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Weathering versus atmospheric sources of strontium in ecosystems on young volcanic soils

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Abstract We used isotopes of Sr to quantify weathering versus atmospheric sources of foliar Sr in 34 Hawaiian forests on young volcanic soils. The forests varied widely in climate, and in lava flow age and texture. Weathering supplied most of the Sr in most of the sites, but atmospheric deposition contributed 30–50% of foliar Sr in the wettest rainforests. A stepwise multiple regression using annual precipitation, distance from the ocean, and texture of the underlying lava explained 76% of the variation in Sr isotope ratios across the sites. Substrate age did not contribute significantly to variation in Sr isotope ratios in the range of ages evaluated here (11–3000 years), although atmospheric sources eventually dominate pools of biologically available Sr in Hawaiian rainforests in older substrates (≥150,000 years).

Key words Atmospheric inputs · Ecosystem development · Hawaii · *Metrosideros polymorpha* · Rock weathering

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Introduction

Inputs of major cations (Ca, Mg, K) to terrestrial ecosystems are derived from weathering of the underlying soil and rock and by deposition from the atmosphere. Watershed-level studies have demonstrated that atmospheric inputs of cations can be large relative to calculated inputs via weathering (Likens and Bormann 1995), but weathering is very difficult to determine directly. A number of studies suggest that because anthropogenic acidification can drive increased cation losses, the supply of cations is increasingly important to the functioning of some ecosystems (Schulze 1989; Likens et al. 1996; Aber et al. 1998).

Under certain circumstances, strontium isotopes provide a means of tracing the integrated contributions of weathering and atmospheric inputs to cation pools in plants and soils (Graustein and Armstrong 1983; Graustein 1989). Where the ratio of $^{87}Sr/^{86}Sr$ in atmospheric versus weathering sources differs sufficiently and reliably, the contribution of each source to a within-system Sr pool can be calculated using a simple mixing equation (Capo et al. 1998; Stewart et al. 1998). Although Sr itself is of little biological interest, its chemistry and biological cycling are similar enough to those of other alkaline earths, particularly calcium and magnesium, that it can be used as a tracer of their inputs and cycling. Several studies have suggested that atmospheric sources make a relatively large contribution to Sr pools in a variety of forest ecosystems (e.g., Åberg et al. 1989; Miller et al. 1993), although often uncertainty about the atmospheric end-member (due to contributions of both dust and marine aerosol) and especially the weathering end-member (due to incongruent weathering of a heterogeneous assemblage of minerals) constrains the precision of these estimates substantially (Blum and Erel 1995; Bailey et al. 1996).

Recently, Kennedy et al. (1998) used Sr isotopes to evaluate the contribution of weathering versus the

atmosphere to plant and soil Sr pools across a 4.1-million-year soil and ecosystem developmental sequence in the Hawaiian Islands. Hawaii is ideally suited for Sr isotopic studies because the end members have distinct values that do not vary spatially or temporally. Atmospheric Sr is derived mainly from marine aerosol, and the atmospheric end member can be considered equivalent to sea water with a minimal contribution of dust from Central Asia ($^{87}Sr/^{86}Sr = 0.7093$, Kennedy et al. 1998). The basaltic substrate is too young to have been measurably changed by the growth of radiogenic ^{87}Sr; it provides a weathering end-member of 0.7035 from all mineral phases. Kennedy et al. (1998) showed that plant and soil $^{87}Sr/^{86}Sr$ ratios were near the weathering end-member in 300- and 2100-year-old sites; they were intermediate between the weathering and atmospheric sources in a ~20,000-year-old site (0.7055), and they approached the atmospheric end-member in sites ≥150,000 years. They concluded that weathering is the primary source of Sr in young sites (up to several thousand years), but that atmospheric sources predominate in old sites (Kennedy et al. 1998) – a pattern consistent with the rapid decline in Ca and Mg pools observed by 20,000 years in the soils, and the disappearance of primary minerals by 150,000 years (Vitousek et al. 1997).

The conclusion that ecosystems on young substrates derive their cations from weathering while atmospheric sources dominate ecosystems on older substrates is clear for the sequence observed by Kennedy et al. (1998) (volcanic ash soils, 1200 m elevation, 2500 mm annual precipitation), but it is not necessarily a general conclusion. For example, drier sites (< 1500 mm annual precipitation) on a 160,000-year-old substrate in Hawaii have Sr isotope ratios close to the weathering end-member (Capo et al. 1998). It is also possible that atmospheric sources of cations could be important in young sites where: (1) rates of weathering are relatively low as a consequence of the structure or chemistry of rock; and/or (2) where atmospheric inputs of Sr are greater than those in the sites considered by Kennedy et al. (1998).

In this paper, we evaluate the relative importance of atmospheric versus weathering sources of Sr in young ecosystems developing on lava flows across a wide range of climates on Mauna Loa and Hualalai volcanoes, Hawaii. Weathering rates on lava flows should be lower than those on volcanic ash, because the lava presents a much lower surface area accessible to weathering than does volcanic ash. These sites also extend to sites that are much wetter (up to 5800 mm $year^{-1}$ versus 2500 mm $year^{-1}$) than the young volcanic ash sites reported by Kennedy et al. (1998); they also reach closer to the ocean (as near as 2 km), where marine aerosol is more concentrated Duce et al. 1965. The range in the contribution of atmospheric sources of Sr to young, developing Hawaiian ecosystems should be evident in these sites.

Materials and methods

Sites

Most of the sites sampled are located on Mauna Loa, an active shield volcano 4169 m tall on the island of Hawaii. Mauna Loa has been utilized extensively for ecological studies, because it allows many of the important controls over ecosystem structure and functioning to be held constant, while others vary in wide but very well defined ways (Vitousek et al. 1995). Factors that can be held constant include the chemistry of parent material, topography, and dominant vegetation. The surface of Mauna Loa is composed of tholeiitic basalt, which erupts in frequent, relatively fluid flows with a gentle angle of repose; coarse-scale topography is absent over most of the mountain. The native vegetation is dominated by a few widely distributed species – the myrtaceous tree *Metrosideros polymorpha* in particular is the most abundant tree in most of the native forest, from sea level to treeline and from semi-arid woodland to wet rainforest (Aplet et al. 1998).

Variable factors on Mauna Loa include climate, the texture of parent material, and substrate age. Temperature varies with elevation, from a mean annual temperature of 24°C at the coast to near 5°C at the summit. Precipitation varies with elevation and exposure to the prevailing northeast trade winds, from < 400 mm $year^{-1}$ to > 6000 mm $year^{-1}$ (Giambelluca et al. 1986; Juvik and Juvik 1998). The lava flows on Mauna Loa range from very young (most recently 1984) to > 10,000 years, and they have been mapped and dated with a precision that is unmatched for any other large volcano (Lockwood 1995; Wolfe and Morris 1996). Finally, Mauna Loa lava flows differ dramatically in texture, from smooth, ropy-surfaced pahoehoe flows to rough, rubbly aa flows. The chemistry of these flows is similar, but the surface area accessible to weathering is much greater on aa.

We made use of sets of sites that had been utilized by earlier studies on Mauna Loa. At each site, we collected fully-expanded sun leaves of *M. polymorpha*, which dominated or co-dominated everywhere. Leaves were collected by hand in short-statured or open forests, and by using a slingshot or shotgun in taller closed-canopy forests. Leaves were collected from at least five trees per site, and analyzed for a range of nutrients. Leaves were then lumped by site prior to Sr analyses; independent samples were analyzed for five sites to provide information on within-site variation.

Of our 34 sites 26 were from the Mauna Loa environmental matrix (Vitousek et al. 1992), which consists of a young (< 150 years in 1995) versus an old (> 2800 years) flow of aa versus pahoehoe textures on the wet east flank of Mauna Loa versus the dry northwest – all sampled from treeline to the lower limit of native forest (or the end of the flow). A second young pahoehoe flow on the wet east flank also is included in this matrix, to provide replication. Patterns in climate, foliar and soil nutrients, biomass and species composition, decomposition, and productivity and nutrient cycling have been reported for most of these sites (Vitousek et al. 1992, 1994; Nullet et al. 1995; Raich et al. 1997; Aplet et al. 1998).

In addition, we utilized sites from a well-characterized moisture gradient and from a 3000-year gradient of substrate age. The moisture gradient consisted of six sites at a single elevation/substrate age (~700 m, 2300–3000 years), arrayed around Mauna Loa (and nearby Hualalai Volcano), in which annual precipitation ranged from 500 to 5500 mm $year^{-1}$ (Austin and Vitousek 1998). The age gradient included five aa flows at a single elevation on the wet east flank of Mauna Loa; these ranged from 11 to ~3000 years old in 1995. Species composition, biomass, and foliar nutrients in these sites are summarized in Drake and Mueller-Dombois (1993), Aplet and Vitousek (1994), and Kitayama et al. (1995). Characteristics of all of the sites are summarized in Table 1.

Methods

Leaf samples were dried, ground, and ashed in a muffle furnace prior to digestion in ultra-pure $HClO_4$ + HNO_3. Sr was purified

Table 1 Characteristics of the sites sampled. More complete information on the Mauna Loa matrix can be found in Vitousek et al. (1992) and Aplet et al. (1998); on the precipitation gradient in Austin and Vitousek (1998); and on the age gradient in Kitayama et al. (1995)

Sites	Age in 1995	Elevations (m)	Distances from the ocean (km)	Precipitation (mm year^{-1})	Texture (Pahoehoe versus aa)
Mauna Loa matrix					
1881 flow	114	80, 305, 700, 1160, 1740, 2410	2, 7, 13, 21, 32, 43	3400, 4600, 5800, 4400, 2400, 1000	Pah
1855 flow	140	700, 1160, 1740, 2410	13, 21, 32, 43	5800, 4400, 2400, 1000	Pah
Punahoa flow	3400	700, 1160, 1740, 2410	13, 21, 32, 43	5800, 4400, 2400, 1000	Pah
1852 flow	143	1160, 1740	21, 32	4400, 2400	Aa
Old aa flow	3000	700, 1160, 1740	13, 21, 32	5500, 4400, 2400	Aa
1859 pah flow	136	700, 1580	11, 31	500, 600	Pah
Old pah flow	3000	1580	31	600	Pah
1859 aa flow	136	700, 1580	11, 31	500, 600	Aa
Kaniku flow	2800	700, 1580	12, 31	500, 600	Aa
Precipitation gradient[a]					
Kaupulehu	2800	700	9	900	Aa
Manuka	2330	700	11	1500	Aa
Kaloko	2300	700	9	2000	Aa
Honaunau	2300	700	6	2800	Aa
Age gradient[b]					
1984 flow	11	1160	21	4400	Aa
1942 flow	53	1160	21	4400	Aa
300-year-oldflow	300	1160	21	4400	Aa
Other					
1868 flow	127	650	12	2000	Pah

[a] The precipitation gradient also includes the 700-m Kaniku site and the 700-m old aa site from the Mauna Loa matrix
[b] The age gradient also includes the 1160-m 1852 flow site and the 1160-m old aa flow site from the Mauna Loa matrix

using standard techniques on Sr-Spec ion exchange resin. Isotope ratios were determined on similar VG-4 mass spectrometers at either UCLA or Cornell University, using dynamic multi-collection. Corrections for mass fractionation were made using $^{86}Sr/^{88}Sr = 0.1194$. $^{87}Sr/^{86}Sr$ ratios are normalized to a common standard value of NBS-987 = 0.71025, to correct for any minor inter-laboratory differences. Analytical precision is typically < 0.00002, although for some small samples it is ≤ 0.00003.

Analysis

Results were analyzed statistically using stepwise multiple regression (SYSTAT 8.0, 1998, SPSS Inc., Chicago, Ill., USA), with log-transformed strontium isotope ratios as the dependent variable. Annual precipitation and the distance from each site to the coast were treated as continuous independent variables, and flow texture (aa versus pahoehoe) and substrate age (young flows < 300 years, all but one site < 150 years, versus old flows > 2300 years) were treated as categorical independent variables.

Results and discussion

Metrosideros trees on some young sites on the Mauna Loa matrix derive more of their Sr from the atmosphere than do the young sites on the developmental sequence evaluated by Kennedy et al. (1998). Between-site differences are much greater than the analytical precision (0.00003 or better). Within-site variation also is larger than analytical precision – for the five sites for which independent samples were collected and analyzed differences between the samples averaged 0.0005 (± 0.0002) – but within-site variation is substantially smaller than some of the between-site variation.

High-rainfall sites on the Mauna Loa matrix support the greatest atmospheric contribution (Fig. 1), of up to 50% of foliar Sr; drier sites at high elevation or on the leeward side are dominated by weathering-derived sources of Sr. Similarly, *Metrosideros* trees in the two wettest sites on the moisture gradient described by Austin and Vitousek (1998) have a substantial contribution of Sr from marine aerosol, while the drier sites are nearly wholly weathering-dominated (Fig. 2); the transition occurs between 2000 and 3000 mm year^{-1} on these several thousand year old aa flows. In contrast, Sr on a moisture gradient on older substrate (~160,000 years) in the Kohala Mountains is mostly rock-derived at annual precipitation below 1500 mm year^{-1}, then undergoes a rapid transition to mostly atmospherically derived Sr in wetter sites (Capo et al. 1998).

We evaluated the overall pattern of variation in $^{87}Sr/^{86}Sr$ across these sites using stepwise multiple regression. Annual precipitation was the best single predictor of Sr isotope ratios; variation in precipitation accounted for 56% of the variation in foliar Sr isotopes ($P < 0.001$). The influence of distance from the ocean explained a significant fraction of the remaining variation ($P < 0.001$), increasing the overall r^2 to 0.71. Sites closer to the ocean have a greater concentration of marine aerosol in the atmosphere, and in precipitation; the influence of this marine aerosol is illustrated by the fact that Sr isotopes continue to have a relatively strong

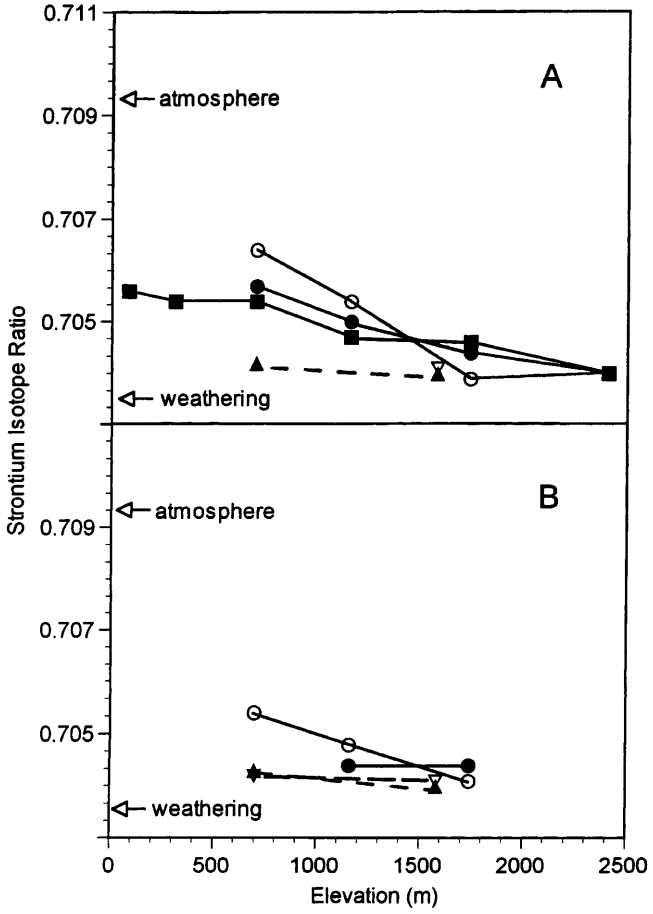

Fig. 1A,B $^{87}Sr/^{86}Sr$ in leaves of *Metrosideros polymorpha* on the Mauna Loa environmental matrix, Hawaii. Weathering sources of Sr have a ratio of 0.7035; atmospheric deposition from marine aerosol and (to a minor extent) Asian dust is 0.7092 (Kennedy et al. 1998). The sites are described in Vitousek et al. (1992) and summarized in Table 1. **A** Sites on pahoehoe flows. Young flows on the wet east flank are indicated with *solid symbols and lines*, a young flow on the dry northwest flank with a *solid symbol and dashed line*, an old (~3400 years) flow on the wet flank with a *hollow symbol and solid line*, and an old flow on the dry northwest with an *open symbol*. **B** Sites on aa lava flows; symbols and lines as in **A**

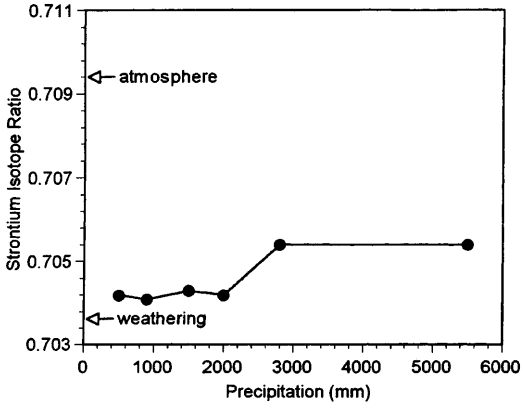

Fig. 2 $^{87}Sr/^{86}Sr$ in leaves of *M. polymorpha* on a moisture gradient around Mauna Loa and Hualalai volcanoes, Hawaii. All the sites are native forests developed on aa lava flows 2300–3000 years old. The sites are described in Austin and Vitousek (1998) and summarized in Table 1

atmospheric (marine aerosol) signature in the lowest-elevation wet sites, even though annual precipitation is lower at 80 m than at 700 m elevation (3400 vs. 5800 mm $year^{-1}$) (Fig. 1, Table 1).

Consideration of lava flow texture (aa versus pahoehoe) explained another significant fraction of the variation in Sr isotope ratios ($P < 0.05$), raising the overall r^2 to 0.76. The aa flows are covered by a deep layer of more or less fist-sized rocks; they present a substantially greater surface area to weathering than do more massive pahoehoe flows, and rock-derived Sr makes up a larger proportion of foliar Sr on aa flows. Volcanic ash soils have a still greater surface area than does aa, and foliar Sr is almost wholly rock-derived in young ash-derived sites (Kennedy et al. 1998).

Substrate age had no consistent effect on strontium isotope ratios, within the range of ages evaluated on Mauna Loa. This result suggests that primary minerals in the substrate had not been depleted in any of these sites. On longer time scales (20,000 years and longer) in volcanic ash-derived soils, primary minerals are exhausted and atmospheric sources of Sr become increasingly important (Kennedy et al. 1998).

Overall, these results show that weathering remains the most important source of Sr in most sites on young (< 3000 years) Mauna Loa substrates – even where annual precipitation is very high, the ocean provides a nearby source of seasalt aerosols, and the underlying rock exposes little surface area to weathering. Consequently, it is unlikely that atmospheric inputs of Ca or Mg contribute substantially to rates of productivity or other biological processes here; foliar Ca and Mg concentrations are relatively high in these young volcanic sites (Vitousek et al. 1992) and decline substantially in the much older sites where both calculated Ca budgets and Sr isotopes (Kennedy et al. 1998) show that atmospheric sources of alkaline earth elements dominate plant and soil pools.

Nevertheless, 30% of the plant available Sr in some Mauna Loa sites can be derived from the atmosphere in little more than a century (Fig. 1), despite conditions that should lead to relatively high weathering rates (warm, wet climate, and fresh surface basalt flows). In sites with rocks more resistant to weathering than is Hawaiian basalt a similarly rapid impact of atmospheric deposition on the biological Sr pool could be important to ecosystem function. The early importance of atmospheric deposition also has implications for the use of Sr isotopes in weathering profiles as indicators of rock weathering rates, suggesting that failure to account quantitatively for atmospheric deposition could lead to significant errors in weathering-rate calculations, even over short (100 years) time scales.

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