Applied Geochemistry 24 (2009) 574–586

Contents lists available at ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

Sr isotopes in natural waters: Applications to source characterisation and water–rock interaction in contrasting landscapes

P. Shand [a,*], D.P.F. Darbyshire [b], A.J. Love [c], W.M. Edmunds [d]

[a] CSIRO Land and Water/CRC LEME, Private Bag 2, Glen Osmond, SA 5064, Australia
[b] NERC Isotope Geosciences Laboratory, Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG, UK
[c] Department of Water, Land and Biodiversity Conservation, P.O. Box 2843, Adelaide 5001, Australia
[d] School of Geography, Oxford University Centre for the Environment, South Parks Road, Oxford, UK

ARTICLE INFO

Article history:
Available online 14 February 2009

ABSTRACT

Strontium isotopes ($^{87}Sr/^{86}Sr$) are routinely measured in hydrochemical studies to determine sources and mixing relationships. They have proved particularly useful in determining weathering processes and quantifying end-member mixing processes. A number of routine case studies are presented which highlight that Sr isotopes represent a powerful tool in the geochemists toolbox helping to constrain weathering reactions, weathering rates, flow pathways and mixing scenarios. Differences in methodologies for determining the weathering component in natural environments, inherent differences in weathering rates of different minerals, and mineral heterogeneity often cause difficulties in defining the weathering component of different catchments or aquifer systems. Nevertheless, Sr isotopes are useful when combined with other hydrochemical data, to constrain models of water–rock interaction and mixing as well as geochemical processes such as ion-exchange. This paper presents a summary of recent work by the authors in constraining the sources of waters and weathering processes in surface catchments and aquifers, and indicates cases where Sr isotopes alone are insufficient to solve hydrological problems.

© 2009 Published by Elsevier Ltd.

1. Introduction

The application of Sr isotope ratios as a natural tracer in water–rock interaction studies and in assessing mixing relationships is now well established as indicated by the large number of journal publications and review articles (e.g. Graustein, 1988; Capo et al., 1998; Stewart et al., 1998; McNutt, 2000; Blum and Erel, 2005). The latter add weight to the maturity of Sr isotopes as a useful technique in de-convoluting the complex behaviour of solutes and water–rock interactions in natural environments. A wealth of unpublished data also exist, publication limited for example by difficulties in interpreting a large scatter of data (too complex systems, sample-scaling issues), lack of understanding of the system (e.g. flow system) or lack of detailed understanding of Sr geochemistry of for example interactions with solid materials.

Over the past few years, detailed field-based studies of weathering (Bain and Bacon, 1994; Bullen et al., 1997; Hogan and Blum, 2003; Négrel, 2006; Shand et al., 2007) have been augmented by laboratory (Brantley et al., 1998) and modelling (Fritz et al., 1992; Johnson and DePaolo, 1997) studies, and both have vastly improved understanding of Sr isotope behaviour; modifying paradigms due to realisation of more realistic complex behaviour and heterogeneous systems. Strontium isotopes are a powerful tool in the geochemists toolbox for constraining and testing geochemical and hydrological models. However, as many authors have stressed over the past decade, multi-isotope/tracer application (Bullen and Kendall, 1998) represents the most powerful approach to solving problems. Perhaps the most common limiting problem in dealing with Sr isotope data is the lack of sufficient information on solid phases, both in individual minerals and on exchange complexes.

The aim of this paper is to present some recent work by the authors in hydrological applications of Sr isotopes in constraining or solving hydrological problems. It presents some cases where Sr isotopes have been useful and others where their application is somewhat limited e.g. due to lack of isotopic variation. Nevertheless, even where Sr isotope data show little variation or are not fully understood, they can still place powerful constraints on conceptual hydrological models.

2. Sr isotopes in water

2.1. Sr isotopes and weathering

Strontium is a divalent cation that shows similar geochemical behaviour to Ca. It has 4 natural isotopes: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr, all of which are stable. However, the isotopic abundances in rocks are variable because of the formation of radiogenic ^{87}Sr by the beta decay of naturally occurring ^{87}Rb which has a half-life of 4.88×10^{10} a

* Corresponding author. Fax: +61 8 8303 8550.
E-mail address: paul.shand@csiro.au (P. Shand).

0883-2927/$ - see front matter © 2009 Published by Elsevier Ltd.
doi:10.1016/j.apgeochem.2008.12.011

(Faure, 1977). Although the minerals in igneous and metamorphic rocks may have identical Sr isotope ratios at the time of formation, the decay of ^{87}Rb to ^{87}Sr leads, over time, to differences in ^{87}Sr/^{86}Sr (Fig. 1). The increase in isotope ratio is proportional to the Rb/Sr ratio, forming the basis of dating rocks using the isochron method. Hence older rocks, particularly those with high Rb/Sr ratios tend to have larger variations between different minerals and higher ^{87}Sr/^{86}Sr ratios than younger rocks.

In freshwater systems, the residence times of waters are sufficiently short (days to 10^{2-3} a) compared to the half-life of ^{87}Rb, that radioactive decay of ^{87}Rb can be ignored.

It is commonly assumed that the isotopes of Sr do not exhibit detectable mass fractionation during chemical processes, unlike those of the lighter elements such as H, C, N, O and S. Any instrumentally produced mass discrimination during Sr isotope analysis by thermal ionisation mass spectrometry is corrected by using ^{86}Sr/^{88}Sr = 0.1194 as a normalizing ratio. Double or triple filament loading assemblies allow greater control on ionisation and vapourisation during analysis and generally give a more stable atomic ratio than is obtained when using a single filament.

Ohno and Hirata (2007) document isotope fractionation during the chemical separation of Sr by cation exchange and by extraction chromatography. They observed that the earliest fractions of eluent were systematically enriched in the heavier isotope. The authors attributed the fact that this effect was less pronounced in extraction chromatography using Sr spec resin than in cation exchange with Biorad AG-50 to the smaller number of theoretical plates in the former column. However, provided the yields from the columns were sufficiently high (<95% in the case of cation exchange, <90% for extraction chromatography), the isotope fractionation was within the level of uncertainty of the measurement of the isotope ratio.

Mass dependent fractionation was first observed in cosmogenic samples (Patchett, 1980) and subsequently in biogenic processes (Aggarwal, 2006, T.D. Bullen, pers comm). Advances in plasma ionisation multicollector mass spectrometry together with new methods developed for determining the mass discrimination effect on ^{88}Sr/^{86}Sr (Ohno and Hirata, 2007; Fietzke and Eisenhauer, 2006) have enabled natural variations to be shown in the ^{88}Sr/^{86}Sr ratio. Fietzke and Eisenhauer (2006) demonstrated a temperature-dependent isotope fractionation during $CaCO_3$ precipitation. They analysed natural corals and found a 0.033‰ shift per °C compared with 0.0054‰ for aragonite samples inorganically precipitated under temperature control. Ohno and Hirata (2007) analysed a series of geochemical reference samples and found no significant variations within ^{88}Sr/^{86}Sr ratios for the igneous rocks but an isotope fractionation of 0.1‰/amu between the carbonate samples and seawater. These degrees of fractionation are small in comparison with those observed in stable isotope studies of the lighter elements and need to be investigated further. Nevertheless Sr isotope data can be normalised to a specific ^{88}Sr/^{86}Sr ratio (e.g. chondritic value of 8.37521) removing such effects and enabling comparisons to be made. This makes Sr isotopes a particularly useful natural tracer of biological or low temperature chemical processes, and the isotope ratios are therefore a function of mixing or exchange between different reservoirs.

Differences in solute Sr isotope ratios are controlled by variations in initial (atmospheric) inputs, differences in mineralogy along flowpaths, mineral dissolution characteristics and residence time. The ^{87}Sr/^{86}Sr ratio in waters will therefore be a function of the "weatherable Sr" and the efficiency of exchange (Åberg et al., 1989). The reaction kinetics of mineral dissolution vary over orders of magnitude, and the Sr isotope ratios of solutes will be dominated by the most easily weathered minerals i.e. solute ^{87}Sr/^{86}Sr is unlikely to be in 'isotopic equilibrium' with the whole rock (Fig. 1). One of the main problems for Sr isotope tracer studies lies in defining the isotope composition of the weathering-derived Sr. Whole rock or soil dissolution does not give a fair representation of the weathering ratio because of 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 or processes. A range of leachate and extraction techniques, usually employing organic acids, have been used to determine the weathering component of Sr in soils (Åberg et al., 1989; Wickman and Jacks, 1992). Care must also be taken in relating the origin of Sr to the origin of water, since many assumptions and knowledge of processes along flow pathways are usually required in addition to knowledge of the Sr concentrations in

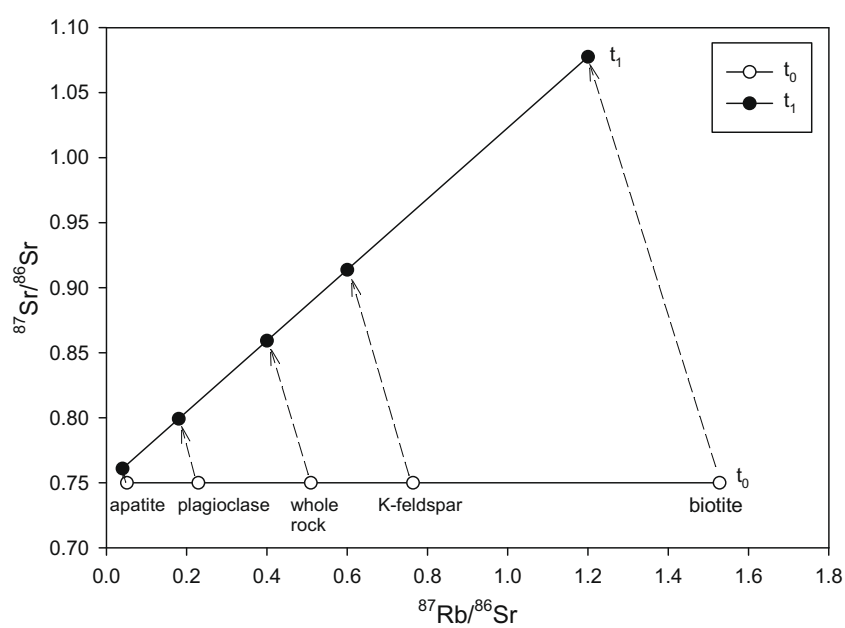

Fig. 1. Theoretical evolution of Sr isotopes in a rock (e.g. from a magma or metamorphic rock) from the time of initial formation (t_0) where the isotopes are homogeneous, to time (t_1) where the ^{87}Sr/^{86}Sr ratio has increased due to decay from ^{87}Rb.

'end-members' during mixing. For example, Sr isotope ratios may vary as a function of time due to differences in the proportions of weathering minerals e.g. where saturation with one phase occurs (Fritz et al., 1992). It is possible, but not commonly demonstrated (Taylor et al., 2000), that radiogenic ^{87}Sr derived from ^{87}Rb may be preferentially leached from minerals: Rb having a higher ionic radius occupies large sites in crystal lattices from which Sr may be more easily weathered.

The degree to which Sr isotopes can be used as tracers or as good indicators of mixing is partly dependent on the ratio of Sr concentration in the fluid relative to that in the rock (Cs/Cf) (Johnson and DePaolo, 1996) and the reactivity of the Sr in a particular environment. For example, where Sr-rich waters move from a carbonate aquifer into a granite aquifer, the relative stability of granite minerals means that Sr isotope ratio may retain a memory of its past geochemical evolution, hence it acts as a good tracer. In contrast, a groundwater with low Sr concentrations moving from a granitic aquifer into a carbonate aquifer may rapidly become swamped with Sr due to carbonate dissolution. A valid interpretation of the Sr isotope ratio therefore requires a sound knowledge of the potential hydrogeochemical processes operating along its flowpath.

A complete review of Sr isotopes is beyond the scope of this paper and the reader is referred to recent reviews (e.g. Graustein, 1988; Capo et al., 1998; Stewart et al., 1998; McNutt, 2000; Blum and Erel, 2005). The marine Sr isotope record is now fairly well established from studies of carbonate minerals of different age (McArthur and Howarth 2004 and references therein). Early studies of terrestrial systems applied Sr isotopes to estimate soil-exchange processes (Miller et al., 1993) weathering rates of Sr, and also used Sr as a surrogate for the essential alkali earth element Ca (Graustein and Armstrong, 1983; Åberg et al., 1989), based on the assumption that Ca exhibits the same ratio of deposition to weathering as Sr (Jacks et al., 1989). Strontium isotopes have also

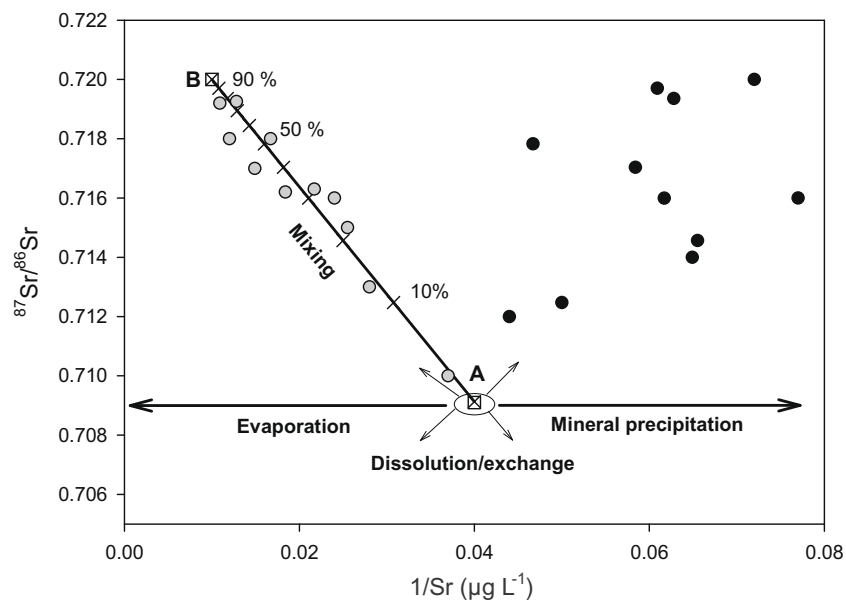

Fig. 2. Mixing on a plot of ^{87}Sr/^{86}Sr vs. (1/Sr) produces a straight line but processes other than mixing can cause changes in isotope ratio. A and B are hypothetical mixing end-members and percentages are mixing proportions of component B mixed with component A. Two data sets are shown: those with grey symbols are consistent with simple mixing whilst black symbols indicate other end-members or processes.

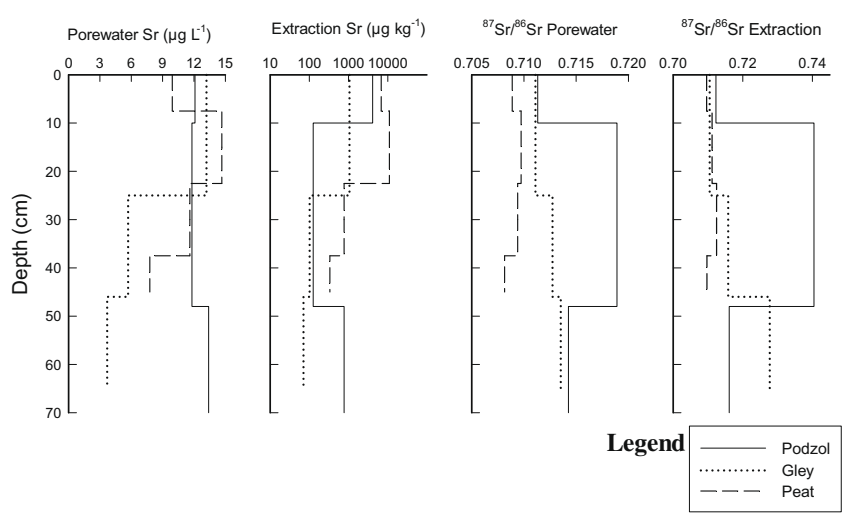

Fig. 3. Variations in ^{87}Sr/^{86}Sr in pore waters and on the exchange complex of soils in the Plynlimon catchment. Whole rock ratios of the dominant lithology are about 0.74.

been used to assess the origin of salinity in highly saline waters (McNutt et al., 1990; Négrel and Casanova, 2005; Vengosh et al., 2007).

Differences in isotope ratios, reflecting mixing, have provided valuable information on sources, pathways and mixing (Bullen et al., 1997; Frost et al., 2002; Hogan and Blum, 2003; Frost and Toner, 2004; Négrel and Petelet-Giraud, 2005; Brinck and Frost, 2007) and surface water–groundwater interactions in catchments and groundwater systems (Land et al., 2000; Shand et al., 2007). Strontium isotopes have also proved useful in helping to quantify silicate vs. carbonate weathering fluxes (Blum et al., 1998; Chamberlain et al., 2005). Experimental studies are helping to understand the complexities of Sr behaviour and mineral dissolution kinetics (Brantley et al., 1998; Taylor et al., 2000) and they are proving valuable in correcting ^{14}C ages (Bishop et al., 1994; Johnson and DePaolo, 1996).

2.2. Graphical display of Sr isotope data

Correlations between Sr isotope data and concentrations with other isotopes and solute data are useful for assessing hydrochemical relationships, and hence deductions about the source of Sr and weathering processes. The mixing of two end-members on a $^{87}Sr/^{86}Sr$ vs. Sr plot produces a series of curves depending on relative Sr concentrations, but plotting the isotope ratio against the reciprocal of Sr produces a straight line, hence it is useful to assess if there are more components or processes other than mixing are important. This is illustrated in Fig. 2 where hypothetical end-

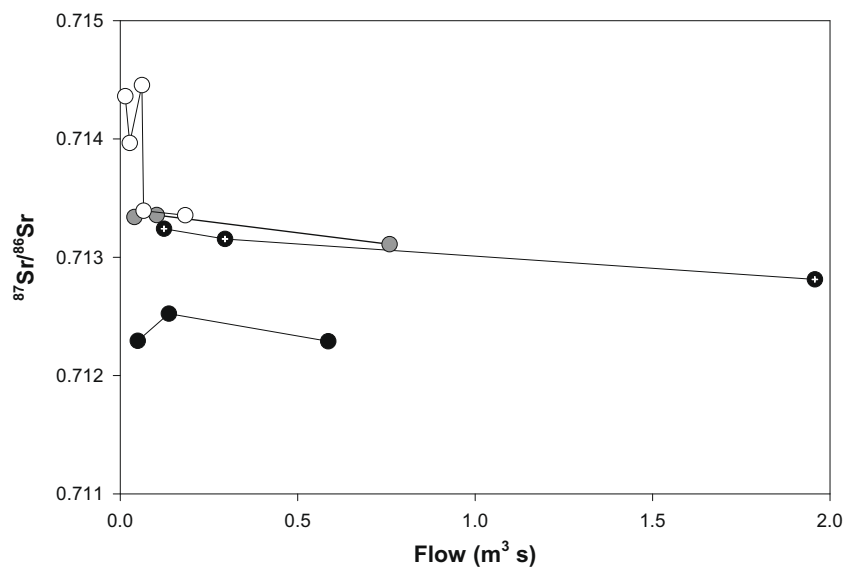

Fig. 4. Changes in $^{87}Sr/^{86}Sr$ with flow in monitored streams of the Plynlimon catchment. Apart from the small Tanllwyth tributary underlain by gley soils, the rivers display little change with flow.

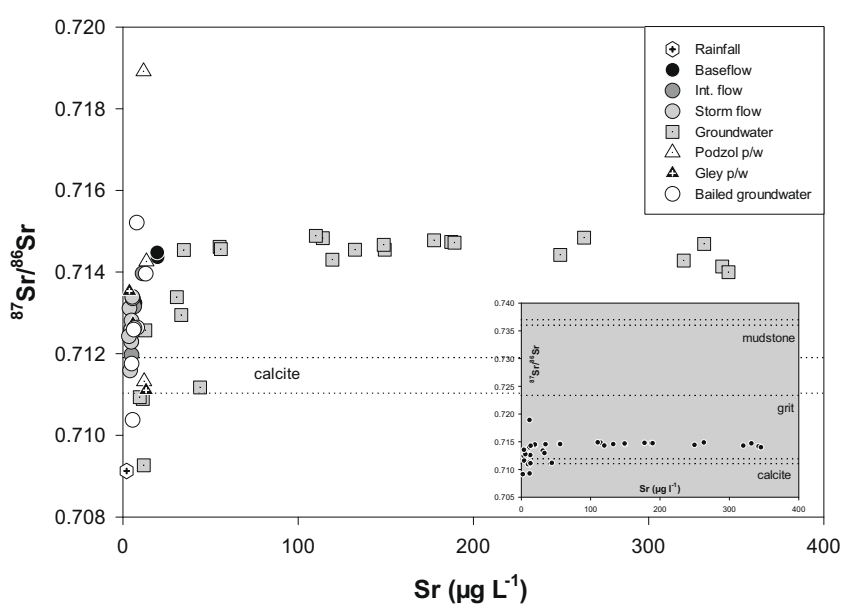

Fig. 5. Changes in $^{87}Sr/^{86}Sr$ with Sr concentration in waters and soils of the Plynlimon catchment, highlighting the constant $^{87}Sr/^{86}Sr$ in deep groundwaters with increase in Sr concentration.

members are used to illustrate mixing and other hydrogeochemical processes. Mineral precipitation and evaporation do not modify the Sr isotope ratio whereas mineral dissolution and exchange are likely to modify the ratio in water depending on the isotopic composition of the reacting phases. Such a plot can be used to provide a rapid assessment of whether simple two-component mixing is viable or whether more end-members or processes are required to explain data trends (Fig. 2).

3. Examples of the application of Sr isotopes during hydrological studies

3.1. Catchment studies in hard rock terrains

Most hard rock upland catchment studies have traditionally assumed that the underlying bedrock is impermeable, with temporal variations in stream water chemistry being a function of mixing between surface flow and soil waters or between different soil members. Strontium isotope studies are proving useful tracers in constraining end-members and elucidating flow pathways through such catchments, particularly where solute concentrations are similar between different components.

3.1.1. Weathering rates and flow pathways in an upland forested catchment in Wales, UK

The Plynlimon forested catchment in Wales is underlain by thin acidic soils overlying fractured Ordovician and Silurian meta-sediments, mainly siltstones and shales. Recent studies have suggested that the thin (mainly podzolic) soils and especially peat present in the upper reaches of the catchment are not the dominant flow sources of water during storm events as previously postulated (Shand et al., 2001, 2004, 2005, 2007; Haria and Shand, 2004, 2006).

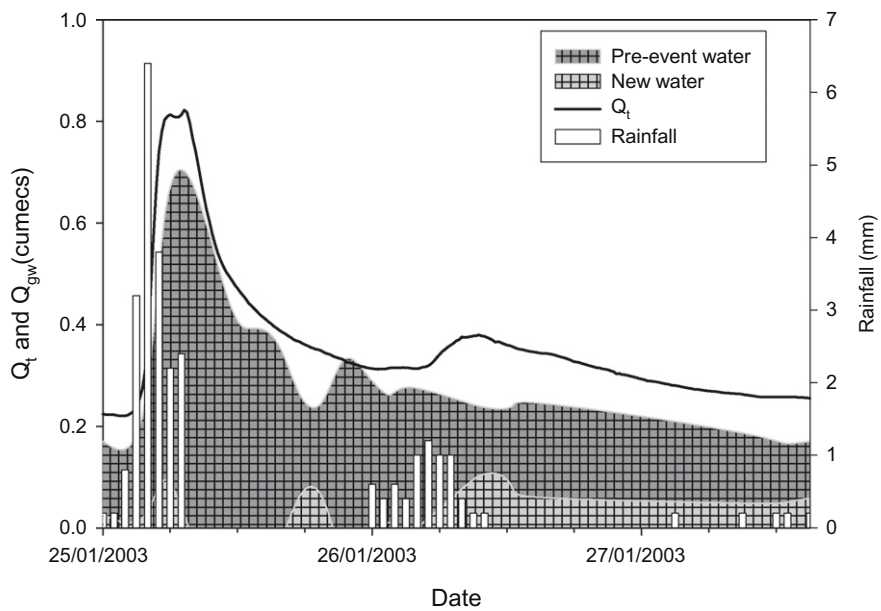

Fig. 6. Hydrograph separation using δ^2H for the Afon Hafren showing that this particular storm event was dominated by pre-event water i.e. that which fell on the catchment prior to the rainfall event responsible for increased flow.

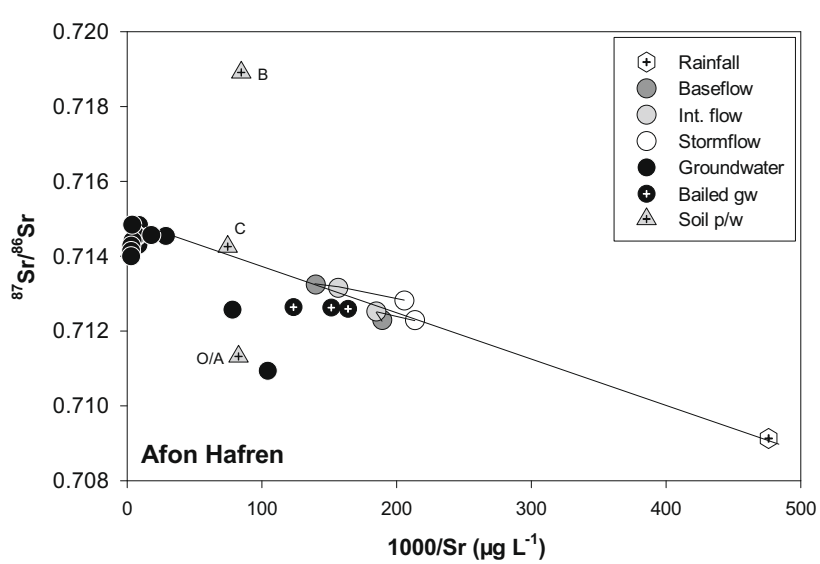

Fig. 7. Changes in ^{87}Sr/^{86}Sr with reciprocal of Sr concentration in waters and soils of one of the Plynlimon catchments. The letters O/A, B and C refer to soil horizons of a podzol, the dominant soil type in the catchment.

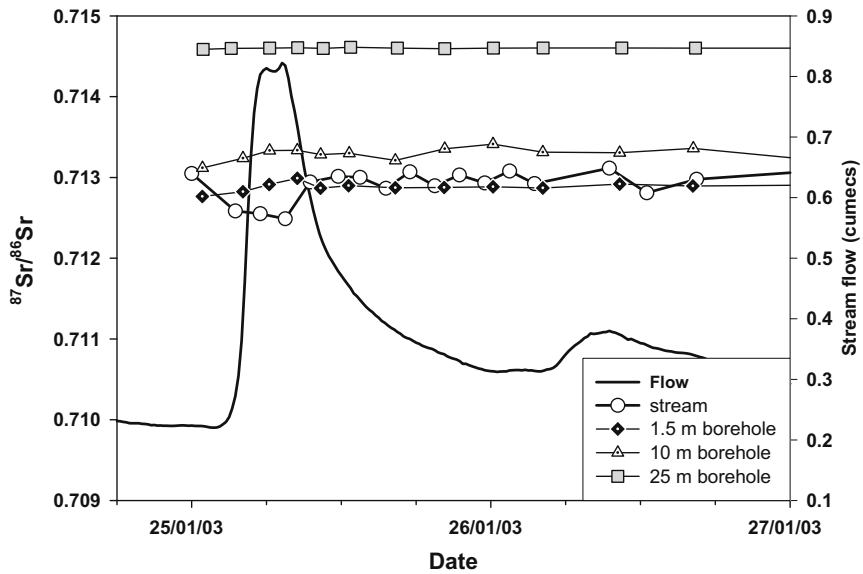

Fig. 8. $^{87}Sr/^{86}Sr$ variations in the Afon Hafren stream during a winter storm event, indicating a relatively homogeneous isotopic store within the catchment. The stream isotope composition was very similar to those found in shallow groundwaters.

Table 1
Weathering rates of Sr and Ca in two Plynlimon sub-catchments compared with traditional mass balance (output–input). Sr in g ha^{-1} a^{-1} and Ca in kg ha^{-1} a^{-1}.

Stream	Estimate based on $^{87}Sr/^{86}Sr$		Estimate based on mass balance	
	Sr	Ca	Sr	Ca
Hafren	57	8.5	51	10.6
Hore	74	16.3	52.1	18.4

The soils in the catchment are highly variable in terms of their $^{87}Sr/^{86}Sr$ ratios in pore waters and on the exchange complex (Fig. 3). Peat deposits in the upper parts of the catchment had relatively unradiogenic Sr, only slightly higher than rainfall. This implies little water–rock interaction with the dominant Sr-bearing minerals in the bedrock (illite, chlorite). Furthermore the organic O horizon isotope ratios were similar to those found in the headwater peat deposits. Higher Sr isotope ratios were present in the other soil types at depth but, apart from exchangeable Sr in the podzol B-horizon, were much lower than the whole rock ratio (ca. 0.737). In general, the isotope ratios of the pore water extractions were not in isotopic equilibrium with the exchangeable Sr (weak mineral acid or ammonium acetate extractions), possibly due to the heterogeneous nature of the clay-rich soils (with varying K_d), temporal disequilibrium because of the range of residence

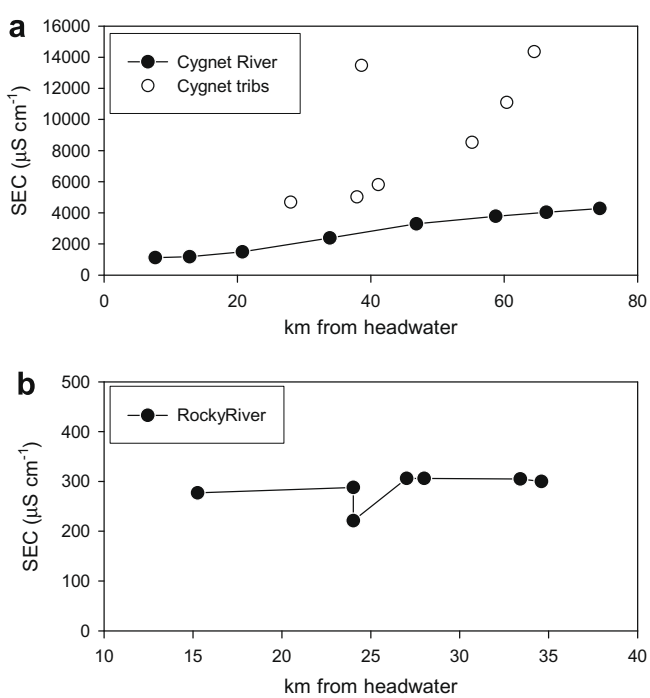

Fig. 9. Specific electrical conductance (SEC): (a) the Cygnet river and its tributaries and (b) the Rocky River showing the contrast between the cleared Cygnet and pristine Rocky River catchments.

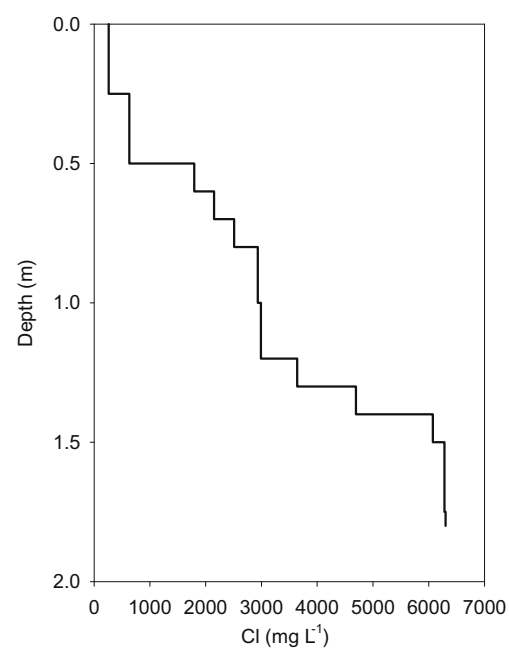

Fig. 10. Porewater Cl concentration in soils at a site 20 m from the Rocky River.

times in different pore sizes of the soil, complexation reactions with acetate or preferential flowpaths through the soil.

The main stream sites showed relatively little change with flow, but varied across the catchment (Fig. 4); although the Tanllwyth is a smaller tributary underlain by gley soils and shows a larger change, probably dilution from shallow interflow. The $^{87}Sr/^{86}Sr$ ratio increased from the headwaters (where it was closer to the rainfall value of 0.7092) downstream. Shallow groundwaters (<15 m) displayed variable $^{87}Sr/^{86}Sr$, increasing with depth and overlapping with the streams. The deeper groundwaters were more constant and reached a plateau, much lower than the whole rock, despite large increases in Sr concentration (Fig. 5). Shand et al. (2007) interpreted this as due to the dominance of a single-mineral controlling phase (epidote or relict plagioclase).

Stable isotope (δ^2H, $\delta^{18}O$) and CFC data (Shand et al., 2004) showed that the storm hydrograph was dominated by pre-event water, implying significant storage in the catchment (Fig. 6). A plot of $^{87}Sr/^{86}Sr$ vs. 1000/Sr (Fig. 7) shows that (a) the streams lie on a mixing line between rainfall and groundwater, (b) the streams are displaced from pore waters in the peat deposits and O/A horizons, and (c) mixing between soil waters cannot explain trends in the data which are consistent following different antecedent conditions, e.g. samples collected during storm flow in different years have almost identical Sr isotope ratios. Strontium isotope variations were monitored over a winter storm event and also displayed little variation, consistent with a well mixed source (Fig. 8). The isotope data combined with the CFC and stable isotope data, suggest that the only consistent model involves mixing and storage of waters within the underlying fractured bedrock.

Strontium isotopes were also used to determine weathering rates for Sr and Ca in the catchment. Estimates for Sr weathering rates using Sr isotopes were based on the choice of "weathering-derived" Sr (using the plateau groundwater maximum shown in Fig. 5 and soil pore water in the C-soil horizon, combined with the flux of Sr from the catchment outlet), and the Sr isotope ratio for rainfall. Measurements of atmospheric inputs in traditional mass balance are made difficult by the problem of accurate determination of dry deposition. The application of Sr isotopes uses the following equation (Wickman and Jacks, 1992), where W % is the percentage of Sr derived from weathering

$$W\ \% = \frac{\left[\left(\frac{^{87}Sr}{^{86}Sr}\right)_R - \left(\frac{^{87}Sr}{^{86}Sr}\right)_D\right]}{\left[\left(\frac{^{87}Sr}{^{86}Sr}\right)_W - \left(\frac{^{87}Sr}{^{86}Sr}\right)_D\right]} \times 100 \quad (1)$$

and R, D and W refer to runoff, deposition and weathering, respectively. Weathering rates for Ca are calculated assuming similar behaviour for Sr and Ca

$$\text{Weathering rate}_{Sr,Ca} = F_{Sr,Ca} \times W\ \% \quad (2)$$

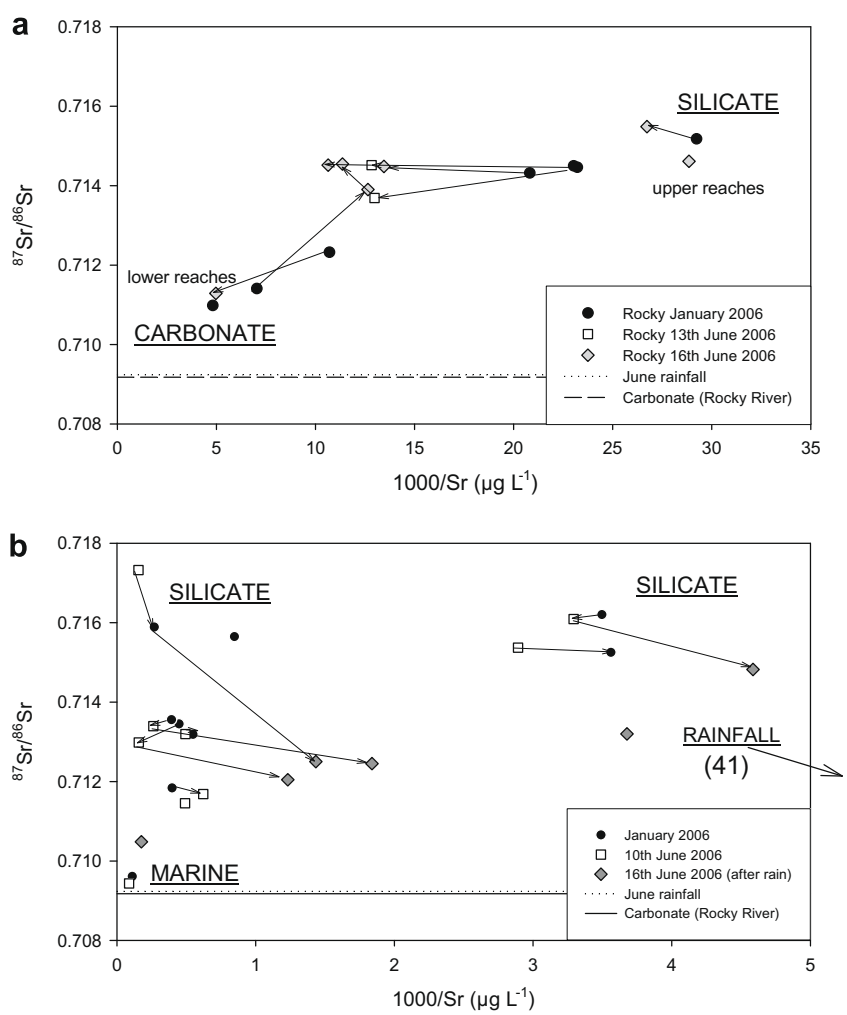

Fig. 11. Contrasting $^{87}Sr/^{86}Sr$ in streams between the pristine Rocky River catchment (top) and cleared Cygnet River (bottom) catchments. Arrows indicate temporal order of sample collection.

where F_{Ca} is the long term flow weighted Sr or Ca flux. Weathering rates for the study catchment (Hafren) were similar to long term mass balance studies (Table 1), taking into account the different approaches and problems with measuring deposition rates. However, when applied to an adjacent catchment (Hore), rates for Ca were significantly different (Table 1). It is not yet established whether this is related to different weathering end-members (groundwater and soil data were only measured in the Hafren catchment), but im-

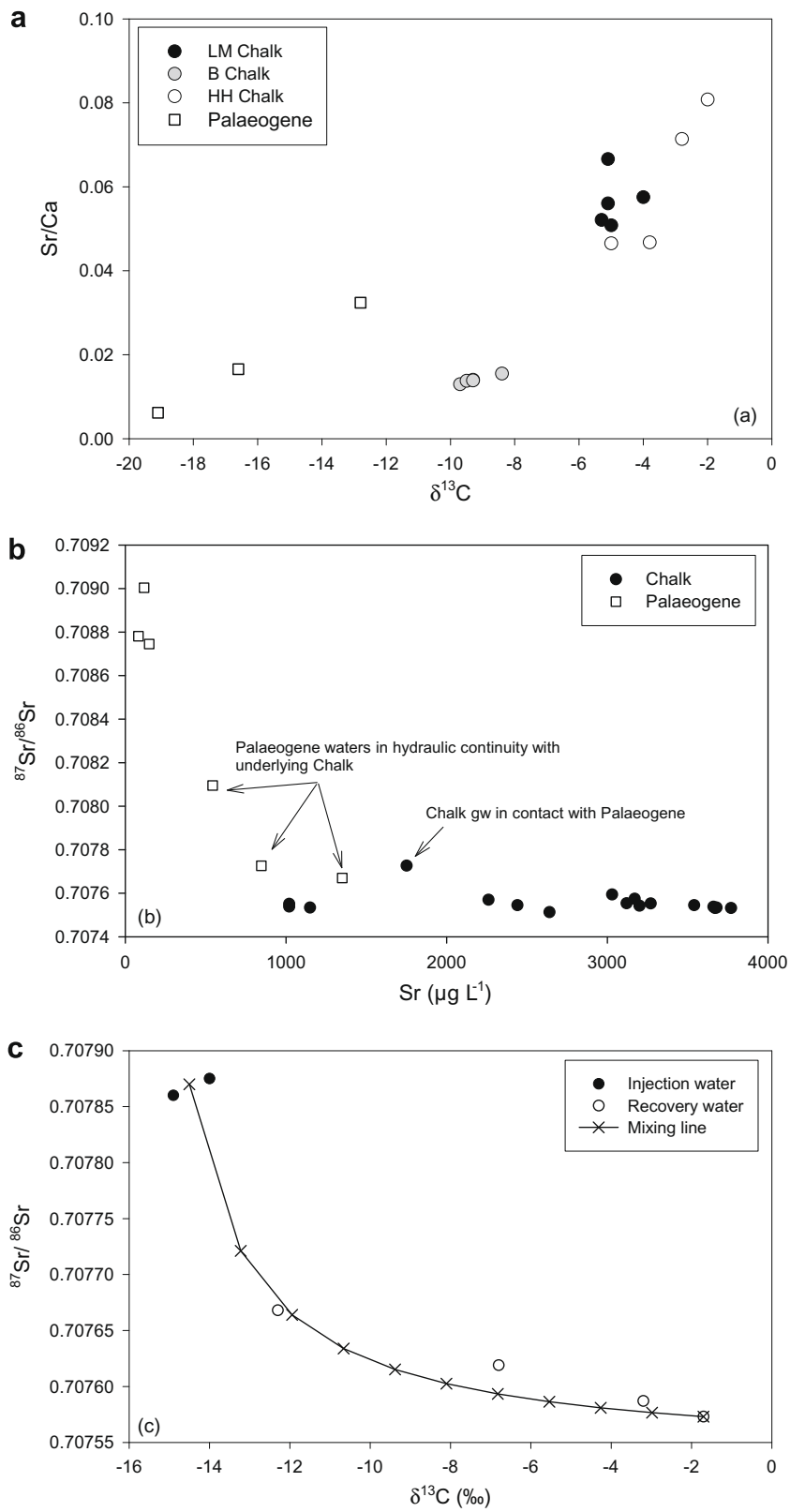

Fig. 12. (a) Sr/Ca vs. $\delta^{13}C$ indicating evolution by incongruent dissolution of calcite; (b) Sr isotope variations in Chalk and Palaeogene groundwaters; (c) mixing of injection and recovery waters during ASR testing.

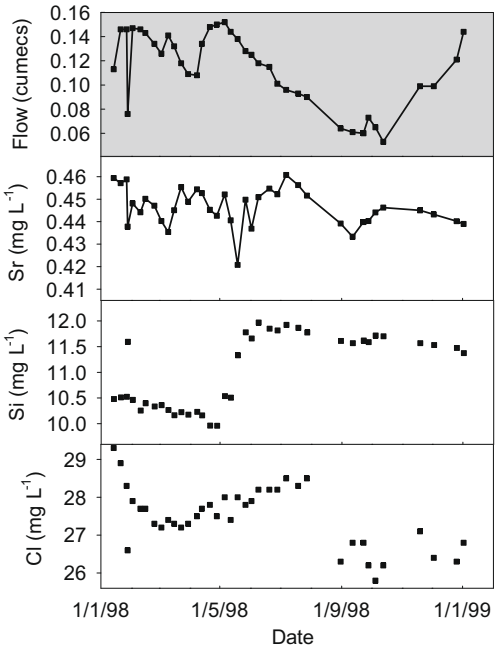

Fig. 13. Seasonal variations in flow and solute concentrations in a Chalk spring.

plies that care must be taken when extrapolating across similar catchments without applicable data.

The above study highlights how Sr isotopes can provide a useful tool to determine weathering rates and flow pathways in upland catchments. In catchments with varied lithologies, Sr isotopes may provide an excellent means of determining complex spatial inputs, but it may be difficult to determine weathering rates with a reasonable degree of confidence if end-member compositions are not assessed.

3.1.2. Vegetation clearance impacts of flow path-ways on Kangaroo Island, Australia

The relationship between native vegetation clearance and increases in groundwater and surface water salinities is well established in sedimentary basins in the semi-arid regions of Australia (Allison et al., 1990). Although the causes of these processes are well established, detailed research on catchment functioning, especially flowpaths through the soil and regolith, is lacking largely because of difficulties in measuring macropore flow, heterogeneities at all scales in soils and landscapes, and their impact of streamflow generation processes (Love and Shand, 2007). The clearance of deep rooted native vegetation and intensive use of tillage typically leads to reduced macropore space. As a result, greater surface runoff, increased diffuse recharge and stream salinisation have occurred. A preliminary study, comparing cleared and pristine

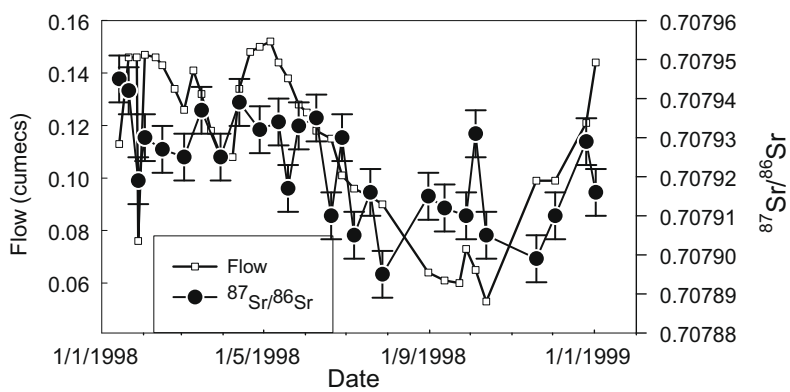

Fig. 14. Seasonal variations in flow and $^{87}Sr/^{86}Sr$ in spring discharge water.

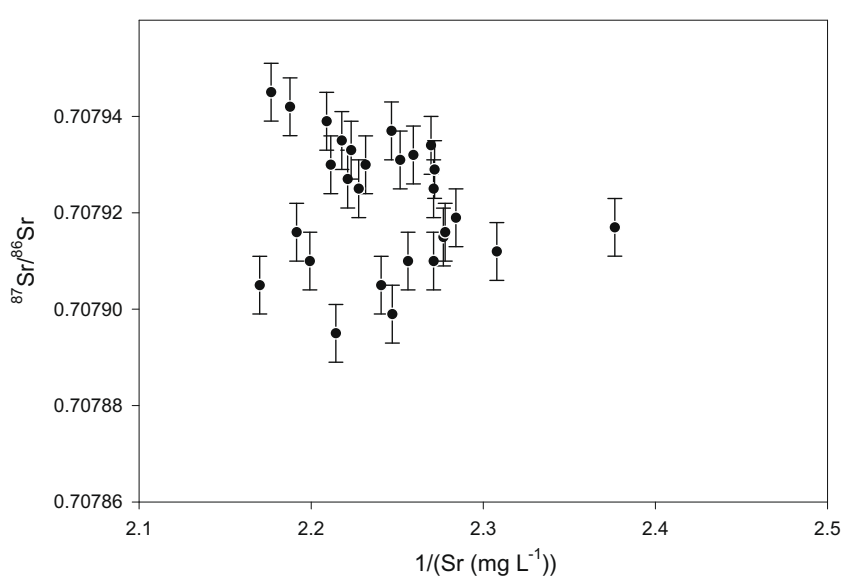

Fig. 15. Plot of $^{87}Sr/^{86}Sr$ against 1/Sr showing that simple two-component mixing cannot explain the variations in spring water quality.

catchments on Kangaroo Island, South Australia (Shand et al., 2006) highlighted large differences in surface water chemistry in these catchments underlain by Cambrian metamorphic rocks.

The pristine Rocky River in the Flinders Chase National Park generally flows all year round and had remarkably fresh water during sampling (SEC ca. 400 μS cm^{-1}, Fig. 9), despite a large salt store being present in the soils (Fig. 10). In contrast, streams in a nearby cleared catchment (Cygnet River) varied from only moderately fresh to saline (SEC from 1000 to 15000 μS cm^{-1}). Strontium isotope variations in the pristine catchment were interpreted as being derived from silicate weathering, with carbonate inputs close to the coast (Fig. 11a). The Sr isotope ratios observed in the lower reaches were similar to seawater (and rainfall). However, increases in Sr and Ca concentrations and Sr/Cl and Ca/Cl ratios in the stream waters suggest that carbonate dissolution rather than rainfall/sea spray is the dominant source of Sr. The low salinities in the upper reaches were interpreted as being due to by-pass macropore flow through the soils and regolith into the fractured bedrock system, with lack of time for significant mixing with the higher Cl in the soils. The end-member is too radiogenic to be rainfall-derived and appears dominated by the metamorphic siliceous rocks, although mineral data are not available at present (whole rock ratios varied from 0.724 to 0.741).

The data for Cygnet River were much more heterogeneous (Fig. 11b). It is probable that four end-members are needed to explain the data: a dilute radiogenic component similar to that in the Rocky River (from silicate weathering), a saline radiogenic component, a saline non-radiogenic component (soil salt store) and a non-radiogenic dilute component (rainfall-runoff). During intense storms, Hortonian overland flow was observed in fields of the Cygnet catchment, but not in the pristine forested Rocky catchment. The mobilisation of salinity (the saline radiogenic component) cannot simply be caused by a decrease in the water table depth, but is likely to be due to more diffuse flow through the salt store caused by a loss of rapid macropore flow due to vegetation clearance and soil compaction (Shand et al., 2005). High salinities in Australian environments are commonly assumed to be from the remobilisation of stored salt formed during high evaporation/transpiration rates (the saline non-radiogenic component), but the radiogenic Sr component implies that much of the Sr is derived from silicate mineral weathering.

3.2. Applications to a carbonate (Chalk) system

The application of $^{87}Sr/^{86}Sr$ as a tracer for mixing in carbonate systems is often limited because of the typical lack of Sr isotope variations compared to many silicate systems (McNutt, 2000). However, the ability to measure Sr isotope ratios with high precision makes them useful as a tracer in environments where minor sources other than carbonate (rainfall, exchangeable Sr or contaminants) are present. Several examples are presented from a relatively pure carbonate aquifer, the Chalk of southern England, where Sr isotopes have proved a useful tracer. The Chalk is composed of fine-grained, highly porous soft limestone that contains large volumes of groundwater. The Chalk consists dominantly of relatively pure calcite ($CaCO_3$). However, small amounts of other elements (Mg, Sr, Mn, Fe) are present in the calcite structure, which helped to stabilise the carbonate in the marine environment. These impurities in the carbonate lattice play an important role in the evolution of the groundwater chemistry, since they are slowly released to the groundwater as the Chalk recrystallises under freshwater conditions. The Chalk forms a dual porosity aquifer with high matrix porosity (20–40%) but very low permeability (Downing et al., 2005). Although most of the groundwater storage is within the matrix, the flow is dominated by fracture and fissure flow.

3.2.1. Mixing of Chalk and overlying Palaeogene waters

A background study on an Artificial Storage and "Recovery (ASR) scheme in southern England was undertaken in a confined part of the aquifer to assess chemical variations and hydraulic connection between the Chalk and overlying Palaeogene sand and clay sediments (Buckley et al., 1998). Although hydrochemical (major and trace element) and isotopic ($\delta^{13}C$, Sr/Ca ratio, Fig. 12a) data showed that the geochemical evolution of the Chalk groundwaters is dominated by incongruent calcite dissolution and ion exchange (Buckley et al., 1998), they were inconclusive on the degree of mixing and connectivity. The Sr isotope data (Fig. 12b) show that the deeper groundwaters in the Palaeogene aquifer, thought to be in hydraulic contact with the Chalk, are indeed influenced by upward flow from the Chalk, consistent with strong upward heads at the site. The data also showed that some Chalk groundwaters close to the contact are influenced by minor amounts of Palaeogene-derived Sr (Fig. 12b). The high precision of Sr isotope analysis in combination with dissolved solutes and stable isotopes also allowed mixing to be demonstrated between two different Chalk groundwaters (original and injection) during testing of the ASR scheme (Fig. 12c).

3.2.2. Variable seasonal sources in a Chalk spring

The flow processes from natural spring discharges are often difficult to assess, typically comprising mixtures of water derived from different flow paths and of different residence times. A Chalk spring was monitored for one year, and displayed significant differences in flow and chemistry (Fig. 13). Trends in solute concentrations were variable for different elements, making interpretation difficult, and most showed very little correlation with spring discharge.

Strontium isotopes were more consistent, varying over a small range and showing an increase during the winter recharge period when flows were high (Fig. 14). Simple mixing calculations indi-

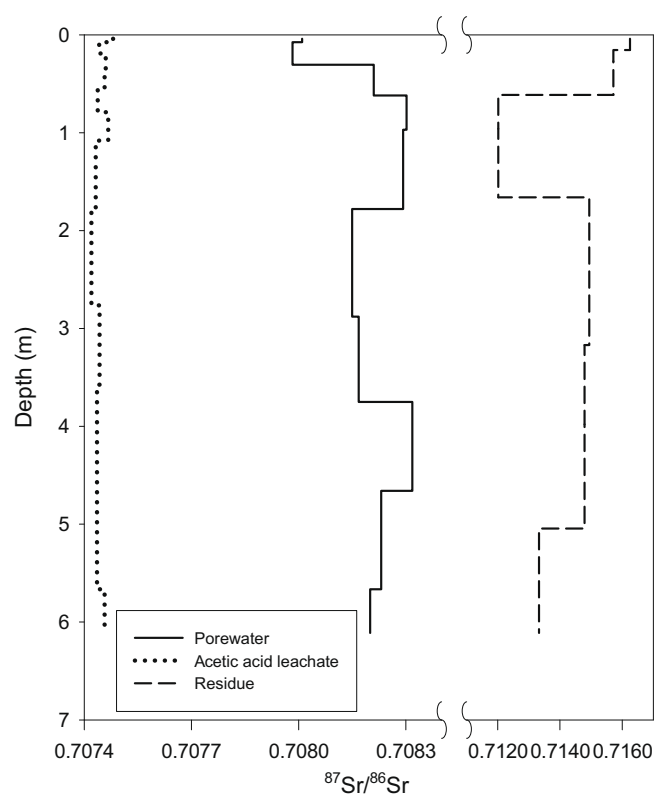

Fig. 16. $^{87}Sr/^{86}Sr$ in Chalk pore water, acetic acid extractions and residue from acetic extract.

cated that the high $^{87}Sr/^{86}Sr$ ratios could not be due to dilution with rainfall ($^{87}Sr/^{86}Sr$ of ca. 0.709) as Sr concentrations remained too high. In addition, $^{87}Sr/^{86}Sr$ ratios were much higher than expected for Chalk (where Sr is considered to be dominated by the carbonate matrix), and those analysed in groundwaters found elsewhere in the Chalk, implying an additional radiogenic component. Correlations between $^{87}Sr/^{86}Sr$ and Sr (or 1/Sr) were also poor, and show that simple two-component mixing of different Chalk groundwaters cannot explain the data (Fig. 15).

Samples of Chalk pore water, acetic acid extracts and residue were analysed from a cored profile upslope of the spring (Fig. 16). The carbonate fraction (acetic acid soluble) was as expected for the Cretaceous Chalk but the insoluble residue (clays) much more radiogenic. The pore waters extracted from the matrix were similar to that in the spring, being intermediate between the calcite matrix and clay component. It appears that shallow sources of Chalk groundwater are strongly influenced by the weathering or exchange with clays, consistent with higher Si. If correct, then it implies at least a shallower component or components become more important during the winter discharge period. It is possible that the radiogenic component is Sr derived from fertiliser applications, however $^{87}Sr/^{86}Sr$ shows a negative correlation with NO_3^-

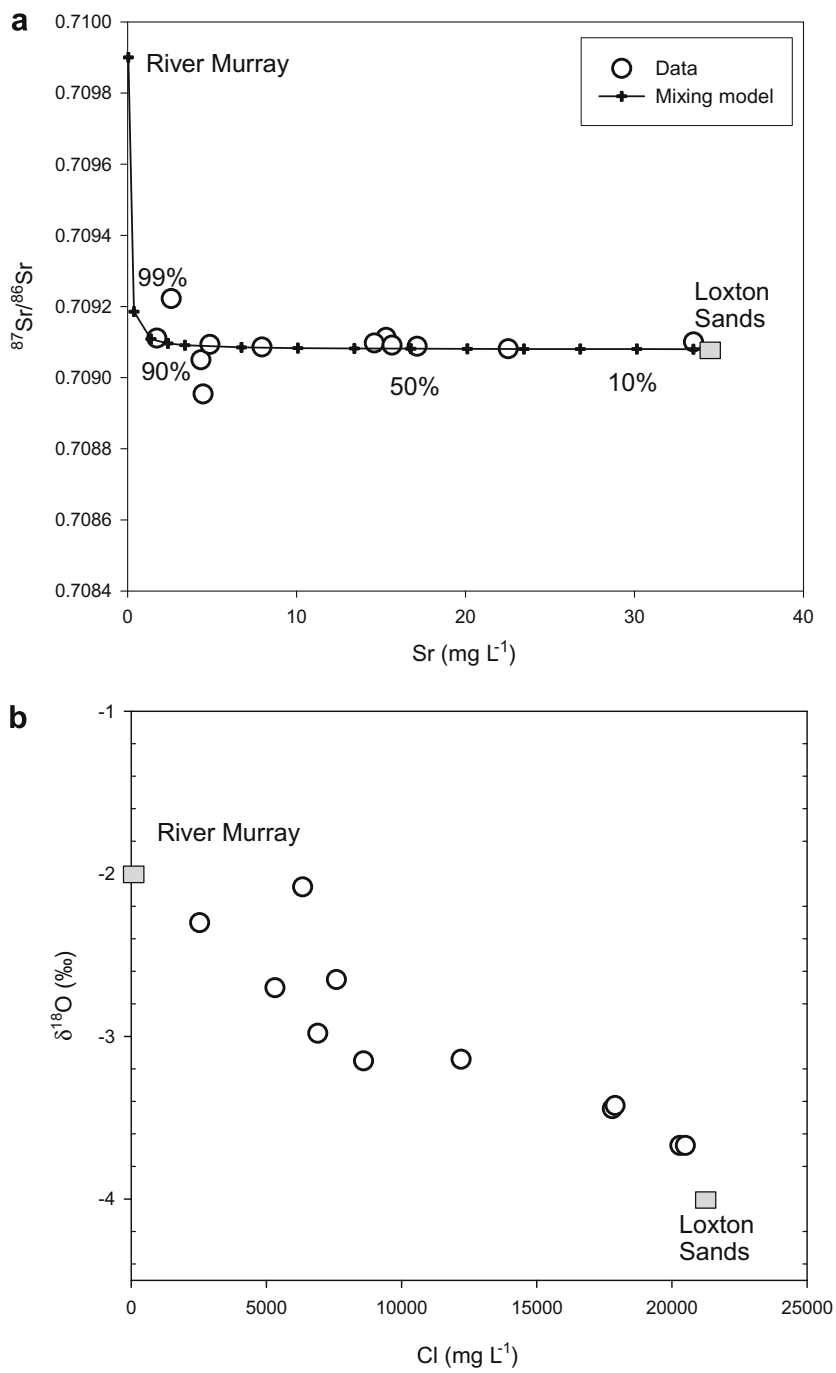

Fig. 17. (a) $^{87}Sr/^{86}Sr$ in groundwaters beneath an irrigation mound at Loxton, Murray Basin and (b) $\delta^{18}O$ vs. Cl for the same samples which lie on a mixing line between irrigation (River Murray) water and original Loxton Sands groundwater.

and this hypothesis is yet to be tested. Nevertheless, Sr isotopes appear to show a much simpler behaviour than most other solutes and potentially a better indicator of mixing processes in the Chalk.

3.3. Irrigation mound in the Murray Basin, Australia

The final case study presents an example which highlights a limitation of the approach developed in the paper, and where reliance had to be based on other tracers. Several decades of irrigation farming using water from the River Murray in Australia led to the development of irrigation mounds in the underlying Tertiary Loxton Sands aquifer. The original water in the aquifer was saline and has become fresher due to enhanced recharge beneath the irrigation areas. An example is shown of groundwaters sampled close to Loxton (Fig. 17). Although the waters display a large range in Cl concentrations (2530–20,500 mg L^{-1}), the $^{87}Sr/^{86}Sr$ ratios showed little variation, i.e. $^{87}Sr/^{86}Sr$ is insensitive because it is dominated by the very high Sr concentrations of the groundwater (Fig. 17a). Modelling indicated that variations were only likely to occur where the irrigation water was present in amounts exceeding ca. 99%. In this case, other tracers such as stable isotopes and Cl proved better indicators of the mixing process (Fig. 17b).

This latter study highlights that the application of Sr isotopes as a mixing tool is most beneficial where end-members can be sufficiently resolved and where the mixing is not dominated by the Sr from one component. Where such dominance is present, Sr isotopes may be more useful as a tracer of pathways.

4. Summary and conclusions

The case studies presented here highlight the use of $^{87}Sr/^{86}Sr$ as a tracer of weathering processes and flow pathways in surface and ground waters in different landscapes. Strontium isotopes were used to estimate weathering rates in an upland catchment in Wales, and showed good agreement with long-term mass balance studies. They also proved useful in constraining flow pathways, and indicated that sub-surface flow through bedrock fractures is important in a catchment previously assumed to be impermeable beneath the soil horizons. Studies in more arid environments in Australia also indicted changes in flow pathways following vegetation clearance and showed that the source of mobilised salinity is from both cyclic (atmospheric) and lithogenic sources. The application of Sr isotopes was also shown to be useful in carbonate terrains e.g. the British Chalk, where changes in the dominant weathering processes vary with depth. This indicated that Sr derived from clays or agricultural inputs may form a significant proportion of this solute at shallow depths. An example of a study where Sr isotopes is less useful was presented, highlighting that where Sr is dominated by one end-member (saline groundwater), it was not possible to assess mixing proportions. In this case, Sr is a good tracer of the saline component in the aquifer system.

A pre-requisite of using Sr isotopes as a tracer of weathering processes and determination of flow pathways is that that the solid phase and potential end-member solution phases are characterised. The whole rock values of Sr isotopes in the host lithologies are in general not particularly useful for assessing sources and end-member compositions, and a range of techniques including mineral separation and selective leaching are more effective. For the range of environmental applications undertaken, the choice of technique should be determined on the basis of the aims of the study. Strontium isotopes generally provide additional evidence to that provided by solute concentrations alone. Even in carbonate terrains, where isotope variations may be small, the high precision of modern mass spectrometers means that small changes can be analysed routinely.

Most of the examples illustrated were used in combination with other isotope and solute tracers, as well as physical measurements. The power of the multi-tracer approach remains the preferred methodology since the best tracers of mixing may be poorer at deciphering weathering processes, the number of operative processes may be large or there is little difference between end-members. Further studies of mineral dissolution processes, particularly selective leaching of ^{87}Sr from Rb-containing minerals may yet limit detailed interpretation of solute Sr in some terrains, but to date there have been a sufficient number of case studies to demonstrate the power of Sr isotopes in hydrological studies.

Acknowledgements

We are extremely grateful to C.D. Frost, B.D. Marshall, R.H. Merry, R.G. Creswell and an anonymous reviewer for constructive reviews which have greatly improved the manuscript.

References

Åberg, G., Jacks, G., Hamilton, P.J., 1989. Weathering rates and $^{87}Sr/^{86}Sr$ ratios: an isotopic approach. J. Hydrol. 109, 65–78.
Aggarwal, J.K., 2006. Mass-dependent strontium isotopic fractionation. Geochim. Cosmochim. Acta 70, A3.
Allison, G.B., Cook, P.G., Barnett, S.R., Walker, G.R., Jolly, I.D., Hughes, M.W., 1990. Land clearance and river salinisation in the Western Murray Basin. J. Hydrol. 119, 1–20.
Bain, D.C., Bacon, J.R., 1994. Strontium isotopes as indicators of mineral weathering in catchments. Catena 22, 201–214.
Bishop, P.K., Smalley, P.C., Emery, D., Dickson, J.A.D., 1994. Strontium isotopes as indicators of the dissolving phase in a carbonate aquifer: implications for ^{14}C dating of groundwaters. J. Hydrol. 154, 301–321.
Blum, J.D., Erel, Y., 2005. Radiogenic isotopes in weathering and hydrology. In: Drever, J.I. (Ed.), Surface and Ground Water, Weathering, and Soils. Treatise on Geochemistry. Elsevier, pp. 365–392.
Blum, J.D., Gazis, C.A., Jacobsen, A.D., Chamberlain, C.P., 1998. Carbonate versus silicate weathering in the Raikhot watershed within the high Himalayan crystalline series. Geology 26, 411–414.
Brantley, S.L., Chesley, J.T., Stillings, L.L., 1998. Isotopic ratios and release rates of strontium measured from weathering feldspars. Geochim. Cosmochim. Acta 62, 1493–1500.
Brinck, E.L., Frost, C.D., 2007. Detecting infiltration and impacts of introduced water using strontium isotopes. Ground Water 45, 554–569.
Buckley, D.K., Shand, P., Gale, I.N., 1998. Geophysical and geochemical investigations related to the ASR trial at Lytchett Minster, Dorset. British Geological Survey Technical Report WD/98/27C.
Bullen, T.D., Kendall, C., 1998. Tracing of weathering reactions and water flowpaths: a multi-isotope approach. In: Kendall, C.K., McDonnell, J.J. (Eds.), Isotope Tracers in Catchment Hydrology. Elsevier, pp. 611–646.
Bullen, T., White, A., Blum, A., Harden, J., Schulz, M., 1997. Chemical weathering of a soil chronosequence on granitoid alluvium: II. Mineralogic and isotopic constraints on the behaviour of strontium. Geochim. Cosmochim. Acta 61, 201–306.
Capo, R.C., Stewart, B.W., Chadwick, O.A., 1998. Strontium isotopes as tracers of ecosystem processes: theory and methods. Geoderma 82, 197–225.
Chamberlain, C.P., Waldbauer, J.R., Jacobsen, A.D., 2005. Strontium, hydrothermal systems and steady-state chemical weathering in active mountain belts. Earth Planet. Sci. Lett. 238, 351–366.
Downing, R.A., Price, M., Jones, G.P. (Eds.), 2005. The Hydrogeology of the Chalk of North-west Europe. Clarendon Press, Oxford.
Faure, G., 1977. Principles of Isotope Geology. John Wiley & Sons.
Fietzke, J., Eisenhauer, A., 2006. Determination of temperature-dependent stable strontium isotope ($^{88}Sr/^{86}Sr$) fractionation via bracketing standard MC-ICP-MS. Geochem. Geophys. Geosyst., vol. 7 (AR Q08009).
Fritz, B., Richard, L., McNutt, R.H., 1992. Geochemical modelling of Sr isotopic signatures in the interaction between granitic rocks and natural solutions. In: Kharaka, Y.K., Maest, A.S. (Eds.), Proc. 7th Internat. Symp. Water–Rock Interaction. Balkema, pp. 927–930.
Frost, C.D., Toner, R.N., 2004. Strontium isotopic identification of water–rock interaction and groundwater mixing. Ground Water 42, 418–432.
Frost, C.D., Pearson, B.N., Ogle, K.M., Heffern, E.L., Lyman, R.M., 2002. Sr isotopic tracing of aquifer interactions in an area of coal and methane production, Powder River Basin, Wyoming. Geology 30, 923–926.
Graustein, W.C., 1988. $^{87}Sr/^{86}Sr$ ratios measure the sources and flow of strontium in terrestrial ecosystems. In: Rundel, P.W., Ehleringer, J.R., Nagy, K.A. (Eds.), Stable Isotopes in Ecological Research Ecological Studies, Vol. 68. Springer-Verlag, New York, pp. 491–512.
Graustein, W.C., Armstrong, R.L., 1983. The use of strontium-87/Strontium-86 ratios to measure atmospheric transport into forested watersheds. Science 219, 289–292.

Haria, A., Shand, P., 2004. Evidence for deep sub-surface flow routing in forested upland Wales: implications for contaminant transport and stream flow generation. Hydrol. Earth Syst. Sci. 8, 334–344.

Haria, A.H., Shand, P., 2006. Near-stream soil water–groundwater coupling in the headwaters of the Afon Hafren, Wales: Implications for surface water quality. J. Hydrol. 331, 567–579.

Hogan, J.F., Blum, J.D., 2003. Tracing hydrologic flow paths in a small forested watershed using variations in $^{87}Sr/^{86}Sr$, [Ca]/[Sr], [Ba]/[Sr] and delta $\delta^{18}O$. Water Resour. Res. 39, 1282–1293.

Jacks, G., Åberg, G., Hamilton, P.J., 1989. Calcium budgets for catchments as interpreted by strontium isotopes. Nordic Hydrol. 20, 85–96.

Johnson, T.M., DePaolo, D.J., 1996. Reaction-transport models for radiocarbon in groundwater: the effect of longitudinal dispersion and the use of Sr isotope ratios to correct for water–rock interaction. Water Res. Res. 32, 2203–2212.

Johnson, T.M., DePaolo, D.J., 1997. Rapid exchange effects on isotope ratios in groundwater systems 1. Development of a transport-diffusion-exchange model. Water Resour. Res. 33, 187–195.

Land, M., Ingri, J., Andersson, P.S., Öhlander, B., 2000. Ba/Sr, Ca/Sr and 87Sr/86Sr ratios in soil water and groundwater: implications for relative contributions to stream water discharge. Appl. Geochem. 15, 311–325.

Love, A.J., Shand, P., 2007. River chemistry in cleared and pristine catchments: where does the salt come from? Kangaroo Island, Australia. In: Bullen, T.D., Wang, Y. (Eds.), Water–Rock Interaction, vol. 11. Taylor & Francis, London, pp. 759–762.

McArthur, J.M., Howarth, R.J., 2004. Strontium isotope stratigraphy. In: Gradstein, F.M., Ogg, J.G., Smith, A.G. (Eds.), A Geological Timescale 2004. Cambridge University Press, Cambridge, pp. 96–105.

McNutt, R.H., 2000. Strontium Isotopes. In: Cook, P.G., Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, pp. 234–260.

McNutt, R.H., Frape, S.K., Fritz, P., Jones, M.G., MacDonald, I.M., 1990. The $^{87}Sr/^{86}Sr$ values of Canadian Shield brines and fracture minerals with application to groundwater mixing, fracture history and geochronology. Geochim. Cosmochim. Acta 54, 205–215.

Miller, E.K., Blum, J.D., Friedland, A.J., 1993. Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes. Nature 362, 438–441.

Négrel, P., 2006. Water–granite interaction: clues from strontium, neodymium and rare earth elements in soil and waters. Appl. Geochem. 21, 1432–1454.

Négrel, P., Casanova, J., 2005. Comparison of the Sr isotopic signatures in brines of the Canadian and Fennoscandian shields. Appl. Geochem. 20, 749–766.

Négrel, Ph., Petelet-Giraud, E., 2005. Strontium isotopes as tracers of groundwater-induced floods: the Somme case study (France). J. Hydrol. 305, 99–119.

Ohno, T., Hirata, T., 2007. Simultaneous determination of mass-dependent isotopic fractionation and radiogenic isotope variation of strontium in geochemical samples by multiple collector-ICP-mass spectrometry. Anal. Sci. 23, 1275–1280.

Patchett, P.J., 1980. Sr isotopic fractionation in Ca-Al inclusions from the Allende meteorite. Nature 283, 438–441.

Shand, P., Darbyshire, D.P.F., Gooddy, D.C., Darling, W.G., Neal, C., Haria, A.H., Dixon, A.J., 2001. The application of Sr isotopes to catchment studies: The Plynlimon upland catchment of Central Wales. In: Cidu, R. (Ed.), Water–Rock Interaction, 10. Balkema, Rotterdam, pp. 1577–1580.

Shand, P., Darbyshire, D.P.F., Gooddy, D.C., Haria, A.H., 2007. $^{87}Sr/^{86}Sr$ as an indicator of flowpaths and weathering rates in the Plynlimon experimental catchments, Wales. UK Chem. Geol. 236, 247–265.

Shand, P., Griffiths, K., Darbyshire, D.P.F., Haria, A.H., Davies, J., 2004. Streamflow generation in upland impermeable catchments–is there a need to think deeper? In: Wanty, R.B., Seal, R.R. (Eds.), Water–Rock Interaction, 11. Balkema, Rotterdam, pp. 1391–1395.

Shand, P., Haria, A.H., Neal, C., Griffiths, K.J., Gooddy, D.C., Dixon, A.J., Hill, T., Buckley, D.K., Cunningham, J.E., 2005. Hydrochemical heterogeneity in an upland catchment: further characterisation of the spatial, temporal and depth variations in soils, streams and groundwaters of the Plynlimon forested catchment Wales. Hydrol. Earth Syst. Sci. 9, 621–644.

Shand, P., James-Smith, J., Love, A.J., Nilson, T., Thomas, D., 2006. Hydrogeochemistry of surface waters and groundwaters, Kangaroo Island. Department of Water, Land and Biodiversity Conservation Report.

Stewart, B.W., Capo, R.C., Chadwick, O.A., 1998. Quantifying strontium isotope models for weathering, pedogenesis and biogeochemical cycling. Geoderma 82, 173–195.

Taylor, A.S., Blum, J.D., Lasaga, A.C., MacInnis, I.N., 2000. Kinetics of dissolution and Sr release during biotite and phlogopite weathering. Geochim. Cosmochim. Acta 64, 1191–1208.

Vengosh, A., Hening, S., Ganor, J., Mayer, B., Weyhenmeyer, C.E., Bullen, T.D., Paytan, A., 2007. New isotopic evidence for the origin of groundwater from the Nubian Sandstobe Aquifer in the Negev, Israel. Appl. Geochem. 22, 1052–1073.

Wickman, T., Jacks, G., 1992. Strontium isotopes in weathering budget. In: Kharaka, Y.K., Maest, A.S. (Eds.), Proc. 7th Internat. Symp. Water–Rock Interaction. Balkema, pp. 611–614.