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Identifying calcium sources at an acid deposition-impacted spruce forest: a strontium isotope, alkaline earth element multi-tracer approach

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Abstract. Depletion of calcium from forest soils has important implications for forest productivity and health. Ca is available to fine feeder roots from a number of soil organic and mineral sources, but identifying the primary source or changes of sources in response to environmental change is problematic. We used strontium isotope and alkaline earth element concentration ratios of trees and soils to discern the record of Ca sources for red spruce at a base-poor, acid deposition-impacted watershed. We measured $^{87}Sr/^{86}Sr$ and chemical compositions of cross-sectional stemwood cores of red spruce, other spruce tissues and sequential extracts of co-located soil samples. $^{87}Sr/^{86}Sr$ and Sr/Ba ratios together provide a tracer of alkaline earth element sources that distinguishes the plant-available fraction of the shallow organic soils from those of deeper organic and mineral soils. Ca/Sr ratios proved less diagnostic, due to within-tree processes that fractionate these elements from each other. Over the growth period from 1870 to 1960, $^{87}Sr/^{86}Sr$ and Sr/Ba ratios of stemwood samples became progressively more variable and on average trended toward values that considered together are characteristic of the uppermost forest floor. In detail the stemwood chemistry revealed an episode of simultaneous enhanced uptake of all alkaline earth elements during the growth period from 1930 to 1960, coincident with reported local and regional increases in atmospheric inputs of inorganic acidity. We attribute the temporal trends in stemwood chemistry to progressive shallowing of the effective depth of alkaline earth element uptake by fine roots over this growth period, due to preferential concentration of fine roots in the upper forest floor coupled with reduced nutrient uptake by roots in the lower organic and upper mineral soils in response to acid-induced aluminum toxicity. Although both increased atmospheric deposition and selective weathering of Ca-rich minerals such as apatite provide possible alternative explanations of aspects of the observed trends, the chemical buffering capacity of the forest floor-biomass pool limits their effectiveness as causal mechanisms.

Introduction

Calcium (Ca) is an essential plant nutrient that is delivered to trees via uptake through fine feeder roots in the organic-rich forest floor and underlying mineral soils of forested watersheds. The sensitivity of trees to natural or anthropogenically induced environmental change in part reflects the sensitivity of their fine roots to changes in both root tip vitality and the availability of nutrients such as Ca (Momoshima and Bondietti, 1990). Over the past century, increased atmospheric deposition of acid anions (Mayewski et al. 1986) has negatively impacted the Ca status of sensitive forest ecosystems, due to both depletion of readily available Ca on soil exchange sites (Shortle and Bondietti 1992; Likens et al. 1996, 1998; Markewitz et al. 1998; Huntington 2000) and mobilization of monomeric aluminum (Al_i) that is toxic to fine roots (Lawrence et al. 1995). Either Ca deficiency or aluminum toxicity may lead to an increased importance of the upper forest floor relative to deeper Al_i-impacted organic and mineral soils as a Ca source for fine roots (cf., Joslin and Wolfe 1992). Chemical and isotopic approaches that can reveal transitions of Ca sources for tree roots would be useful for determining the historic timing of, systemic response to and potential recovery from soil acidification.

Red spruce (*Picea rubens* Sarg.) is a dominant tree throughout both high and low elevation spruce-fir forests across the northeastern USA and eastern Canada, with high ecological as well as economic importance (White and Cogbill 1992). Growth reductions in red spruce have been documented across the northeastern USA and have been variously attributed to stressors such as reduced uptake of base cation nutrients (e.g., Ca, Mg) in response to soil acidification as well as to natural growth patterns (Shortle and Smith 1988; Johnson et al. 1994; Reams and Van Duesen 1995). The role of base cation nutrition in spruce growth dynamics is suggested by the association of anomalous dendrochemical base cation patterns and biochemical stress indicators (Shortle et al. 1997), the role of Ca depletion in reduction of cold hardiness (DeHayes et al. 1999), and documentation of a regional decline of plant-available Ca in soils of red spruce forests over the last century (Shortle and Bondietti 1992; Johnson et al. 1994; Bailey et al. 1996; Lawrence et al. 1997). Thus, red spruce represents an ideal species with which to test the effectiveness of proxy tracers of Ca sources in acid-impacted systems.

Both conventional wisdom (e.g., Lawrence et al. 1995) and the preponderance of field observations to date (e.g., Smith et al. 1995; W.C. Shortle, pers. comm.) suggest that the majority of fine roots of red spruce are concentrated in the forest floor. Thus, the forest floor is likely to be an important source of Ca nutrition for red spruce, and changes in its Ca status may have significant implications for the heath of the spruce ecosystem. On the other hand, recent studies have demonstrated that ectomycorrhizal mycelia associated with fine roots of conifers are able to penetrate micropores in, and draw nutrients from minerals that are components of the mineral and lowermost organic soils (e.g., Van Breeman et al. 2000; Wallander 2000; Wallander et al. 2002). Blum et al. (2002) used chemical and isotopic approaches to argue that ectomycorrhizal hyphae associated with roots of red spruce at the Hubbard Brook Research Watershed are able to penetrate into the deepest mineral soils and selectively weather the calcium-phosphate mineral apatite. They suggested that apatite may be an important, and perhaps the predominant source of Ca nutrition for red spruce at Hubbard Brook and similar base-poor forested watersheds; however, this hypothesis has been controversial (e.g., Comment on Blum et al. 2002 by Watmough and Dillon, (2003); Reply by Blum et al. (2003)).

Isotopic and chemical tracers that can distinguish contributions of nutrients from the various soil nutrient pools and minerals would have considerable value in assessments of root system development patterns and response to environmental stresses. For example, the alkaline earth element strontium (Sr) behaves similarly to Ca during nutrient uptake by fine spruce roots due to similar ionic radius ($r_{\mathrm{Sr}}/r_{\mathrm{Ca}} = 1.13$) and charge (Elias et al. 1982; Aberg et al. 1989; Bailey et al. 1996; Poszwa et al. 2000). By analogy, the alkaline earth element barium (Ba) should behave similarly to Sr during nutrient uptake, due to similar ionic radius ($r_{\mathrm{Ba}}/r_{\mathrm{Sr}} = 1.17$) and charge. Therefore, ratios of neighboring alkaline earth elements (e.g., Ca/Sr and Sr/Ba ratios) as well as Sr isotope (^{87}Sr/^{86}Sr) ratios of tree tissues may prove useful for identifying sources of alkaline earth elements if there is systematic variability of these ratios in plant-available pools down the soil profile.

Sr isotopes are increasingly being used in biogeochemical studies of forested ecosystems (e.g., Aberg et al. 1990; Miller et al. 1993; Bailey et al. 1996; Blum et al. 2002; Kennedy et al. 2002). ^{87}Sr/^{86}Sr of 'plant-available' Sr in the organic soils will differ from that in the underlying mineral soils if: (1) there is a significant difference in ^{87}Sr/^{86}Sr of atmospherically derived and mineral weathering-derived Sr, and (2) biological cycling of Sr does not homogenize the Sr isotope signal. Given these conditions, temporal changes in the relative contributions of Sr (and Ca) from the organic and mineral soils should be recorded as changing ^{87}Sr/^{86}Sr in tree growth rings. For example, Aberg et al. (1990) suggested that lower ^{87}Sr/^{86}Sr of outer wood relative to that of core wood in a Norway spruce sample from Sweden resulted from acidification-induced reduction in the relative supply of Sr (and Ca) from the mineral soil exchange pool as the tree grew. In this case, ^{87}Sr/^{86}Sr values changed toward that of atmospheric input that should have an important influence on plant-available pools in the forest floor.

However, if ^{87}Sr/^{86}Sr ratios of weatherable soil minerals span a range that overlaps that of atmospheric deposition, ^{87}Sr/^{86}Sr alone may not provide an effective discriminant of nutrient contributions from the various soil pools. In this case, a 'multi-tracer' approach using ^{87}Sr/^{86}Sr together with additional tracers such as Ca/Sr and Sr/Ba ratios may prove far more effective. For example, Blum et al. (2002) suggested that the high Ca/Sr ratios of spruce foliage relative to those of NH_4Cl-exchangeable and HF/HNO_3-acid digestible fractions of the underlying soils at Hubbard Brook result from preferential ectomycorrhizal weathering of the high-Ca/Sr mineral apatite in deep mineral soils. To support this hypothesis, they experimentally isolated a high-Ca/Sr, P-rich component of the deepest mineral soils from several sampling sites in the watershed using a 1 N HNO_3 leach procedure. The similarity of ^{87}Sr/^{86}Sr of the experimental leachates to that of the spruce foliage provided support for their hypothesis. For this study they assumed that the Ca/Sr ratio of foliage is similar to that of the soil source pool for Ca (and Sr), and that there is little discrimination between Ca and Sr along the transpiration stream.

Tracers such as Ca/Sr and Sr/Ba ratios of tree tissues will be most effective if there is no fractionation between the alkaline earth elements along the transpiration stream. However, Poszwa et al. (2000) reported that the Ca/Sr ratio of foliage from a Norway spruce was 8 times that of roots sampled from the B-horizon at a European watershed having soils developed on granitic materials. Bailey et al. (1996) reported a roughly 8-fold variation in the Ca/Sr ratio of red spruce tissues at the Cone Pond watershed (New Hampshire) that likewise has soils developed on granitic materials. However, at Cone Pond roots and foliage had Ca/Sr ratios 6.2 and 9.2 times that of stemwood, respectively. In both cases, Ca/Sr ratios of stemwood were similar to or slightly greater than those of soil waters. Momoshima and Bondietti (1990) found that the Sr/Ba ratio of stemwood from a red spruce was 25% greater at 17.4 m height compared to that at 1.4 m height. Thus, there is clear evidence of fractionation between the alkaline earth elements, and particularly between Ca and Sr, within spruce following uptake from soil nutrient pools.

Momoshima and Bondietti (1990) suggested that collecting tree core samples from a single height (e.g., at breast height) across a population of trees should minimize uncertainty due to variability in biogeochemical behavior of the alkaline earth elements along the transpiration stream. Using this approach, we sought to develop a robust, widely applicable method for determination of the depth of alkaline earth element uptake by tree root systems, similar to the nitrogen stable isotope approach used by Nadelhofer et al. (1996) in their assessment of nitrogen uptake by tundra plants. The fundamental premise of our present study is that at steady-state there will be a consistent change of composition in Sr isotope, alkaline earth element ‘multi-tracer space’ of plant-available pools with depth through the soil profile. For example, the chemistry of the Oi horizon is dominated by that of litter material, but is shifted toward values that are characteristic of atmospheric deposition. The chemistry of the Oa horizon is in part determined by that of decomposed organic material displaced downward, but is shifted toward values that are characteristic of mineral weathering in the uppermost mineral soils. As long as atmospheric deposition and mineral weathering maintain distinct Sr isotope and alkaline earth element ratios, the compositional differences of plant-available pools with depth should persist. The chemistry of trees will reflect an intermediate composition determined by the distribution and relative cation uptake of fine roots throughout the soil profile, overprinted by within-tree and soil disturbance processes that require additional understanding.

Our present study had two main objectives: first, to determine whether Sr isotope and alkaline earth element ratios of spruce tissues and spatially associated soils can be used to infer sources of Ca taken up by trees; and second, to determine whether changes in Sr isotope and alkaline earth element ratios in spruce stemwood cores can be used to infer changes in sources of Ca taken up by trees during their life span. For this study, we focused on the base-poor Cone Pond watershed, where earlier work suggested that atmospheric deposition of inorganic acidity has caused depletion of Ca from soil nutrient pools

(Bailey et al. 1996) and where a lack of direct human activity (e.g., logging, agriculture) has provided an undisturbed forest stand with a long time period recorded in the growth rings of old spruce.

Study area and methods

The Cone Pond watershed consists of 53 ha of all-aged (maximum tree age, 270 years) forest within the White Mountain National Forest. The watershed cover is 80% mixed conifer forest, 15% northern hardwood forest, and 5% bedrock outcrop. The watershed is underlain by sillimanite-grade metapelites of the Silurian Perry Mountain Formation. Bedrock is exposed along ridges, while the remainder of the watershed is mantled by glacial till (< 2.5 m thick) derived primarily from local granitic and metapelitic rocks (Bailey and Hornbeck 1992). The soils are Aquic, Lithic, and Typic Haplorthods, and have developed in a thin (< 2 m), firm, slowly permeable, dense basal till which limits deep percolation of drainage waters. As a result, hydrologic flowpaths that feed streamflow are largely confined to upper soil horizons.

Soil profiles typically consist of a ~12 cm thick forest floor, including an Oi horizon of the least decomposed plant litter, an Oe horizon of intermediate decomposition and a well decomposed Oa horizon. Mineral content determined by loss on ignition ranges from < 5% in the Oi horizon to 30% in the Oa horizon. The underlying mineral soils typically consist of a highly leached E horizon overlying a spodic B horizon, where iron and aluminum sesqui-oxides and organic matter coat mineral surfaces. Primary minerals in the soils, in order of decreasing modal abundance, are quartz, plagioclase feldspar (average composition, An_{26}), K-feldspar, muscovite, biotite, chlorite and hornblende. Pyroxene, garnet, epidote and apatite are present in minor to trace amounts (Bailey et al. 1996; Hyman et al. 1998). Unlike many neighboring watersheds such as Hubbard Brook, the Cone Pond watershed was not logged during the 19th and early 20th centuries. Rather, the main environmental disturbances of historical record, other than acid deposition, include blowdown from a major hurricane in 1815 and subsequent fire *circa* 1820, and lesser damage from a hurricane in 1938 (Buso et al. 1985).

We analyzed soils collected from four sites (1, 8, 10 and 26; Figure 1) along an elevational transect and spanning the depth range from the surficial litter layer to the deep mineral soils. The elevational range sampled was small (~100 m), and thus our purpose was to establish site variability rather than elevational trends. Soil samples collected at sites 1 and 8 have been previously discussed by Bailey et al. (1996). Soils were subjected to a three-stage extraction-digestion procedure that produced soil components referred to here as the ‘exchangeable’, ‘leachable’ and ‘digestible’ fractions (cf., Blum et al. 2002). To obtain the ‘exchangeable’ fraction, approximately 5 g of sieved (< 2 mm fraction), oven-dried soil was equilibrated with 50 ml of 1 *N* ammonium acetate for several days. Each solution was filtered and the residue rinsed with

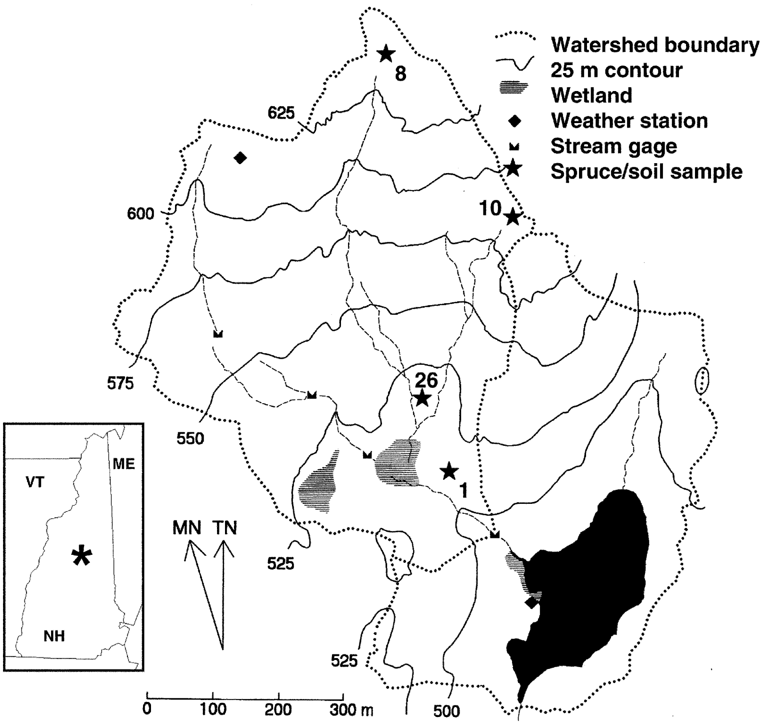

Figure 1. Map of the Cone Pond watershed, showing tree and soil sampling sites. Inset map shows location of the watershed in New Hampshire.

distilled water. The filtered solutions (including rinsates) were evaporated, and each extract was treated with a mixture of concentrated, Teflon-distilled HNO_3 and Ultrex H_2O_2 on a hot plate to eradicate organic compounds. The residue was re-dissolved in 3 ml of 2%HNO_3 and reserved for analysis.

To obtain the 'leachable' fraction, 1 g of the soil remaining from the exchange procedure was allowed to sit in 10 ml of 1 *N* HNO_3 for a period of 24 h on a hot plate set to 30 °C. As described in the Results section below, the Sr isotope and chemical compositions of the 'leachable' fraction obtained using this procedure were significantly different from those obtained by Blum et al. (2002) for lithologically similar soils from Hubbard Brook using a similar technique but at 20 °C. In an effort to explain the discrepancy, we repeated the 1 *N* HNO_3 leaching procedure described above on the mineral soil samples at 'room temperature' (~20 °C) and, for a subset of the deepest mineral soils, 'at freezing' in the freezer space of a small refrigerator (~0 °C). For each leaching procedure, the resulting leachate was then extracted using a syringe filter and evaporated to dryness on a hot plate. The residue was dissolved in 3 ml of 2% HNO_3 and reserved for analysis.

The 'digestible' fraction was determined on samples from the Oa horizon downward through the deepest mineral soils. To obtain the digestible fraction, the soil remaining from the first (30 ° C) leaching procedure was rinsed with distilled water, dried, carefully transferred to a crucible and ashed at 650 °C in a muffle furnace to eradicate organic compounds. The resulting material was then digested over several days in a mixture of concentrated HF (5 ml) and HNO_3 (1 ml) on a hot plate set to 30 °C. The resulting solution was evaporated on a hot plate, the remaining material was re-dissolved in 10 ml of 6 *N* HCl, allowed to sit for several days, again evaporated on a hot plate, and finally re-dissolved in 2% HNO_3 and reserved for analysis.

In addition, we analyzed the Sr isotope and chemical compositions of dated stemwood, bark, foliage and roots from red spruce collected at three sites (8, 10 and 26) shown in Figure 1. Samples of spruce stemwood were collected using a 5 mm-bore tree corer. Cores were collected at breast height from six individual trees. The sample set was supplemented by two 3-tree composites collected at site 10 that were prepared for an earlier study and for which the individual decadal increments were combined and homogenized (Shortle et al. 1997). The time periods spanned were 1750–1995 for two samples, 1850–2000 for three samples, 1910–1995 for one sample and 1870–1990 for the 3-tree composites. The cores were air-dried and separated into decadal increments ranging from 10 to 150 mg. Bark was collected from the six individual trees. Roots, stemwood, bark and foliage were collected from four additional small, variously aged sub-canopy spruce at sites 8 and 10. All spruce samples were totally digested in 5 ml of concentrated Teflon-distilled HNO_3 over a period of 24 h. Following evaporation of the HNO_3 on a hot plate, each sample was treated with a mixture of concentrated HNO_3 and Ultrex H_2O_2 to eradicate organic compounds, the residue was re-dissolved in 3 ml of 2% HNO_3 and the solution was reserved for analysis.

One-tenth of each 2% HNO_3 solution was used for determination of element concentrations on a Perkin Elmer Elan 6000 inductively coupled plasma mass spectrometer. All samples were analyzed for Mg, Al, K, Ca, Sr and Ba; in addition, all soil fractions were analyzed for Na, the leachable fraction was analyzed for Si, P and Fe, and the digestible fraction was analyzed for P, Fe and Nb. Synthetic mixtures of pure element solutions were used as standards for analysis of the tree samples and exchangeable and 1 *N* HNO_3-leachable soil fractions. U.S.G.S. rock standards BIR, BHVO, BCR, AGV, QLO and G2, subjected to the HF/HNO_3-dissolution technique, were used as standards for analysis of the digestible soil fractions. Reported concentrations for all elements are precise to 3% or better. Sr was separated from the remaining 2% HNO_3 solutions of tree core digests and soil fractions using AG50X8 cation resin with 2 *N* HCl as the eluant. $^{87}Sr/^{86}Sr$ was measured on a Finnigan MAT 261 thermal-ionization mass spectrometer, with a 2-sigma internal precision of 0.00003 or better. The average value for 50 measurements of N.I.S.T. SRM987 on this mass spectrometer during the course of this study was 0.71023, with a 2-sigma external precision of 0.00002.

Element concentrations and $^{87}Sr/^{86}Sr$ ratios of the exchangeable, leachable and digestible fractions of the soil samples are given in Table 1. Sr isotope and chemical compositions of all spruce stemwood, bark, root and foliage samples, as well as sample weights of decadal stemwood core increments, are available in Appendix 1. Decadal averages of chemical compositions and $^{87}Sr/^{86}Sr$ ratios of the stemwood core samples are given in Table 2. For completeness we report all of the stemwood core data collected for this study, but note that we do not include the data for one tree (tree 10–2) in the following statistical evaluation due to its short life relative to the rest of the sample population. In addition, although two of the trees (26-1 and 26-3) have dated wood extending back to the mid-1700's, we only include data on these trees for the post-1820 increments in the following plots, statistical evaluation and discussion. For both of these trees, the time period around 1820 corresponds to their probable emergence from the understory as a result of the fire that occurred in the watershed in the late 1810's, as indicated by the substantial increase of their decadal increment masses at that time (Appendix 1).

Results

Soils

Concentrations of exchangeable Mg, Ca, Sr and Ba, as well as Ca/Sr and Sr/Ba ratios of exchangeable fractions are generally greatest in the organic soils and decrease with depth in the mineral soils (Table 1). $^{87}Sr/^{86}Sr$ ratios of exchangeable fractions display no consistent depth trends, although at each site values of the Oi and Oe horizons are always less than that of the Oa horizon. Below this depth, the variations tend to be erratic.

Concentrations and ratios of alkaline earth elements in the leachable fractions exhibit variable trends (Table 1). For example, concentrations of leachable Ca are greatest in the upper organic and deepest mineral soils, and least in the lower organic and upper mineral soils. Concentrations of leachable Sr are greatest in the upper organic soils and generally decrease with depth. Concentrations of leachable Ba and Mg, as well as K and Rb, are highly variable and show no clear systematic down-profile trends. The down-profile distribution of Ca/Sr ratios of the leachable fractions is similar to that of Ca, while that of Sr/Ba ratios is similar to that of Sr. $^{87}Sr/^{86}Sr$ ratios of the leachable fractions generally increase with depth in the organic soils, and either continue to increase or decrease slightly in the mineral soils. Alkaline earth element concentrations and $^{87}Sr/^{86}Sr$ ratios of both leachable and exchangeable fractions in the forest floor generally decrease with increasing elevation in the watershed. The concentration trends are consistent with previous regional-scale studies of forest floor compositions (Arthur et al. 1999; Yanai et al. 1999).

Compositional variability of leachable fractions is in part due to a dependence on the temperature of the leaching procedure, with the higher temper-

Table 1. Data for exchangeable, leachable, and digestible fractions of soils.

	$^{87}Sr/^{86}Sr$	Ca/Sr	Sr/Ba	Na	Mg	Al	Si	P	K	Ca	Fe	Rb	Sr	Nb	Ba
Exchangeable fraction															
Site 1															
Oi	0.71952	495	1.26	5.2	120.5	24.0			933.0	1891.5		5.75	8.34		9.99
Oe	0.71985	424	4.34	7.7	88.6	40.3			658.3	324.2		5.01	1.67		2.53
Oa	0.72071	312	4.27	14.6	44.7	256.5			344.0	79.1		3.49	0.55		1.79
E	0.72174	205	0.67	5.5	3.6	39.1			32.0	2.1		0.08	0.02		0.26
Bh	0.72113	225	3.63	4.1	2.6	79.1			29.9	1.3		0.33	0.01		0.20
Bs	0.72099	90	1.95	3.3	2.0	52.6			21.9	0.5		0.21	0.01		0.24
Cd	0.72080	38	2.53	1.6	0.6	17.5			6.5	0.2		0.30	0.01		0.26
Site 26															
Oi	0.71925	302	0.56	12.9	308.9	7.1			876.9	2791.4		6.10	20.23		23.96
Oe	0.71932	276	0.99	16.0	179.6	6.0			655.6	1492.3		6.61	11.82		14.57
Oa	0.71946	66	0.69	27.3	63.0	9.6			337.2	195.6		3.95	6.52		12.49
Bhs	0.72042	68	0.35	7.0	15.4	56.3			60.8	11.9		0.23	0.38		1.41
Bs	0.71962	107	0.48	3.5	4.7	302.3			37.9	15.4		0.27	0.31		1.23
Site 10															
Oi	0.71896	407	2.01	11.3	157.5	20.1			828.5	1106.2		6.60	5.94		7.19
Oe	0.71936	198	7.93	20.4	99.6	101.3			625.7	107.8		9.22	1.19		2.54
Oa	0.71675	121	6.64	40.6	37.4	419.4			282.3	17.0		3.98	0.31		1.31
Bh	0.71746	382	4.27	3.3	2.0	90.1			32.0	2.1		0.41	0.01		0.21
Bs	0.71921	312	1.28	2.1	1.5	74.9			29.0	1.6		0.24	0.01		0.41
Bw	0.71929	219	0.47	1.1	1.0	20.0			21.0	0.9		0.21	0.01		0.98
Site 8															
Oi	0.71831	463	3.61	15.0	99.4	17.9			785.1	560.3		6.37	2.64		3.86
Oe	0.71906	94	2.16	35.4	85.4	37.1			531.7	80.8		5.60	1.89		5.66
Oa	0.71957	85	1.06	17.8	45.8	155.1			216.6	20.6		1.12	0.53		2.30
E	0.71997	119	0.37	1.6	2.0	2.3			32.0	2.4		0.06	0.04		0.33
Bhsm	0.71972	125	0.74	3.5	5.4	87.2			53.5	13.0		0.43	0.23		1.27

Table 1. Continued.

	$^{87}Sr/^{86}Sr$	Ca/Sr	Sr/Ba	Na	Mg	Al	Si	P	K	Ca	Fe	Rb	Sr	Nb	Ba
Leachable fraction															
Site 1															
Oi	0.71928	566	1.23	5.6	129	862	1960	350	39	3593	480	0.62	13.87		24.61
Oe	0.71953	130	0.67	9.6	118	5605	1310	472	46	460	520	1.15	7.72		25.12
Oa	0.72382	141	0.22	26.3	233	10800	1050	497	22	77	15260	1.93	1.19		11.85
E (30 °C)	0.71934	115	0.29	52.0	53	2458	570	89	114	50	2390	1.83	0.96		7.26
E (20 °C)	0.72052	128	0.17	6.9	17	1894	70	46	40	24	1280	0.31	0.41		5.11
Bh (30 °C)	0.73037	122	0.17	51.3	49	10487	2000	1013	282	73	41570	5.28	1.31		16.47
Bh (20 °C)	0.72094	172	0.12	8.4	9	6587	320	417	51	40	16350	0.64	0.50		9.17
Bs (30 °C)	0.74048	195	0.23	79.3	749	12536	2810	272	408	112	29950	6.65	1.25		12.14
Bs (20 °C)	0.71900	335	0.17	5.9	28	9300	250	78	22	55	12730	0.35	0.36		4.58
Cd (30 °C)	0.73925	424	0.24	81.0	1188	12721	4590	218	491	282	13040	11.17	1.45		13.24
Cd (20 °C)	0.72060	732	0.37	17.4	256	11506	2620	230	95	322	6510	2.32	0.96		5.61
Site 26															
Oi	0.71916	383	0.87	11.2	111	284	930	436	62	3728	420	0.70	21.30		53.78
Oe	0.71918	327	0.77	11.2	86	391	650	357	62	2073	530	0.85	13.87		39.47
Oa	0.72250	368	0.26	21.3	342	15983	450	1124	309	344	11850	5.28	2.04		17.28
Bhs (30 °C)	0.72350	381	0.12	18.1	403	13004	430	1009	252	280	25420	4.51	1.60		30.31
Bhs (20 °C)	0.71910	76	0.29	7.6	10	2264	70	118	20	24	5700	0.09	0.70		5.32
Bs (30 °C)	0.72852	187	0.17	9.1	434	10206	200	384	194	92	36130	3.69	1.07		13.43
Bs (20 °C)	0.71850	138	0.19	12.8	35	5772	140	81	41	45	9880	0.58	0.72		8.20
Site 10															
Oi	0.71846	580	1.22	13.4	272	1036	970	770	132	3091	530	0.99	11.64		20.92
Oe	0.71888	220	0.46	19.9	125	7072	850	1100	217	263	1170	1.83	2.61		12.47
Oa	0.71964	106	0.44	20.3	200	18803	600	1358	291	180	6380	3.97	3.71		18.51
Bh (30 °C)	0.72157	99	0.26	17.6	403	26272	665	1334	249	195	30650	5.68	4.32		36.98
Bh (20 °C)	0.72113	107	0.28	10.0	56	19336	460	411	102	139	10480	1.36	2.85		22.15
Bs (30 °C)	0.72887	183	0.15	9.9	519	37276	1240	545	221	109	51760	4.07	1.31		18.91
Bs (20 °C)	0.72165	190	0.17	8.6	16	22969	1130	106	28	71	12220	0.37	0.81		10.27

Bw (30 °C)	0.73451	933	0.16	9.8	704	20697	3640	425	274	463	13020	4.93	1.08		15.07
Bw (20 °C)	0.72264	1211	0.24	13.5	245	19710	1500	271	90	437	7970	1.52	0.79		7.13
Bw (0 °C)	0.71800	1429	0.29	12.4	5	11950	1110	205	9	388	3780	0.25	0.59		4.45
Cd (30 °C)	0.75688	749	0.21	114.1	2143	12820	7650	474	1519	903	10370	24.56	2.63		27.75
Cd (20 °C)	0.72465	1568	0.33	19.0	410	12111	2360	505	284	1100	3400	4.84	1.53		10.17
Cd (0 °C)	0.71735	1980	0.38	10.2	16	11603	1950	440	20	864	1110	0.53	0.95		5.53
Site 8															
Oi	0.71819	555	0.79	17.1	124	930	2610	567	63	1096	1240	0.86	4.32		11.91
Oe	0.71811	127	0.39	14.1	110	2841	1980	723	160	169	1660	1.60	2.91		16.34
Oa	0.71876	204	0.33	13.0	162	3673	310	818	341	526	3770	3.87	5.65		37.70
E (30 °C)	0.73702	372	0.27	13.0	47	580	60	70	59	39	250	0.88	0.23		1.86
E (20 °C)	0.71960	122	0.36	5.5	1	280	30	30	9	3	15	0.05	0.06		0.38
Bhs1 (30 °C)	0.75614	368	0.18	14.7	489	8571	430	886	482	153	3640	5.87	0.91		11.17
Bhs1 (20 °C)	0.72050	314	0.28	7.1	37	6465	190	711	29	104	1560	0.42	0.72		5.59
Bhs2 (30 °C)	0.74497	965	0.20	25.8	808	18339	2100	989	651	831	4780	9.16	1.88		20.26
Bhs2 (20 °C)	0.72185	1167	0.26	10.2	168	16999	1855	787	130	733	1900	1.83	1.37		11.63
Bhs2 (0 °C)	0.71937	1570	0.28	5.2	8	16503	1500	754	12	892	1000	0.39	1.24		9.61
BC (30 °C)	0.73233	1016	0.17	18.5	842	13788	5780	503	265	486	3450	4.46	1.05		13.51
BC (20 °C)	0.72193	1515	0.21	9.8	283	12274	2360	457	87	525	1050	1.69	0.76		7.89
BC (0 °C)	0.71620	1833	0.23	12.3	9	12138	2570	418	19	549	500	0.41	0.65		6.29
Digestible fraction															
Site 1															
Oa	0.72221	113	0.67	5520	991	24753		468	8310	2705	9250	43.2	52.5	19.7	171.6
E	0.72147	105	0.63	8397	1070	33884		136	11417	3453	6000	53.1	72.1	29.0	251.5
Bh	0.72419	108	0.62	9580	1530	44286		207	16916	4773	14170	91.0	96.7	28.3	343.1
Bs	0.72217	113	0.72	11819	1482	43244		249	15526	5593	11360	85.7	107.8	22.4	327.9
Cd	0.71944	119	0.83	14113	2394	43108		155	15966	7677	12100	89.5	141.5	33.0	372.2

Table 1. Continued.

	$^{87}Sr/^{86}Sr$	Ca/Sr	Sr/Ba	Na	Mg	Al	Si	P	K	Ca	Fe	Rb	Sr	Nb	Ba
Site 26															
Oa	0.72299	114	0.76	4142	727	16510		300	5434	1658	3520	26.4	31.8	7.0	91.1
Bhs	0.72315	107	0.78	7040	949	25352		229	7511	2488	6410	41.7	51.0	12.0	142.1
Bs	0.72266	124	0.76	11139	1609	39537		218	14032	4678	7520	71.1	82.4	17.8	235.5
Site 10															
Oa	0.71615	102	0.76	1526	353	6531		224	2157	686	2000	6.4	14.7	7.3	42.4
Bh	0.72150	113	0.71	3898	852	16613		241	5993	1714	5240	26.7	33.0	6.4	101.1
Bs	0.72185	125	0.67	6815	1577	27697		240	9262	3154	7740	44.4	55.3	12.2	179.9
Bw	0.72312	138	0.85	12436	2230	41601		188	15685	5796	8870	84.8	91.6	15.8	235.9
Cd	0.72097	138	0.74	14670	1827	44912		98	15952	7829	10680	93.0	124.3	26.2	368.5
Site 8															
Oa	0.72443	85	0.51	2000	323	10096		206	3596	678	2220	16.6	17.5	6.6	75.7
E	0.72505	138	0.63	10483	646	34226		118	15115	4443	4660	68.9	70.5	16.1	246.3
Bhs1	0.72375	148	0.75	11431	1004	35914		148	14796	5308	5120	71.7	78.4	10.5	229.7
Bhs2	0.72268	148	0.80	12013	1325	36641		85	14280	5525	6410	70.3	81.7	9.9	224.1
BC	0.72022	173	0.89	13994	1987	42364		132	13357	7694	9490	70.3	97.1	16.6	239.5

Element concentrations are given in terms of $\mu g/g$ of dry soil. Ca/Sr and Sr/Ba ratios are given in molar proportions.

Table 2. Data for weighted average of decadal increments for trees having dated wood from 1870 to 1990 (see text for details of weighting).

	Wood mass	$^{87}Sr/^{86}Sr$	Ca/Sr	Sr/Ba	Ca	Mg	Sr	Ba	K	Al
1870's	0.1290	0.72017	419	0.55	848	97.9	4.42	12.71	203	4.66
1880's	0.1188	0.72004	432	0.56	810	89.4	4.10	11.46	201	3.81
1890's	0.1178	0.72002	431	0.58	806	88.4	4.09	11.08	202	3.87
1900's	0.1110	0.71990	435	0.60	765	84.5	3.84	10.15	193	4.61
1910's	0.1092	0.71988	429	0.61	736	81.1	3.75	9.69	186	4.27
1920's	0.1117	0.71978	426	0.62	704	77.2	3.61	9.24	188	4.28
1930's	0.1126	0.71963	427	0.63	700	78.3	3.58	9.02	183	4.13
1940's	0.1054	0.71955	436	0.62	696	78.7	3.49	8.80	182	4.06
1950's	0.1058	0.71936	472	0.63	726	81.1	3.37	8.40	184	6.43
1960's	0.1070	0.71922	460	0.65	674	80.3	3.20	7.71	218	4.11
1970's	0.0934	0.71922	447	0.69	613	77.1	2.99	6.84	317	5.00
1980's	0.0854	0.71925	398	0.72	522	69.0	2.87	6.25	401	4.87

Wood mass for decadal increments is given in grams; element concentrations are given in terms of μg/g of dry wood. Ca/Sr and Sr/Ba ratios are given in molar proportions.

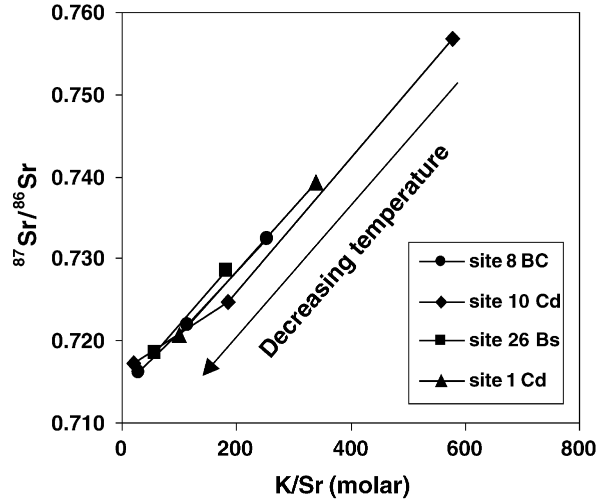

Figure 2. $^{87}Sr/^{86}Sr$ versus K/Sr_{molar} ratios of leachable fractions of deepest mineral soils sampled from each site, showing values for leach obtained at 30 and 20 °C for all sites and at 0 °C for sites 8 and 10. For each site, $^{87}Sr/^{86}Sr$ and K/Sr_{molar} ratios decrease with decreasing temperature of leach procedure.

ature leachates having the greatest Mg, K, Rb, Sr and Ba concentrations and $^{87}Sr/^{86}Sr$ ratios (Table 1). In Figure 2 we compare the $^{87}Sr/^{86}Sr$ and K/Sr ratios of the leachates of the deepest mineral soil from each site. On this diagram, mixing trajectories plot as straight lines and thus the data array can describe mixing between low-K/Sr, low $^{87}Sr/^{86}Sr$ and high-K/Sr, high $^{87}Sr/^{86}Sr$

end-member components. Based on simple linear regression through the data in Figure 2, $^{87}Sr/^{86}Sr$ of the inferred ‘K-free’ component is approximately 0.714 (95% confidence interval: 0.7125–0.7155). Furthermore, based on the chemical data for the 0 °C leachates of the deepest mineral soils at sites 8 and 10 (Table 1), this inferred ‘K-free’ component has a P/Ca ratio equal to or slightly greater than that of apatite (0.60) and a Ca/(Ca + Na) ratio substantially greater than that of plagioclase in Cone Pond soils (0.19–0.24, based on data for digestible fractions in Table 1). Therefore, Ca in these 0 °C leachates may have been supplied largely through dissolution of apatite having $^{87}Sr/^{86}Sr$ of ~0.714 (cf., Blum et al. 2002). The chemical and Sr isotope variations resulting from leaching temperature differences are thus consistent with dissolution of apatite and variable leaching of a soil mineral having high Mg, K, Rb and Ba concentrations and K/Sr and $^{87}Sr/^{86}Sr$ ratios, such as biotite. We note that Mg/K ratios of the 20 and 30 °C leachates range from ~1 to 3, similar to the value for biotite (~2) and considerably less than that for hornblende (~25) separated from Cone Pond soils (Hyman et al. 1998). The substantial Al (and Fe) in the leachates at all temperatures may be due to dissolution of oxyhydroxide coatings on mineral surfaces.

Concentrations of all elements (except P) and Ca/Sr and Sr/Ba ratios of digestible fractions generally increase with depth. $Ca/(Ca + Na)_{molar}$ ratios range from 0.19 to 0.24, close to the average value for plagioclase (0.26) observed by Hyman et al. (1998) during an earlier study of soils at the Cone Pond watershed. There are no consistent trends of $^{87}Sr/^{86}Sr$ with depth, but as shown in Figure 3a the data define a robust ‘isochron’ when plotted against $^{87}Rb/^{86}Sr$

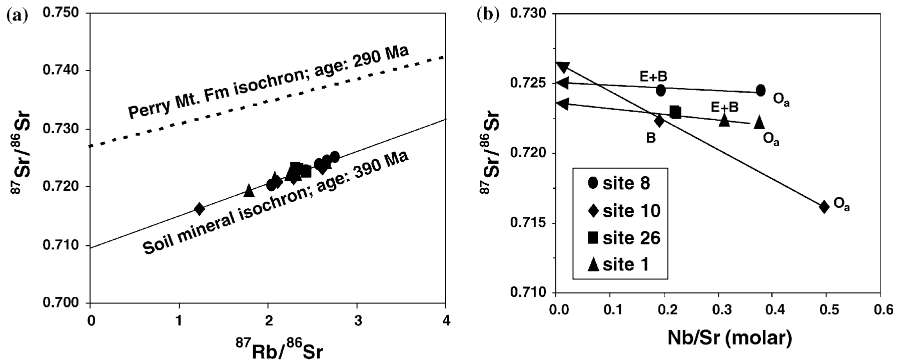

Figure 3. (a) $^{87}Sr/^{86}Sr$ versus ^{87} $Rb/^{86}Sr$ ‘isochron’ plot for digestible fractions of soils from sampled profiles. Soil minerals define an isochron giving an age since mineral formation of ~390 Ma, and initial $^{87}Sr/^{86}Sr$ ~0.7094. Also included is the isochron defined by minerals of the Perry Mountain Formation (Bailey et al. 1996) that gives an age since mineral formation of ~290 Ma. (b) $^{87}Sr/^{86}Sr$ versus Nb/Sr for digestible fractions of upper mineral and O_a horizon soil samples. For sites 1, 8 and 10, the arrow extends from the composition of the O_a horizon sample through the average composition of the B- (or B- and E-) horizon soils. The arrowhead points to the $^{87}Sr/^{86}Sr$ ratio of the Sr that has been extracted from the digestible fraction of the mineral soils to produce the composition of the digestible fraction of the O_a horizon.

ratios of the digestible fractions. The age implied by the slope of the soil mineral isochron is approximately 390 Ma, appropriate to the Devonian age of the granitic rocks from which the majority of pebbles in the till mantle at this watershed were derived (Bailey and Hornbeck 1992). The isochron defined by minerals of the Perry Mt. Formation, the bedrock on which the till was deposited (Bailey et al. 1996), is included in Figure 3a for comparison. The separation of the two isochrons provides strong evidence that the minerals controlling the soil mineral isochron were derived from the granitic rock source, and not from the local bedrock.

The initial Sr isotope composition of the granitic minerals, given by the $^{87}Sr/^{86}Sr$ intercept determined by simple linear regression through the data plotted in Figure 3a, is 0.7097 (95% confidence interval: 0.7085–0.7109). We note that minerals derived from the granite that are essentially Rb-free (e.g., plagioclase and apatite) will not develop significant additional radiogenic ^{87}Sr following crystallization, and should have $^{87}Sr/^{86}Sr$ close to the initial value. Bailey et al. (1996) reported that plagioclase separated from Cone Pond soils had a $^{87}Sr/^{86}Sr$ ratio of 0.7122, in close agreement with the initial value of the granitic minerals. Although we have not physically separated and analyzed apatite from the Cone Pond soils, our geochemical regression approaches suggest that its $^{87}Sr/^{86}Sr$ ratio should be between $\sim$0.7095 and 0.714 and similar to that of plagioclase. We note that this value is substantially less than that inferred for apatite ($\sim$0.722) at the nearby Hubbard Brook watershed (Blum et al. 2002).

In addition to providing information about the Sr isotope composition of specific minerals, linear regression of digestible component data can be used to infer the isotopic composition of Sr released during weathering of one soil component to form another. For example, we suggest that the digestible fraction of the Oa horizon represents a reasonable long-term weathering residue of underlying mineral soils. In Figure 3b we compare $^{87}Sr/^{86}Sr$ and Nb/Sr ratios of the digestible fraction of the Oa horizon with those of the average of underlying weathered mineral soils (B- or (B + E)-horizons) from each soil profile. Nb is used as a concentration index due to its immobility during weathering processes. We prefer to use Nb as the immobile index element in such calculations because, compared to titanium (Ti) and zirconium (Zr) concentrations, Nb concentrations in soils are less likely to be biased by accumulation or loss of heavy minerals such as titanomagnetite and zircon due to preferential translocation. By using the Nb/Sr ratio to index Sr losses, a straight line drawn in Figure 3b from the composition of the digestible fraction of the Oa horizon through that of the underlying mineral soils and projected to the $^{87}Sr/^{86}Sr$ axis intersects the isotopic ratio of Sr that was lost from the underlying mineral soils due to weathering to form the mineral component of the Oa horizon (Bullen et al. 1999). Based on this graphical approach, the $^{87}Sr/^{86}Sr$ ratio of Sr derived from weathering of the mineral soils ranges from $\sim$0.724 to 0.726. These values lie within the range proposed by Bailey et al. (1996) for mineral weathering on a watershed scale at Cone Pond ($^{87}Sr/^{86}Sr$ = 0.723–0.727), and provide additional confidence in that range of values.

$^{87}Sr/^{86}Sr$ ratios, Ca concentrations (representative of the alkaline earth elements) and K concentrations of the decadal tree core increments are plotted in Figure 4a–c, respectively. K concentration patterns are included here to demonstrate the lack of elevated abundances in old wood. Elevated abundances of K that are not simply compensatory for decreasing alkaline earth element abundances (i.e., in a charge-balance sense) are indicative of infection that can allow remobilization of metals in red spruce (Ostrofsky et al. 1997), a situation that would severely limit our ability to make meaningful interpretations of the data.

There is considerable inter-tree variability in ranges of $^{87}Sr/^{86}Sr$ and element concentrations that makes inter-comparison of relative temporal trends

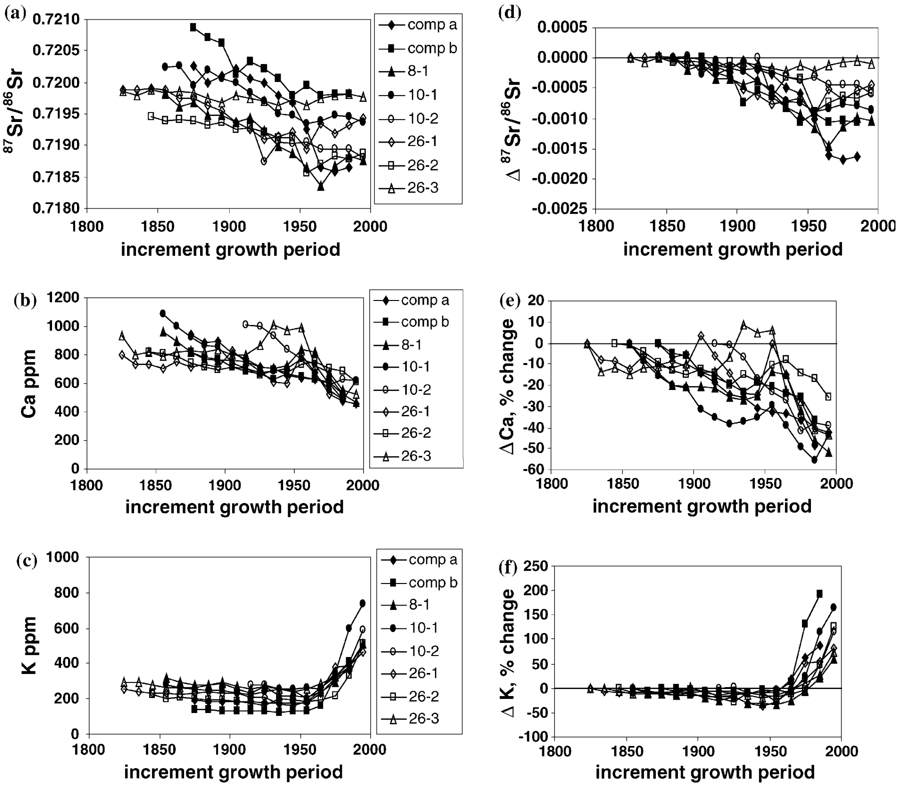

Figure 4. $^{87}Sr/^{86}Sr$ ratios, Ca concentrations and K concentrations of decadal increments of spruce stemwood cores plotted as function of increment growth period in terms of absolute values (a–c, respectively) and in terms of a 'delta' factor d–f, respectively) which compares the absolute value for each decadal increment to the absolute value for the oldest decadal increment of each core.

difficult. In order to more effectively compare relative trends, the data are plotted in Figure 4d–f in terms of a 'delta' factor that gives the absolute difference in ^{87}Sr/^{86}Sr and the percentage difference in element concentrations of the individual decadal increments relative to the composition of the oldest decadal increment of each individual tree. Using this approach, we observe that ^{87}Sr/^{86}Sr ratios and alkaline earth element concentrations tend to be greatest in the oldest decadal increments and least in the youngest decadal increments of each tree. K concentrations display much less variability compared to the alkaline earth elements, although concentrations increase substantially over the last several decades. This late-stage K concentration increase is a common feature of healthy red spruce that may reflect either charge-balance compensation for the decreasing alkaline earth concentrations or an increase of cytoplasmic K in the younger stemwood (Momoshima and Bondietti 1990).

Previous work by tree physiologists has demonstrated that the pattern of decreasing alkaline earth element concentrations with decreasing growth ring age and increasing tree radius is typical of normal growth conditions. Development of this pattern is generally ascribed to the progressive decrease in the number of pectate sites available for binding of these and other metals (Momoshima and Bondietti 1990), although biotic sequestration through stand development may likewise play a role (Johnson et al. 1994). However, the patterns for Ca (and the other alkaline earths elements) are clearly non-linear with age, and display varying deviations toward greater concentrations at various times during the period from 1900 to 1960. There is no clear relationship between the timing of these excursions and tree age. For example, Ca concentrations in stemwood from trees 10-1 and 26-3 both begin to increase in the 1920–1930's, even though they differ in age as canopy trees by 30 years. Moreover, tree 26-1 actually exhibits two distinct episodes of increasing Ca concentration of stemwood, in the 1900's and the 1950's, at different times than similarly aged tree 26-3. Overall, the alkaline earth element concentration patterns appear to reflect local environmental influences rather than tree age.

Five of the individual trees and the two 3-tree composites have dated wood ranging from 1870 to 1990. Combining the data for these samples allows a more straightforward evaluation of compositional variability and trends for the tree population, and eliminates potential bias when comparing patterns for individual trees and the composite samples (Table 2). In Figure 5a–f, the weighted average of the decadal increments (i.e., 3-times weighting for the 3-tree composites, 1-time weighting for the individual trees) and the standard deviation of the population for each decade are plotted for Mg, Ca, Sr and Ba concentrations, and ^{87}Sr/^{86}Sr and Sr/Ba$_{\mathrm{molar}}$ ratios, respectively. Again, the data are plotted in terms of a 'delta' factor that compares the weighted average composition of increments for each decade to the weighted average composition of the 1870's decadal increments, on a percentage difference basis for Mg, Ca, Sr, Ba and Sr/Ba$_{\mathrm{molar}}$ ratios and on an absolute difference basis for ^{87}Sr/^{86}Sr.

Using this approach, several important features of the temporal patterns are revealed. First, variability of alkaline earth element concentrations generally increases with time and reaches a maximum in the period from 1940 to 1960. Second, the overall patterns of decreasing concentrations of all alkaline earth elements display inflections toward leveling to increasing concentrations during the period from 1930 to 1960. The inflections for the nutrient cations Mg and Ca are substantially greater than those for the non-nutrient cations Sr and Ba, and given the pattern for Sr/Ba$_{\mathrm{molar}}$, the inflection for Ba is greater than that for Sr. Third, by the 1920's Δ ^{87}Sr/^{86}Sr of stemwood became statistically less than that of pre-1900's wood ($p < 0.01$; Student's t-test comparing individual

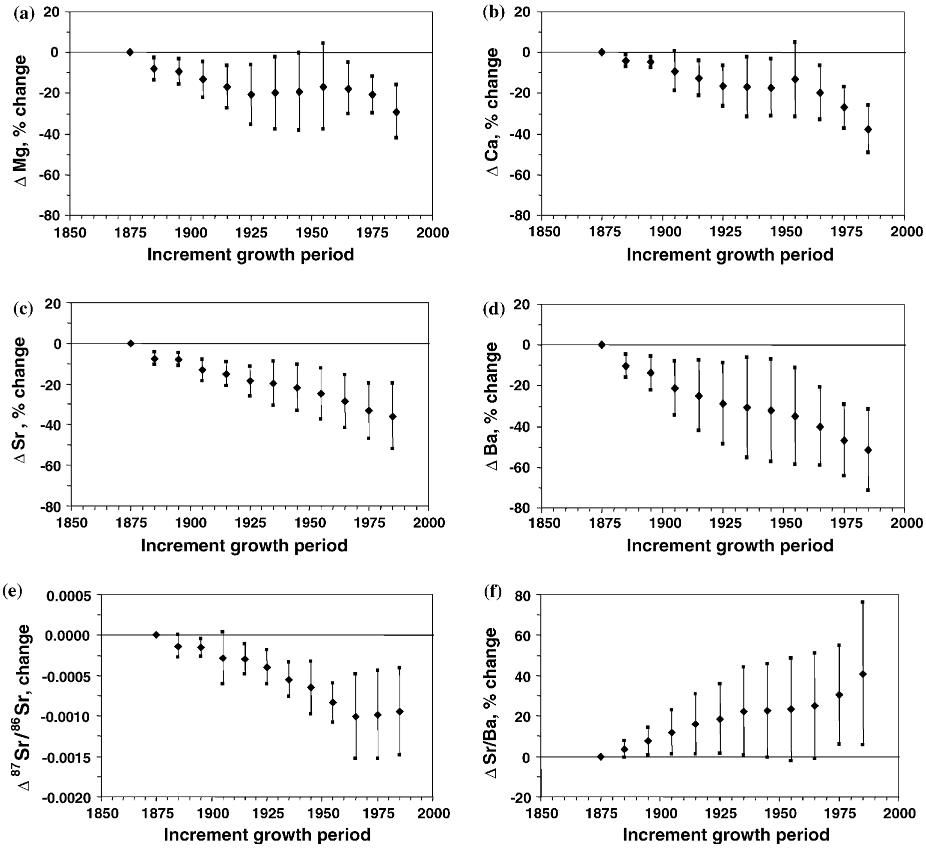

Figure 5. Weighted average (solid diamonds) and standard deviation (lines above and below diamonds) of relative Mg, Ca, Sr and Ba concentrations, ^{87}Sr/^{86}Sr and Sr/Ba$_{\mathrm{molar}}$ ratios for spruce stemwood cores having dated wood from 1870 to 1990 (Table 2). Concentrations are plotted in terms of a 'delta' factor that compares the absolute value of the weighted average of increments for each decade to the absolute value for the weighted average for the 1870's decadal increments. The two 3-tree composites are given a three-times weighting compared to the samples from individual trees.

decade and pre-1900's sample populations), suggesting a transition to a new alkaline earth element uptake regime characterized by lower $^{87}Sr/^{86}Sr$ ratios. Fourth, although not plotted here, there is an excellent correlation between average decadal increment wood mass and Ca concentration ($R^2 = 0.91$, $n = 12$; Table 2). In detail, average decadal increment wood mass actually increased during the period from 1920 to 1940 after having progressively decreased during the period from 1870 to 1920. Fifth, trees sampled from the same site can have markedly different stemwood composition patterns (e.g., trees 26-2 and 26-3), suggesting heterogeneities at the plot scale for soil composition and the inter-tree scale for nutrient uptake depth. Sixth, given that Sr and Ba should behave similarly during root uptake and neither cation plays an active nutritional role, the considerable variability of Sr/Ba ratios in the stemwood population should reflect similar variability in the soil source pools.

Bark and foliage have significantly greater concentrations of all analyzed elements compared to stemwood and roots. Bark samples from the canopy trees ($n = 7$) have Ca/Sr ratios that are 1.5 to 3 times those of the youngest stemwood increment, but Sr/Ba ratios that are approximately 0.8 times (i.e., more similar to) those of the youngest stemwood increment of their corresponding trees. These data suggest that bark formation is an important process that can fractionate the alkaline earth elements, and particularly Ca and Sr, with respect to each other at a given height of the tree. The foliage samples of the sub-canopy trees have greater Ca/Sr ratios but similar Sr/Ba ratios compared to those of stemwood or roots. Alkaline earth element concentrations of foliage increase with increasing needle age, as do (in general) Ca/Sr and Sr/Ba ratios (Appendix 1). In the two sub-canopy trees for which both stemwood and roots were analyzed, Ca/Sr ratios of the stemwood are 1.5 to 2 times greater than those of the roots, while Sr/Ba ratios are similar. Taken together, these new data for the sub-canopy trees confirm the results of earlier studies (e. g., Bailey et al. 1996; Poszwa et al. 2000) that alkaline earth element fractionation, particularly between Ca and Sr, can occur within healthy spruce after uptake from soil nutrient pools. The data further suggest that Sr/Ba ratios of stemwood may provide a better proxy of root composition than Ca/Sr ratios.

Discussion

Alkaline earth element source pool identification

Chemical approaches for identification of nutrient sources require an understanding of the nutrient pools that are actually available to fine roots in soils. The conventional approach is to consider the exchangeable ions in soils to be the most 'plant available' (e.g., Suarez 1996), although any laboratory procedure for the determination of exchangeable inventories is strictly operational and may not truly approximate nutrient uptake by fine roots. On the other hand, Kennedy et al. (2002) found that plants rooted in shallow soil at a Chilean watershed did not take up isotopically labeled Sr residing on shallow soil exchange sites during the two years following application of the tracer to a forest plot. They suggested that the plants obtained alkaline earth elements predominantly from decomposing soil organic matter, rather than from the exchange sites. Moreover, a growing body of research has suggested that fine roots and their fungal associates are able to derive nutrients directly from minerals, utilizing chemical exudates that are more aggressive than typical salt extractants (e.g., Van Breeman et al. 2000; Wallander 2000; Wallander et al. 2002).

We suggest that a more reasonable estimate of plant-available soil pools is obtained by considering the operational exchangeable and leachable fractions of the soils together as a bulk pool. The distribution of Ca in the individual organic soil horizons provides an argument in favor of this approach. As shown in Table 1, Ca is concentrated in the Oi horizon of all profiles but is effectively removed from both the exchangeable and leachable fractions of the soils as organic matter decomposition proceeds, such that Ca concentrations of those fractions in the Oa horizons are 3–35 times less than those in the Oi horizons. Moreover, Ca is removed preferentially relative to Sr, such that the Ca/Sr_{molar} ratio of the fraction removed during the Oi to Oa conversion varies from 400 to 870, a range that essentially encompasses the range observed in spruce stemwood (Appendix 1; Figure 6a). For each organic soil profile there is considerably more Ca in the leachable fraction than in the exchangeable fraction, and subtraction of exchangeable Ca alone is insufficient to account for the lower concentrations in the Oa horizons relative to those in the Oi horizons. We recognize that on the time scale of organic soil decomposition, the leachable nutrients may partially cycle onto the exchange complex prior to root uptake, but in terms of operational considerations both the exchangeable and leachable fractions of the organic soils in total are ultimately available to fine roots.

Determination of the availability of nutrients to fine roots in mineral soils is more problematic. Nutrient availability may be controlled by the ability of nutrients to enter soil water through weathering processes that are enhanced by the chemical activity of plant root tips or fungal hyphae. In this regard, we note that Bailey et al. (1996) reported a $^{87}Sr/^{86}Sr$ ratio of 0.7442 for a stream water sample collected at extreme base flow at Cone Pond. This $^{87}Sr/^{86}Sr$ ratio is considerably greater than that for monthly weighted stream flow ($\sim$0.720) as well as for the range of exchangeable Sr in our soil sample set ($\sim$0.717–0.722), but lies within the range of leachable Sr for the deeper mineral soils (Table 1). We suggest that this base flow sample represents discharge of relatively deep soil water, and that our operational leaching procedure effectively approximated its Sr isotope composition. An alternative explanation is that this base flow sample represents discharge from fractures in the underlying bedrock, which contains several minerals having $^{87}Sr/^{86}Sr$ greater than 0.750 (Bailey et al. 1996). Regardless, we note that Blum et al. (2002) needed the leaching

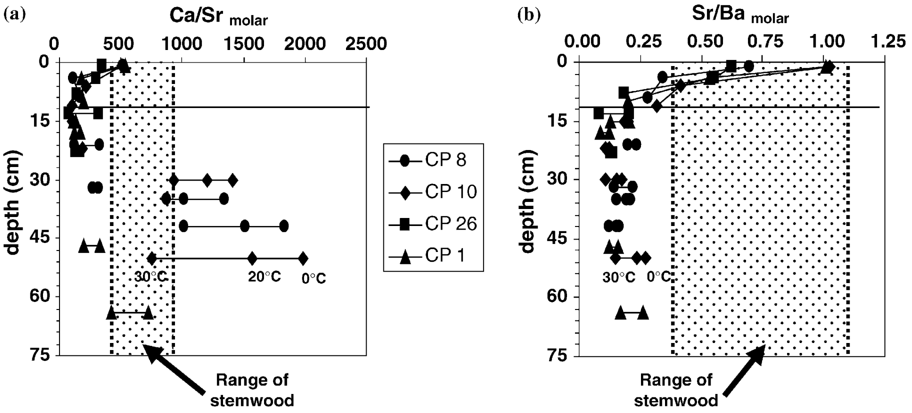

Figure 6. (a) Ca/Sr_{molar} and (b) Sr/Ba_{molar} ratios of plant-available fractions of soils plotted as a function of sample depth. Plant-available fractions were determined by combining values for exchangeable and leachable fractions at any depth. Data for samples having multiple-temperature treatments of the leachable fraction are connected by horizontal tie-lines; in each case, point at far right is 0 °C data, and temperature of treatment increases to the left. Line at ~12 cm depth in each figure corresponds to the organic soil-mineral soil boundary. Shaded region gives the range of stemwood sample compositions.

procedure employed in this study to selectively extract apatite, their favored nutrient source for ectomycorrhizal species, from the mineral soils at Hubbard Brook. Apparently, plant root exudates may be similarly aggressive in order to effectively accomplish dissolution of apatite and other primary minerals in mineral soils.

Based on these observations, we approximate plant-available alkaline earth element pools as a simple combination of the exchangeable and leachable fractions of any soil horizon. Ca/Sr_{molar} ratios of these pools (Figure 6a) decrease with depth from the Oi horizon through the upper mineral soils, but are highly variable in the lower mineral soils. Sr/Ba_{molar} ratios of these pools (Figure 6b) similarly decrease with depth from the Oi horizon through the upper mineral soils, but remain low with increasing depth through the lower mineral soils. $^{87}Sr/^{86}Sr$ ratios of these pools (Figure 7a and b) increase with depth through the organic soils, but are highly variable in the mineral soils. The variability of the Ca/Sr ratios of the mineral soil pools is complementary to that of their $^{87}Sr/^{86}Sr$ ratios, and based on the above experimental evidence is due to the variable influences of apatite dissolution and leaching of radiogenic Sr from minerals such as biotite. We contend that this variability compromises the use of Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of stemwood together in a 'multi-tracer' approach for determination of nutrient source depths. Moreover, recognition that Ca may fractionate from Sr and Ba within plants suggests that the use of Ca/Sr (or Ca/Ba) ratios of plant tissues for identification of soil Ca sources may be problematic. On the other hand, Sr/Ba ratios appear to effectively discriminate between organic and mineral soil plant-available

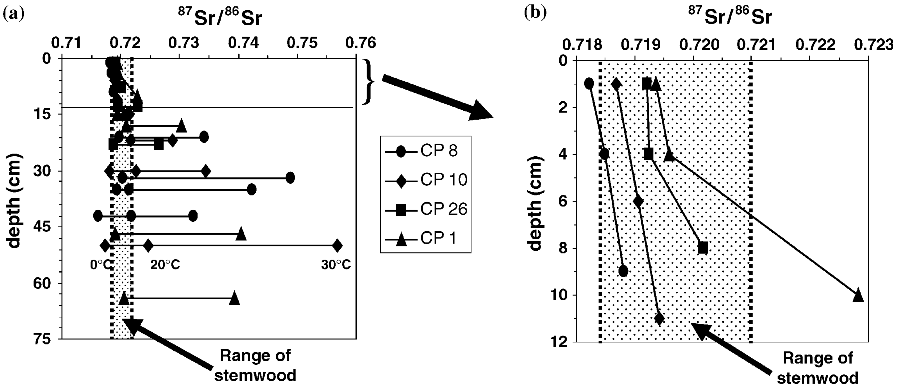

Figure 7. $^{87}Sr/^{86}Sr$ ratios of plant-available fractions of soils (calculated as in Figure 6) plotted as function of sample depth. (a) data for all samples; (b) organic horizon samples only. Shaded region gives the range of stemwood sample compositions.

alkaline earth element pools as defined here. Thus, Sr/Ba ratios of stemwood may provide an ideal tracer of nutrient source depths (i.e., organic versus mineral soil depths) particularly when considered together with $^{87}Sr/^{86}Sr$ ratios of stemwood. Unfortunately, Sr/Ba and $^{87}Sr/^{86}Sr$ ratios of stemwood considered together are unlikely to be useful for determining contributions of nutrients from soil minerals such as apatite, hornblende and Ca-oxalate that typically contain meager amounts of Sr and Ba on a total mass basis.

In Figure 8, $^{87}Sr/^{86}Sr$ and Sr/Ba_{molar} ratios of spruce stemwood are plotted in relation to our estimate of plant-available pools using the compositions for the leachable fractions obtained at 20 °C. The range of $^{87}Sr/^{86}Sr$ and Sr/Ba_{molar} ratios of the stemwood population overlaps that of the organic soils and is distinct from that of the mineral soils. In addition, although not shown in Figure 8, the data for the roots of the sub-canopy spruce samples lie within the ranges of the organic soils at their respective sites (Appendix 1). We note that the temporal trend of average stemwood composition from 1870 to 1990 (solid arrow) is toward that of the Oi horizon plant-available pool. Using data for the leachable soil fractions obtained at 30 °C (dashed arrow) or 0 °C does not affect this observation.

Causal mechanisms

The temporal patterns of alkaline earth element concentrations in the spruce stemwood (Figure 5) reflect the interplay of multiple processes. For example, overall decreasing concentrations of all alkaline earth elements in stemwood from 1870 to 1990 is consistent with an expected decreasing number of pectate sites available for cation binding in progressively younger wood (Momoshima and Bondietti 1990). Overall increasing Sr/Ba_{molar} ratios and decreasing

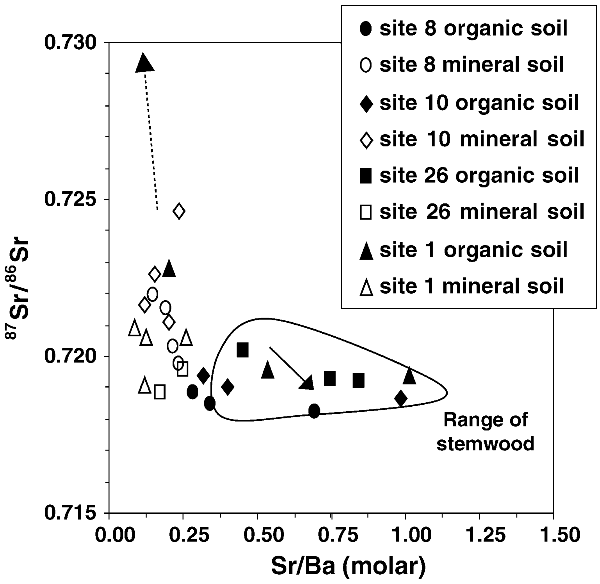

Figure 8. $^{87}Sr/^{86}Sr$ versus Sr/Ba_{molar} for plant-available fractions of soil samples (organic soils, closed symbols; mineral soils, open symbols) and stemwood samples (shown as field). Plant-available fractions determined by combining values for exchangeable and 20 °C-leachable fractions at each depth. For reference, organic soil samples having the greatest Sr/Ba_{molar} ratios at each site correspond to the Oi horizon; mineral soil samples having the greatest $^{87}Sr/^{86}Sr$ ratios at each site correspond to the deepest mineral soil. Solid arrow shows the trend of the weighted average for spruce stemwood cores having dated wood from 1870 to 1990 (Table 2); tail of arrow corresponds to 1870's data; tip of arrow corresponds to 1980's data. Dotted arrow shows the direction of offset of data for the leachable fraction obtained at 30 °C compared to that obtained at 20 °C.

$^{87}Sr/^{86}Sr$ ratios during this period (Figures 6b and 7b) are consistent with progressive shallowing of the effective depth of alkaline earth element uptake by the evolving root systems. Trends indicating shallowing of nutrient sources might reflect progressively increasing fine root density in the shallow forest floor relative to that in the lower organic and upper mineral soils over this time period, and may be a normal feature of a healthy spruce forest.

On the other hand, the pattern of leveling to increasing concentrations of all alkaline earth elements in stemwood dated from 1930 to 1960 is consistent with an abnormal enhanced mobilization of these elements from plant-available soil pools during this period. The resulting elevation of alkaline earth element concentrations in soil water leads directly to a transient increase in their concentrations in tree sap water, allowing enhanced partitioning onto wood exchange sites (Shortle et al. 1995). The coincident leveling of Sr/Ba ratios of stemwood during this period (Figure 5f) is consistent with enhanced mobilization of alkaline earth elements from plant-available pools in the mineral soils. Enhanced mobilization of cations, particularly from soil exchange sites, is an expected result of increased inorganic acidity in the soils (Shortle and

Bondietti 1992; Shortle et al. 1997; Markewitz et al. 1998; Huntington 2000). We note that the concentration increases of Mg and Ca during this period are noticeably greater on a percentage basis than those for Sr and Ba (Figure 5c and d). This is consistent with a soil acidification scenario, in that the relative efficiency of alkaline earth element mobilization from soil exchange sites due to proton transfer decreases with increasing atomic radius (Jenny and Reitemeier 1935).

Increased soil acidity could result from either a regional-scale stressor such as atmospheric deposition of inorganic acidity ('acid rain'), or a more local, transitory impact such as severe soil freezing (e.g., Mitchell et al. 1998). The timing of the deviation of alkaline earth element concentrations in stemwood from the 'normal' decreasing trend is critical for deciding between these possible causes. Evidence from the distribution of ^{90}Sr in spruce reveals that its stemwood may continue to transpire nutrients for up to 30 years following its formation (Bondietti et al. 1989). Thus, the acidification event may have occurred as many as 30 years after the formation of the earliest stemwood increment observed to have greater than expected concentrations of alkaline earth elements. Based on the average stemwood compositions (Figure 5), deviation from the trend of decreasing alkaline earth element concentrations at Cone Pond occurred in the 1930's, and thus the acidification event happened at some specific time or over some period within the 1930–1960 time frame.

Similar trends of Mg and Ca enrichment in spruce stemwood over the growth period from 1930 to 1960 have been observed in red spruce populations from throughout northern New England (Shortle et al. 1997). This period in particular was characterized by substantially increased atmospheric deposition of SO_2 and NO_x compounds relative to earlier decades (Mayewski et al. 1986; NAPAP 1993), and there is evidence that acid rain was prevalent over much of New England by the early 1950's (Cogbill and Likens 1974). On the other hand, there is no compelling evidence from climatological records from 1930 to 1960 for exceptionally cold, dry winters that would foster widespread soil freezing. Thus, we suggest that increased atmospheric deposition of inorganic acidity after 1930 followed by soil acidification is the more likely cause of alkaline earth element mobilization from soil pools as recorded in the chemistry of spruce stemwood dated from 1930 to 1960.

Strong decreases in Mg and Ca concentrations of stemwood after 1960 suggest that these nutrients may have been depleted from plant-available soil pools to such an extent that pre-acidification homeostatic concentrations in sap water were unable to be reestablished (Shortle et al. 1995; Smith and Shortle 2001). On the other hand, a generally accepted consequence of mineral soil acidification is the mobilization of monomeric aluminum (Al_i) that can poison fine root tips in contact with soil water primarily in the upper mineral and lower organic soils (Shortle and Smith 1988; Smith et al. 1995). Aluminum toxicity severely restricts or destroys the ability of fine roots to take up nutrients including alkaline earth elements. We note that the decrease of Ca concentrations in stemwood after 1960 is greater than that of Mg concentrations, consistent with laboratory physiology studies of acid-induced Al toxicity that demonstrate enhanced exclusion of Ca relative to Mg at damaged root tips (Thornton et al. 1987). Finally, the return to increasing Sr/Ba ratios during this period (Figure 5f) is consistent with renewed shallowing of the effective depth of alkaline earth element uptake.

Alternative causal mechanisms

The important temporal trends observed in the Cone Pond spruce stemwood include: (1) overall decreasing concentrations of alkaline earth elements from the 1870's to the present; (2) deviation from this 'normal' trend toward increasing concentrations of all alkaline earth elements, primarily during the period from 1930 to 1960, followed by strongly decreasing concentrations of those elements from 1960 to the present; and (3) progressively decreasing $^{87}Sr/^{86}Sr$ ratios from the 1870's to the 1960's. Although we have proposed an internally consistent set of causal mechanisms for these trends in the discussion above, there are viable alternative scenarios that must be considered. For example, depletion of Ca and other alkaline earth elements from mineral soil pools due to stand development has been hypothesized to lead to decreasing concentrations of these elements available for uptake by roots and incorporation into stemwood (Hamburg et al. 2003). However, this process was probably not important in the case of the Cone Pond spruce forest that was never logged, and thus has probably been at or near 'steady-state' at least for centuries. We prefer the explanation of Momoshima and Bondietti (1990), that overall decreasing concentrations of alkaline earth elements in progressively younger spruce stemwood is due to a decreasing number of pectate binding sites.

An alternative process that might cause deviations from this normal pattern is enhanced dissolution of nutrient-rich minerals by ectomycorrhizal fungi associated with the fine roots in response to an environmental stimulus. Van Breeman et al. (2000) suggested that nutrients derived from such biologic weathering processes can be translocated to the roots through the fungal network, even bypassing Ai_i-rich soil solutions resulting from acidification and eliminating competition for nutrient uptake by other organisms. Enhanced dissolution of Ca-rich minerals such as apatite and plagioclase can explain transient increases in Ca concentration as well as decreasing $^{87}Sr/^{86}Sr$ of stemwood, particularly given that $^{87}Sr/^{86}Sr$ of these Rb-free minerals in the Cone Pond soils is probably less than 0.714 and thus less than stemwood values. However, this scenario does not explain the similar behavior of all alkaline earth elements in stemwood during the growth period from 1900 to 1960, because Mg and Ba are not significant constituents of apatite and plagioclase. Enhanced dissolution of hornblende, the only Ca–Mg soil mineral derived from the granitic mineral source, can explain the similar behavior of Ca and Mg, but cannot explain the Sr isotope trends because $^{87}Sr/^{86}Sr$ of hornblende separated from soils at Cone Pond (0.7225; Bailey et al. 1996) is greater than that of any of the stemwood samples. Enhanced dissolution of a combination of these minerals can explain the Sr isotope trends in the stemwood from 1900 to 1960, but cannot explain the Ba systematics and should result in a greater increase of Ca concentrations compared to Mg concentrations in stemwood, and in fact the opposite is observed. We prefer the soil acidification scenario outlined above as an effective means of mobilizing all alkaline earth elements.

Although we attribute decreasing $^{87}Sr/^{86}Sr$ in spruce stemwood over the period from 1875 to 1965 to progressive shallowing of the effective depth of nutrient uptake by roots, we note that changes in atmospheric deposition may influence the Sr isotope composition of the forest floor. If $^{87}Sr/^{86}Sr$ of plant-available Sr in the forest floor changed over time due to changing amounts of atmospheric deposition, that change would have been recorded in stemwood without requiring a change of effective rooting depth. To test the ability of increased atmospheric deposition of relatively unradiogenic Sr to account for the trend of decreasing $^{87}Sr/^{86}Sr$ observed in the Cone Pond spruce stemwood population, we used a simple mass balance approach to model the Sr isotope composition of the forest floor, using present-day Sr pools and fluxes as the baseline.

In this model, the $^{87}Sr/^{86}Sr$ ratio of the forest floor in any year is given by the expression:

$$\frac{X_{ff}*I_{ff}+X_{ppt}*I_{ppt}+X_{tf}*I_{tf}+X_{lit}*I_{lit}+X_{wth}*I_{wth}-X_{upt}*I_{ff}-X_{lch}*I_{ff}-(X_{ppt}-X_{ppt,base})*I_{ff}}{X_{ff}+X_{ppt}+X_{tf}+X_{lit}+X_{wth}-X_{upt}-X_{lch}-(X_{ppt}-X_{ppt,base})}$$

where ‘X’ terms are Sr pool sizes (mol/ha) or annual Sr fluxes (mol/ha-y^{-1}), ‘I’ terms are $^{87}Sr/^{86}Sr$ ratios of pools or annual fluxes, and subscripts denote the following ecosystem components: ff, forest floor; ppt, precipitation; tf, throughfall; lit, litter; wth, mineral weathering; upt, biomass uptake; lch, leaching losses; ppt, base, baseline precipitation value. Sr pool sizes and annual fluxes were calculated by dividing Ca pool sizes and annual fluxes given in Bailey et al. (1996) by the following Ca/Sr molar ratios: forest floor, 350; precipitation, 700; throughfall, 800; litter, 500; mineral weathering, 200; biomass uptake, 500; leaching losses, 350. $X_{ppt,\ base}$ was taken to be equivalent to the Sr flux in precipitation measured at Cone Pond during the 1990’s. This finite difference model assumes that spruce take up Sr from the forest floor only, and that changing atmospheric deposition of Sr is offset by equal adjustment of biologic uptake and leaching loss terms, such that the size of the forest floor Sr pool remains fixed. The model further assumes that $^{87}Sr/^{86}Sr$ ratios of litter and throughfall in any year are equal to that of average uptake during the previous 50 years of forest growth, that the flux of Sr to the forest floor from mineral weathering is constant and has $^{87}Sr/^{86}Sr = 0.725$, and that $^{87}Sr/^{86}Sr$ of atmospheric deposition is 0.710 (Bailey et al. 1996).

In order to approximate the average trend of $^{87}Sr/^{86}Sr$ of the spruce stemwood over the period from 1875 to 1985 (Table 2) with the calculated Sr

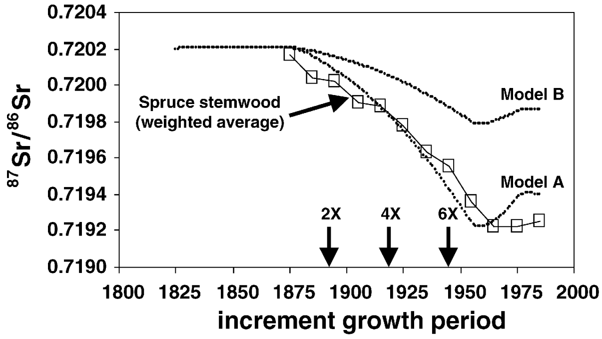

Figure 9. Results of mass balance model describing evolution of $^{87}Sr/^{86}Sr$ of the forest floor in response to changing atmospheric deposition of Sr. Sr deposition was assumed to be equal to the 'baseline' value (present-day Sr deposition flux) from 1825 to 1875. Beginning in 1875, Sr deposition was increased annually by a set increment, reaching a maximum in 1955. After 1955, Sr deposition was decreased annually by a set increment, returning to the baseline value in 1975. Curve labeled 'model A' shows result when the maximum deposition value was adjusted to give agreement between model results and the trend of weighted average spruce stemwood compositions (Table 2; open squares). 'X-factor' arrows show year in which Sr deposition for this model reached 2 times, 4 times and 6 times baseline levels. Curve labeled 'model B' shows result when the maximum deposition value was taken to be that measured at Hubbard Brook watershed from 1963 to 1966 (Likens et al. 1998).

isotope composition of the forest floor, it was necessary to progressively increase atmospheric deposition of Sr from the baseline level (0.029 mol/ha-y^{-1}) in 1875 to 0.205 mol/ha-y^{-1} in 1955 (i.e., by 0.0022 mol/ha-y^{-1}). Atmospheric deposition of Sr was then decreased back to the baseline level by a fixed amount annually over the period from 1955 to 1975, consistent with our knowledge of regional trends based on work at Hubbard Brook (Likens et al. 1998). In Figure 9, the results of this calculation ('model A') are compared to the average trend of the spruce stemwood data.

The ~7-fold increase of Sr (and Ca) flux from atmospheric deposition over baseline values required by the model is consistent with the ~6-fold difference between Ca concentration measured in regional precipitation in 1955–1956 (12.5 μmol/*l*; Junge and Werby, 1958) and that measured in precipitation at Cone Pond during the early 1990's (2 μmol/l; Bailey et al. 1996). However, apart from this single measurement of Ca in pre-1960's precipitation, there is no compelling evidence that the long-term concentration of Ca in regional precipitation ever exceeded the well-constrained levels measured during the early years of monitoring at Hubbard Brook (6.6 μmol/*l* for the period from 1963 to 1966; Likens et al. 1998). Using this latter value to determine maximum Sr deposition for the model produces the curve labeled 'model B' in Figure 9, which clearly does not provide a good fit with the stemwood data. Moreover, in order to account for decreasing $^{87}Sr/^{86}Sr$ of stemwood prior to 1917, 'model A' requires that atmospheric deposition of Sr would have quadrupled over baseline levels by that time (Figure 9), an increase that we view as highly unlikely and for which there is no independent evidence. Finally, little is known about the timeframe of bioavailability of cations in atmospheric deposition, making it difficult to judge the reasonability of any particular model result. Although changes in atmospheric deposition of Sr may have had some effect on the ^{87}Sr/^{86}Sr ratios observed in spruce at Cone Pond, it is unlikely to have been the major controlling factor due to the substantial chemical buffering capacity of the large pool of Ca in both the forest floor and in litter derived largely from older biomass and returned to the forest floor on an annual basis.

Implications

Our results suggest that the spruce forest at Cone Pond depends on the forest floor as its primary source of Ca and other alkaline earth elements, consistent with the observations of Kennedy et al. (2002) in their study of a pristine forest ecosystem in southern Chile. This conclusion provides an alternative view of Ca nutrition dynamics compared to that of Blum et al. (2002), whose study at the nearby Hubbard Brook watershed emphasized the importance of selective weathering of apatite by ectomycorrhizal hyphae associated with fine spruce roots in the deepest mineral soils. The contrast of conclusions is intriguing, particularly given that the lithologies comprising the till mantle at Hubbard Brook are essentially identical to those at Cone Pond (Bailey and Hornbeck 1992; Bailey et al. 2003), and thus any assessment of soil source pools of Ca at one watershed should be largely applicable to the other.

Based on the assumption of negligible discrimination of Ca from Sr within spruce, Blum et al. (2002) suggested that selective apatite dissolution was the primary cause of high Ca/Sr ratios of spruce foliage compared to those of the bulk mineral soils at Hubbard Brook. In support of selective apatite weathering, they noted that experimental leachates of the deepest mineral soils, using 1 *N* HNO_3 at 20 °C, had the P/Ca stoichiometry of apatite and ^{87}Sr/^{86}Sr similar to that of the spruce foliage. In contrast, we contend that foliar Ca/Sr ratios of spruce grown in soils developed on granite are likely to be poor indicators of soil Ca sources. Our data, considered together with that of Bailey et al. (1996) and Poszwa et al. (2000), reveal that in such settings Ca/Sr ratios of spruce foliage are significantly greater than those of stemwood, primarily due to preferential sequestration of Ca in foliage as it ages. We point out that stemwood has Ca/Sr ratios similar to or slightly greater than that of the plant-available fraction of the forest floor, the main rooting zone of spruce. Finally, the results of our multiple-temperature leachate experiments and the mineral soil isochron calculation indicate that the ^{87}Sr/^{86}Sr ratio of apatite at Cone Pond is less than 0.714, substantially less than that observed in any spruce tissue.

Although mixing calculations based on Ca/Sr ratios indicate that some ecosystem pools including soil water and plants must derive a large percentage of their Ca from a high-Ca/Sr source such as apatite (cf., Blum et al. 2002), there are other soil minerals such as hornblende and Ca-oxalate that have high Ca/Sr ratios that must likewise be considered in the mixing analysis. For example, hornblende at Cone Pond has $Ca/Sr_{molar} \sim 13{,}000$ (unpublished data), and at Hubbard Brook, Ca in hornblende constitutes essentially the same proportion of total soil Ca as does Ca in apatite (Nezat et al. 2004. We view selective apatite weathering as a potentially important, but subordinate Ca nutrition supply mechanism. Moreover, we view the use of Ca/Sr ratios of plant tissues as indicators of nutrient source pools to be problematic at best, and urge caution in their further application to forest nutrition studies.

Ca appears to be more tightly recycled within the spruce biomass-forest floor system than the other alkaline earth elements, based on the substantially greater Ca/Sr, Ca/Mg and Ca/Ba ratios of both exchangeable and leachable fractions of the Oi horizon relative to those of deeper plant-available organic soil pools. The importance of recycled forest floor Ca as the primary source of Ca for spruce nutrition is consistent with the watershed-scale view of the Ca cycle at Cone Pond (Bailey et al. 1996) and Hubbard Brook (Likens et al. 1998) which shows that Ca fluxes associated with uptake, litterfall and decomposition are at least an order of magnitude greater than input to the ecosystem from atmospheric deposition and mineral weathering and output to streamflow. Furthermore, although uptake of Ca directly from granitic and metamorphic minerals contained in the lower organic and mineral soils is likely to be ongoing and of varying relative importance, we find no evidence that either suggests or requires selective weathering of any primary soil mineral to explain the temporal trends of alkaline earth element chemistry and $^{87}Sr/^{86}Sr$ observed in our stemwood core population. Uptake of Ca by fine spruce roots from easily weathered, high Ca/Sr minerals such as apatite and hornblende may have been the predominant nutritional mechanism when the spruce forest or its precursor was first established on the fresh glacial till mantle and prior to the establishment of a thick forest floor. However, these minerals were probably a component of a mineral weathering assemblage that included other alkaline earth element-bearing minerals such as plagioclase and biotite. Thus, the overall elevated Ca/Sr and Sr/Ba ratios of the spruce forest and underlying forest floor relative to those of the bulk mineral soils and granitic/metamorphic substrate are probably long-lived characteristics of the forest, perhaps accentuated by within-tree processes and maintained by tight cycling of alkaline earth elements and concentration of fine roots in the forest floor.

This multi-tracer approach is a promising technique both for determining historic nutrient uptake trends and for assessing the impacts of, and responses to anthropogenic disturbances such as clear-cutting. For example, Hamburg et al. (2003) demonstrated that the initial response to forest harvesting is an extended period of Ca enrichment in the forest floor, presumably due to enhanced weathering of, and nutrient uptake directly from easily weathered, Ca-rich primary minerals in the C-horizon. They proposed that the operationally defined leachable fraction of C-horizon material is likely to be representative of the plant-available pool in this situation. Given our data for the leachable fractions of the deepest mineral soils at sites 8 and 10 at Cone Pond (Table 1), the proposed nutrient uptake from the C-horizon should be recorded in stemwood growth rings immediately after harvesting as increased Ca/Sr ratios, decreased $^{87}Sr/^{86}Sr$ ratios and perhaps decreased Sr/Ba ratios relative to pre-harvesting compositions. Alternatively, we note that enhanced uptake of Ca from apatite-poor plant-available pools in the B-horizon is likewise consistent with their data. In this case, nutrient uptake from the B-horizon should result in decreased Sr/Ba ratios, but only minor differences in Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of new wood. In addition to helping resolve such issues, this multi-tracer technique may be especially useful as a cost-effective means of monitoring the effectiveness of efforts to remediate anthropogenic activities, if manipulation of nutrient uptake depths is a goal of those efforts.

Summary

We used $^{87}Sr/^{86}Sr$ and Sr/Ba ratios of spruce tissues and soil fractions in a multi-tracer approach to demonstrate that the spruce forest at Cone Pond is obtaining Ca and other alkaline earth elements predominantly from the forest floor and only subordinately from mineral soil pools. Temporal trends of $^{87}Sr/^{86}Sr$ and Sr/Ba ratios in stemwood point to an increased proportion of recycled alkaline earth elements from the upper forest floor during the past 130 years, consistent with progressive shallowing of the effective depth of alkaline earth element uptake. This apparent shallowing may have been due to preferential growth and expansion of the shallow fine root network, but likewise may have occurred in response to Ca depletion and/or Al_i mobilization in the lower forest floor and upper mineral soil horizons. The timing of dendrochemical changes that suggest a response to soil acidification in stemwood dated from 1930 to 1960 is consistent with the established history of inorganic acid deposition in northeastern North America. Our results indicate that alkaline earth elements, and especially Ca are tightly recycled within this forest floor-spruce ecosystem, and thus that environmental stressors that affect the forest floor may have considerable impact on the spruce nutritional cycle. Future monitoring of $^{87}Sr/^{86}Sr$ and Sr/Ba ratios in spruce stemwood may allow us to recognize the onset or continuation of ecosystem disturbance, as well as to track the recovery of impacted systems to pre-disturbance conditions.

Acknowledgements

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Appendix 1. Data for canopy and sub-canopy tree samples. The first number in each sample name indicates the sampling site. Wood mass for decadal increments of stemwood cores is given in grams; element concentrations of all samples are given in μg/g of dried material; Ca/Sr and Sr/Ba ratios are given in molar proportions. Composites 10-A and 10-B are composites of cores from three trees each collected for a previous study (Shortle et al., 1997); other canopy trees are represented by a single core. All cored trees were dominant or co-dominant in the forest canopy.

	Wood mass	^{87}Sr/^{86}Sr	Ca/Sr	Sr/Ba	Ca	Mg	Sr	Ba	K	Al
Tree 8-1:										
1850's	0.1241	0.71981	548	0.61	963	105.9	3.8	9.9	319	1.9
1860's	0.2370	0.71961	573	0.63	893	96.3	3.4	8.6	295	1.0
1870's	0.1992	0.71968	569	0.69	822	88.6	3.2	7.2	281	3.3
1880's	0.1416	0.71947	587	0.76	773	79.7	2.9	6.0	276	1.6
1890's	0.1319	0.71947	619	0.82	763	77.2	2.7	5.2	287	2.0
1900's	0.0765	0.71937	634	0.85	766	76.4	2.6	4.9	257	4.6
1910's	0.0810	0.71944	638	0.87	756	75.0	2.6	4.7	236	2.2
1920's	0.0940	0.71924	652	0.91	716	71.7	2.4	4.1	268	1.6
1930's	0.1051	0.71899	677	0.90	704	73.7	2.3	4.0	220	1.9
1940's	0.0863	0.71888	731	0.84	722	79.0	2.2	4.1	217	1.7
1950's	0.0705	0.71866	961	0.71	834	89.1	1.9	4.2	211	1.1
1960's	0.0524	0.71835	979	0.66	819	89.5	1.8	4.4	238	1.7
1970's	0.0773	0.71867	957	0.70	651	80.9	1.5	3.3	296	2.3
1980's	0.0692	0.71883	756	0.77	521	84.2	1.5	3.1	389	1.5
1990's	0.0515	0.71877	681	0.71	467	90.5	1.5	3.3	509	2.6
bark		0.71854	1832	0.46	17825	721.1	21.3	72.3	1576	13.7
Tree 10-1:										
1850's	0.0935	0.72023	375	0.62	1090	130.7	6.3	16.2	277	3.5
1860's	0.1184	0.72027	376	0.62	996	119.7	5.8	14.8	260	3.8
1870's	0.1153	0.71995	383	0.64	922	110.6	5.3	13.0	252	2.5
1880's	0.1045	0.72019	382	0.67	870	103.1	5.0	11.6	249	2.4
1890's	0.0902	0.72005	387	0.72	860	98.4	4.9	10.7	247	3.1
1900's	0.1319	0.72000	368	0.75	745	87.8	4.4	9.3	230	2.8
1910's	0.1292	0.71984	366	0.78	705	79.3	4.2	8.5	227	2.5
1920's	0.1233	0.71971	365	0.82	673	77.3	4.0	7.7	240	2.2
1930's	0.1454	0.71951	371	0.79	682	85.1	4.0	8.1	252	1.6
1940's	0.0860	0.71948	374	0.88	707	98.8	4.1	7.4	256	1.4
1950's	0.0532	0.71935	399	0.94	771	114.9	4.2	7.1	265	1.7
1960's	0.0530	0.71939	337	0.94	665	111.2	4.3	7.3	253	3.5
1970's	0.0479	0.71947	324	0.93	551	85.1	3.7	6.3	346	2.6
1980's	0.0530	0.71945	267	0.88	482	75.6	3.9	7.1	597	3.6
1990's	0.0504	0.71937	329	0.73	616	106.9	4.1	8.8	736	4.6
bark		0.71890	697	0.50	15774	108.4	49.5	156.3	259	56.1

Appendix 1. Continued.

	Wood mass	^{87}Sr/^{86}Sr	Ca/Sr	Sr/Ba	Ca	Mg	Sr	Ba	K	Al
Tree 10-2:										
1910's	0.2331	0.71938	419	0.46	1005	122.1	5.2	18.1	276	3.9
1920's	0.2572	0.71873	418	0.47	998	117.5	5.2	17.4	281	4.8
1930's	0.2005	0.71906	442	0.49	936	115.6	4.6	14.7	253	5.1
1940's	0.2293	0.71902	475	0.49	837	109.8	3.9	12.3	251	5.9
1950's	0.2634	0.71905	430	0.63	771	99.8	3.9	9.8	201	3.2
1960's	0.2291	0.71893	497	0.55	736	100.6	3.2	9.2	262	3.5
1970's	0.2184	0.71894	532	0.54	588	79.6	2.4	7.0	328	3.1
1980's	0.2825	0.71895	580	0.50	627	79.5	2.4	7.5	404	3.2
1990's	0.3028	0.71880	657	0.53	615	83.4	2.0	6.0	590	2.8
Inner bark		0.71881	1261	0.45	13192	481.5	22.9	79.3	3512	11.5
Outer bark		0.71888	897	0.33	4797	114.5	11.7	55.3	378	15.1
Composite 10-A:										
1870's	0.1121	0.72026	429	0.56	947	118.0	4.8	13.5	197	5.7
1880's	0.1084	0.72000	450	0.57	884	99.8	4.3	11.8	186	4.7
1890's	0.1140	0.72010	438	0.61	894	100.4	4.5	11.6	189	4.6
1900's	0.1092	0.72022	443	0.64	809	96.0	4.0	9.8	182	5.8
1910's	0.1144	0.72007	431	0.70	771	90.7	3.9	8.8	184	5.1
1920's	0.1132	0.72000	419	0.73	718	82.4	3.7	8.1	175	5.1
1930's	0.1108	0.71978	414	0.82	703	84.3	3.7	7.1	180	5.2
1940's	0.1116	0.71968	412	0.84	657	79.3	3.5	6.6	177	5.2
1950's	0.1153	0.71926	421	0.85	638	75.9	3.3	6.1	178	4.7
1960's	0.1124	0.71865	433	0.89	630	86.8	3.2	5.7	234	4.8
1970's	0.1108	0.71858	428	0.92	604	91.9	3.1	5.3	319	5.6
1980's	0.1110	0.71864	375	1.09	486	81.9	2.8	4.1	367	4.9
Composite 10-B:										
1870's	0.1147	0.72086	450	0.52	821	82.3	4.0	12.0	139	6.1
1880's	0.1119	0.72071	466	0.56	783	76.6	3.7	10.3	138	4.8
1890's	0.1162	0.72061	465	0.58	773	74.0	3.6	9.8	134	4.8
1900's	0.1199	0.72012	457	0.63	710	67.2	3.4	8.5	131	5.3
1910's	0.1098	0.72033	457	0.65	689	64.4	3.3	8.0	130	5.5
1920's	0.1120	0.72022	467	0.64	663	59.5	3.1	7.6	129	5.5
1930's	0.1113	0.72005	480	0.65	629	53.7	2.9	7.0	125	4.8
1940's	0.1126	0.71979	512	0.64	668	53.9	2.9	7.0	134	4.8
1950's	0.1207	0.71995	522	0.65	650	56.8	2.7	6.6	130	4.8
1960's	0.1127	0.71980	546	0.63	627	58.4	2.5	6.3	159	4.9
1970's	0.1113	0.71982	550	0.64	608	62.1	2.4	5.9	322	6.3
1980's	0.1133	0.71981	550	0.64	523	52.7	2.1	5.1	408	6.1
Tree 26-1:										
1740's	0.0283	0.71994	367	0.42	829	145.0	4.9	18.7	262	15.8
1750's	0.0556	0.71979	355	0.37	739	127.3	4.6	19.3	242	13.9
1760's	0.0209	0.71977	306	0.42	628	130.0	4.5	16.7	259	20.3
1770's	0.0111	0.71969	341	0.42	696	125.0	4.5	16.9	268	44.1
1780's	0.0294	0.71972	318	0.44	642	121.2	4.4	15.8	262	12.1
1790's	0.0287	0.71961	346	0.44	713	120.0	4.5	16.0	278	14.8
1800's	0.0464	0.71981	339	0.44	689	114.1	4.5	16.0	263	10.0

Appendix 1. Continued.

	Wood mass	^{87}Sr/^{86}Sr	Ca/Sr	Sr/Ba	Ca	Mg	Sr	Ba	K	Al
1810's	0.0787	0.71989	370	0.45	676	106.6	4.0	14.0	263	7.7
1820's	0.1142	0.71987	426	0.45	799	108.0	4.1	14.2	254	6.8
1830's	0.1253	0.71988	390	0.45	736	101.0	4.1	14.4	239	6.2
1840's	0.1176	0.71991	403	0.46	730	94.2	4.0	13.6	233	5.9
1850's	0.1136	0.71987	407	0.47	701	91.2	3.8	12.7	234	4.8
1860's	0.0983	0.71974	378	0.40	749	92.0	4.3	16.9	228	6.0
1870's	0.1126	0.71975	380	0.48	716	83.6	4.1	13.7	229	6.0
1880's	0.0837	0.71963	405	0.46	732	82.0	4.0	13.5	239	5.8
1890's	0.0940	0.71955	384	0.48	710	78.0	4.0	13.2	232	5.3
1900's	0.0633	0.71936	451	0.45	828	81.8	4.0	14.2	235	7.3
1910's	0.0607	0.71925	406	0.41	750	82.1	4.0	15.5	208	7.7
1920's	0.0667	0.71910	393	0.40	683	76.5	3.8	14.9	211	7.7
1930's	0.0607	0.71915	362	0.41	607	82.2	3.7	14.0	174	8.0
1940's	0.0471	0.71920	358	0.41	603	88.2	3.7	14.2	161	8.4
1950's	0.0615	0.71893	435	0.45	797	85.0	4.0	14.0	184	36.1
1960's	0.0776	0.71935	363	0.47	680	81.0	4.1	13.8	249	5.8
1970's	0.0382	0.71919	276	0.49	523	81.5	4.1	13.4	383	9.5
1980's	0.0261	0.71933	247	0.49	478	80.4	4.2	13.5	391	10.1
1990's	0.0262	0.71944	237	0.53	461	86.1	4.3	12.7	466	9.8
bark		0.71938	707	0.40	11531	254.9	35.7	141.2	681	18.1
Tree 26-2:										
1840's	0.2560	0.71945	462	0.40	820	88.1	3.9	15.3	225	1.1
1850's	0.1814	0.71938	439	0.41	811	89.4	4.0	15.6	203	2.1
1860's	0.2372	0.71940	437	0.41	786	88.8	3.9	15.1	210	2.0
1870's	0.2442	0.71939	434	0.41	745	89.2	3.7	14.3	205	2.4
1880's	0.2235	0.71931	437	0.41	712	86.1	3.6	13.8	194	1.9
1890's	0.2052	0.71937	449	0.41	700	85.0	3.4	13.2	192	2.1
1900's	0.1675	0.71926	453	0.42	718	85.0	3.5	12.9	189	2.0
1910's	0.1600	0.71927	456	0.44	704	81.0	3.4	12.2	180	2.1
1920's	0.1509	0.71922	433	0.46	658	75.4	3.3	11.5	163	2.8
1930's	0.1634	0.71913	436	0.46	698	79.0	3.5	12.0	203	3.0
1940's	0.2020	0.71911	456	0.43	672	75.7	3.2	11.7	193	2.3
1950's	0.2000	0.71855	525	0.38	732	76.3	3.0	12.7	184	2.1
1960's	0.2567	0.71870	602	0.39	754	79.9	2.7	11.1	196	1.7
1970's	0.1400	0.71882	645	0.46	702	73.2	2.4	8.2	216	1.9
1980's	0.0781	0.71878	574	0.51	681	61.0	2.6	8.1	333	2.2
1990's	0.0752	0.71888	525	0.44	608	61.1	2.5	9.1	508	1.3
bark		0.71903	1035	0.35	14664	296.2	31.0	139.6	818	6.8
Tree 26-3:										
1750's	0.0564	0.71965	274	0.59	1014	124.9	8.1	21.6	334	3.2
1760–1770's	0.0333	0.71980	275	0.60	975	120.6	7.7	20.5	319	3.4
1780–1790's	0.0399	0.71590	277	0.60	1009	122.3	8.0	20.9	323	3.3
1800–1810's	0.0376	0.71990	273	0.60	977	119.9	7.8	20.4	306	3.0
1820's	0.1004	0.71986	274	0.61	929	113.4	7.4	19.1	296	2.5
1830's	0.1133	0.71978	286	0.62	803	106.6	6.1	15.5	291	16.2
1840's	0.1074	0.71987	288	0.63	820	104.8	6.2	15.7	279	1.9
1850's	0.1066	0.71984	299	0.62	788	102.1	5.8	14.7	261	2.0

Appendix 1. Continued.

	Wood mass	^{87}Sr/^{86}Sr	Ca/Sr	Sr/Ba	Ca	Mg	Sr	Ba	K	Al
1860's	0.0778	0.71986	303	0.61	822	102.5	5.9	15.2	262	1.9
1870's	0.0675	0.71983	306	0.62	825	103.8	5.9	15.0	261	1.7
1880's	0.0923	0.71974	310	0.62	823	104.0	5.8	14.8	280	1.5
1890's	0.0837	0.71968	322	0.59	840	110.6	5.7	15.3	298	1.9
1900's	0.0944	0.71980	316	0.57	801	108.8	5.5	15.4	270	0.8
1910's	0.0976	0.71974	325	0.56	804	109.1	5.4	15.3	254	0.8
1920's	0.1184	0.71970	335	0.54	870	122.4	5.7	16.5	273	1.0
1930's	0.0972	0.71963	355	0.52	1011	127.4	6.2	18.9	254	0.7
1940's	0.0658	0.71973	343	0.52	976	124.5	6.2	18.7	240	1.0
1950's	0.0703	0.71964	375	0.55	988	128.7	5.8	16.4	256	1.3
1960's	0.0620	0.71974	305	0.65	721	86.5	5.2	12.5	285	3.2
1970's	0.0577	0.71979	313	0.71	673	65.6	4.7	10.4	324	3.0
1980's	0.0397	0.71981	265	0.76	550	53.9	4.5	9.5	378	3.1
1990's	0.0421	0.71977	262	0.58	528	59.6	4.4	12.0	514	3.7
bark		0.71973	568	0.51	17785	436.8	68.4	210.2	1817	31.3
Sub-conopy:										
Tree 8-2 (0.7 m):										
bark		0.71919	736	0.36	19187	526.4	57.0	251.1		
Inner wood		0.71934	401	0.43	1035	105.5	5.6	20.9		
Roots		0.71975	278	0.36	1979	817.5	15.6	67.7		
Tree 10-3 (2.6 m)										
Current foliage		0.71953	339	0.59	962	536	6.2	16.6		
1 yr old foliage		0.71942	497	0.68	3236	667	14.2	33.0		
2 yr old foliage		0.71940	604	0.63	3316	623	12	30.3		
3 yr old foliage		0.71957	775	0.78	5273	880	14.9	30.2		
Tree 10-4 (0.3 m):										
Current foliage		0.71953	358	0.62	776	508.8	4.7	12.0		
1 yr old foliage		0.71933	336	0.78	2106	834.7	13.7	27.6		
2 yr old foliage		0.71944	548	0.76	3138	723.4	12.5	26.1		
Inner wood		0.71956	314	0.68	811	140.6	5.6	13.1		
Roots		0.71990	149	0.77	683	455.2	10.0	20.5		
Tree 10–5 (seedling):										
Current foliage		0.71929	739	0.51	1329	492.7	3.9	12.2		
1 yr old foliage		0.71906	572	0.62	3112	828.7	11.9	30.0		
Roots		0.71935	432	0.57	2795	468.3	14.1	38.8		

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