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SYNTHESIS AND EMERGING IDEAS

Use of foliar Ca/Sr discrimination and ^{87}Sr/^{86}Sr ratios to determine soil Ca sources to sugar maple foliage in a northern hardwood forest

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Abstract Calcium/strontium and ^{87}Sr/^{86}Sr ratios in foliage can be used to determine the relative importance of different soil sources of Ca to vegetation, if the discrimination of Ca/Sr by the plant between nutrient sources and foliage is known. We compared these tracers in the foliage of sugar maple (*Acer saccharum)* to the exchange fraction and acid leaches of soil horizons at six study sites in the White Mountains of New Hampshire, USA. In a previous study, sugar maple was shown to discriminate for Ca compared to Sr in foliage formation by a factor of 1.14 ± 0.12. After accounting for the predicted 14% shift in Ca/Sr, foliar Ca/Sr and ^{87}Sr/^{86}Sr ratios closely match the values in the Oie horizon at each study site across a 3.6-fold variation in foliar Ca/Sr ratios. Newly weathered cations, for which the Ca/Sr and ^{87}Sr/^{86}Sr ratios are estimated from acid leaches of soils, can be ruled out as a major Ca source to current foliage. Within sites, the ^{87}Sr/^{86}Sr ratio of the soil exchange pool in the Oa horizon and in the 0–10 cm and 10–20 cm increments of the mineral soil are similar to the Oie horizon and sugar maple foliar values, suggesting a common source of Sr in all of the actively cycling pools, but providing no help in distinguishing among them as sources to foliage. The Ca/Sr ratio in the soil exchange pool, however, decreases significantly with depth, and based on this variation, the exchange pool below the forest floor can be excluded as a major Ca source to the current sugar maple foliage. This study confirms that internal recycling of Ca between litter, organic soil horizons and vegetation dominate annual uptake of Ca in northern hardwood ecosystems. Refinement of our understanding of Ca and Sr uptake and allocation in trees allows improvement in the use of Ca/Sr and ^{87}Sr/^{86}Sr ratios to trace Ca sources to plants.

Keywords Foliage · Soil · Ca/Sr · ^{87}Sr/^{86}Sr · Sugar maple · *Acer saccharum*

Introduction

In the past decade interest in the biogeochemistry of Ca in forests has grown dramatically, and studies have pointed to the potential effects of Ca on a wide range of ecosystem processes (Likens et al. 1998;

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McLaughlin and Wimmer 1999; Schaberg et al. 2001). Calcium levels have been implicated as key to such factors as organic matter decomposition (Reich et al. 2005), winter frost injury to trees (Hawley et al. 2006), rates of mycorrhizal infection (Juice et al. 2006) and snail abundances (Hamburg et al. 2003). Sugar maple (*Acer saccharum* Marsh.) is a widespread and abundant tree in the northern hardwood forest, and is valued for timber, maple syrup production and fall foliar colors. In many areas sugar maple has experienced declines (Houston 1999) and deficiency of Ca often accompanies this decline (Mader and Thomson 1969; Kolb and McCormick 1993; Horsley et al. 2000). Depletion of base cations has been hypothesized as an impact of acid deposition (Likens et al. 1996) and forest harvest removes significant quantities of Ca from forest ecosystems (Johnson et al. 1992; Federer et al. 1989). Identifying the sources and pathways of Ca cycling in forest ecosystems can advance our understanding of the effects of environmental perturbations and lead to methods for ameliorating their impacts.

Given the importance of Ca to forest ecosystems, tools to track the sources, pathways and bioavailability of Ca are essential. The trace element Sr, which like Ca is an alkaline earth element, is taken up by plants in similar ways to Ca and can he used to aid in distinguishing among various sources of Ca through the use of Ca/Sr and ^{87}Sr/^{86}Sr ratios (e.g. Graustein and Armstrong 1983; Gosz and Moore 1989; Åberg et al. 1989; Miller et al. 1993; Bailey et al. 1996). Whereas Ca has important physiological functions, Sr is not known to have any function and is believed to simply substitute for Ca (Elias et al. 1982). In some ecosystem processes, such as ion exchange on clays, Ca and Sr behave almost identically (Appelo and Postma 1993) due to their divalent charge and similar hydrated radius ($r_{Ca} = 0.272$ nm vs. $r_{Sr} = 0.274$ nm; Marcus and Kertes 1968). In other processes, such as ion exchange on soil organic matter, Ca may be retained preferentially over Sr to a small degree (Baes and Bloom 1988). The ^{87}Sr/^{86}Sr ratio does not fractionate significantly upon biological uptake or ion exchange, and what little fractionation may occur is corrected during mass-spectrometer mass-bias correction (e.g. Blum et al. 2000).

Many previous studies have explored the use of Ca/Sr and ^{87}Sr/^{86}Sr ratios of foliage in forest biogeochemistry. Until recently most studies assumed that the Ca/Sr ratio did not change appreciably upon plant uptake ($\leq$a factor of 1.4) based on studies of nutrient uptake from solutions into crop plants (Runia 1987), but recently several studies have showed more widely variable Ca/Sr ratios across various tree tissues (Poszwa et al. 2000; Watmough and Dillon 2003; Bullen and Bailey 2005; Drouet and Herbauts 2007). Studies in a wide range of locations have used ^{87}Sr/^{86}Sr ratios to determine Sr sources to foliage and wood and to then infer Ca sources based on the assumption that Ca/Sr discrimination was not large (Dambrine et al. 1997; Poszwa et al. 2002, 2004; Kennedy et al. 2002; Blum et al. 2002; Dijkstra et al. 2003; Drouet et al. 2005; Berger et al. 2006). In a few recent studies, ^{87}Sr/^{86}Sr ratios in soils and trees were used to determine spatial and temporal variability in the input of Sr from atmospheric deposition and weathering, but this was not used to infer Ca sources due to the complexities of discrimination between Ca and Sr during uptake by some plant species (Porder et al. 2005; Bullen and Bailey 2005).

In a recent whole-watershed $CaSiO_3$ addition experiment at the Hubbard Brook Experimental Forest, Dasch et al. (2006) found that various plant species accumulate Ca and Sr in foliage and roots in a constant proportion relative to their nutrient source. They determined discrimination factors [$DF = (Ca/Sr_{plant\ tissue})/(Ca/Sr_{nutrient\ source})$] for foliage and roots of sugar maple and some other herb, shrub and tree species. Sugar maple was found to discriminate for Ca over Sr in foliage ($DF_{foliage} = 1.14 \pm 0.12, 1\sigma$) but to discriminate for Sr over Ca in root formation ($DF_{root} = 0.60 \pm 0.07, 1\sigma$). Dasch et al. (2006) suggested that once the discrimination factor is empirically determined for a particular plant species and tissue, Ca/Sr ratios could be used as a tracer of the sources of Ca for that species.

Previous investigations bring to light several common themes and cautions in the use of Ca/Sr and ^{87}Sr/^{86}Sr ratios to indicate Ca sources to trees. (1) Different tree species at the same site can vary in the Ca/Sr ratios in foliage, suggesting that they either take up Ca from different sources or fractionate Ca/Sr differentially. (2) Discrimination of Ca/Sr among plant tissues within a tree species can differ significantly. (3) Different soil fractions and depths at the same site may vary in Ca/Sr, depending on soil parent materials and other soil properties. (4) Use of the ^{87}Sr/^{86}Sr ratio to ascertain the proportions of Sr from atmospheric versus weathering sources can be confounded by difficulties in determining compositions released by weathering of parent materials containing a variety of minerals.

In this study, we sampled and analyzed soils at six sites with varying parent material, in even-aged forest stands ranging in age from 16 to 66 years. We limited our study to foliage of a single tree species, sugar maple, for which a foliar Ca/Sr discrimination factor had been determined previously in a whole-watershed $CaSiO_3$ addition experiment. In this report we first characterize the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of sugar maple foliage, soil organic horizons, and both the exchangeable and acid-leachable soil nutrient pools as a function of soil depth at each study site. Next, we use the previously determined foliar Ca/Sr discrimination factor and the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios measured in this study to constrain the source of Ca to sugar maple foliage. Finally, we use the Ca/Sr and $^{87}Sr/^{86}Sr$ tracers to gain insight into Ca cycling in soil organic matter and the soil exchange pool.

Materials and methods

Study sites

This study was conducted primarily in six northern hardwood stands in the White Mountain National Forest. Three of the six stands (H1, H4, and H6) are located within 2 km of each other in the Bartlett Experimental Forest, and the remaining three stands are located 20 km north (M5), 14 km southwest (M6), and 11 km north-northeast (T30) of the Bartlett Forest (Fig 1). A seventh stand (C2, located ~1 km northeast of H1) was used to compare the Ca/Sr ratios of fresh foliage and litter. The seven stands are part of a larger study to investigate nutrient cycling as a function of stand age following forest harvest (Yanai et al. 2000, 2006), and thus range in age (the time between cutting and sample collection) from 16 to 66 years. Due to differences in successional status, species composition varies among the stands (Yanai et al. 2000), but most stands include sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Ehrh.), yellow birch (*Betula alleghaniensis* Britt.), white birch (*Betula papyrifera* Marsh.), red maple (*Acer rubrum* L.) and white ash (*Fraxinus Americana*). Younger stands also include the early successional species pin cherry (*Prunus pensylvanica* L.f.). Soils are coarse-loamy, mixed, frigid, Typic Haplorthods developed on glacial till derived from local igneous and metamorphic bedrock. The forest floor horizons (Oie and Oa) are 5–13 cm in thickness in these six sites and overlie mineral soils that are 48–82 cm in thickness (Yanai et al. 2006). The study sites are 25–50 km from Hubbard Brook Experimental Forest (Fig. 1).

Foliage collection and processing

It is difficult to collect representative samples of fresh foliage from an area large enough to correspond to the scale of soil sampling. Therefore, in this study we used freshly fallen litter to represent sugar maple foliage. In October 2003, litter was collected from fifteen 0.23 m^2 litter baskets at each of the main study sites (H1, H4, H6, M5, M6 and T30) and composited to form a single sample from each site. To test for changes in Ca/Sr with leaf senescence, foliar litter was collected in the fall of 2004 in an additional site (C2), where fresh canopy foliage was also sampled. At this site (C2), samples from each litter basket were analyzed separately. Both fresh foliage and litter from all sites were separated by species, oven dried at 50°C, and finely ground to increase sample homogeneity and facilitate digestion. Approximately 0.5 g of each foliage sample was digested in ultra-pure distilled HNO_3 and HCl using high-pressure microwave digestion in reinforced XP-1500 Teflon vessels (MARS 5, CEM Corporation, Matthews, NC), evaporated to dryness, and re-dissolved in ultra-pure 5% HNO_3 for analysis.

Soil collection and processing

Soils were collected at each of the main sites in the summer of 2003 from three soil pits per site positioned in the same plots as the litter baskets. Forest floor horizons were distinguished and sampled as Oie and Oa, and mineral soil was collected by depth from 0–10 cm, 10–20 cm, 20–30 cm and 30 cm to the C-horizon; a C-horizon sample was also collected. Samples of the Oa horizon and mineral soil (through the C-horizon) were sieved through 6 mm and 2 mm screens, respectively, then thoroughly mixed and subsampled. To reduce the effects of soil heterogeneity, subsamples were composited by horizon from each

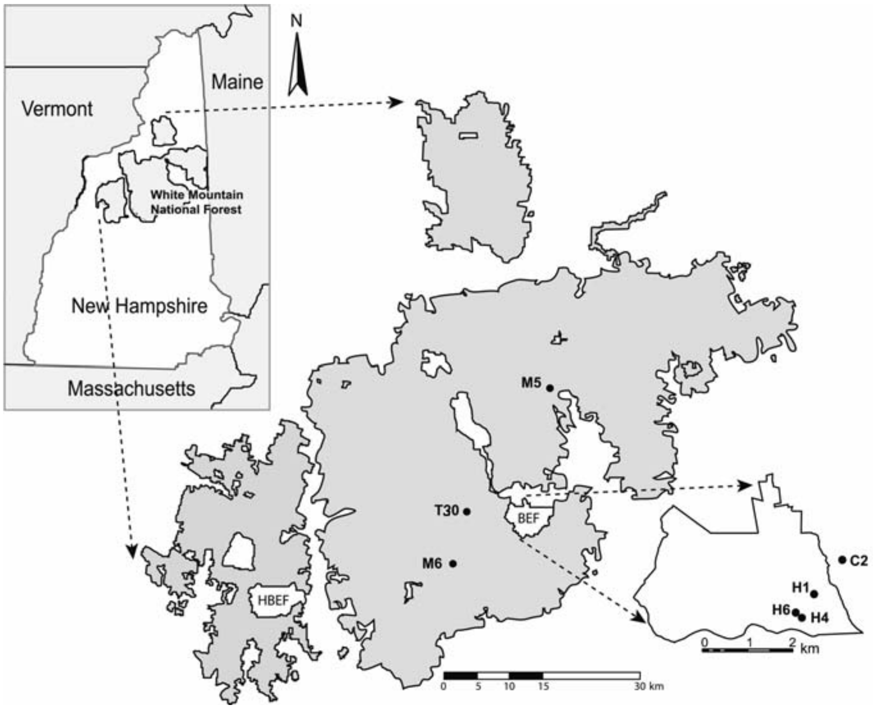

Fig. 1 Sample locations in the White Mountain National Forest, central New Hampshire, USA. The Hubbard Brook Experimental Forest (HBEF) and the Bartlett Experimental Forest (BEF) are highlighted in white. BEF is magnified in the lower right

of the three pits at each site, either by physically mixing samples before analysis or by averaging of individual chemical analyses. A 0.5 g subsample from each Oie horizon sample was digested using the same method as that for litter. The Oa and mineral horizons were extracted in 5 ml of ultrapure 1 M NH_4Cl for 20 h to determine the exchangeable fraction and this was followed by extraction of an acid-leachable fraction using 5 ml of 1 M ultrapure HNO_3 for 20 h at 10°C. The Ca released by the 1 M NH_4Cl treatment is widely used to approximate the plant-available soil pool, but we caution that this assumption is difficult to verify. The cold 1 M HNO_3 leach (hereafter described as "acid leach") is believed to release the recent products of mineral weathering, which include mainly feldspars at shallow depths but also apatite (Ca-phosphate) where this mineral is present deeper in the soil (Nezat et al. 2007).

Chemical analyses

Elemental concentrations were measured using a simultaneous collection inductively coupled plasma optical emission spectrometer (ICP-OES; PE-3300DV, Perkin Elmer, Norwalk, CT). Five- to eight-point linear calibration curves had R^2 values greater than 0.9999. One in-house standard and two High-Purity® solutions (Trace Metals in Drinking Water and CRM Soil Solution A) were analyzed for quality control before and after each 10-sample sequence. Analyses agreed with certified values to within ±5%.

Strontium isotope ratios were determined on aliquots of Sr separated from each sample (using cation exchange chromatography) with a thermal ionization mass spectrometer (TIMS, MAT-262, Finnigan, Bremen, Germany). A more detailed description of methods of chemical separation and isotope ratio measurement of Sr can be found in Dasch et al. (2006). Between 100 and 200 isotope ratios were measured for each sample, yielding a mean $^{87}Sr/^{86}Sr$ ratio with an analytical uncertainty of less than ± 0.000030 ($\pm 2\sigma$). Repeated measurements of NBS-987 during the period of analysis resulted in a mean $^{87}Sr/^{86}Sr$ value of 0.710237 ± 0.000025 ($\pm 2\sigma$, $n = 138$).

Results and discussion

Comparison of Ca/Sr ratios between foliage and litter

In this study we use recently fallen litter to indicate foliar Ca/Sr. To assess the suitability of this substitution, we analyzed litter and fresh foliage from a single study site (C2). Sugar maple foliage was not sampled in 2004 at this site and thus could not be compared, but a comparison of Ca/Sr ratios between litter and foliage was made for yellow birch, white birch, American beech, red maple and pin cherry. For each species, 4–6 canopy samples and 8–15 litter samples (from different baskets) were analyzed. An almost two-fold difference in foliar Ca/Sr ratios was observed across species, but the mean values for fresh foliage and litter from each individual species agreed within 2–15% (Table 1). For three species, litter had lower mean Ca/Sr than foliage and for two species litter had a higher mean Ca/Sr than foliage. The standard error of the mean of litter Ca/Sr ratios (from individual litter baskets) gives an estimate of the uncertainty of mean foliar values at our main study sites, where we composited litter from 15 litter baskets. The standard errors range from 3 to 13% of the mean Ca/Sr ratios (Table 1), indicating that the differences we see between canopy and litter Ca/Sr ratios are within the natural variability of samples from each site. This comparison indicates that litter and fresh foliage Ca/Sr ratios can be used interchangeably for the purposes of this study.

Table 1 Comparison of Ca/Sr ratios of fresh leaves and litter for American beech, pin cherry, red maple, white birch and yellow birch from study site C2

Species	Sample	*n*	Mean Ca/Sr	RSE (%)
Pin cherry	Canopy	4	752	7
	Litter	10	737	6
	Δ		−2%	
White birch	Canopy	6	825	4
	Litter	10	876	4
	Δ		+6%	
Yellow birch	Canopy	6	895	3
	Litter	8	968	7
	Δ		+8%	
Red maple	Canopy	6	1341	7
	Litter	9	1160	12
	Δ		−15%	
Amer. beech	Canopy	6	1489	13
	Litter	13	1349	7
	Δ		−10%	

The number of samples (*n*), mean Ca/Sr ratios, percent difference in Ca/Sr between canopy and litter samples (Δ), and relative standard error (RSE) are given

Ca/Sr and ^{87}Sr/^{86}Sr of sugar maple foliage across the White Mountains, NH

The Ca/Sr ratios of foliar litter of sugar maple varied across sites by a factor of 3.6 (239–856 mol/mol; Fig. 2). Calcium concentrations varied by only a factor of 1.6 (8.9–14.3 mg/g), whereas Sr concentrations varied by a factor of 5.8 (22.7–131 μg/g). Thus, Ca concentrations in sugar maple foliage at our six study sites appeared to be less variable, whereas Sr varied more widely, reflecting its abundance in soil nutrient sources.

The ^{87}Sr/^{86}Sr ratio of sugar maple foliage varied from 0.714186 to 0.720023 across the six study sites (Fig. 3), reflecting differences in the mixture of sources of Sr to the trees (Blum et al. 2000). The ratios reflect the age and Rb/Sr ratio of soil minerals as well as differences in the input of Sr to the ecosystem from wet and dry atmospheric deposition (e.g., Miller et al. 1993; Bailey et al. 1996).

Comparison of Ca/Sr and ^{87}Sr/^{86}Sr ratios of sugar maple foliage with soil pools

The primary goal of this study was to use Ca/Sr and ^{87}Sr/^{86}Sr ratios to investigate which soil nutrient pools supply Ca to the current foliage of sugar maple. We begin by comparing the Ca/Sr ratio of sugar maple foliage with the Ca/Sr ratio of the Oie horizon as well as the exchange pool and acid leach fraction of the Oa horizon and mineral soil from different depths. These data are plotted on Fig. 2 along with a line of slope = 1 and a wedge-shaped area defined by lines of slope = 1.14 ± 0.12, which is the previously determined ratio between the Ca/Sr ratio of sugar maple foliage and its nutrient source ($\mathrm{DF}_{\mathrm{foliage}}$) and the associated uncertainty in that relationship (Dasch et al. 2006). Several important trends are apparent in Fig. 2. All of the soil components that have higher Ca/Sr than foliage are acid leaches of the mineral soil. The Oie and Oa horizons, as well as exchange fractions from the mineral soil, all have lower Ca/Sr than foliage. Finally, data from the Oie horizon of all six sites fall within the wedge-shaped area defined by the empirically determined 1.14 ± 0.12 value for $\mathrm{DF}_{\mathrm{foliage}}$. The simplest explanation for these observations is that the Oie horizon is the main source of Ca and Sr for constructing current sugar maple

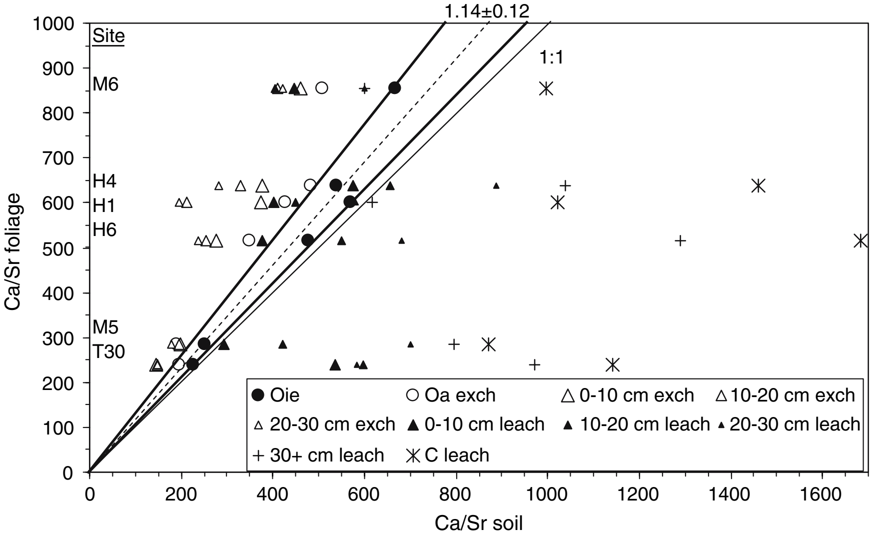

Fig. 2 For each of the six study sites the molar Ca/Sr ratio of sugar maple foliage is plotted against the molar Ca/Sr ratio of various soil fractions. Soil fractions include exchange fractions and acid leaches of each soil horizon. Also plotted is a line of slope = 1 and a shaded wedge-shaped area defined by lines of slope = 1.14 ± 0.12, which is the relationship between the Ca/Sr ratio of sugar maple foliage and the nutrient source predicted by Dasch et al. (2006). Note that samples of the Oie horizon fall within the wedge-shaped area for each site

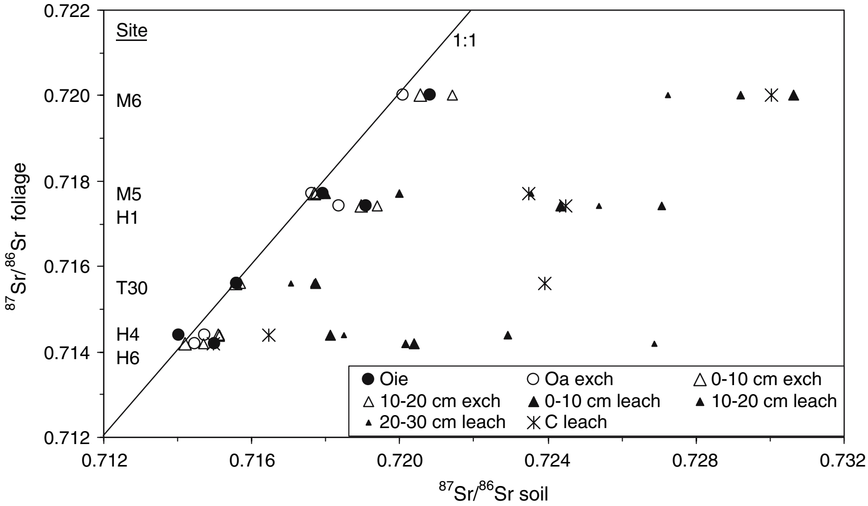

Fig. 3 For each of the six study sites the $^{87}Sr/^{86}Sr$ ratio of sugar maple foliage is plotted against the $^{87}Sr/^{86}Sr$ ratio of various soil fractions. Soil fractions include exchange fractions and acid leaches of each soil horizon. Also plotted is a line of slope = 1. Note that samples of the Oie horizon and the exchange pool of most soil horizons plot close to the slope = 1 line for 5 of the 6 sites

foliage. The Oa horizon Ca/Sr ratios are only slightly lower than the Oie horizon values and for most sites a mixture of the Oie horizon with up to ~50% Ca from the Oa horizon could explain the foliar Ca/Sr ratios. It is also possible, but seems less likely, that the Ca and Sr in foliage are composed from a mixture of the soil exchange pool and mineral weathering sources (i.e., the acid leach of the C horizon), which happen to mix in the proportion necessary to give the same ratio as the Oie horizon.

Next we turn to a comparison of $^{87}Sr/^{86}Sr$ ratios between foliage and soils to see if this helps to clarify the source of Ca and Sr to sugar maple foliage. These data are plotted on Fig. 3 along with a line of slope = 1. At each site, the $^{87}Sr/^{86}Sr$ ratios of the Oie horizon, the Oa horizon, and mineral soil exchange fractions are close to the $^{87}Sr/^{86}Sr$ ratio of sugar maple foliage (Fig. 3). At site H1, the $^{87}Sr/^{86}Sr$ ratio of the Oie horizon differs from that of foliage by ~0.0015, suggesting that Sr isotope ratios are somewhat more heterogeneous at this study site and that the average of samples from our three soil pits may not adequately reflect the average $^{87}Sr/^{86}Sr$ available to the trees that were sampled. Nevertheless, the $^{87}Sr/^{86}Sr$ data are consistent with the Ca/Sr data which suggest that the Oie and/or Oa horizons are the main source of Ca and Sr to current sugar maple foliage. A mixture of the soil exchange pool and mineral weathering sources (i.e., the acid leach of the C horizon), mixing proportionally to give the same Ca/Sr ratio as the Oie horizon (as proposed above), is not compatible with the $^{87}Sr/^{86}Sr$ data because the weathering source would drive the foliar $^{87}Sr/^{86}Sr$ to higher values than the Oie and Oa horizons.

All of the acid leaches of the mineral soil, except one, have $^{87}Sr/^{86}Sr$ ratios much higher than foliage; the exception is the C-horizon sample at site H6 which has a value similar to the foliage. Acid leaches of the mineral soil should reflect the range of $^{87}Sr/^{86}Sr$ ratios released by mineral weathering reactions (Miller et al. 1993; Bullen and Bailey 2005; Nezat et al. 2007). In addition to mineral weathering, Sr is supplied to forest ecosystems in wet and dry atmospheric deposition, which in the vicinity of the study sites has a $^{87}Sr/^{86}Sr$ ratio of approximately 0.710 (Miller et al. 1993; Bailey et al. 1996). This low $^{87}Sr/^{86}Sr$ source of Sr, which has been added to the ecosystem for thousands of years, has mixed with the higher $^{87}Sr/^{86}Sr$ source of Sr from mineral weathering to produce the intermediate $^{87}Sr/^{86}Sr$ ratios observed in vegetation and in the various soil nutrient pools.

Our suggestion that most of the Ca in current sugar maple foliage is derived from the Oie and Oa horizons raises the question of the sources of Ca to the combined vegetation and forest floor pools. Over the course of secondary forest succession following harvest, both the vegetation and the forest floor accumulate Ca (Yanai et al. 1999) from some combination of mineral soil and atmospheric sources. We can make estimates of the amount of Ca needed to build these pools, compared to the amount cycling annually through foliage and litterfall, to estimate the relative importance of annual Ca influx from other sources.

In the six stands we studied, the accumulation rate of Ca in the forest floor averaged 86 mol/ha/year (more in the younger stands, less in the older stands) (Yanai et al. 1999). The accumulation rate of Ca in the vegetation in the aggrading forest at nearby Hubbard Brook was estimated to be 135 mol/ha/year, and 43 mol/ha/year in the older forest (Likens et al. 1998). The annual cycling of Ca through foliage and litterfall is large compared to these accumulation rates, ranging from 555 to 836 mol/ha/year in the six stands we studied (unpublished data). This litterfall flux amounts to only about 4% of the total Ca in the forest floor in these stands (15–25 kmol/ha; Yanai et al. 1999). Atmospheric deposition is very small, even compared to the uptake into foliage: ~5 mol/ha/year of Ca before 1950 (Junge and Werby 1958; Hedin et al. 1994) and ~29 mol/ha/year in more recent times (Likens et al. 1998). Similarly, weathering inputs may be only ~3.5 mol/ha/year, assuming that the total amount of Ca weathered from soil profiles at Hubbard Brook (~49 kmol/ha, Nezat et al. 2004) was released over 14,000 years of soil formation. Estimates of Ca weathering based on present-day stream fluxes are higher, at 54–132 mol/ha per year at Hubbard Brook (Bailey at al. 2003), but weathering fluxes that supply stream export are not relevant to our calculation of sources of Ca to aggrading ecosystems. Even considering the highest estimates of annual Ca input from weathering and atmospheric deposition, these Ca inputs amount to <1% of the Ca in the forest floor and vegetation and <20% of the Ca cycled through foliage and back into the forest floor each year. With annual Ca inputs from weathering and atmospheric deposition small compared to annual Ca fluxes through vegetation, it is not surprising that sugar maple foliage could obtain Ca mostly by recycling through the Oie and Oa horizons. We note that we have investigated only one tree species in this mixed hardwood forest. Other species have differing behavior with respect to Ca acquisition and Ca/Sr discrimination (Dasch et al. 2006).

Ca/Sr in the forest floor horizons and exchange pool

In the previous section we suggested based on Ca/Sr and $^{87}Sr/^{86}Sr$ ratios that the soil Oie and Oa horizons are the dominant source of Ca and Sr to sugar maple foliage. In this section we consider in more detail the Ca/Sr ratios of the Oie horizon and Oa and mineral soil exchange pools in order to gain insight into Ca and Sr dynamics in soils. On Fig. 4 we plot the Ca/Sr ratio of sugar maple foliage and soil exchange fractions (at each depth sampled), divided by the Ca/Sr ratio of the Oie horizon at each site (thus at each site the Oie horizon plots at 1). Also plotted on Fig. 4 is a region representing the range of Ca/Sr ratios that would be expected for foliage assuming that the Oie was the sole nutrient source and the foliar discrimination factor was 1.14 ± 0.12, as independently determined for sugar maple in the Hubbard Brook Ca fertilization study (Dasch et al. 2006). At five out of six sites, sugar maple foliage falls within the range predicted from the Hubbard Brook study ($DF_{foliar} = 1.14 \pm 0.12$). At all sites, the Ca/Sr ratio of the soil exchange pool decreases with increasing depth, and this does not seem to depend on forest age. Recall that although there is some heterogeneity, the Oie and all soil exchange fractions have similar $^{87}Sr/^{86}Sr$ ratios (Fig. 3).

The observed decrease in the Ca/Sr ratio of the soil exchange complex with depth (Fig. 4) may be related to ion exchange processes. Laboratory studies have shown that Ca can be retained in preference to Sr by ion exchange on peat (Baes and Bloom 1988). If this preference applies generally to soil organic matter, then Ca may be more strongly retained than Sr in the upper, more organic-rich, soil horizons. As Ca and Sr released by decomposition move downward in the soil horizon they may become partially separated by ion exchange processes. We do not observe a difference in Ca/Sr gradients as a function of forest age in the chronosequence that we studied (Fig. 4), which suggests that these gradients have accumulated over longer time scales than that of secondary succession following forest harvest. We also observe that trees exhibit the same Ca/Sr discrimination behavior over an age range of 16–66 years. Quantitative estimates of changes in Ca/Sr with soil depth using a mass-balance approach will require more information on foliar and root chemistry of the other important species in the mixed hardwood forest, better information on Ca and Sr fluxes and pathways in the soils, and more information on Ca and Sr ion exchange in forest soils.

Summary and conclusions

Across six study sites separated by up to 30 km in the White Mountains of New Hampshire (USA), we found that 1 M cold nitric acid leaches of soils (believed to be representative of cations available for release by weathering) had widely variable Ca/Sr and $^{87}Sr/^{86}Sr$ ratios with no systematic variation in values with depth in soil profiles (Figs. 2, 3). In contrast, we found that the soil exchange complex at each site had Ca/Sr ratios that systematically decreased through the Oie, Oa, and 0–10, 10–20 and 20–30 cm depth mineral soils (Fig. 2). Although the Ca/Sr ratio of the Oie horizon varied across sites by a factor of 3.6, the ratio of Ca/Sr in the Oie to Ca/Sr at each soil depth was relatively constant across sites (Fig. 4). The $^{87}Sr/^{86}Sr$ ratios in the soil exchange complex of the Oie, Oa, and 0–10 and 10–20 cm depth mineral soils varied widely across sites, but all fell within a narrow

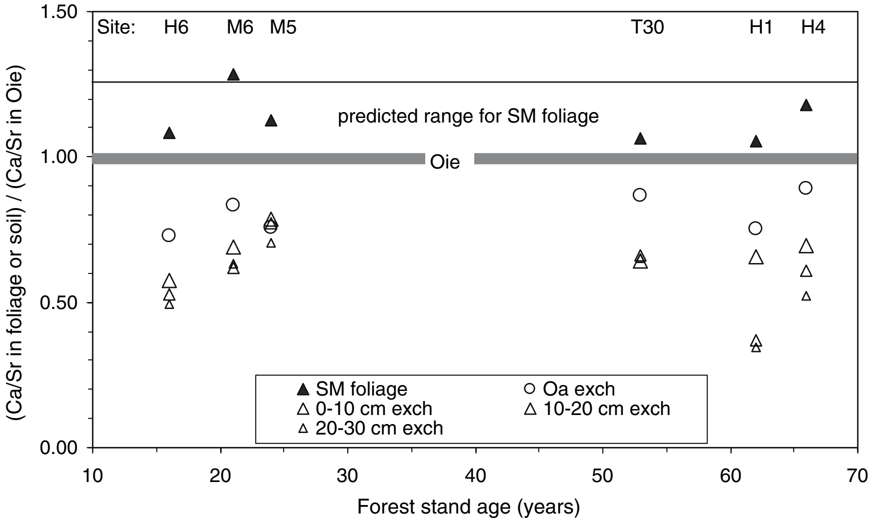

Fig. 4 For each of the six study sites the Ca/Sr ratios for foliage and the soil exchange pool divided by the Ca/Sr ratio of the Oie horizon is plotted against the age of each even-age forest stand. The labelled region represents the predicted Ca/Sr ratios for sugar maple foliage based on the foliar discrimination factor determined by Dasch et al. (2006)

range at each site (Fig. 3). Sugar maple foliage was also measured for Ca/Sr (Fig. 2) and $^{87}Sr/^{86}Sr$ ratios (Fig. 3) at each of the six sites. A previous Ca fertilization study (Dasch et al. 2006) showed that sugar maple foliage discriminates in favor of Ca compared to Sr by a factor of 1.14 ± 0.12; accounting for this discrimination, we conclude that the major sources of Ca and Sr for the annual construction of sugar maple foliage are the Oie and Oa horizons. This study supports the long-standing view that internal recycling of Ca through organic matter supplies most of the annual requirement of Ca in northern hardwood ecosystems. At each of the six sites, $^{87}Sr/^{86}Sr$ ratios released by weathering were much higher than vegetation and all samples of the cation exchange complex, which confirms the importance of atmospheric deposition in addition to mineral weathering in contributing Sr, and by inference Ca, to the actively cycling pool.

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