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Distinguishing sources of base cations in irrigated and natural soils: evidence from strontium isotopes

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Abstract. Strontium isotope ratios ($^{87}Sr/^{86}Sr$) of soil solids, soil cation extracts, irrigation water and plant material are used to determine strontium and therefore cation sources and fluxes in irrigated and natural soil–plant systems. Strontium isotopes of soil solids from four soil profiles (two irrigated vineyard soils and two 'natural' profiles from nearby reserves) show large differences between soil horizons with depth. These differences are not reflected in $^{87}Sr/^{86}Sr$ ratios of soil labile cations, which show both little variation down-profile and much lower ratios than soil solids. In the undisturbed, natural soil profiles, labile cation $^{87}Sr/^{86}Sr$ ratios are close to the ratio of modern seawater, indicating that solutes of marine origin from precipitation are the primary input of strontium (and calcium) to the labile cation pool. In the irrigated soil profiles, $^{87}Sr/^{86}Sr$ ratios of labile cations are consistently shifted towards that of the irrigation water. Mass-balance calculations using $^{87}Sr/^{86}Sr$ ratios of the different inputs to the labile cation pool indicate more than 90% of labile strontium is derived from precipitation solutes in unirrigated soils, and up to 44% from irrigation water solutes as an additional source in irrigated soils. The $^{87}Sr/^{86}Sr$ ratios of grapes grown in irrigated soils match precisely with those of the labile soil cations, demonstrating that cation nutrients are drawn wholly from the labile cation pool and have the same mix of precipitation, irrigation, and soil solid sources. The $^{87}Sr/^{86}Sr$ ratios of grapes grown in the irrigated soils may therefore vary over time depending on (1) the changing mix of irrigation water and local precipitation and (2) potential change to irrigation water. These findings suggest limitations to the use of strontium isotopes in the tracing of grapes and wines to their soil of origin.

Introduction

An understanding of soil cation fluxes and the identity and magnitude of cation sources and sinks can be used to assess a variety of effects of environmental change on terrestrial ecosystems. The elements present in the soil, water and plants of an ecosystem are ultimately sourced from a combination of atmospheric deposition (wet and dry precipitation) and weathering of soil parent rock material (Stewart et al. 1998). Subsequent to these primary inputs, elements may undergo transfer and recycling between soil solution, plants, soil organic matter, secondary minerals, and the soil cation exchange complex (Figure 1). Losses from the system then occur by dissolved and solid removal via water throughflow and runoff, deflation, and grazing by animals.

In the case of an artificially modified soil–plant–water system such as an irrigated crop, additional input of elements as irrigation water solutes, fertilisers and other agricultural additions, and output via harvested crops needs also to be considered.

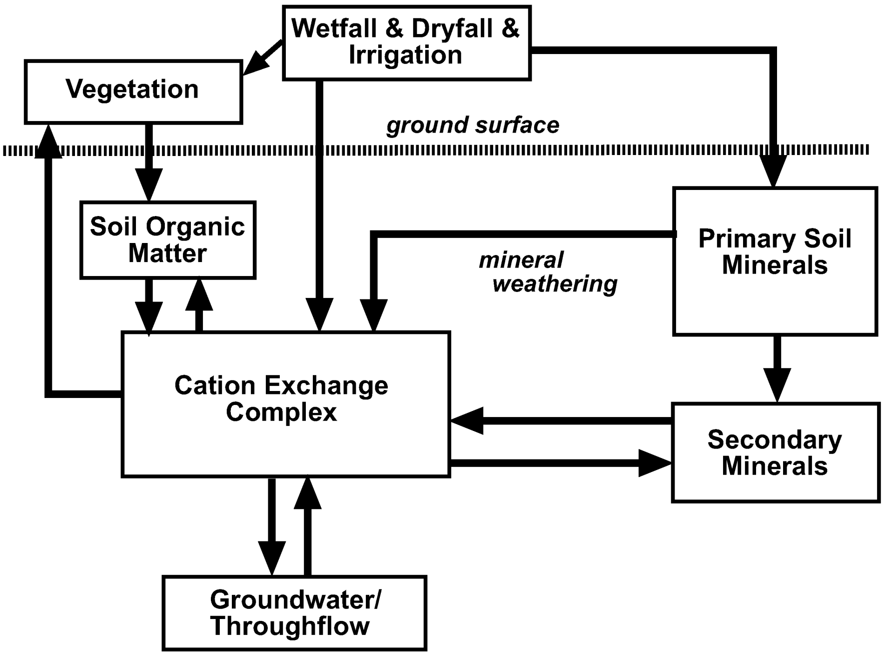

Figure 1. Solute pathways in the soil–water–plant system. Primary inputs of cations to the soil cation exchange complex are from wet and dry precipitation, weathering of soil minerals, and decomposition of soil organic matter. The cation exchange complex then provides the primary source of base cation nutrients for uptake by plants.

The measurement of input and output fluxes of elements in agricultural soils can provide an opportunity to increase our understanding of this system because the treatments are generally known and time frames short.

Key to the monitoring of short-term elemental gains and losses in soils is the analysis of the soil cation exchange complex, which consists of base cations, primarily Na^+, K^+, Mg^{2+}, Ca^{2+}, held within the soil matrix by electrostatic attraction to negatively charged surfaces of clay particles and organic matter (Grim 1968). The soil exchange complex cations exist in a dynamic equilibrium with cations in the soil solution. Collectively the cations in the soil solution and the soil cation exchange complex are commonly referred to as labile soil cations (Capo et al. 1998 after Nye and Tinker 1977). Base cations in the soil exchange complex play an important role in regulating pH of soil and buffering acid inputs to the soil from precipitation and plant decomposition. The labile cation pool also provides the primary source of plant macronutrients K^+, Mg^{2+} and Ca^{2+} (Fageria et al. 1991).

Numerous studies have used strontium isotope ratios to trace and quantify the sources and fluxes of base cations in soil, water and plant materials (Aberg et al. 1990; Bailey et al. 1996; Kennedy et al. 1998; Nakano et al. 2001; Stewart et al.

2001). Strontium (Sr) is utilised for this purpose because it is fairly ubiquitous in the natural environment and because two of its stable isotopes, ^{87}Sr and ^{86}Sr, occur in a ratio that varies greatly with the original geological source of the strontium (Capo et al. 1998). As a relatively high-mass element, strontium isotope fractionation by geological or biological processes is very small compared to that in low-mass isotopic systems such as H, C and O. Thus if the strontium isotope ratios of the original sources of strontium to an ecosystem are known, the ratio found in each component of the ecosystem will reflect the proportions of Sr that are derived from each of the strontium sources (Graustein,1988; Capo et al. 1998).

The chemical similarity of strontium to calcium, having similar ionic radius and the same valence, means that strontium tends to behave similarly to calcium in most systems (Bailey et al.1996), although some fractionation of Sr/Ca ratios may occur at successive trophic levels in ecosystems (Blum et al. 2000). The similar behaviour of strontium and calcium allows the use of strontium isotope ratio as a tracer of sources and fluxes of calcium, and to some extent, the base cations as a group. The utility of strontium isotope ratios in tracing the sources of elements in plant material presents the possibility to trace the place of origin of plant materials by comparing their ^{87}Sr/^{86}Sr ratio with that of the soils in which the plant grew.

The application of strontium isotope analyses for the purpose of tracing wine origins has been explored recently in studies by Almeida and Vasconcelos (2001) and by Barbaste et al. (2001). These studies did not however establish or confirm the direct correspondence of ^{87}Sr/^{86}Sr ratio of the wine with that of the soil in which the grapes were grown. Also, the influences on ^{87}Sr/^{86}Sr ratio in wine grapes from irrigation water has not been established. If the primary source of base cations for vines is the soil labile cation pool, then the relative contributions of the factors influencing the composition of this pool, including atmospheric/precipitation inputs and irrigation water as well as the soil parent material, need to be established before any clear correlation between wine and grape origin can be confirmed.

The study presented here explores the use of strontium isotopes as tracers between water, soil, and grapes in irrigated vineyards. Assuming long-term (hundreds of years) rainfall rates have been fairly consistent, the soil will have reached a steady state in which additions from soil parent material weathering and from wet and dry precipitation are approximately equal to the mass of solutes leached (Stewart et al. 1998). However, with summer irrigation using water that is relatively high in solute concentrations, a net addition of solutes to the soil profile is expected after a few years of irrigation. Changes in soil solute concentrations and element ratios will not necessarily be reflected in the grapes because the processes of nutrient uptake and incorporation of elements into plant tissue is selective. However, the change in strontium isotope ratio in the grapes should be similar to that evident in the soil labile cation pool as the plant does not fractionate strontium isotopes by selectively uptaking one strontium isotope over another in the plant nutrient uptake process (Graustein 1988). Hence, examination of grape strontium isotope ratios can provide an indication of the source of cations taken up by the grape vines under the influence of irrigation.

Field sites

Field sites were selected which had similar soil profile types but were sufficiently geographically separate to provide the opportunity for distinguishing soil strontium isotope signatures. It was also required that the sites were close enough to ensure only subtle climatic differences. Two sites with significantly differing irrigation water salinity values were chosen to enable the comparison of the effects of irrigation both on the practicality of wine origin discrimination using strontium isotope ratios, and on the degree of impact that differing irrigation water has on strontium isotope signatures. Two soil profiles were sampled at each site; one in the irrigated area and one in an adjacent reserve area of natural vegetation that has never been irrigated.

One site is within the Coonawarra viticultural area, about 33 km south of Naracoorte (Figure 2). This site has only been established as a vineyard since 1999, having previously been used as sheep grazing land, and has been subject to conservatively managed irrigation for only three growing seasons up to and including 2002 (Haselgrove L., 2002 personal communication). Irrigation water at this site is drawn from a shallow unconfined aquifer in the Tertiary Gambier Limestone (South Australian Government Department of Water Resources, 2002; Haselgrove L., 2002 personal communication), which provides irrigation water with a salinity of about 780 mg/l total dissolved solids (TDS), measured at the time of soil sample collection. The soil profiles sampled at this site are designated Ci (Coonawarra, irrigated) and Cn (Coonawarra, natural).

The second study site is approximately 10 km south of Padthaway township approximately 70 km north of the Coonawarra site (Figure 2). This site has been established as a vineyard for approximately 10 years, during which time drip irrigation has only been in place for approximately 6 years (Haselgrove L., 2002 personal communication). Prior to use as a vineyard, this site has had a varied and less conservative history of irrigation than the Coonawarra site including flood-irrigation of vegetable crops for a period of up to 30 years (Kaye G., 2002, personal communication). Thus the Padthaway site has been subject to varying, and much greater, volumes of the local groundwater over a much longer period of time than the Coonawarra site. The irrigation water at this site, drawn from the near-surface unconfined aquifer in the Pleistocene limestone Coomandook Formation (Cobb et al. 1994), is of higher salinity than that at the Coonawarra site, with a salinity of about 1580 mg/l TDS, measured at the time of soil sample collection. The soil profiles sampled at this site are designated Pi (Padthaway, irrigated) and Pn (Padthaway, natural).

The Coonawarra and Padthaway areas of the South East district of South Australia are renowned high quality grape-growing areas that have characteristic 'Terra Rossa' soil profiles occurring through much of the region. These soils show significant variability across the region, but typically include a horizon of heavy red clay soil over a limestone base and are common in climates with warm, dry Mediterranean summers and cool wet winters. At both sites the soils have strong contrasts between horizons, with a thick sandy-loam A-horizon over a

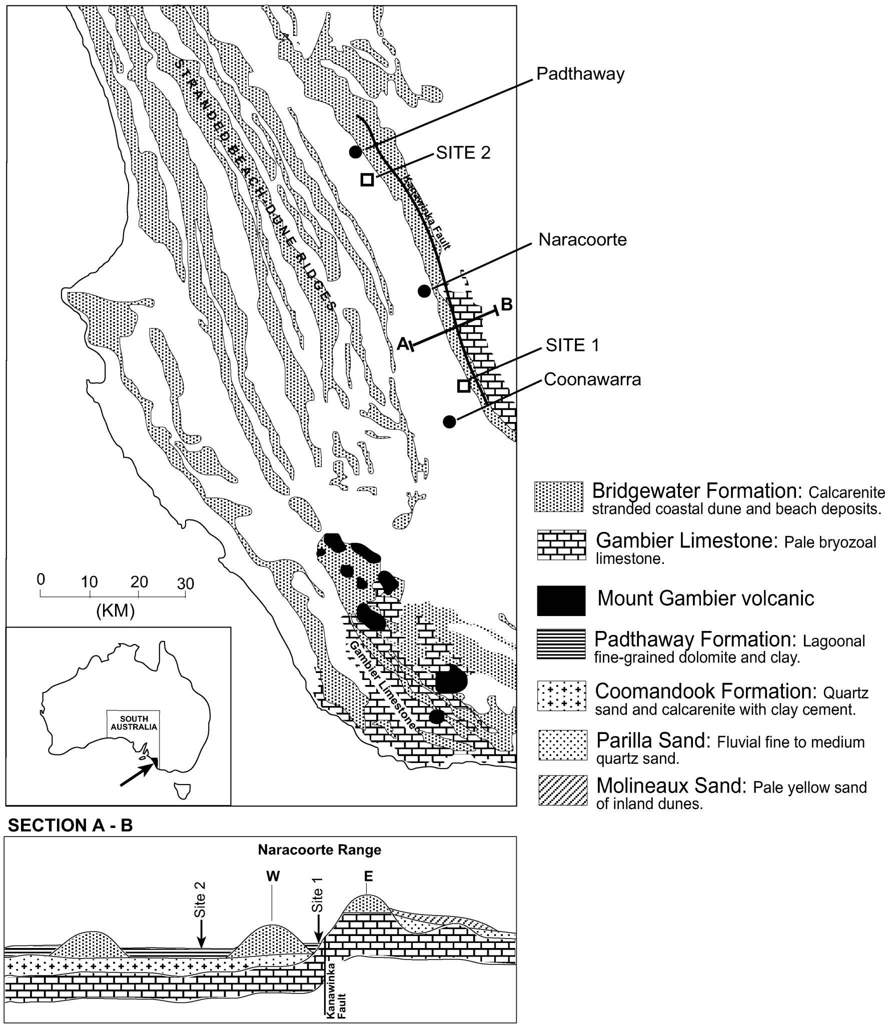

Figure 2. Location map of study sites in South Australia showing distributions of regional geologic and geomorphologic units.

clay B-horizon separated from the underlying limestone by discontinuous zones of pedogenic carbonate (Figures 3 and 4). At both sites A-horizons are dominated by quartz (>99%) with less than 1% feldspar (albite and orthoclase). The clay B-horizon at the Coonawarra site is considerably thicker (70–90 cm) than that at the Padthaway site (25–30 cm). The B-horizons at the Coonawarra site contain 60–80% kaolinite, 11–14% goethite, variable amounts of quartz (4–27%) and trace amounts of anatase and feldspars. The clay B-horizon at the Padthaway site contains 50–60% kaolinite, 20–30% illite, 0–15% smectite, and a few percent of goethite and

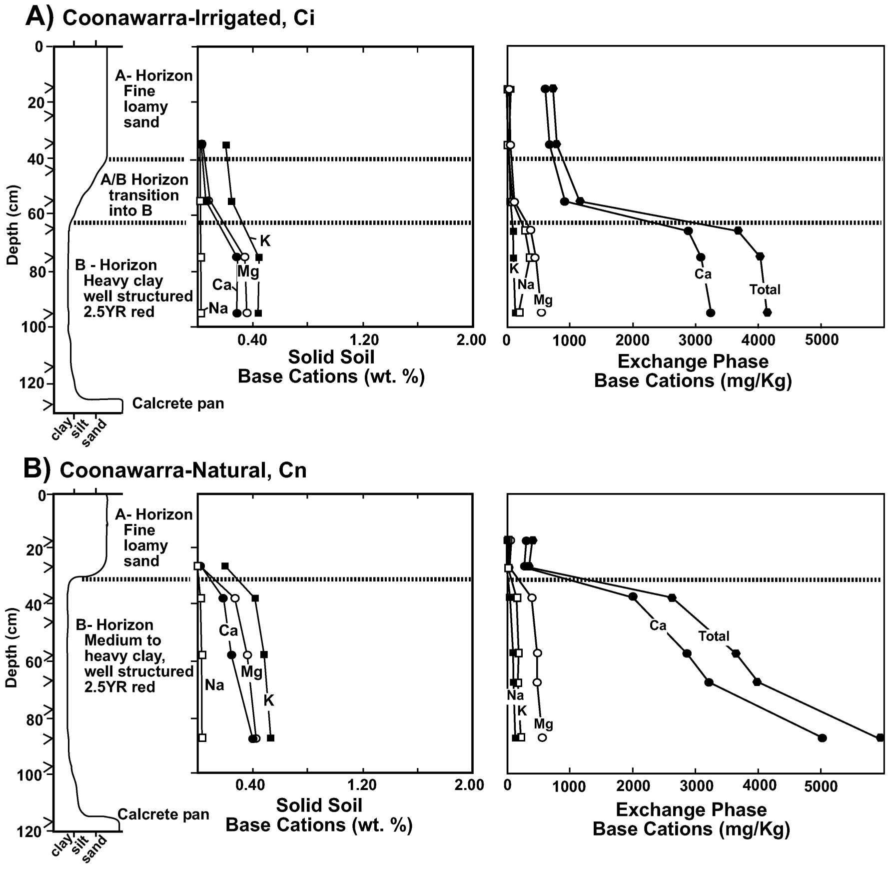

Figure 3. Soil profile and depth profiles of concentrations of major base cations in soil solids and soil exchange phase of (A) Coonawarra-irrigated, Ci and (B) Coonawarra-natural, Cn. Profile on left side of diagram is a grain-size indicator.

hematite, 2–4% orthoclase and albite, and trace amount of anatase (Green 2002). The soil profile types at both sites can be classified as Red Chromosols under the Australian Soil Classification System, or as Xeric Alfisols under the U.S. Department of Agriculture classification system (U.S. Department of Agriculture Soil Conservation Service 1975).

Both sites have gently sloping topography and are approximately 70 km west of the coast and subject to south-westerly prevailing winds. The Coonawarra site is approximately 70 m Australian height datum (AHD) in altitude and has an annual average of approximately 579 mm of rain, while the Padthaway site is at 60 m AHD and receives approximately 508 mm of rain annually (Australian Bureau of Meteorology 2002).

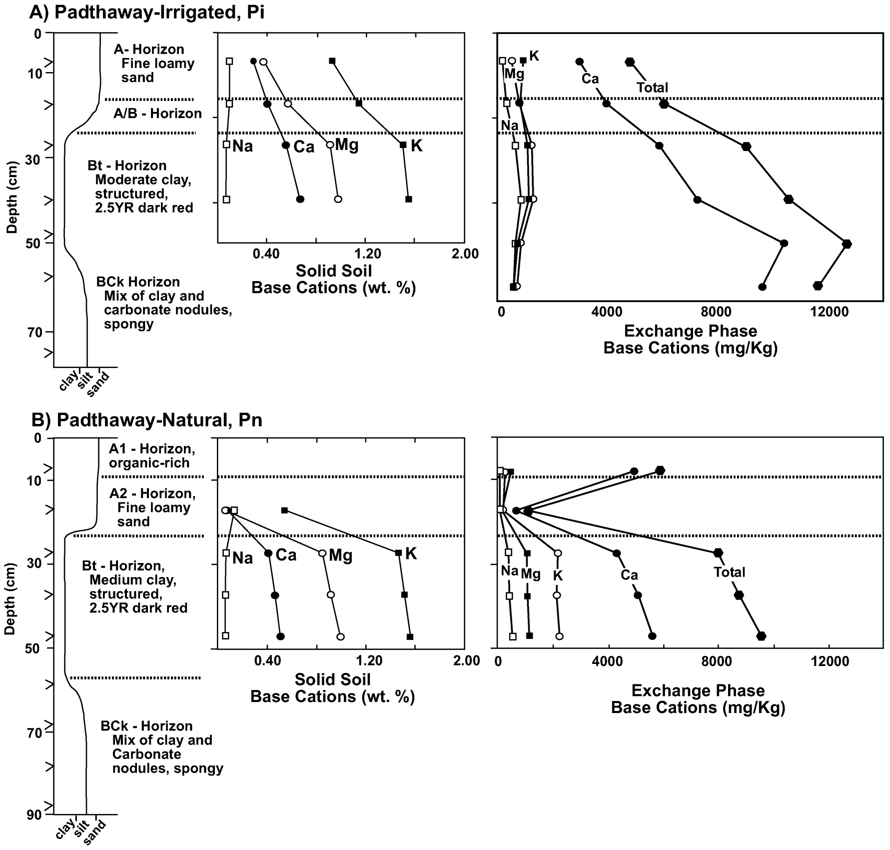

Figure 4. Soil profile and depth profiles of concentrations of major base cations in soil solids and soil exchange phase of (A) Padthaway-irrigated, Pi and (B) Padthaway-natural, Pn. Profile on left side of diagram is a grain-size indicator.

Geological setting

The area encompassing both study sites is underlain to a depth of up to 40 m by the Oligocene–Miocene Gambier Limestone (Rochow et al. 1969) (Figure 2). Overlying the limestone is a widespread Terra Rossa soil profile, in-turn overlain in places by stabilised quartz sand dunes. Recent work on the age and origin of this Terra Rossa soil show that it is dominated by locally derived windblown material sourced from nearby lunette-playa systems over the last 100 k years (Mee 2001; Mee et al. in press).

The surface geological features in the area are dominated by the marine transgression–regression sequence of NE–SW trending topographic ridges of calcarenite beach-dune deposits known as the Bridgewater Formation (Sprigg 1952; Cook et al. 1977). Between these beach-dune ridges are flat lagoonal areas that are typically poorly-drained and filled with imperfectly to poorly-drained soils, marsh, lunette and lake deposits of clay, marl, and silt, locally covered by a sheet of pale grey quartz sand. The Padthaway study site is located in one of these interdunal areas, to the west of the West Naracoorte Range, the oldest (early Pleistocene) and highest of the beach-dune ridges of the Bridgewater Formation in this area (Smith et al. 1995).

The Coonawarra site is on a western foot slope of the Kanawinka escarpment (Figure 2), in an area where the Gambier Limestone is close to the surface. The Terra Rossa soil at the Coonawarra site occurs directly atop the calcarenite Camelback Member of the Gambier Limestone, providing it with exceptional drainage characteristics due to the open framework nature of this limestone unit (Smith et al. 1995).

At the Padthaway site there has been later Miocene and Pliocene exposure and partial erosion of the Gambier Limestone (Harris 1983), with some of the eroded material reworked to form the Pleistocene Coomandook Formation. This formation is a medium-grained quartz sand and calcarenite with clay cement, that underlies the Terra Rossa at this site, and separates the soil from the Gambier Limestone (Rochow et al. 1969).

Methods

Field sampling

At each of the four soil sampling locations, a pit was dug by back-hoe and one face of the pit was cleaned to prevent mixing of soil between horizons. Soil samples were taken from a clean horizontal bench cut into the side of the pit at depth intervals of between 5 and 10 cm.

Water samples were taken from bores regularly used for irrigation at the two vineyards. Bore pump inlet depths were at 9.0 and 16.5 m respectively in the bores sampled at the Padthaway and Coonawarra sites. The bore outlets were situated after a coarse filter and before any chemical treatment or fine filtering apparatus. All samples were filtered in the field with disposable 0.45 μm filters, those intended for Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) analysis were acidified to pH2 with nitric acid.

Grape samples were taken from vines directly above the sampled side of the soil pits. These were immediately stored in sealed plastic containers containing a perforated container of sodium metabisulphite solution. All water and grape samples were stored on ice until they reached the laboratory and then stored in a cold-room at 4 °C.

Soil sample preparation

Samples of soil solid for strontium isotope and elemental composition analysis, were oven-dried at 100–105 °C overnight, ground to a powder, and then leached with 0.01 M HCl (pH2) and rinsed with deionised water to remove carbonates.

Elemental composition analysis

Elemental composition, including major and trace elements, of soil exchangeable cation extracts and bore water (Table 1) were analysed using ICP-AES at CSIRO Science and Technology Centre Laboratory, Lucas Heights, NSW.

Soil exchangeable cation extracts for ICP-analysis were prepared according to the method developed by Lavkulich (1981) and described in Carter (1993). Dried soil samples (not acid leached) were treated with 1.0 M ammonium acetate (NH_4O-Ac) solution and filtered, the collected filtrate being the exchangeable cation extract for analysis. Standard solutions of Mg/Ca and Na/K in NH_4O-Ac solution were prepared to verify the ICP-AES analysis.

Elemental compositions of soil solids (Table 2) were analysed using X-ray fluorescence (XRF) at the University of Adelaide Department of Geology and Geophysics. Soil samples were acid-leached to remove carbonates, combusted overnight at 960 °C, and then re-weighed to determine loss on ignition (LOI) values for the loss of organic material. Sub-samples of 1.0 g were then prepared for XRF-analysis of major element composition at the University of Adelaide using a Philips PW1480 X-ray Fluorescence Spectrometer with an analysis program calibrated against international and local Standard Reference Materials.

Strontium isotope analysis

Strontium isotope analysis was carried out at the University of Adelaide using a Finnigan Mat 262 thermal ionisation mass spectrometer (TIMS). Strontium standard NIST987 was measured with each batch of samples. The average $^{87}Sr/^{86}Sr$ for NIST987 standards was 0.710276 with SD of 0.000014.

Samples of soil solids, soil cation extract, soil carbonate, irrigation water and grapes were analysed for strontium isotope ratios. The soil solid samples were oven-dried, ground (<0.212 mm), acid-rinsed and combusted at 500 °C. Sub-samples of 200 mg were then prepared for strontium isotope analysis. Soil solids were dissolved in a combination of distilled hydrofluoric acid (50% HF) and nitric acid (6 M HNO_3) at 160 °C, then evaporated to dryness and the precipitate re-dissolved in hydrochloric acid (6 M HCl) at 140 °C. Strontium chlorides were isolated from the resulting solution by passing the solution two times through columns of 2 ml AG50W X8 200–400 mesh Biorad cation exchange resin, which was leached with distilled HCl (6 M) between passes. The product of the second pass through the cation exchange columns was collected in cleaned teflon vials and evaporated to dryness, resulting in refined strontium chloride ($SrCl_2$) for spectroscopic analysis.

This sample preparation process was carried out in teflon vials cleaned by successive boiling in 6 M HNO_3 and 6 M HCl. The refined $SrCl_2$ samples were dissolved in 1 µl of Birck's solution and evaporated onto single tantalum filaments pre-primed with 2 µl of pure Birck's solution, then loaded into the sample carousel of the mass spectrometer.

Table 1. ICP-AES results. Elemental concentrations of soil extracts and irrigation waters.

Profile	Depth (cm)	Na	Mg	K	Ca	Si	P	Sr	Ba	Mn	Fe	S
Soil cation extract concentrations (mg/kg dry soil)												
Ci Coonawarra irrigated	15	32.7	55.2	61.4	654.7	8.2	8.2	3.5	2.9	1.2	0.8	–
	35	75.6	73.6	12.3	715.3	12.3	6.1	4.3	4.1	0.4	0.4	–
	55	130.5	117.9	42.1	968.2	6.3	2.1	7.2	6.3	–	–	–
	65	335.6	413.3	100.2	2955.5	5.0	5.0	23.3	16.5	–	–	–
	75	409.4	480.3	105.0	3149.3	5.2	5.2	22.6	17.3	–	–	26.2
	95	241.9	560.9	132.9	3296.4	5.3	5.3	17.5	18.3	–	–	26.6
Cn Coonawarra natural	17	28.5	42.7	40.7	317.4	4.1	4.1	4.5	3.7	0.4	–	–
	27	24.4	36.6	40.6	272.2	4.1	4.1	2.8	2.4	0.4	–	–
	37	76.8	405.4	155.9	2015.2	4.8	4.8	9.8	13.9	–	–	–
	57	132.5	503.6	180.2	2862.8	5.3	5.3	11.7	21.5	–	–	–
	67	138.5	483.3	173.8	3204.0	8.1	5.4	11.9	23.1	–	–	27.2
	87	181.0	569.8	228.5	4985.8	14.8	5.9	16.3	35.0	–	–	29.7
Pi Padthaway irrigated	7	373.6	601.6	987.0	3101.9	54.0	4.7	31.5	18.1	0.5	–	23.5
	17	649.3	860.5	860.5	4094.1	52.2	5.2	40.2	28.4	–	–	26.1
	27	1050.7	1328.8	1205.2	6026.1	34.0	6.2	67.7	53.8	1.2	–	61.8
	40	1293.2	1356.3	1198.6	7380.9	22.1	6.3	83.0	60.9	–	–	63.1
	50	1262.0	909.8	733.7	10565.9	23.5	5.9	84.8	43.1	–	–	88.0
	60	1138.4	783.4	623.4	9758.1	21.7	5.4	77.8	30.6	–	–	108.4

Pn Padthaway natural	7	274.0	552.2	339.8	5309.6	46.7	10.6	38.2	10.0	9.8	1.1	21.2
	17	142.7	112.1	203.8	774.4	30.6	8.2	10.4	6.1	1.4	0.6	–
	27	926.3	1122.8	2386.0	4659.6	39.3	5.6	103.9	35.6	1.1	–	84.2
	37	962.4	1166.6	2362.3	5453.7	32.1	5.8	122.5	49.6	0.3	–	58.3
	47	1068.7	1246.8	2374.8	6115.1	29.7	8.9	130.6	45.7	0.9	–	59.4
	95	924.3	1082.8	977.2	9507.4	31.7	5.3	87.2	37.5	–	–	52.8
Irrigation water solute concentrations (mg/l)												
Coonawarra 1		97.0	18.4	2.2	114.8	11.9	–	0.71	0.02	–	0.20	6
Coonawarra 2		98.0	17.9	2.2	115.7	11.6	–	0.66	0.02	–	0.22	6
Padthaway 1		252.0	42.0	5.0	144.4	11.8	–	0.92	0.04	–	0.02	19
Padthaway 2		252.0	42.0	5.2	145.2	11.8	–	0.94	0.04	–	0.02	18

– indicates value below detection limit.

Table 2. Quantitative XRF results. Elemental concentrations of soil solid fraction.

Profile	Depth (cm)	K (%)	K (mg/kg)	Na (%)	Na (mg/kg)	Mg (%)	Mg (mg/kg)	Ca (%)	Ca (mg/kg)	Sr (mg/kg)
Ci	35	0.209	2092	0.012	118	0.030	301	0.029	286	12
(Coonawarra	55	0.245	2453	0.018	177	0.072	724	0.071	714	17
irrigated)	75	0.447	4467	0.024	236	0.350	3497	0.286	2857	40
	95	0.438	4382	0.024	236	0.362	3618	0.293	2929	36
Cn	27	0.199	1985	0.012	118	0.024	241	0.000	0	11
(Coonawarra	37	0.413	4127	0.018	177	0.271	2713	0.186	1857	33
natural)	57	0.481	4808	0.024	236	0.362	3618	0.250	2500	34
	87	0.531	5311	0.024	236	0.428	4281	0.407	4071	36
Pi	7	0.926	9261	0.094	944	0.374	3738	0.293	2929	54
(Padthaway	17	1.139	11388	0.083	826	0.579	5789	0.414	4143	63
irrigated)	27	1.504	15040	0.071	708	0.923	9226	0.564	5643	81
	40	1.554	15543	0.071	708	0.983	9829	0.679	6786	92
Pn	7	0.513	5134	0.100	1003	0.151	1507	0.821	8214	68
(Padthaway	17	0.540	5396	0.130	1297	0.054	543	0.079	786	30
natural)	27	1.464	14636	0.071	708	0.850	8502	0.414	4143	114
	37	1.521	15210	0.059	590	0.923	9226	0.464	4643	123
	47	1.561	15607	0.059	590	1.001	10009	0.514	5143	122

The samples of cation extract, irrigation water, soil carbonate and grapes were subject to a modification of this procedure. Cation extract samples for strontium isotope ratio analysis were prepared by the same method as those for the elemental composition analysis. The soil sample quantity and ammonium acetate (NH_4O-Ac) solution concentration were adjusted to provide sufficient NH_4O-Ac in 100 ml of solution to leach the majority of cations from a 25 g soil sample without creating an over-burden of NH_4O-Ac in the extract sample for the strontium sample preparation process. Samples were then evaporated to dryness and subjected to the process of acid-dissolution, cation-exchange and filament loading described above with the exception of the initial HF and HNO_3 dissolution stages, deemed unnecessary for these highly soluble samples.

Irrigation water samples were evaporated to a dry precipitate and prepared for Sr analysis using the same process of acid-dissolution, cation-exchange and filament loading used for the soil cation extract samples.

Solid fragments of soil carbonate (calcrete) from the base of each of the four sample pits were partially dissolved in 0.01 M HCl, then filtered and the filtrate evaporated to provide a solid residue. The solid residue was prepared for strontium isotope analysis using the same process of acid-dissolution, cation-exchange and filament loading used for the soil cation extract samples.

For strontium isotope analysis of grapes, a homogenised blend of grape skins, flesh and seeds was oven-dried then combusted at 550 °C. The resulting ash was prepared for strontium analysis using the same process of acid-dissolution, cation-exchange and filament loading used for the soil solid samples, including the

Table 3. TIMS results. Strontium isotope ratios of soil solids, soil extracts, irrigation water and grapes.

Sample type	Profile Ci				Profile Cn				Profile Pi			Profile Pn		
	Depth (cm)	$^{87}Sr/^{86}Sr$	2SE	Total error	Depth (cm)	$^{87}Sr/^{86}Sr$	2SE	Total error	Depth (cm)	$^{87}Sr/^{86}Sr$	2SE	Depth (cm)	$^{87}Sr/^{86}Sr$	2SE
Soil solid	35	0.7268173	0.0000914	0.0000914	27	0.7275834	0.0000707	0.0000707	7	0.7178454	0.0000166	7	0.7157472	0.0000188
Soil solid	55	0.7214509	0.0000121	0.0000121	37	0.7156484	0.0000655	0.0000655	17	0.7159739	0.0000155	17	0.7257120	0.0000137
Soil solid	75	0.7137736	0.0000653	0.0000653	57	0.7134844	0.0000421	0.0000421	27	0.7131266	0.0000168	27	0.7128528	0.0000147
Soil solid	95	0.7141276	0.0000212	0.0000212	87	0.7143962	0.0000667	0.0000667	40	0.7125709	0.0000155	37	0.7122856	0.0000165
Soil solid	–	–	–	–	–	–	–	–	–	–	–	47	0.7121780	0.0000198
Cation Extract	35	0.7092241	0.0000387	0.0000897	27	0.7096705	0.0000173	0.0000683	7	0.7092557	0.0000140	7	0.7093617	0.0000162
Cation Extract	55	0.7095102	0.0000137	0.0000647	37	0.7096848	0.0000124	0.0000124	17	0.7092351	0.0000161	17	0.7093293	0.0000119
Cation Extract	75	0.7095837	0.0000172	0.0000172	57	0.7097360	0.0000170	0.0000170	27	0.7092412	0.0000134	27	0.7093329	0.0000139
Cation Extract	95	0.7095721	0.0000161	0.0000161	87	0.7096942	0.0000207	0.0000207	40	0.7092440	0.0000127	47	0.7093505	0.0000153
Irrigation Water*	–	0.7086214	0.0000132	0.0000132	–	–	–	–	–	0.7091094	0.0000162	–	–	–
Grapes*	–	0.7095089	0.0000150	0.0000150	–	–	–	–	–	0.7092566	0.0000181	–	–	–
Carbonate	100	0.7096743	0.0000181	0.0000181	100	0.7099167	0.0000165	0.0000165	55	0.7093347	0.0000168	56	0.7094109	0.0000147

*$^{87/86}$Sr ratios for irrigation water and grapes are average of two samples with similar results.

2SE = 2 × standard error of 100 TIMS ratio measurements.

Total error = 2SE + procedural error (refer text).

HF and HNO_3 dissolution stages, which were found to be necessary to dissolve the ash.

Strontium isotope ratios are reported (Table 3) with a standard error for each measurement based on the results of between 60 and 100 analyses carried out by the TIMS for each sample. To determine the degree of strontium contamination introduced to the soil cation extract samples by the ammonium acetate solution, a ^{84}Sr-spiked sample of ammonium acetate solution was prepared for Sr analysis simultaneously with the soil cation extract samples. The ^{84}Sr/^{86}Sr ratio of the spiked sample was analysed and the total mass of contaminant strontium was calculated by comparing the measured ^{84}Sr/^{86}Sr ratio with natural abundances of ^{84}Sr and ^{86}Sr. Contamination was considered to be significant for any sample in which the mass of strontium contamination exceeded 0.1% of the mass of strontium in the sample. This limit was exceeded only in some soil cation extract samples in which Sr concentration was particularly low. For these samples a 'procedural error' was calculated in which:

$$\text{Procedural error} = \pm\left(\frac{[\mathrm{Sr}_{(\text{contaminant})}]}{[\mathrm{Sr}_{(\text{sample})}]}\Delta\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\max}\right)$$

Where $\Delta(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\max}$ equals the maximum probable range of contaminant Sr ratios. The limits of this range were considered for this purpose to be 0.70360–0.74700. Total error for these samples is reported as 2 × standard error + procedural error (Table 3).

Results

Elemental concentrations of soil solids

Elemental concentrations of soil solids were used to evaluate the contribution to the exchangeable cation complex of elements weathering from soil minerals. The analysis here examines only the major base cations and compares these to the concentrations and elemental ratios of the exchange phase base cations (Tables 1 and 2).

The relative proportions of Ca, Mg, K and Na in the soil solids differ considerably from the proportions observed in the exchange phase, with K and Mg being the dominant cations in the solid phase (Figures 3 and 4). Overall the soil solids at Padthaway have higher concentrations of these elements than those at Coonawarra because the Padthaway soils contain a greater variety of clays than Coonawarra soils and include illite (Green 2002), the structure of which includes K as well as Mg substituting for Al or Fe (Grim 1968). The clay minerals present at both sites contain minimal Ca and Na, hence in nearly every sample K and Mg concentrations in the soil solids dominate over Ca and Na concentrations. Although the soil solid samples were leached with weak acid prior to XRF analysis, some exchange phase cations probably still remain and form a proportion of the

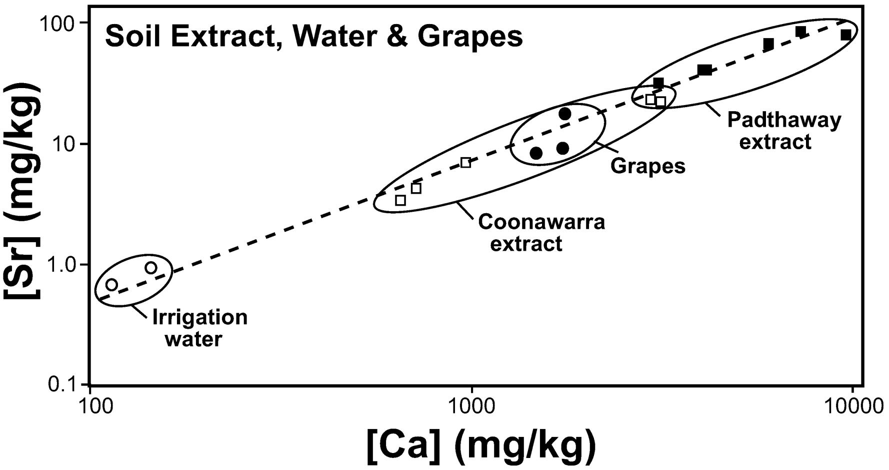

Figure 5. Scatter plot on log–log scale of Sr concentrations versus Ca concentrations in irrigation waters, grapes, and soil extracts from irrigated profiles. The proximity of all data points to the regression line ($r^2 = 0.955$) indicates a consistent Sr/Ca ratio (approximately 0.009) in all samples, suggesting parallel behaviour of both elements.

percentage of the Na, Ca, K and Mg detected in the soil solid samples by the XRF analysis. As the Na and Ca concentrations detected by the XRF are very low (Table 2), it is possible that a significant proportion of these are residual exchange phase Na^+ and Ca^{2+}. The Mg and K concentrations however are an order of magnitude higher in the soil solids than in the exchange phase.

Strontium isotope ratios

Since strontium is to be treated in this study as an analogue for calcium, it must first be confirmed that these elements behave similarly in their movements between the plants, soil and water of the system studied. A linear relationship was observed between strontium and calcium mass concentrations in the irrigation water, grapes and soil cation extracts from the irrigated profiles at both locations (Figure 5). The proximity of all the data points to the linear regression line indicates a highly consistent ratio of Sr/Ca in all the samples. The slope of approximately 0.008 indicates a consistent ratio of Sr/Ca (mg/mg) in these samples. In view of these results, it is assumed that strontium exhibits parallel behaviour to calcium in the soil–plant–water system studied, and that strontium can therefore be considered analogous to calcium.

In order to evaluate the use of strontium isotope ratios as a tracer of soil types, each horizon is characterised by its $^{87}Sr/^{86}Sr$ isotope ratio and its strontium concentration (plotted as its reciprocal of strontium concentration). Linear relationships are observed between $^{87}Sr/^{86}Sr$ and 1/[Sr] of samples from various depths at both

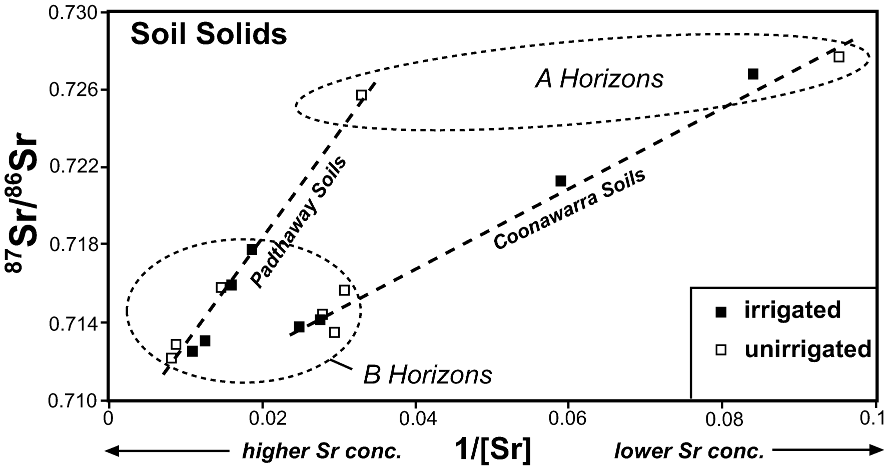

Figure 6. Variation of strontium isotope ratios with strontium concentration in soil solids indicates mixing of two soil horizons with distinct Sr isotope ratios.

locations (Figure 6), indicating a simple mixing of two end-member soil types with differing $^{87}Sr/^{86}Sr$ isotope ratios. At Coonawarra the end-members are the near-surface sand, with 1/[Sr] of 0.095 and $^{87}Sr/^{86}Sr$ ratio of 0.7276, and the clay B-horizon material, with 1/[Sr] of close to 0.0275 and $^{87}Sr/^{86}Sr$ ratio of about 0.7140. The distinct difference between $^{87}Sr/^{86}Sr$ ratios of the A- and B-horizon materials indicates a different geological source for the soil material in the two horizons. The position of each sample on the mixing line in Figure 6 provides an indication of the fraction of each end member material contributing to the soil in the sample. Because many of the soil values fall on a line between the end members, they are probably a mixture of only the two end member materials. This concurs with field observations. Samples from the A–B transition zone in a profile that had been mechanically mixed for vine planting or located at the top of the clay B-horizon, where some degree of natural mixing with the overlying A-horizon can be expected, appear at positions on the mixing line between the A- and B-horizon end member materials.

Soil depth profiles of strontium isotope ratios show a clear difference between soil solids and soil exchangeable cation extract (Figure 7; Table 3). Soil solids have higher $^{87}Sr/^{86}Sr$ ratios than soil cation extracts and vary considerably with depth. The variation with depth is related to the different percentages of minerals in the soil horizons. A-horizons, dominated by quartz sand and coarse silt, but with small amounts of feldspar (Green 2002), have significantly higher strontium isotope ratios than the B horizons. The clayey B horizons from both the Coonawarra and Padthaway sites have strontium isotope ratios within the same overall range, however the Padthaway site has slightly, yet significantly, lower ratios. Strontium isotope ratios of soil extracts, on the other hand, do not appear to vary significantly down profile when compared to the variation observed in soil solids.

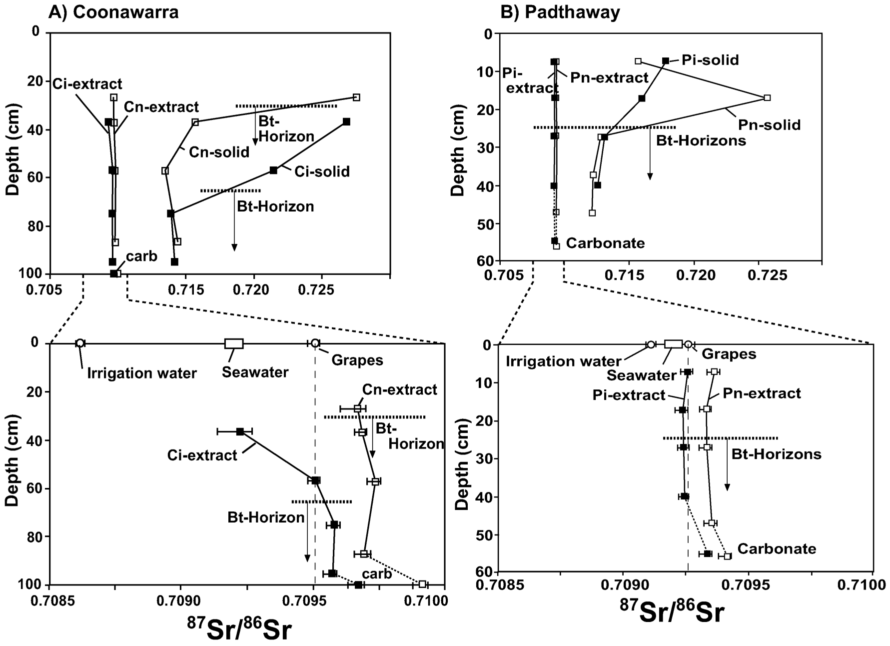

Figure 7. Soil depth profiles of strontium isotope ratios of soil solids and soil cation extracts from (A) Coonawarra irrigated and natural profiles (Ci, Cn) and (B) Pathaway irrigated and natural profiles (Pi, Pn). The lower graphs show the data on an expanded ^{87}Sr/^{86}Sr axis and with the soil solid data omitted. These illustrate that the small differences between Sr ratios of the soil cation extract between irrigated profiles and natural are consistent with depth and exhibit a shift in irrigated profiles towards Sr ratios of irrigation water.

The soil cation extracts, irrigation water, grapes and soil carbonates all have fairly similar ^{87}Sr/^{86}Sr ratios and occupy a narrow range of values at both locations (Figure 7). At Coonawarra there is a greater range of values for these components (0.70860–0.70990) than at Padthaway (0.70910–0.70940). However, on the scale of ^{87}Sr/^{86}Sr ratio values occupying the horizontal axis of these graphs, the soil cation extracts vary minimally with depth, particularly those for the undisturbed natural soil profiles. However, when plotted on an expanded scale (Figure 7) the differences within the narrow range of values for cation extracts, water, grapes and soil carbonate can be examined. The trends displayed by the data are remarkably consistent, both from one profile to another and from one site to the other. In both the natural and irrigated profiles at Padthaway, the soil cation extracts have ^{87}Sr/^{86}Sr ratios that are nearly constant through the whole depth of the A- and B-horizons (Figure 7). However the soil cation extracts from the irrigated profile are shifted by 0.001 towards a lower ratio (less radiogenic). The irrigation water applied to this profile has a ^{87}Sr/^{86}Sr ratio a further 0.0012 lower than the cation extracts. The ratios of the soil cation extracts in the irrigated profile thus lie approximately half way between the ratio of the irrigation water and the ratios of the extractable cations in the natural profile.

The $^{87}Sr/^{86}Sr$ ratios of the soil cations, carbonate, water and grape samples from the Coonawarra site follow a similar pattern to the Padthaway samples, but with some subtle differences. On the expanded $^{87}Sr/^{86}Sr$ scale in Figure 7, the values for soil cations in the irrigated profile at Coonawarra vary systematically with depth. Similar to the Padthaway soils, the ratios of soil cations in the irrigated Coonawarra profile (Ci) are all shifted to lower ratios than those in the natural soil profile (Cn). However in the irrigated profile at Coonawarra they decrease from 0.70960 between 75 and 95 cm depth to a less radiogenic 0.70920 at 35 cm depth. The irrigation water applied to this profile has a $^{87}Sr/^{86}Sr$ ratio significantly lower than the labile cations in the natural soil. The soil cations closer to the surface in the irrigated profile are closer to the irrigation water value than those at depth.

The $^{87}Sr/^{86}Sr$ ratio of the grapes from Padthaway is within 1.1×10^{-5} of the ratios of the soil cations in the irrigated profile in which they grew (Figure 7(A)). This is close to the limit of the accuracy of the TIMS analysis and thus these ratios are considered to be indistinguishable. Similarly, the $^{87}Sr/^{86}Sr$ ratio of grapes from the Coonawarra site (Figure 7B) is indistinguishable, within the accuracy of the method, to that of the soil cations at the 55 cm depth in the Ci soil profile. Soil salinity data for this profile (Green 2002) show this depth to be the point where soil solution salinity peaks, indicating that this is the depth of greatest uptake by the vine roots. Thus the majority of the strontium in the plant should be taken up from soil at this depth further confirming the match between grape $^{87}Sr/^{86}Sr$ ratio and the soil cation extract $^{87}Sr/^{86}Sr$ ratio.

The soil carbonate in the Padthaway irrigated profile (Pi) exhibits a shift to a $^{87}Sr/^{86}Sr$ ratio about 0.001 lower than the carbonate in the natural profile (Pn), similar to the change observed in the soil cation $^{87}Sr/^{86}Sr$ ratios. The soil carbonates in the Coonawarra profiles follow a similar pattern to those from Padthaway, with the $^{87}Sr/^{86}Sr$ ratio of carbonate from the irrigated slightly lower than that in the natural profile. In all four profiles the soil carbonates have $^{87}Sr/^{86}Sr$ ratios that are slightly higher than those of the soil cations. Quade et al. (1995) measured strontium isotope ratios of soil carbonates and cation extracts from five soil profiles sampled in South Australia and Victoria and found soil carbonate $^{87}Sr/^{86}Sr$ ratios to be grossly similar to those of soil cations. However, they did not examine differences in the order of 10^{-4}, which are consistent in the data presented here.

The small but consistent differences between soil cation extracts and soil carbonates may be an artefact of the carbonate separation method. The method of preparing soil carbonate samples for strontium isotope analysis may have caused some higher-ratio strontium to be leached from the silicate particles within the carbonate samples. The $^{87}Sr/^{86}Sr$ ratios then measured for the carbonate samples would then represent a mix of strontium from (1) soil carbonate, probably with an identical $^{87}Sr/^{86}Sr$ ratio to the exchangeable cations, and (2) soil silicates with a higher $^{87}Sr/^{86}Sr$ ratio.

Discussion

Key to the tracing of dissolved solids in the soil–water–plant system is the evaluation of contributions from mineral weathering, precipitation, and irrigation water. The results of XRF analysis show that K and Mg are much more significant than Na and Ca as components of the soil minerals at both sites. If weathering of soil minerals is a major contributor to the soil cation pool, the amounts of K and Mg would be expected to be significant and the amount of Ca or Na would be less. The soil samples with higher concentrations of K or Mg in the solid phase would therefore have higher proportions of K^+ and Mg^{2+} in the exchange phase. However, comparison of soil solid and exchange phase proportions (Figures 3 and 4) indicates minimal correlation between percentages in soil minerals and in the exchange phase, suggesting that the products of soil mineral weathering have a minimal effect on exchange phase cation concentrations.

The results of the strontium isotope ratio analyses support the above findings of the major element analysis and indicate that exchange phase fractions of these soils are probably dominated by cations contributed by precipitation. The addition of irrigation water in irrigated soils is a significant additional input source to the exchange phase, while the contribution from soil mineral weathering is very small.

If soil mineral weathering were a significant contributor to the exchangeable cation pool, the vertical variations in $^{87}Sr/^{86}Sr$ ratios of soil solids would influence the $^{87}Sr/^{86}Sr$ ratios of exchangeable cations to vary correspondingly, as demonstrated by Kennedy et al. (1998). Such an influence is not observed in the four soil profiles studied. While the $^{87}Sr/^{86}Sr$ ratios of soil solids reduce significantly with depth in all four profiles, the cation extract $^{87}Sr/^{86}Sr$ ratios are either constant or, in the case of profile Ci, actually increase slightly with depth. This suggests that in these soils either: (1) weathering of soil solid material has a minimal influence on exchangeable strontium and that exchangeable cations in the unirrigated soils are derived mostly from precipitation, or (2) exchangeable cations, including strontium, are vertically cycled within the soil causing mixing through the soil profile of strontium from precipitation and mineral weathering. The work of Graustein (1988) suggests vegetation causes cycling of exchangeable cations between the root zone and the surface, thus integrating strontium with different isotope ratios. However, since the cation extract $^{87}Sr/^{86}Sr$ ratios are constant with depth in both of the natural soil profiles, the latter explanation requires that plant roots at these sites extend to the full depth sampled.

For most of the year these soils are subject to rainfall rates that are much lower than the potential evaporation rate (Australian Bureau of Meteorology 2002) so that most infiltrating rainwater evaporates from within the soil profile and there is very little drainage below the soil. It may be that in these circumstances input of strontium from precipitation overwhelms the input from weathering of soil parent material. If this is correct then the $^{87}Sr/^{86}Sr$ ratio of the exchangeable cations in the undisturbed profile is close to the ratio of the local rainfall.

Strontium isotope ratios of the cation extracts, soil minerals and the precipitation may be used to quantify the relative proportions of strontium contributed to the

Table 4. Calculation of percentages of labile Sr contributed by soil mineral weathering, based on ^{87}Sr/^{86}Sr ratios.

Soil profile	Depth (cm)	^{87}Sr/^{86}Sr soil solid	^{87}Sr/^{86}Sr cation extract	% Exchangeable Sr from soil minerals
Cn (Coonawarra natural)	27	0.7275834	0.7096705	2.5
	37	0.7156484	0.7096848	7.4
	57	0.7134844	0.7097360	12.3
	87	0.7143962	0.7096942	9.3
Pn (Padthaway natural)	7	0.7157472	0.7093617	2.3
	17	0.725712	0.7093293	0.7
	27	0.7128528	0.7093329	3.3
	37	0.7122856	0.7093505	4.3

cation pool from these sources using an equation of isotope mass balance of two end-members:

The ^{87}Sr/^{86}Sr of a mixture of two components 1 and 2 is:

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{mix}} = \frac{\mathrm{M_1}^{\mathrm{Sr}} \cdot (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_1 + \mathrm{M_2}^{\mathrm{Sr}} \cdot (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_2}{\mathrm{M_1}^{\mathrm{Sr}} + \mathrm{M_2}^{\mathrm{Sr}}} \tag{1}$$

where $\mathrm{M}_1^{\mathrm{Sr}}$ and $\mathrm{M}_2^{\mathrm{Sr}}$are the masses of strontium from end members 1 and 2 and $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{mix}}$ is the ^{87}Sr/^{86}Sr ratio of the mixture of $\mathrm{M}_1^{\mathrm{Sr}}$ and $\mathrm{M}_2^{\mathrm{Sr}}$. Rearranged, this formula gives the proportion of component 1 in the mixture of components as (Modified from Stewart et al. 1998):

$$\frac{\mathrm{M}_1^{\mathrm{Sr}}}{\mathrm{M}_1^{\mathrm{Sr}} + \mathrm{M}_2^{\mathrm{Sr}}} = \frac{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{mix}} - (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_2}{(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_1 - (^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_2} \tag{2}$$

Table 4 shows the percentages of strontium in the exchange phase that could have been derived from the soil minerals in the two unirrigated profiles (Cn and Pn) if the only two inputs of strontium are considered to be from precipitation and weathering of soil minerals. In calculating these figures, end-member 1 is the strontium contributed by soil mineral weathering, end-member 2 is strontium contributed by precipitation and the strontium in the soil cation extract is considered to be a mixture of these two contributors. These calculations use an estimated precipitation ^{87}Sr/^{86}Sr ratio identical to that of modern seawater, 0.709211 (Elderfield 1986). The findings of Quade et al. (1995) indicated that in the soils of this region strontium in both the exchangeable cation pool and the soil carbonate is derived from precipitation with solutes dominated by marine sources and that ^{87}Sr/^{86}Sr ratios of soil carbonates generally increase inland in the direction of the prevailing south-westerly winds, indicating a diminishing proportion of marine strontium and increasing influence of higher ^{87}Sr/^{86}Sr ratio dust in precipitation. As the soil surface materials at both sites have much higher ^{87}Sr/^{86}Sr ratios than seawater, and precipitation ^{87}Sr/^{86}Sr ratios tend to increase with the influence of windblown dust, the estimate used here is the lowest ratio that could be considered reasonable. The resulting percentages of labile cations derived from soil minerals range from 0.7% up to 12.3%, with higher percentages overall occurring in the Coonawarra soils. However, if the estimate for the precipitation ^{87}Sr/^{86}Sr ratio is increased only slightly to account for some influence of silicate dust in the precipitation then the calculated percentages from soil mineral weathering rapidly diminish to zero.

Given the above parameters, these results suggest that the influence of soil mineral weathering on the ^{87}Sr/^{86}Sr ratio of the soil labile cations is very small and that the consistent ratios determined for the extractable cations in the unirrigated soil profiles at both sites are largely reflective of the solutes, or easily dissolvable material in the local wet and dry deposition.

With closer attention to the small differences between the ^{87}Sr/^{86}Sr ratios of the soil cation extracts, those in the irrigated profile at Padthaway (Figure 7(B)) are shifted in the direction of the irrigation water compared to those of the natural soil profile. This shift to lower ratios may be simply due to natural soil variation within the vineyard, however the data strongly suggest that solutes in the irrigation water have affected the cation composition. This soil profile has been subject to various amounts of irrigation from the same groundwater source for over 10 years, so a degree of equilibrium between the exchangeable cations in the natural soil and those in the irrigation water can be expected through the whole of the shallow soil profile.

If this interpretation of the results is correct, then the trend of ^{87}Sr/^{86}Sr values for exchangeable cations in the Coonawarra profiles (Figure 7(B)) is consistent with a soil profile that is increasingly influenced by irrigation water strontium, with far more influence currently apparent towards the top of the profile than at the bottom. This profile has only been subject to minimal irrigation for 3 years, before which it was unirrigated pasture (Haselgrove L. 2002, personal communication). It could be that the soil cations here are still in a state of transition from the natural state seen in profile Cn, to a state similar to the irrigated profile at Padthaway, in which the exchangeable cation ^{87}Sr/^{86}Sr ratio values do not vary with depth in the profile and are all about mid-way between the ^{87}Sr/^{86}Sr ratio values of the exchangeable cations in the natural soil and the value for the irrigation water. If this is correct then it is fitting that the ^{87}Sr/^{86}Sr values toward the top of the profile, where the soil is more sandy and cation exchange capacity is much lower, should be influenced to a greater extent by the irrigation water.

The wider range of exchange phase ^{87}Sr/^{86}Sr ratios at Coonawarra thus seems to be caused by the influence of the low ^{87}Sr/^{86}Sr ratio of 0.70862 in the irrigation water. The soil surface materials here have the highest ratios of any component measured in this study, so the local precipitation (wet- and dry-fall) is unlikely to be affected by low ^{87}Sr/^{86}Sr ratio of wind-blown dust from the basalts around Mount Gambier (Quade et al. 1995) as this would be evident in the ^{87}Sr/^{86}Sr ratio of the soil surface materials. Hence, local precipitation is likely to have a ^{87}Sr/^{86}Sr ratio that is at least as high as the 0.709211 of modern seawater. The low ratio observed in the groundwater used for irrigation must therefore be influenced by another strontium source with a ratio considerably lower than that of modern seawater. Irrigation water at the Coonawarra site is drawn from an aquifer in the upper part of the Gambier Limestone Formation, which was deposited from the late Eocene to mid Miocene (Smith et al. 1995) and should have a ^{87}Sr/^{86}Sr ratio similar to seawater at that time (Faure 1986). The ^{87}Sr/^{86}Sr isotope ratio of seawater has varied over geological time and has had a substantial, well known increase over the last 50 million years (Burke et al. 1982; Elderfield 1986). The Coonawarra groundwater has a ^{87}Sr/^{86}Sr ratio very close to that expected for the youngest Gambier Limestone. It is therefore concluded that the Coonawarra groundwater gains its ^{87}Sr/^{86}Sr isotope ratio from strontium dissolved from the aquifer matrix of the upper Gambier Limestone.

The Padthaway groundwater is drawn from an aquifer in the Pleistocene Coomandook formation, with regional flow via the Bridgewater formation beneath the West Naracoorte range (Cobb et al. 1994). This groundwater has a ^{87}Sr/^{86}Sr ratio of 0.70911, very close to that of recent (Pleistocene) or modern seawater.

Thus, at both study sites, the groundwater used for irrigation has a ^{87}Sr/^{86}Sr ratio that is significantly lower than the ^{87}Sr/^{86}Sr ratio of the soil cation exchange complex. The consistent shift of exchangeable cation ^{87}Sr/^{86}Sr ratios towards lower values in the irrigated soil profiles indicates a partial replacement of strontium in the exchange complex with strontium contributed by the irrigation water.

The two end-member mass balance approach (Eq. 2) can be used to provide estimates of the relative proportions of exchangeable strontium in the irrigated soil profiles that are contributed by (1) natural sources, represented by the ^{87}Sr/^{86}Sr ratios of labile cations in the unirrigated profiles, and (2) irrigation water solutes (Table 5). Here one end member is the ^{87}Sr/^{86}Sr ratio of the labile cations in the unirrigated soil profiles and the other is the ^{87}Sr/^{86}Sr ratio of the irrigation water solutes. The ^{87}Sr/^{86}Sr ratio of the labile cations in the irrigated profiles is considered to be a mixture (^{87}Sr/^{86}Sr$_{(\mathrm{mix})}$) of these two end members.

It must be considered that the observed shift in ^{87}Sr/^{86}Sr ratio values may be only a seasonal response occurring during the irrigation season in response to the input of irrigation water with a lower ^{87}Sr/^{86}Sr ratio. Given this scenario, the amount of strontium required to cause the observed shift in the exchangeable strontium isotope ratio would have to be no more than the amount delivered in the irrigation water in 1 year. The mass of irrigation-derived strontium in the A- and B-horizons beneath each square metre of the soil surface can be approximated by applying the percentages of irrigation-derived labile strontium shown in Table 5 to the concentrations of strontium in the labile cation pool over discrete depth ranges. Similarly, the mass of strontium applied to the soil in the irrigation water over the past year can be approximated from the recorded irrigation quantities, and strontium concentration (from ICP-AES data) of the irrigation water.

The mass of irrigation-derived labile strontium in the soil of each of the irrigated profiles was found to be approximately one order of magnitude greater than has been applied to the soil in irrigation water in the past year. This large difference

Table 5. Calculation of percentages of labile Sr contributed by irrigation water solutes, based on $^{87}Sr/^{86}Sr$ ratios in irrigated soil profiles.

Soil profile	Depth (cm)	$^{87}Sr/^{86}Sr$ Exchangeable Sr natural	$^{87}Sr/^{86}Sr$ Exchangeable Sr irrigated	$^{87}Sr/^{86}Sr$ irrigation water	% Exchangeable Sr from irrigation water
Ci	35	0.709685	0.709224	0.708621	43
(Coonawarra	55	0.709736	0.709510	0.708621	20
irrigated)	75	0.709694	0.709584	0.708621	10
	95	0.709694	0.709572	0.708621	11
Pi	7	0.709362	0.709256	0.709109	42
(Padthaway	17	0.709329	0.709235	0.709109	43
irrigated)	27	0.709333	0.709241	0.709109	41
	40	0.709351	0.709244	0.709109	44

between the estimated mass of exchangeable strontium in the soil profile and the mass delivered to the soil in irrigation water in 1 year is acceptable for the Padthaway site, where the soils have been irrigated for up to 30 years with highly varying annual amounts of irrigation water (Haselgrove L., 2000 personal communication). For the Coonawarra site, the difference can not be explained by the 3 years of irrigation at this site. This finding highlights the need to consider that the estimates of exchangeable strontium contributed by the irrigation water may be strongly influenced by:

(1) spatial variability in the occurrence of irrigation solutes in the soil profile; and
(2) natural differences occurring between the $^{87}Sr/^{86}Sr$ ratios of the soil exchangeable cations from the natural and irrigated profiles, which are taken here to be only due to the influence of irrigation.

The preferred interpretation is that spatial variability in the accumulation of irrigation solutes due to the drip irrigation method has locally enhanced the shift of $^{87}Sr/^{86}Sr$ ratios.

However, even allowing for a large margin of error in the estimated mass and distribution of irrigation-derived strontium in the exchange phase, the amounts of strontium delivered to the soil in irrigation water in 1 year are not sufficient to influence the $^{87}Sr/^{86}Sr$ ratio of soil exchange complex to the extent observed. This implies that the change in ratio of the labile strontium must occur over several years of irrigation water input, rather than being a seasonal response to other mechanisms.

If the soil cations in the irrigated profile at Coonawarra are changing over time towards a lower strontium isotope ratio between the values for the natural soil cations and the irrigation water, then the soil exchangeable cations in this profile will, in time, have a $^{87}Sr/^{86}Sr$ ratio that is similar to that in the irrigated profile at Padthaway. This drift of soil $^{87}Sr/^{86}Sr$ ratios in response to irrigation has serious implications for any method using strontium isotope ratios to distinguish between wines from different areas within a fairly similar geologic setting such as this. The results indicate two potential confounding factors:

(1) The exchangeable cations in the highly weathered soils of the south east district of south Australia are derived mostly from wet- and dry-fall precipitation. The variations in soil minerals between one region and another thus have minimal effect on the ^{87}Sr/^{86}Sr ratio of soil exchangeable cations. Hence, exchangeable cation ^{87}Sr/^{86}Sr ratios may be found to be very similar over a large area, exhibiting a ratio almost the same as seawater.

(2) The significant influence of irrigation water solutes on the ^{87}Sr/^{86}Sr ratio of the soil cations means that ^{87}Sr/^{86}Sr ratios of soil cations and grapes within a particular vineyard may vary from year to year. Potential variables affecting the ^{87}Sr/^{86}Sr ratio of grapes from a particular vineyard then become:

  - how long the vineyard has been irrigated;
  - how much difference exists in the irrigation water ^{87}Sr/^{86}Sr and that of the natural exchangeable soil cations;
  - whether the source of irrigation water is the same each year;
  - whether irrigation water from the same source retains the same ^{87}Sr/^{86}Sr signature each year. This may be affected by changes in depth from which the water is drawn within a particular bore, if different levels of the aquifer have different sedimentary deposits. Alternatively, piped-in water may be mixed with, or substituted for, bore water in some years.

Thus, even if there is a small but significant difference between the ^{87}Sr/^{86}Sr ratios of soil cations at two vineyards in their natural state, it appears that the addition of irrigation water with a different ratio can cause a drift of soil cation Sr ratios that may obscure or nullify any distinguishing difference between grapes from different areas.

Conclusions

The strontium isotope ratios of the soil cation extracts support the conclusion that irrigation influence has a major effect on the soil cation exchange complex. The lack of variation of exchangeable cation ^{87}Sr/^{86}Sr ratios with depth in the natural soil profiles studied here strongly supports the hypothesis that precipitation solutes are the primary source of strontium to the soil cation exchange complex. However, soil cation extracts from the irrigated soil profiles at both locations were found to have ^{87}Sr/^{86}Sr ratios between those of the exchangeable cations in the natural profile and the irrigation water, suggesting that dissolved strontium in the irrigation water has affected the ^{87}Sr/^{86}Sr ratio of strontium in the cation exchange complex.

Comparison of the ^{87}Sr/^{86}Sr ratios of soil exchangeable cations, which are nearly constant through the whole soil depth, with soil solids, which vary significantly with depth, suggests that soil mineral weathering has minimal influence in the provision of base cations to the soil exchange complex. This is supported by the comparison of solid phase element concentrations, which show minimal relationship between exchange phase and solid phase percentages of individual elements.

Grapes from both locations were found to have ^{87}Sr/^{86}Sr ratios that were the same as the cation extracts of the soil taken from the main root zone of the soil profile in which the grapes were growing. This supports the findings of other researchers (Bailey et al. 1996; Kennedy et al. 1998) that the isotope ratio of strontium taken up by plants is the same as that of the soil exchange complex, the major source of base cations for plant nutrient uptake. The results here demonstrate that a grape sample or a wine sample (if no strontium contamination occurs in the wine making process), should have a ^{87}Sr/^{86}Sr ratio that closely matches that of the cation extract of soil from the vineyard of origin. However, the alteration of exchangeable cation ^{87}Sr/^{86}Sr ratios by irrigation is shown to be a confounding factor in the potential use of strontium isotope ratios to trace the regional origin of grapes and wines. If strontium isotope ratios were used to confirm wine origin in this region, the method would have to rely on a regularly-updated database of ^{87}Sr/^{86}Sr ratios for soil cation extracts in specific vineyards. The method would then only provide a non-unique strontium isotope signature for each vineyard. A wine sample could thus be excluded from many vineyards with differing strontium isotope signatures, but could probably not be attributed to a specific vineyard or area as there may be several areas with nearly identical signatures.

In summary, this study provides an understanding of the effects of irrigation on the labile cation composition of soils at two study sites and explores the use of strontium isotope ratios to trace the transfer of base cations between water, soil and plants in artificially irrigated ecosystems. It is shown that the ^{87}Sr/^{86}Sr isotope ratio of the labile cations in a soil may change quite rapidly in response to a new source of dissolved strontium such as irrigation water. In soils with low cation exchange capacity, a measurable change may occur within only a few years of the introduction of a new strontium source. The results reveal important limitations to the use of strontium isotope ratios to trace the regional origin of grapes and wines, and explain some important geochemical relationships in the provenance of exchangeable cations in soils of this region.

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