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Geoderma 82 (1998) 197–225

GEODERMA

Strontium isotopes as tracers of ecosystem processes: theory and methods

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Accepted 15 April 1997

Abstract

The strontium (Sr) isotope method can be a powerful tool in studies of chemical weathering and soil genesis, cation provenance and mobility, and the chronostratigraphic correlation of marine sediments. It is a sensitive geochemical tracer, applicable to large-scale ecosystem studies as well as to centimeter-scaled examination of cation mobility within a soil profile. The ^{87}Sr/^{86}Sr ratios of natural materials reflect the sources of strontium available during their formation. Isotopically distinct inputs from precipitation, dryfall, soil parent material, and surface or groundwater allow determination of the relative proportions of those materials entering or leaving an ecosystem. The isotopic compositions of labile (soil exchange complex and soil solution) strontium and Sr in vegetation reflect the sources of cations available to plants. Strontium isotopes can be used to track the biogeochemical cycling of nutrient cations such as calcium. The extent of cation contributions from in situ weathering and external additions to soil from dust and rain can also be resolved with this method. In this paper, we review the geochemistry and isotopic systematics of strontium, and discuss the use of this method as a tracer of earth surface processes. © 1998 Elsevier Science B.V.

Keywords: Strontium; isotopes; biogeochemistry; weathering; soil; eolian; atmosphere

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PII S0016-7061(97)00102-X

1. Introduction

Soils lie at the interface of the atmosphere, biosphere, hydrosphere and lithosphere, and are a key component of global biogeochemical cycles. Thus quantification of the processes involved in weathering and pedogenesis is a crucial aspect of element cycling models. On a watershed scale, information about cation fluxes and the identity and the magnitude of their sources and sinks is used to assess the effects of environmental change on terrestrial ecosystems.

The variation of isotope abundances in the Earth provides a means of tracing physical and chemical processes that have operated over geologic time. Isotopic tracer studies provide an extra dimension for tracking the fate of specific elements or families of elements; thus isotopic analysis is an increasingly important technique in environmental studies. Radioactive isotopes have long been used as a direct dating tool; for pedologic studies, radiocarbon and U-series methods have been successfully used to date Quaternary sediments and soils (see Faure, 1986). Cosmogenic isotopes (e.g., ^{10}Be, ^{14}C, ^{26}Al, ^{32}Si, ^{36}Cl) can yield information pertaining to sedimentation rate, the age of biogenic carbon, and the timing of subaerial exposure. Variations in the stable isotopic composition of light elements such as carbon, oxygen, hydrogen, nitrogen and sulfur are useful indicators of environmental temperature variations and biologic processes (see Hoefs, 1987).

Radiogenic isotopes, which are the isotope products of radioactive decay, can be used as geochemical tracers. In recent years, natural variations in isotope ratios of strontium (Sr) have been increasingly applied to studies of earth surface processes. These studies have shown that Sr isotopes can be a powerful tool in studies of chemical weathering and soil genesis, cation provenance and mobility, and the chronostratigraphic correlation of marine sediments. In this paper, we review the geochemistry and isotopic systematics of strontium in earth surface materials, and discuss analytical considerations in the measurement of Sr isotopes and its use as an ecosystem tracer. A companion paper (Stewart et al., 1998) details the application of Sr isotopes to models of soil–vegetation–atmosphere cation cycling.

2. Strontium isotope systematics

2.1. Rubidium–strontium mineral chemistry

Strontium (atomic number 38) is a divalent alkaline earth element. Its ionic radius (1.18 Å) is similar to that of calcium (1.00 Å), and Sr substitutes for Ca in minerals including plagioclase feldspar, apatite, sulfates such as gypsum and anhydrite, and carbonates (calcite, dolomite and especially aragonite). In some minerals Sr^{2+} can also substitute for K^{+} when Si^{4+} is replaced by Al^{3+} (e.g.,

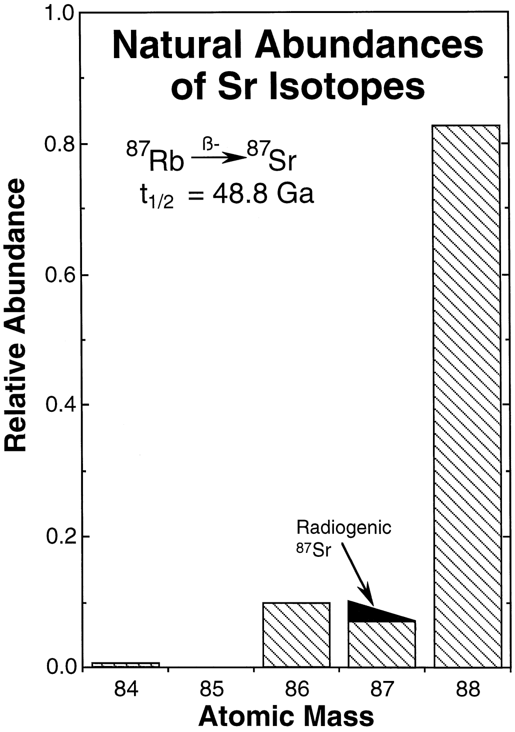

Fig. 1. Isotopes of strontium. Strontium has four naturally occurring stable isotopes; variations in the relative proportions of Sr isotopes (expressed as the ratio of 87-strontium to 86-strontium, or $^{87}Sr/^{86}Sr$) are due to the formation of radiogenic ^{87}Sr from the natural β^- decay of ^{87}Rb (half-life = 48.8 Ga).

vermiculite, smectite). Strontium has four naturally occurring isotopes, with approximate abundances as follows: ^{84}Sr, 0.56%; ^{86}Sr, 9.87%; ^{87}Sr, 7.04%; and ^{88}Sr, 82.53%. All four isotopes are stable, although the fraction of ^{87}Sr varies due to radioactive decay of ^{87}Rb (Fig. 1). A small amount of ^{90}Sr, a short-lived (half-life ~30 years) radioactive isotope produced by fission reactions, is present in the modern environment.

Rubidium (Rb; atomic number 37) is an alkali metal and a large ion lithophile element; its ionic radius (1.52 Å) is similar to that of potassium (1.38 Å). It occurs in highest abundance in K-bearing minerals including muscovite, biotite, alkali feldspars (orthoclase and microcline), clays (illite) and evaporites (sylvite, carnallite). Rubidium has two naturally occurring isotopes, ^{85}Rb and ^{87}Rb. ^{87}Rb undergoes radioactive β^- decay to stable ^{87}Sr (half-life $\sim 48.8 \times 10^9$ years; decay constant $\lambda = 1.42 \times 10^{-11}$ year^{-1}). This decay is the basis for the Rb–Sr dating method, used to determine the time of crystallization of igneous rocks such as granites (Faure and Powell, 1972; Faure, 1986).

2.2. Concentrations of Sr and Rb in natural materials

Table 1 shows the average concentrations of rubidium, strontium, potassium, and calcium in common natural materials. Rb averages 90 ppm in crustal rocks, but its concentration ranges from < 1 ppm in most carbonates to ~ 200 ppm in some granites. The average Rb content of soils is 70 ppm, with a general range of 20–500 ppm (Bohn et al., 1979). The average concentration of Sr in crustal rocks is 370 ppm, but can vary from 1 ppm in some ultramafic rocks to several

Table 1
Average or ranges of concentrations of strontium, calcium, rubidium, and potassium in earth materials

	Sr	Ca	Rb	K	Reference[a]
Geologic (ppm)					
Average crust	370	41,000	90	21,000	1
Exposed upper crust	337		95		2
Soil:					
Soil minerals	240	24,000	67	15,000	1
Soil (labile)	0.2–20				3, 4
Individual rock types:					5
Ultramafic rock	1	25,000	0.2	40	
Sandstone	20	39,100	60	10,700	
Low-Ca granite	100	5,100	170	42,000	
Deep-sea clay	180	29,000	110	25,000	
Syenite	200	18,000	110	48,000	
Shale	300	22,100	140	26,600	
High-Ca granite	440	25,300	110	25,200	
Basalt	465	76,000	30	8,300	
Carbonate	610	302,300	3	2,700	
Deep-sea carbonate	2,000	312,400	fs10	2,900	
Biologic (ppm)					
Wood	8–2,500				3, 6–9
Roots (spruce)	19				9
Conifer needles	2–20				3, 8
Hydrologic ($\mu g\ l^{-1}$)					
Seawater	7,620	414,000	110	425,000	10
Rivers	6–800	15,000	1.3	2,300	10–13
Rain	0.7–383	800–56,000		55–1,340	3, 6–8, 14
Snow [b]	0.01–0.76	8–75		5–20	15, 16

[a] 1 = Sposito (1989); 2 = Goldstein and Jacobsen (1988); 3 = Miller et al. (1993); 4 = Bullen et al. (1997); 5 = Faure (1986); 6 = Graustein and Armstrong (1983); 7 = Gosz et al. (1983); 8 = Åberg et al. (1989); 9 = Åberg et al. (1990); 10 = Holland (1984); 11 = Wadleigh et al. (1985); 12 = Goldstein and Jacobsen (1987); 13 = Yang et al. (1996); 14 = Herut et al. (1993); 15 = Andersson et al. (1990); 16 = Baisden et al. (1995).

[b] Determined on volume of melted snow.

percent in some aragonitic corals. The average concentration of Sr in soils is 240 ppm, but can fall below 10 ppm or exceed 1000 ppm in some cases (Bohn et al., 1979). Soil retention of divalent cations is generally greater than retention of monovalent cations; K^+ is generally more readily exchangeable than Ca^{2+}, and Sr^{2+} is relatively strongly adsorbed to phyllosilicates and organic matter in soil. Soil retention of monovalent alkali ions tends to increase with atomic weight: $Cs > Rb > K > Na > Li$. For divalent alkaline earth ions, soil retention increases in the order $Ba > Sr > Ca > Mg$. This can result in some fractionation of Rb from K and Sr from Ca under certain conditions. Seawater has ~ 8 ppm Sr and ~ 0.1 ppm Rb. River water and precipitation generally have < 0.1 ppm Sr and an order of magnitude less Rb (Bohn et al., 1979; Sposito, 1989; Faure, 1986).

2.3. Evolution of $^{87}Sr/^{86}Sr$ in geologic systems

If Rb and Sr are incorporated into a mineral or rock at its formation and the system remains closed with respect to those elements, then the amount of ^{87}Sr increases over time as radioactive ^{87}Rb decays; the amounts of ^{84}Sr, ^{86}Sr, and ^{88}Sr remain constant. Therefore, older rocks will in general have higher $^{87}Sr/^{86}Sr$ ratios than younger ones with the same initial Rb/Sr ratio. Over geologic time, rocks of a given age composed of minerals with a high Rb/Sr (e.g., granites in the continental crust), will develop a higher $^{87}Sr/^{86}Sr$ than rocks with a lower Rb/Sr (e.g., oceanic basalt) (Fig. 2). Thus, $^{87}Sr/^{86}Sr$ ratios in geologic materials are indicators of both age and geochemical origin.

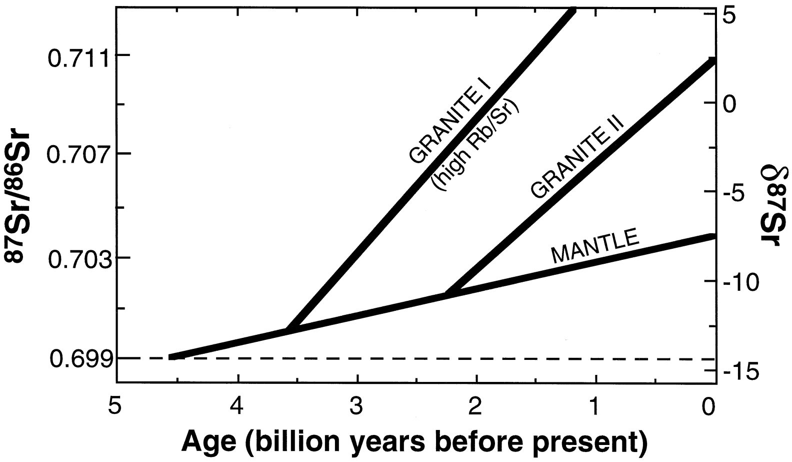

Fig. 2. Evolution of $^{87}Sr/^{86}Sr$ over geologic time. A hypothetical granite that crystallized around 3.6 Ga ago from a mantle-derived melt (Granite I) evolves along a steep trajectory toward high $^{87}Sr/^{86}Sr$ values because of its high Rb/Sr ratio; Granite II also evolves along a steep trajectory, but its $^{87}Sr/^{86}Sr$ measured today is lower than that of Granite I because it crystallized later. Two rocks of the same age but with different Rb/Sr ratios will evolve along different trajectories, with the lower Rb/Sr rock yielding a lower $^{87}Sr/^{86}Sr$.

2.4. Applicability to the study of ecosystem processes

Strontium is a relatively high-mass element, and therefore fractionation from geologic and biological processes is very small compared to that in low-mass isotopic systems (e.g., H, C, O, S). Moreover, mass-dependent fractionation of Sr isotopes (whether natural or instrument-induced) is corrected for during mass spectrometric measurement by normalization of the non-radiogenic isotopes to known values (see Appendix A). Therefore, the measured $^{87}Sr/^{86}Sr$ ratio reflects only variations in the amount of radiogenic ^{87}Sr present in the sample, which is a function of its source. The net result is that the strontium isotopic composition of a sample yields information about provenance or geologic interactions, unobscured by local temperature variations or internal biologic processes. Rb–Sr systematics are well understood because of their extensive application to geochronological studies, and a large database exists for the estimation of $^{87}Sr/^{86}Sr$ ratios of potential source materials to ecological systems (Faure and Powell, 1972; Graustein, 1989). Strontium is ubiquitous in nature, and is one of the most abundant of the trace elements in surficial deposits and rocks (Sposito, 1989; Table 1). Although Sr is of little significance itself as a nutrient, it can be used as a chemical proxy for Ca because of its chemical similarity to that element.

The ability to resolve differences between the isotopic composition of two samples is limited by the analytical precision of the isotopic ratio measurement, with a typical 2σ uncertainty of 0.0015 to 0.003% (15–30 ppm), and by the isotopic value and variability of the different sources of Sr to the system. Sensitivity is increased in ecosystems that have isotopically distinct sources with a narrow range of variability. Applicability of the method is limited in systems where the isotopic composition of different sources overlap. In this paper, Sr isotopic compositions are expressed both as $^{87}Sr/^{86}Sr$ and as $\delta^{87}Sr$, where:

$$\delta^{87}\mathrm{Sr} = 10^3\left[\frac{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SAMPLE}}}{^{87}\mathrm{Sr}/^{86}\mathrm{Sr}_{\mathrm{SEAWATER}}} - 1\right]$$

See Appendix B for a discussion of Sr isotope ratio notation and normalization.

3. Strontium isotopes in earth surface materials

3.1. The strontium cycle

Strontium in rocks is released by weathering, cycled through vegetation and animals, and eventually enters the oceans, primarily by rivers. Strontium leaves the oceans, the largest reservoir of dissolved Sr, primarily by deposition in marine carbonate. A small amount of Sr is also transferred directly from the oceans to the atmosphere and transferred to the continents in precipitation.

The Sr isotopic composition of the Earth's rivers reflects the nature of the exposed crust undergoing alteration. For example, subaerial exposure of Precambrian shield granites provides weatherable minerals with higher $^{87}Sr/^{86}Sr$ ratios than young basalts. Tectonic activity and climate change can strongly affect the amount and isotopic composition of Sr entering oceans through rivers by changing the intensity of weathering processes as well as the type of rocks subject to weathering (Armstrong, 1971; Capo and DePaolo, 1990; Berner, 1991; Raymo and Ruddiman, 1992; Palmer and Edmond, 1992).

To use strontium isotopes as an ecosystem tracer, the isotopic composition of all sources of Sr to the system and the extent of isotopic variation within individual sources must be determined. To characterize a soil–vegetation system, it is necessary to determine the isotopic composition of the soil parent material, of local rain and dust, and of groundwater and surface waters that come in contact with the soil. This requires an understanding of the geochemical cycling of Sr, and of the processes that generate the Sr isotopic ratios and patterns observed in nature. Quantification of fluxes into and out of the soil system is discussed in the companion paper by Stewart et al. (1998).

3.2. Terrestrial rocks and minerals

Weathering of bedrock or sediments can be a significant source of strontium to soil. Soil parent materials often have distinct Sr isotopic signatures. Precambrian granitic bedrock and alluvial sands derived from similar felsic rocks generally have high $^{87}Sr/^{86}Sr$ values (≥ 0.71; $\delta^{87}Sr > 1.1$) that reflect their high Rb/Sr ratios and the age of the continental crust from which these rocks and sediments were derived. The upper continental crust exposed to weathering has an average Sr concentration of ~ 340 ppm and $^{87}Sr/^{86}Sr$ ratio of 0.716 ($\delta^{87}Sr \approx +9.6$; Goldstein and Jacobsen, 1988). As discussed below, Sr derived from the weathering of Phanerozoic limestone and dolomite has a relatively low $^{87}Sr/^{86}Sr$ (~ 0.707 to 0.709, $\delta^{87}Sr \approx -3$ to 0; Burke et al., 1982). Young oceanic basalts and sediments derived from them will generally have even lower $^{87}Sr/^{86}Sr$ values (typically 0.702 to 0.705; $\delta^{87}Sr \sim -10$ to -6). Continental basalts have variable $^{87}Sr/^{86}Sr$ ratios that depend on the age and the extent of their pre-eruption interaction with continental crust. Table 2 lists typical values for common geologic materials.

Minerals within a crystalline rock or sediment generally have variable Rb/Sr ratios and therefore a range of $^{87}Sr/^{86}Sr$ ratios. Rb/Sr ratios in basalt, granite, and lithic sediments can increase greatly during weathering due to preferential alteration of Sr-rich, Rb-poor minerals like plagioclase. Chemical weathering generally lowers the calculated Rb–Sr ages of both mineral separates and whole rocks, although the $^{87}Sr/^{86}Sr$ ratio of the bulk weathered rock is not always

Table 2
Ranges and average $^{87}Sr/^{86}Sr$ ratios of some geologic materials

	$^{87}Sr/^{86}Sr$		$\delta^{87}Sr$		Reference[a]
	average	range	average	range	
Continental crust	0.716		9.7		1
Continental volcanics		0.702–0.714		−10.1 to +6.8	2
Oceanic island basalts	0.704	0.702–0.707	−7.3	−10.1 to −3.1	2
River water	0.712	0.704–0.922	4.0	−7.3 to 300	3–8
Modern seawater	0.7092		0		9–10
Phanerozoic seawater		0.707–0.709		−3.1 to +0.2	9, 11–13
Proterozoic seawater		0.702–0.709		−10.1 to +0.2	14, 15

[a] 1 = Goldstein and Jacobsen (1988); 2 = Faure (1986); 3 = Brass (1976); 4 = Wadleigh et al. (1985); 5 = Goldstein and Jacobsen (1987); 6 = Palmer and Edmond (1989); 7 = Palmer and Edmond (1992); 8 = Krishnaswami et al. (1992); 9 = Burke et al. (1982); 10 = Capo and DePaolo (1992); 11 = Hess et al. (1986); 12 = DePaolo (1986); 13 = Elderfield (1986); 14 = Veizer et al. (1983); 15 = Derry et al. (1992).

significantly altered (Kulp and Engels, 1963; Goldich and Gast, 1966; Bottino and Fullagar, 1968; Fullagar and Ragland, 1975). Decomposition of a high Rb/Sr mineral such as biotite during early stages of granite weathering can result in pore water enriched in ^{87}Sr and a weathered residuum depleted in ^{87}Sr relative to the whole-rock (Fritz et al., 1992; Blum et al., 1993), whereas early chemical weathering of Ca-plagioclase could result in the opposite effect. Thus differential weathering rates for primary minerals can affect the isotopic composition of Sr released to the soil; realistic models must take parent rock mineralogy into account (Dasch, 1969; Brass, 1975; Graustein, 1989).

3.3. Rivers

The concentration of Sr in river water varies from ~6 to 800 ppb, and averages ~60 ppb; Rb is even less abundant (~1–2 ppb; Stallard, 1985). Surface and groundwater isotopic composition is a function of bedrock weathering and atmospheric inputs. Strontium from rivers in general has a high $^{87}Sr/^{86}Sr$ (~0.711; Wadleigh et al., 1985), and reflects weathering and erosion rates of continents, which in turn are affected by sea level and climatic change (Dasch, 1969; Brass, 1976; Holland, 1984; Palmer and Edmond, 1989). The rapid rise in the seawater $^{87}Sr/^{86}Sr$ ratio over the last 2 million years is primarily due to a change in the Sr entering the oceans from rivers. This could result from an increase in the overall amount of chemical weathering on the continents, which would release more Ca and Sr into rivers, or by an increase in chemical weathering of old, highly radiogenic portions of the continental crust, which would increase the $^{87}Sr/^{86}Sr$ in the rivers entering the oceans (DePaolo, 1986; Capo and DePaolo, 1990; Hodell et al., 1990; Blum et al., 1993). Fluvial input is influenced by changes in rainfall, chemical weathering and the lithology of major drainage basins (e.g., Goldstein and Jacobsen, 1988; Palmer and Edmond, 1992; Krishnaswami et al., 1992).

3.4. Seawater and marine carbonates

Strontium in the oceans has a residence time of several million years and oceanic mixing time is on the order of a thousand years, so the Sr isotopic composition of today's oceans should be very homogeneous (Holland, 1984). The uniformity of the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio of modern seawater, at least within the limits of present analytical uncertainty, is confirmed by measurements of Holocene shells and waters from various depths from oceans around the world (Burke et al., 1982; Elderfield, 1986; Capo and DePaolo, 1992). Because of the lack of significant isotopic fractionation of Sr in nature, the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of the hard parts of calcareous marine organisms (such as coccolithophores, foraminifera and mollusks), and phosphatic fish debris, brachiopods, and conodonts record the Sr isotopic composition of all the world's oceans at the time the material formed. Rubidium is a very low-abundance element relative to strontium in carbonate, phosphate and seawater (~ 0.1 ppm). Thus addition of radiogenic $^{87}\mathrm{Sr}$ from decay of $^{87}\mathrm{Rb}$ after fossil formation is generally negligible (Faure, 1986). Ancient seawater Sr ratios can be determined by measurements of unaltered marine fossils, regardless of the environment, water depth, latitudinal range or species of the organism. The strontium isotopic composition of seawater has changed significantly over Earth's history and definition of these time-dependent variations provides a method for global correlation of marine sediments, as well as a tracer that reflects the cycling of material between the continental crust and the oceans (Armstrong, 1971; Brass, 1976; Palmer and Edmond, 1989; Capo and DePaolo, 1990; Hodell et al., 1990). The curve shown in Fig. 3 (modified after Burke et al., 1982), shows that Phanerozoic seawater $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ has fluctuated midway between the average ratio of rivers (~ 0.711; $\delta^{87}\mathrm{Sr} \approx +2.6$) and that of hydrothermally altered oceanic basalt (~ 0.704; $\delta^{87}\mathrm{Sr} \approx -7.3$). Changes in the Sr isotopic composition of the oceans over long time scales (on the order of 10^7–10^9 years) are associated with major tectonic events, such as uplift of the Himalayas (Palmer and Edmond, 1992; Krishnaswami et al., 1992; Richter et al., 1992). Shorter time-scale fluctuations on the order of a million years or less probably reflect climatic change, such as glaciation.

Global correlation of marine sediments and limestones of marine origin can be made by comparison of strontium isotopic compositions with an independently established record of the seawater $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio with time (see DePaolo, 1987). This method has been used to correlate deep-sea sediments and subaerially exposed rocks of marine origin not amenable to dating by biostratigraphic methods. Age resolution ranges from a few million years to less than a

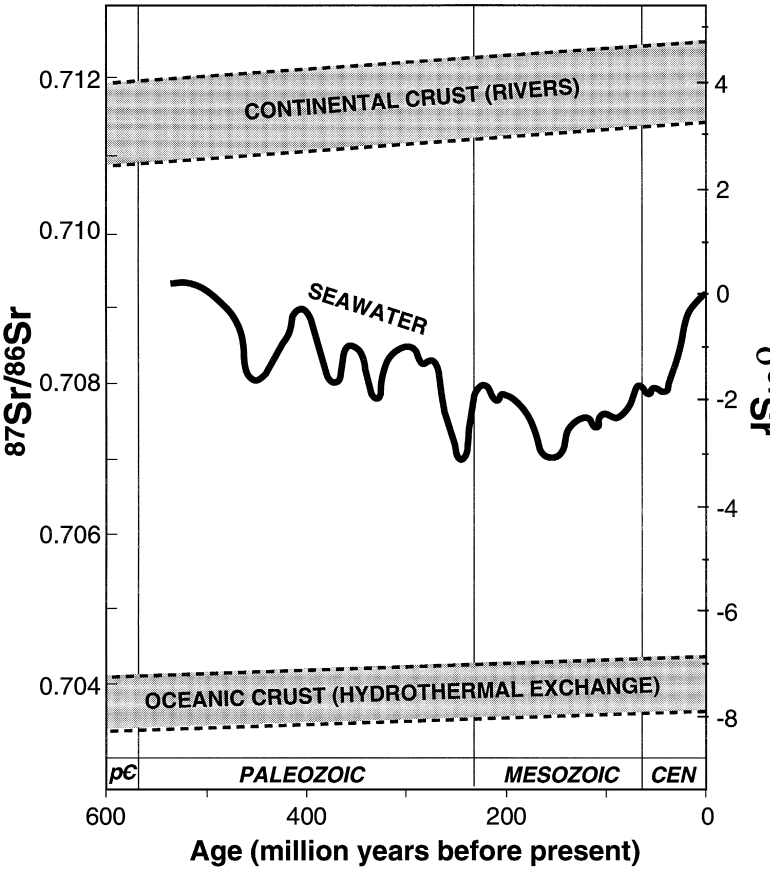

Fig. 3. Variation of the strontium isotopic composition of Phanerozoic oceans (modified from Burke et al., 1982). The $^{87}Sr/^{86}Sr$ of seawater has fluctuated between the average values of terrestrial weathering and hydrothermal exchange with mid-ocean ridge basalts. The isotopic composition at any time in the past reflects that of unaltered marine carbonate of that age. Higher-precision reference data exist for specific periods of the geologic record with a corresponding improvement in age resolution (e.g., references 10–12 in Table 2).

hundred thousand years, depending on the slope of the seawater curve and the precision of the reference curve data. High-resolution seawater Sr curves have been determined for various periods of the Phanerozoic; see Table 2 for references.

3.5. Precipitation and dryfall

Strontium isotopic composition can be used as a chemical tracer to determine the sources of atmospheric contributions to soil cation reservoirs over time

(Graustein and Armstrong, 1983; Åberg et al., 1989; Graustein, 1989; Capo and Chadwick, 1993; Miller et al., 1993). In any given area, locally derived dust will have an $^{87}Sr/^{86}Sr$ ratio similar to the subaerially exposed soil, sediments, and bedrock. However, eolian processes can introduce isotopically distinct minerals to soils, such as zircons (Brimhall et al., 1994), or micas (Dymond et al., 1974). Dust from exposed Phanerozoic marine carbonate will have $^{87}Sr/^{86}Sr$ ratios between 0.707 and 0.709 ($\delta^{87}Sr \approx -3$ to 0). Terrigenous dust can have $^{87}Sr/^{86}Sr$ ratios much higher than seawater; dust from the Sahara, carried across on the northeast trade winds over the northern Atlantic Ocean, has values between 0.715 and 0.747 ($\delta^{87}Sr \approx +8$ to 53; Biscaye et al., 1974; Muhs et al., 1987; Muhs et al., 1990). Fly ash from coal combustion or woodburning can also have distinct $^{87}Sr/^{86}Sr$ ratios (Straughan et al., 1981; Andersson et al., 1990).

Precipitation near ocean basins generally has a strontium isotopic composition similar to that of seawater (0.709; $\delta^{87}Sr = 0$). However, the concentration of Sr in rainfall is generally lower than that in seawater by several orders of magnitude (usually < 1 ppb; Graustein and Armstrong, 1983; Gosz and Moore, 1989; Åberg et al., 1990; Miller et al., 1993). Terrigenous components can also be entrained in precipitation; fine-grained mica and clay can contribute Sr to the dissolved portion of precipitation as well as to the particulate load (Andersson et al., 1990).

Gosz and Moore (1989) analyzed precipitation in a forested ecosystem in New Mexico and found that precipitation volume increased greatly with elevation due to the orographic effect, but the concentration of Sr decreased with elevation. This suggests a uniform input of Sr over the elevation range of the watershed. They also found that the $^{87}Sr/^{86}Sr$ ratios of precipitation showed a considerable seasonal variation (0.7090 to 0.7131; $\delta^{87}Sr \approx -0.3$ to $+5.5$). Graustein and Armstrong (1983) obtained slightly lower values for rainfall in the same area. Precipitation treated with hydrofluoric and perchloric acids yielded higher $^{87}Sr/^{86}Sr$ values (0.7145 to 0.7177; $\delta^{87}Sr \approx +7.5$ to $+12.0$), probably due to the dissolution of clay minerals higher in radiogenic Sr that were present in the precipitation (Graustein, 1989).

Andersson et al. (1990) analyzed a snow profile across Scandinavia and found that $^{87}Sr/^{86}Sr$ ratios increased from 0.7098 to 0.7194 ($\delta^{87}Sr \approx +0.9$ to $+14.4$), and strontium concentrations decrease eastward away from the Atlantic Ocean. They concluded that near the coast, seawater contributes 90% of the Sr to snow, but this decreases to 10–30% 300 km inland. They also found that pollution apparently increases the Sr concentration (from 0.01 to 0.8 $\mu g\ l^{-1}$), as well as that of S and Ca, and that this could be related to emissions from woodburning. Baisden et al. (1995) analyzed snowfall across a transect in the northeastern US and found similar local variations in Sr concentrations (0.007 to 0.2 $\mu g\ l^{-1}$) and in Mn, Ca, and K content; they also linked these variations to woodburning.

3.6. Vegetation and soil

Vegetation takes up strontium available on the soil exchange complex and in the soil solution, which can then be replenished by mineral weathering or atmospheric input. The exchange complex is a reservoir of ions attracted to negatively charged surfaces of organic matter and soil minerals such as clays. The soil solution represents water and ions held by capillary action within the soil. Ions in the soil solution become more concentrated as the water evaporates, and may precipitate secondary minerals. Gravitationally unstable water in saturated soil exchanges to only a limited extent with the soil solution. Leaching a dry soil with reagents such as buffered ammonium chloride in methanol (see Appendix A) will release ions from both the soil exchange and soil solution reservoirs. We refer to this combined source of ions as 'labile' in the sense of Nye and Tinker (1977, p. 33) to ''include the ions in solution and the conventional 'exchangeable' ions...[T]he concentration of ions in the soil solution is buffered by ions adsorbed on the soil surfaces...[and] the overall mobility of labile ions is related to their amounts and mobilities in the solid and solution.''

Bulk soil, soil waters, and secondary soil minerals (e.g., pedogenic carbonate) have the isotopic composition of the parent material, modified by differential weathering of primary minerals and external sources such as dryfall and precipitation. The typical concentration of labile strontium in soil and in solution, expressed as μg Sr leached/g soil, ranges from 0.2 to 20 ppm (Åberg et al., 1990; Miller et al., 1993; Bullen et al., 1997). Biologic processes, whether involved in plant or animal metabolism, do not significantly fractionate strontium isotopes. Therefore terrestrial vegetation will be dominated by the Sr isotopic composition of labile cations in the soil. Strontium is present in vegetation at levels of a few ppm in roots and leaves to 0.2% in some wood samples (Graustein and Armstrong, 1983; Gosz et al., 1983; Åberg et al., 1989, 1990; Miller et al., 1993; Table 1).

4. Analytical methods

The application of Sr isotopes as an ecosystem tracer requires the determination of the isotopic composition of the components of the system as well as the sources to the system. Isotopic analysis of different components in a terrestrial system can require different sampling and extraction techniques. Characterization of a soil system often involves several steps: leaching cations with an exchange reagent, removal of carbonate with acetic acid and dissolution of the silicate residue in hydrofluoric and nitric acids.

Only a small quantity of purified Sr is needed for isotopic analysis. While measurement of several nanograms ($1 \text{ ng} = 10^{-9}$ g) of purified strontium is possible, 0.4 to 1 microgram ($1\ \mu g = 10^{-6}$ g) of Sr can yield several high-precision ($2\ \sigma$ error $\leq 0.003\%$) mass spectrometric analyses. The amount of sample required can range from 1 to 2 l of rainwater, several grams of soil, or a few milligrams of carbonate. This amount can be estimated using the concentrations given in Table 1. In choosing sample size, consideration must also be given to the scale of isotopic homogeneity required and to the necessity of obtaining representative samples.

To avoid contamination of natural materials during trace metal isotopic analysis, care must be taken in sample collection, preparation, and laboratory procedures. Strontium is relatively abundant in many materials in the environment. Although this is an advantage in its use as an ecosystem tracer, it also increases the potential for contamination of those samples that have relatively low Sr concentrations. Water samples are generally collected in prewashed, acid-cleaned plastic bottles, with care taken to avoid the influx of foreign matter. These samples are often filtered in the field and acidified to keep ions in solution. Soil and dust samples are stored in closed, non-metal containers. Ultrapure water or reagents are used if samples require rinsing or etching to remove external contamination. Any necessary grinding or powdering is done using clean agate mortars and pestles or tungsten carbide-coated mills or shatterboxes that are precontaminated with a small amount of sample.

Extraction of Sr for isotopic analysis is carried out under clean laboratory conditions that minimize ambient contamination. Samples are processed in acid-washed Teflon® or polypropylene beakers and vials and evaporated with filtered air. Chromatographic columns are generally constructed of quartz glass, polypropylene or Teflon® rather than Pyrex®, which can contribute measurable amounts of trace metals into the sample by leaching. Reagent purity is also critical; ultrapure reagents can be bought off the shelf, or analytical-grade acids and other reagents can be further distilled. Water is purified by filtration, ion exchange and/or distillation. Procedural blanks ensure that the level of contamination is within acceptable limits; reagent and total chemistry blanks are also monitored. Details of analytical chemistry and mass spectrometry can be found in Appendix A.

5. Strontium isotope tracers of terrestrial processes

Once the isotopic compositions of the sources of strontium to the soil–atmosphere–biosphere system are known, $^{87}Sr/^{86}Sr$ ratios in soil, precipitation, dust, and vegetation can track the geochemical cycling of Sr within and between components. This provides insight into the terrestrial processes that affect the budget of Sr and other elements. The range of Sr isotopic variation in each component determines the resolution of the method.

5.1. Quantification of sources using Sr isotopes

Mass balance techniques (Chadwick et al., 1990; Brimhall et al., 1991) are used to describe the movement of elements into and out of the soil column. This approach can be extended to quantify the proportion of material added to a soil by eolian processes or lost by leaching. Eolian material in a soil can be identified by comparison with dust collected above ground or by the chemistry of labile cations in the soil and abundances of silt and clay at the top of the soil profile. However, because of the complexity of soil-forming processes, quantification of eolian input to a soil, identification of its provenance, and determination of its contribution to pedogenesis relative to in situ parent material weathering can be difficult. For example, dust is the dominant source of calcium involved in the formation of calcrete in some soils of the southwestern U.S. (Gile, 1979; Reheis and Kihl, 1995; Reheis et al., 1995). However, Rabenhorst et al. (1984) and West et al. (1988) found that eolian input was not a significant factor in the development of calcareous soils developed on limestone in central and west Texas.

Mixing equations are used in conjunction with strontium isotope measurements to determine the relative contribution of individual inputs to the reservoir of interest. To extrapolate the Sr isotope results to other components in a system, the concentration and the isotopic composition of Sr in each component must be determined. The isotopic composition, δ_{mix}, of a mixture of n components is given by:

$$\delta_{\text{mix}} = \frac{M_1^{\text{Sr}}\delta_1 + M_2^{\text{Sr}}\delta_2 + \ldots + M_n^{\text{Sr}}\delta_n}{M_1^{\text{Sr}} + M_2^{\text{Sr}} + \ldots + M_n^{\text{Sr}}} \tag{1}$$

where M_n^{Sr} represents the mass of Sr in component n.

This equation is valid for all notations of $^{87}\text{Sr}/^{86}\text{Sr}$ (see Appendix B). For a two-component system, the contribution of Sr from component 1 to a mixture is calculated from the isotopic ratios of the mixture and the endmembers:

$$\frac{M_1^{\text{Sr}}}{M_1^{\text{Sr}} + M_2^{\text{Sr}}} = \frac{\delta_{\text{mix}} - \delta_2}{\delta_1 - \delta_2} \tag{2}$$

This simple relationship can be used to calculate the relative contributions of atmospheric input and soil mineral weathering to vegetation (Graustein and Armstrong, 1983; Gosz and Moore, 1989; Wickman and Jacks, 1993), labile Sr in soil (Graustein, 1989; Åberg et al., 1989; Miller et al., 1993), and soil carbonate (Capo and Chadwick, 1993). In dynamic natural systems, it is often useful to frame problems in terms of fluxes, rather than static mixing of two endmembers. For a system in steady state (i.e., constant source fluxes mixing together into a reservoir in which the output rate is identical to the input rate), an expression similar to Eq. (1) is obtained for combining material from n sources into a single reservoir:

$$\delta_{\mathrm{mix}} = \frac{J_1^{\mathrm{Sr}}\delta_1 + J_2^{\mathrm{Sr}}\delta_2 + \dots + J_n^{\mathrm{Sr}}\delta_n}{J_1^{\mathrm{Sr}} + J_2^{\mathrm{Sr}} + \dots + J_n^{\mathrm{Sr}}} \tag{3}$$

where J_n^{Sr} is the flux of strontium (in μg year^{-1}) from source n. As an example of the application of Eq. (3), the relative fluxes of strontium to a soil profile from precipitation ($J_{\mathrm{P}}^{\mathrm{Sr}}$) and soil mineral weathering ($J_{\mathrm{M}}^{\mathrm{Sr}}$) can be calculated from the isotopic composition of labile soil Sr. The Sr flux from precipitation would be equivalent to $\mathrm{Aj_PC_A}$, where A is watershed area, $\mathrm{j_P}$ is precipitation rate in g cm^{-2} year^{-1}, and $\mathrm{C_A}$ is concentration of dissolved atmospheric Sr in rainwater; the flux of strontium from dissolution or alteration of primary soil minerals would be equivalent to $\mathrm{Aj_MC_M}$, where $\mathrm{j_M}$ is the weathering flux density in g cm^{-2} year^{-1} and $\mathrm{C_M}$ is the concentration of Sr in soil minerals. In principle, Eq. (3) can be rearranged to calculate a weathering rate, provided the exchange factor for Sr between rainwater and the labile fraction of the soil can be determined.

5.2. Strontium as a proxy for calcium

The amount of calcium (or any other element which does not fractionate from Sr) contributed by an endmember in a two-component system can be calculated from the Sr isotope data, provided the Sr/Ca concentration ratio is known for each component. The fraction of Ca contributed to a mixture by component 1 is given by:

$$\frac{M_1^{\mathrm{Ca}}}{M_1^{\mathrm{Ca}} + M_2^{\mathrm{Ca}}} = \frac{(\delta_{\mathrm{mix}} - \delta_2)\mathrm{K}_2}{(\delta_{\mathrm{mix}} - \delta_2)\mathrm{K}_2 + (\delta_1 - \delta_{\mathrm{mix}})\mathrm{K}_1} \tag{4}$$

where K_1 and K_2 are the Sr/Ca concentration ratios for components 1 and 2. Mixing curves for different Sr/Ca ratios of a hypothetical two component system are shown in Fig. 4.

Åberg et al. (1990) used Sr as a Ca proxy to estimate Ca budgets in different media: precipitation, throughfall, runoff, soil water, soil, trees, and mussel shells. However, they found that budgeting Ca inputs and outputs in the soil–vegetation ecosystem is difficult, because of the complications involved in quantifying the weathering of primary minerals. Although pedogenic processes may decouple the behavior of Sr from other elements (even geochemically similar elements like Ca) these complexities can in principle be accounted for by determining the Sr concentration or Sr/element ratio in each of the system endmembers (see Graustein, 1989; Blum et al., 1993). Quantitative modeling of the soil–vegetation–atmosphere system using Sr isotopes, including non-steady

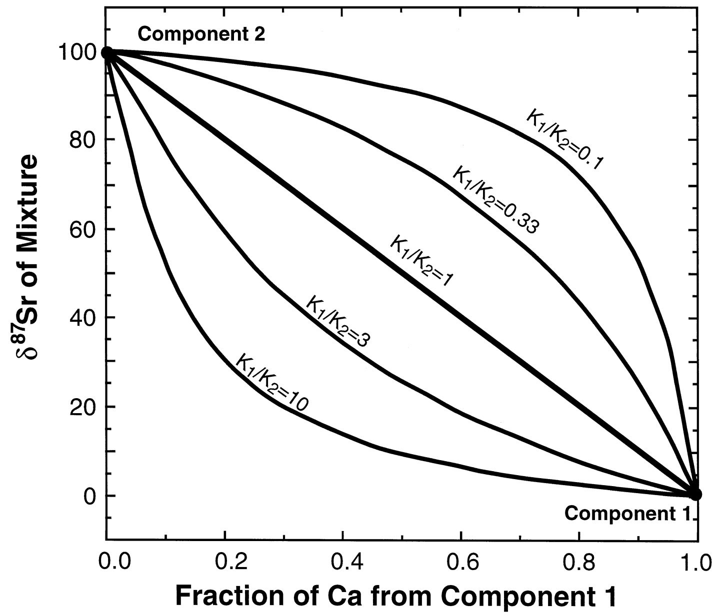

Fig. 4. Mixing curves for different Sr/Ca ratios of a hypothetical two-component system. K_1 and K_2 represent the Sr/Ca ratios of components 1 and 2, respectively. The source of calcium in a two-component mixture can be determined from strontium isotopic data, provided the Sr/Ca of each component is known. In this way, strontium isotopes can be used for the determination of the atmospheric contribution to pedogenic calcium.

state models, is explored in greater depth in a companion paper (Stewart et al., 1998).

5.3. Pedologic systems

The two primary sources of cation nutrients (such as Ca or Mg) to the soil–biomass–water ecosystem are weathering of soil minerals and atmospheric deposition. Thus, mass balance studies of soils depend on an understanding of the rate and processes of weathering and of dust incorporation into surficial deposits. The ^{87}Sr/^{86}Sr ratios of weathering products reflect those of the parent material, so the Sr isotopic composition of secondary clays and soil minerals can be used as a tracer of parent material provenance (Dasch, 1969; Brass, 1976). The strontium isotopic composition of pedogenic carbonate will reflect the sources of strontium available in the soil environment, both from atmospheric and in situ weathering sources (Graustein, 1989; Marshall et al., 1993; Capo and Chadwick, 1993; Marshall and Mahan, 1994; Capo et al., 1995). In some cases, the ^{87}Sr/^{86}Sr ratio can be used to discriminate between terrestrial lacustrine and marine paleoenvironments (McCulloch et al., 1989; Banner et al., 1994; Johnson and DePaolo, 1994). If the external and in situ sources of strontium to the soil have distinct Sr isotopic signatures, the $^{87}Sr/^{86}Sr$ ratio can be used to track the movement and provenance of Sr through the soil–atmosphere system (Graustein, 1989). As a first approximation, knowledge of local bedrock geology can be used to estimate the $^{87}Sr/^{86}Sr$ range of parent materials in a particular area. Because Sr behaves like Ca, Sr can be used as a geochemical proxy for Ca, provided the relative concentrations of Sr and Ca in the system are known (see Section 5.2). With the appropriate assumptions, this can be extended to other major and trace elements in the soil–atmosphere system (Miller et al., 1993; Blum et al., 1993).

Strontium isotopes have been used as a chemical tracer to measure the atmospheric inputs to soils and soil carbonate over time (Graustein and Armstrong, 1983; Åberg et al., 1989; Gosz and Moore, 1989; Miller et al., 1993; Capo et al., 1994; Quade et al., 1995). The $^{87}Sr/^{86}Sr$ ratio of labile Sr in soil provides information about the source of cations within the profile (Åberg et al., 1989, 1995; White et al., 1992; Wickman and Jacks, 1992; Capo et al., 1994; Stewart et al., 1994). Åberg et al. (1989) sampled waters, sieved soil samples and NH_4Ac leached podzols developed on Proterozoic granite bedrock in south-central Sweden. They found high $^{87}Sr/^{86}Sr$ ratios in soil water in the upper 5–10 cm of the soil, indicating the influence of bedrock weathering.

Eolian input can be important in soil development (Gile, 1979; Chadwick and Davis, 1990; Reheis et al., 1995) and in particular to the formation of soil carbonate in desert regions (Gile et al., 1966; Ruhe, 1967; Machette, 1985; McFadden et al., 1991; Reheis and Kihl, 1995). Alkaline dust production is high in the desert southwest; the carbonate dust flux is ~ 0.5 mg cm^{-2} year^{-1} (Mayer et al., 1988; Gillette et al., 1992). Mayer et al. (1988) found that increased precipitation or dust flux at the end of the Pleistocene resulted in major changes in the distribution of soil carbonate. The source of this input to soils can be locally derived (Cahill et al., 1981), but dust can also travel great distances (Brimhall et al., 1994). Asian dust travels across the Pacific (Dymond et al., 1974; Rea and Leinen, 1988; Olivarez et al., 1991; Nakai et al., 1993), and Saharan dust crosses the Atlantic (Biscaye et al., 1974; Muhs et al., 1987, 1990).

Strontium isotopic analysis in concert with mass balance studies can be used to quantify the amount, rate and sources of subsurface carbonate accumulation in desert ecosystems. The sources of solutes (e.g., Sr) for pedogenic carbonate include bedrock, surface and groundwater, airborne dust, precipitation, and seawater (Graustein, 1989). Sr isotopes can be used to characterize the secondary carbonate formed in arid soils and distinguish between eolian vs. in situ weathering components. Capo and Chadwick (1993) determined the Sr isotopic composition for carbonate and silicate fractions from A, upper B and petrocalcic Bkm (K horizon of Gile et al., 1966) of a soil developed on the Pleistocene Upper La Mesa surface in New Mexico (Fig. 5). The $^{87}Sr/^{86}Sr$ ratios of local

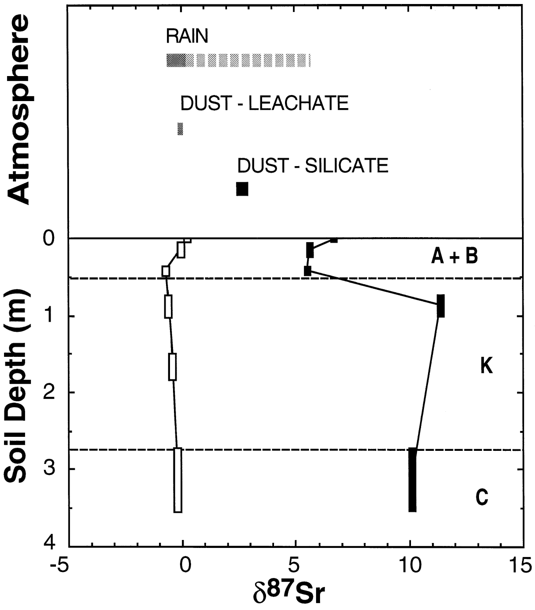

Fig. 5. Strontium isotope data from atmospheric components and soil developed on the Pleistocene Upper La Mesa geomorphic surface in the Desert Project area, New Mexico. The upper region shows atmospheric data, and the lower portion shows soil samples plotted against depth in the profile. Open symbols are the acetic acid soluble leaches of dust and soil, which represent both carbonate and labile Sr. The solid symbols are the $HF–HNO_3$ soluble residue (silicate fraction) of the dust and soil. Error bars are smaller than the size of the symbol. Rain water values are from Graustein and Armstrong (1983) and from Capo and Chadwick (1993).

rain and the acetic acid-soluble fraction of dust (representing carbonate and labile Ca) range from 0.7088 to 0.7090 ($\delta^{87}Sr \approx -0.5$ to -0.2). The silicate fraction of the dust ranges from 0.7109 to 0.7112 ($\delta^{87}Sr \approx +2.4$ to $+2.9$), while the $^{87}Sr/^{86}Sr$ of the parent alluvial sediment is relatively high (0.717; $\delta^{87}Sr \approx +11.0$). The acetic acid-soluble fractions of the A, B, and Bkm soil horizons range from 0.7087 to 0.7093 ($\delta^{87}Sr \approx -0.7$ to $+0.2$), and indicates that the Ca in the pedogenic carbonate is derived primarily from atmospheric sources, with an upper limit of ~ 5% on the silicate weathering contribution to soil carbonate.

On the Kohala Peninsula of Hawaii, Capo et al. (1994) found that the $^{87}Sr/^{86}Sr$ ratios of labile Sr in soils in low-rainfall sites were similar to those of the basaltic parent material (0.704; $\delta^{87}Sr \approx -7.3$). This suggests both lower rates of atmospheric input and higher weathering rates in the Kohala arid site compared to the New Mexico desert site (Stewart et al., 1998). In contrast, the isotopic composition of soils above 200 cm annual rainfall approach rainfall values (Fig. 6). Application of time-dependent Sr flux models suggests that the shift toward atmospheric values in the high-rainfall sites are caused by a

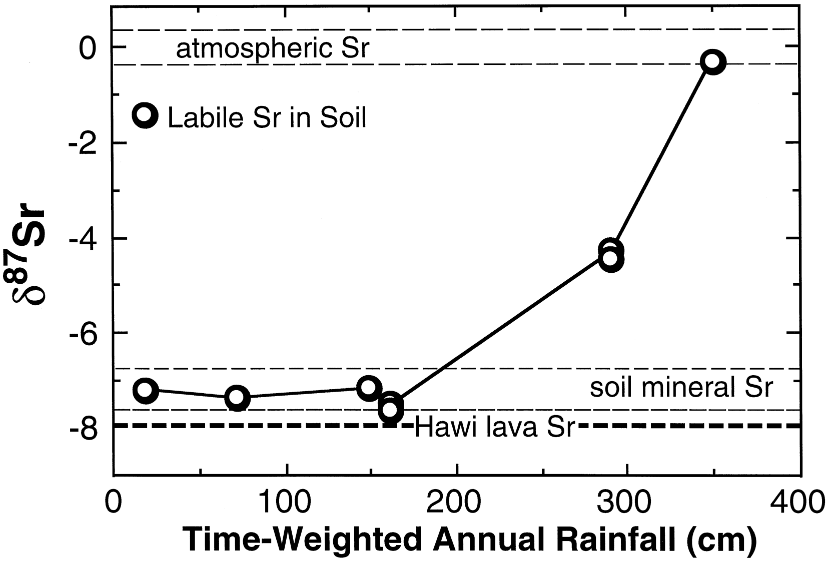

Fig. 6. Isotopic data for labile strontium at ~50 cm depth as a function of time-weighted annual rainfall on the island of Hawaii. The soils are developed on the 170,000 year old Hawi basalt. Soil mineral Sr isotope data are based on analysis of the silicate residue of the soil.

combination of a large flux of atmospheric Sr and simultaneous depletion of the parent material through chemical weathering (Stewart et al., 1998).

5.4. Biologic systems

5.4.1. Vegetation

Strontium isotopes are not fractionated by biological processes; therefore the ^{87}Sr/^{86}Sr ratios of vegetation reflect the sources of Sr (and other nutrients) to the local environment. The flux of strontium available to plants can be dominated by either bedrock weathering (Brass, 1975; Graustein, 1989; Åberg et al., 1995), or atmospheric input (Graustein and Armstrong, 1983; Capo et al., 1994; Kennedy and Derry, 1995). Graustein and Armstrong (1983) and Graustein (1989) studied Sr isotopes in rain, Proterozoic granite regolith, soil, and coniferous and deciduous vegetation from watersheds in the Sangre de Cristo Mountains, New Mexico. They found that $>75\%$ of Sr in the local vegetation is derived from atmospheric input and $<25\%$ from bedrock weathering. Much of the dryfall Sr enters the watershed by way of conifers; deciduous foliage traps little or no Sr-bearing aerosol. The majority of Sr in spruce–fir throughfall came from dissolution of atmospheric particles deposited in foliage. Water and nutrients can be transported to lower soil horizons through macropore flow along root channels, biopores and ped structure interfaces. Graustein (1989) found that isotopic values of stream water were similar to bedrock, which indicates bedrock–water exchange below the rooting zone. However, upper soil horizon isotopic values reflected atmospheric and biomass sources. He concluded that in the New Mexico study area strontium and other nutrients are efficiently recycled between upper soil horizons, forest litter, and standing crop.

Gosz and Moore (1989) quantified the flux and distribution of atmospheric strontium in biomass in a neighboring forested ecosystem in New Mexico. They found that spruce trees exhibited a greater capacity for atmospheric Sr capture than aspen, but that aspen had more total atmospheric Sr in its tissues because of greater uptake rates.

Åberg et al. (1990) and Wickman and Jacks (1993) examined Sr isotopes in trees in Sweden as a method of determining cation nutrient sources and to as a proxy for calcium uptake. They concluded that atmospheric deposition was the dominant source for Sr and Ca (65–75%) for most pine stands growing on undeveloped soil on gneissic bedrock. They linked declining calcium concentrations in trees over the last century with soil impoverishment and acidification.

5.4.2. Animals

Strontium is generally incorporated into the hard parts of animals, such as phosphate in teeth and bone, and carbonate in the shells of aquatic animals. Aquatic and terrestrial animals have isotopic compositions related to their environment and diet. The $^{87}Sr/^{86}Sr$ composition of animal bone has been used to track the migration patterns and dietary habits of a variety of animals. This can be extended to fossil remains as well, although care must be taken to account for post-depositional changes that can alter the original isotopic signature (Nelson et al., 1986; Koch et al., 1995). Open ocean fish (cod and shark) have modern seawater values (0.7092; $\delta^{87}Sr = 0$); fish from the brackish Baltic Sea, influenced by radiogenic terrigenous input, have higher $^{87}Sr/^{86}Sr$ ratios (Schmitz et al., 1991; Åberg, 1995; Åberg et al., 1995).

The strontium isotope ratios of terrestrial herbivores reflect the isotopic composition of labile Sr taken up by plants eaten by the herbivores. In many cases, this is similar to bedrock values. Both freshwater fish and vertebrates from central Sweden have high $^{87}Sr/^{86}Sr$ values (~ 0.735; $\delta^{87}Sr \approx +36$) similar to the felsic Proterozoic parent material of the local soil (Åberg et al., 1995). Animals that live in terrain dominated by limestones or young volcanics generally have lower $^{87}Sr/^{86}Sr$ ratios (van der Merwe et al., 1990; Vogel et al., 1990). A reindeer from Iceland had a $^{87}Sr/^{86}Sr$ value of 0.706 ($\delta^{87}Sr \approx -4$), intermediate between the rainwater value of 0.709 ($\delta^{87}Sr \approx 0$) and that of the grass growing on the soil derived from basalt ($\sim$ 0.703 to 0.704; $\delta^{87}Sr \approx -9$ to -7; Åberg, 1995). Koch et al. (1995) interpreted a negative correlation between the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ ratios of African elephant bones as mixing between low $\delta^{13}C$, C_3 plant-dominated bushlands on soils derived from high $^{87}Sr/^{86}Sr$ Precambrian rock, and higher $\delta^{13}C$, C_4-rich grasslands on soil derived from low $^{87}Sr/^{86}Sr$ volcanic rock and nearby lake beds.

6. Summary

Strontium isotopes can be a powerful tool in ecosystem studies, both as a tracer of nutrient sources and as a monitor of the weathering process. In many cases, isotopic characterization of sources to an ecosystem allows quantification of the relative contributions of in situ weathering and atmospheric inputs to soil and vegetation. The $^{87}Sr/^{86}Sr$ ratio of dust can indicate the source of atmospheric input, with implications for local climate patterns. Strontium isotope analyses, when combined with careful study of all components of a soil–vegetation system, have the potential to provide important new insights into the sources and cycling of cations in terrestrial ecosystems.

Acknowledgements

This paper was improved by the careful reviews and insightful comments of Ariel Anbar and Larry Wilding. We also thank Jean Hsieh, Gene Kelly, Chuck Whipkey and GEOL 3960 for helpful discussions. Lance Lugar provided invaluable library research assistance. This work was funded in part by NSF grant EAR-9614875 and a University of Pittsburgh Central Research and Development grant to R.C. Capo and NASA–JPL Mission to Planet Earth grants to O.A. Chadwick.

Appendix A

A.1. Sample dissolution and extraction of strontium

Before dissolution of the silicate portion of soil or rock, individual components such as evaporites or carbonate can be removed by leaching. Calcium carbonate dissolves in nitric acid (HNO_3) or hydrochloric acid (HCl). However, these acids can also attack associated clay minerals or micas and preferentially remove radiogenic Sr, which could bias an analysis that seeks to determine the isotopic composition of pure carbonate. Dilute acetic acid (HOAc) will also dissolve carbonate but is less destructive to associated minerals (DePaolo et al., 1983). Purified water is used to dissolve evaporite minerals such as gypsum and anhydrite (Müller and Mueller, 1991). To analyze labile Sr, samples are leached with a cation exchange reagent such as ammonium acetate (NH_4OAc) or ammonium chloride in methanol (NH_4Cl–MeOH) buffered (to pH 8) following the methods used in soil analysis described in Jackson (1975). The latter is preferred for leaching calcareous samples as it extracts less soluble salt and carbonate from soil than ammonium acetate. Åberg et al. (1990) and Wickman and Jacks (1993) used a salicylic acid leach to simulate humic acid weathering of bedrock. After leaching of labile cations, solids (soil or rock) are digested in concentrated hydrofluoric acid (HF) with nitric acid (HNO_3) or hydrochloric acid (HCl), sometimes augmented with perchloric acid ($HClO_4$). Vegetation can be digested in acid (HNO_3; $HClO_4$) in sealed Teflon® vials, or ashed and leached with HCl to remove metals (Åberg et al., 1990; Wickman and Jacks, 1993).

Analysis of dryfall involves the same techniques used in solid samples discussed above. Natural water samples (e.g., precipitation, stream water, seawater) containing dissolved strontium are evaporated. Addition of HNO_3 and HF will result in the analysis of both dissolved Sr and Sr held on or in particulate matter carried in the solution. Such total digestion will generally result in a different measured $^{87}Sr/^{86}Sr$ due to the variations in the isotopic composition of the suspended load. Filtration of water samples through 0.45 μm acid-washed

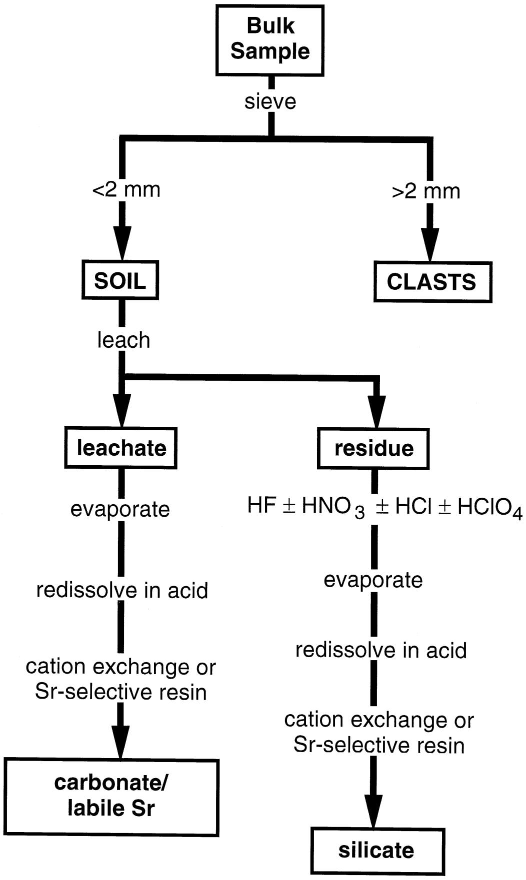

Fig. 7. Analytical chemistry flow chart for strontium isotopic analysis of soil samples. Soils can be leached to extract labile cations with a pH buffered solution such as NH_4Cl or NH_4OAc. Acetic acid is commonly used to remove carbonate.

filters allows separate analysis of the dissolved and the particulate load (Gosz and Moore, 1989; Andersson et al., 1990).

The resulting sample solution can be spiked with an isotopic tracer (usually ^{84}Sr) to precisely determine the Sr concentration by isotope dilution (see Faure, 1986). The sample is then evaporated to remove organics and fluorides and redissolved in dilute acid. Sr is concentrated and purified by ion exchange techniques. The dissolved sample is passed through a chromatographic column containing a cation resin that has been calibrated to separate Sr from other cations. It is eluted with HCl and collected as $SrCl_2$. Alternatively, a Sr-specific resin such as SrSpec® can be used. After other cations have been washed through the column with 3 *N* nitric acid, the purified Sr is eluted with ultrapure water. The sample is then evaporated and is ready for isotopic analysis (Fig. 7).

A.2. Mass spectrometry

A portion of the separated strontium (10 to 1000 ng) is evaporated onto an outgassed, zone-refined metal filament (typically rhenium, tantalum, or tungsten) for measurement on a solid-source thermal ionization mass spectrometer (TIMS). Mass fractionation during measurement is corrected for by normalizing to the ratio of two non-radiogenic isotopes, conventionally ^{86}Sr/^{88}Sr set at 0.1194. This procedure effectively eliminates mass-dependent fractionation, either as an artifact of instrumental analysis or as a result of biological processes. For older geologic samples with significant amounts of Rb, the ^{87}Rb/^{86}Sr ratio must be determined to make corrections for in situ growth of ^{87}Sr from ^{87}Rb decay. Depending on the equipment and number of ratios determined, reported in-run precision for the ^{87}Sr/^{86}Sr ratio ranges from 1 part in 10,000 to better than 1 part in 100,000. Reproducibility of 15 to 30 ppm is standard.

To facilitate interlaboratory comparisons, Sr isotope data are also reported relative to known standards. These include: (1) National Institute of Standards and Technology Sr standard NIST 987 (commonly called NBS987); (2) Eimer and Amend $SrCO_3$ standard; or (3) the measured value for modern seawater, which is equivalent to Holocene carbonate standard EN-1.

Appendix B

B.1. Normalization of ^{87}Sr/^{86}Sr ratios

For ease of comparison, the ^{87}Sr/^{86}Sr ratios of samples can be normalized to a standard. This allows for immediate comparison of data from different laboratories, because normalization corrects for interlaboratory variations in standard ^{87}Sr/^{86}Sr ratios. Several examples of standardization of Sr isotope ratios appear in the literature. One of the early normalizations used was ε notation, in analogy with $\varepsilon_{\mathrm{Nd}}$ (DePaolo and Wasserburg, 1976), where:

$$\varepsilon_{\mathrm{Sr}} = 10^4 \left[\frac{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{SAMPLE}}}{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{CHUR}}} - 1 \right]$$

and CHUR is an assumed bulk earth or chondrite value (${}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{CHUR}} = 0.7045$); this form is most often used in discussions of the evolution of meteorite parent bodies or the earth's mantle. Another standardization for ${}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}$ is $\Delta^{87}\mathrm{Sr}$, which is expressed in the form:

$$\Delta^{87}\mathrm{Sr} = 10^4 \left[\left(\frac{{}^{87}\mathrm{Sr}}{{}^{87}\mathrm{Sr} + {}^{86}\mathrm{Sr}} \right)_{\mathrm{SAMPLE}} - \left(\frac{{}^{87}\mathrm{Sr}}{{}^{87}\mathrm{Sr} + {}^{86}\mathrm{Sr}} \right)_{\mathrm{STANDARD}} \right]$$

and the standard can be an arbitrary local standard or a global standard such as seawater. A third notation is $\delta^{87}\mathrm{Sr}$, which can be written:

$$\delta^{87}\mathrm{Sr} = 10^3 \left[\frac{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{SAMPLE}}}{{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}_{\mathrm{SEAWATER}}} - 1 \right]$$

in a form analogous to normalizations for stable isotopes such as oxygen ($\delta^{18}\mathrm{O}$), carbon ($\delta^{13}\mathrm{C}$), or sulfur ($\delta^{34}\mathrm{S}$). Unlike $\Delta^{87}\mathrm{Sr}$, $\delta^{87}\mathrm{Sr}$ can be used directly and easily in calculations involving decay of ${}^{87}\mathrm{Rb}$ over time (such as isochrons) and is quickly converted to ${}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}$.

In the strictest sense, only the $\Delta^{87}\mathrm{Sr}$ normalization can be used directly in mass balance calculations where total Sr concentrations are used. However, the error introduced by using $\delta^{87}\mathrm{Sr}$ in mixing equations in most natural systems can be shown to be insignificant, given by:

$$\mathrm{E}_1(\%) = 100 \left| \left(\frac{M_1^{\mathrm{Sr}} + M_2^{\mathrm{Sr}}}{M_1^{\mathrm{Sr}} + M_2^{\mathrm{Sr}} \left[1 + 7 \times 10^{-5} (\delta_1 - \delta_2) \right]} - 1 \right) \right| \tag{B1}$$

where E_1 is the percent uncertainty in the calculated mass fraction of component 1, M_1^{Sr} and M_2^{Sr} represent the mass of Sr and δ_1 and δ_2 are the $\delta^{87}\mathrm{Sr}$ of components 1 and 2, respectively. This effect is strongest for the case where $M_2^{\mathrm{Sr}} \gg M_1^{\mathrm{Sr}}$, which then gives:

$$\mathrm{E}_1^{\max}(\%) \approx 100 \left| \left(\frac{1}{1 + 7 \times 10^{-5} (\delta_1 - \delta_2)} - 1 \right) \right| \tag{B2}$$

As an example, a difference of 100 δ units (corresponding to a spread in ${}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}$ ratio of 0.07) leads to a maximum error of 0.7% in the calculated contribution of component 1, which is far greater precision than is warranted by uncertainties in the concentrations and isotopic compositions of endmembers in any natural system. Note that the multiplication factor in the denominator varies with the normalization multiplication factor; thus, this factor would be 7×10^{-6} for ε_{Sr}. In a case where $\delta_1 - \delta_2$ is unusually large, concentrations of a single stable isotope of Sr (e.g., [^{86}Sr]) may be used in place of total Sr concentration in mass balance equations for a rigorously correct calculation. This may be the optimal strategy in cases where a natural system is artificially 'spiked' with an enriched isotope of strontium as a passive tracer.

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