutant inputs on water quality

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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; McDonnel, 2003; 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; 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 CO_2 and consequently important long-term control on climate change. Unlike carbonate weathering, where CO_2 consumed in dissolution is released during precipitation of calcite in the oceans, silicate weathering and subsequent precipitation results in a net loss of CO_2 from the Earths 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 (δ^2H and $\delta^{18}O$ 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; 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; Blum and Erel, 2005).