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Influences of calcium availability and tree species on Ca isotope fractionation in soil and vegetation

Blair D. Page · Thomas D. Bullen · Myron J. Mitchell

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Abstract The calcium (Ca) isotope system is potentially of great use for understanding biogeochemical processes at multiple scales in forest ecosystems, yet remains largely unexplored for this purpose. In order to further our understanding of Ca behavior in forests, we examined two nearly adjacent hardwood-dominated catchments with differing soil Ca concentrations, developed from crystalline bedrock, to determine the variability of $^{44}Ca/^{40}Ca$ ratios (expressed as $\delta^{44}Ca$) within soil and vegetation pools. For both sugar maple and American beech, the Ca isotope compositions of the measured roots and calculated bulk trees were considerably lighter than those of soil pools at these sites, suggesting that the trees were able to preferentially take up light Ca at the root–soil interface. The Ca isotope compositions of three of four root samples were among the lightest values yet reported for terrestrial materials ($\delta^{44}Ca \leq -3.95‰$). Our results further indicate that Ca isotopes were fractionated along the transpiration streams of both tree species with roots having the least $\delta^{44}Ca$ values and leaf litter the greatest. An approximately 2‰ difference in $\delta^{44}Ca$ values between roots and leaf litter of both tree species suggests a persistent fractionation mechanism along the transpiration stream, likely related to Ca binding in wood tissue coupled with internal ion exchange. Finally, our data indicate that differing tree species demand for Ca and soil Ca concentrations together may influence Ca isotope distribution within the trees. Inter-catchment differences in Ca isotope distributions in soils and trees were minor, indicating that the results of our study may have broad transferability to studies of forest ecosystems in catchments developed on crystalline substrates elsewhere.

Keywords Calcium · $\delta^{44}Ca$ · Fractionation · Isotope · Soil · Vegetation

B. D. Page (✉) · M. J. Mitchell
SUNY College of Environmental Science and Forestry,
1 Forestry Drive, Syracuse, NY 13210, USA
e-mail: bdpage1@yahoo.com

M. J. Mitchell
e-mail: mitchell@syr.edu

T. D. Bullen
U.S. Geological Survey, MS 420, 345 Middlefield Rd.,
Menlo Park, CA 94025, USA
e-mail: tdbullen@usgs.gov

Introduction

There have been numerous reports recently indicating wide-spread soil Ca decline in terrestrial ecosystems in North America and Europe (Lawrence et al. 1997; Jandl et al. 2004; Bailey et al. 2005; Watmough et al. 2005). Reduced Ca availability has been linked to sugar maple (*Acer saccharum*) and red spruce (*Picea rubens*) declines in the Northeast U.S. (Lawrence et al. 1997; Bailey et al. 2004; Juice et al. 2006), decreased avian nesting success associated with

reduced mollusk populations (Graveland and Van der Wal 1996), and slow recovery of acidified lakes (Driscoll et al. 2003; Sullivan et al. 2006). Because of the important ecological roles of Ca and potential consequences of its continued depletion, it is critical to understand Ca cycling pathways in order to identify sensitive ecosystems, minimize further losses of Ca, and evaluate potential mitigation strategies.

Most of the Ca in a temperate forested ecosystem is located in the mineral soil and forest floor with a relatively small fraction (<5%) being available for plant uptake (Likens et al. 1998). Calcium uptake in plant roots can be influenced by variables including: (1) water influx driven by transpiration (Bangerth 1979), (2) root structure associated with cation binding sites and membrane Ca channels (White 1998), and (3) root associations with ectomycorrhizal fungi (Blum et al. 2002; Wallander et al. 2006). Calcium requirements can also vary by species. Sugar maple and American basswood (*Tilia americana*) are relatively demanding for base cations including Ca and Mg (Fujinuma et al. 2005; Page and Mitchell 2008b) while American beech (*Fagus grandifolia*) is generally regarded to be less sensitive to growth on sites with reduced soil Ca concentrations (Duchesne et al. 2005). Due to the relatively low mobility of Ca associated with pectate, oxalate, or other binding sites within trees, most of the Ca cycling occurs through litterfall, mineralization, and subsequent re-uptake from the soil (Likens et al. 1998).

Potential mechanisms of Ca loss from forest ecosystems include: (1) removal of biomass through harvesting (Watmough and Dillon 2003); and (2) soil leaching resulting from acidic deposition (Fernandez et al. 2003), continued export of previously accumulated SO_4^{2-} (Gbondo-Tugbawa et al. 2002; Likens et al. 2002; Driscoll et al. 2003) or from other mobile anions formed from biotic processes in the soil including respiration (HCO_3^-) and nitrification (NO_3^-) (Tomlinson 2003; Page and Mitchell 2008a). Increased leaching of Ca from forested sites can also coincide with site disturbances, such as those resulting from timber harvesting (Likens et al. 1998). In addition to reduced Ca concentrations resulting from ecosystem export, declines in soil Ca may also be attributed to decreased atmospheric deposition of base cations (Hedin et al. 1994; Likens et al. 1998). While some Ca loss from a forested ecosystem is expected due to natural metabolic and aging processes (Ulrich and Matzner 1986), the accelerated rate at which current losses have been reported is cause for concern.

Stable isotopes are increasingly being used to study the biogeochemical cycling of numerous elements including H, C, N, O, and S. The research utility of these isotope systems arises from measurable fractionation whereby certain biotic and abiotic processes discriminate against either heavier or lighter isotopes of an element. For example, during biological processing of these elements, organisms generally tend to favor the utilization of the lighter isotope from an energetic standpoint (Kendall and Caldwell 1998). In contrast, during abiotic processing of these elements, solids or more tightly bound phases tend to contain heavier isotopes of these elements relative to the coexisting aqueous phase (Hoefs 2004). On the other hand, metals can be either lighter (e.g., Ca; DePaolo 2004) or heavier (e.g., Mg; Tipper et al. 2006) in the solid phase relative to the coexisting aqueous phase due to a variety of bonding considerations. Finally, some elements such as Sr can be used as tracers due to their long-lived radiogenic characteristics that are considered to be stable on the time scale of ecosystem processes (Bailey et al. 1996; Blum et al. 2000; Bullen and Bailey 2005).

While fractionation of atoms involved in covalent bonding, such as oxygen and hydrogen, can be affected by phase changes and equilibrium reactions (Kendall and Caldwell 1998), the fractionation of Ca results largely from kinetic processes related to reaction rate, solution saturation state, and perhaps ion hydration (e.g., Gussone et al. 2003; LeMarchand et al. 2004). Along food chains, for example, Ca isotopes are fractionated largely through biotic processes which result in progressively lighter isotopic compositions when advancing up the food chain (Skulan et al. 1997). Wiegand et al. (2005) reported that within Ohia trees (*Metrosideros polymorpha*) sampled along a chronosequence in Hawaii, $^{44}Ca/^{40}Ca$ ratios were generally the least in the roots and greatest in the foliage; progressively increasing up the transpiration stream. Using stable Ca isotope ratios, Perakis et al. (2006) suggested that lesser $^{44}Ca/^{40}Ca$ ratios in surface soils relative to those in deeper soils in Douglas-fir (*Pseudotsuga menziesii*) dominated forest sites in Oregon indicated that recycling of isotopically light Ca derived from decaying litter was occurring to meet Ca nutrition demands of the trees.

Given that the use of stable Ca isotopes is relatively new in forest biogeochemical studies, much remains to be learned with respect to the research utility and behavior of Ca isotopes for this purpose. In order to further our understanding of Ca isotope systematics in a well constrained, comparative forest ecosystem setting, we evaluated stable Ca isotope ratio trends in soil and vegetation pools in two nearly adjacent catchments with similar site histories but disparate soil Ca concentrations. Due to their geographic proximity, these two catchments offer a unique opportunity to compare how naturally differing soil Ca concentrations can influence biogeochemical cycling. Our work allows for a comparison of Ca isotope results from this temperate northern-hardwood forest developed on igneous and metamorphic rock-dominated glacial till to recent data from Wiegand et al. (2005) evaluating Ca isotopes in tropical single-species dominated rainforests growing on basaltic parent material along a chronosequence in Hawaii.

Methods

Site description

This study was conducted in two nearly adjacent catchments (termed "14" and "15") in the Arbutus Lake watershed of Huntington Forest, located in the central Adirondack Mountains, New York (Fig. 1). At the Huntington Forest, mean annual temperature and total annual precipitation were 4.8°C and 1,080 mm from 1981 to 2000, respectively (Park et al. 2003). The Adirondack Mountains are part of the Grenville Province with bedrock composed primarily of granitic gneisses and metasedimentary rock. The Huntington Forest and Arbutus Lake watershed are within the Anorthosite Massif, a large igneous intrusion composed of up to 90% calcium-rich feldspar. The surficial geology is dominated by glacial till (Driscoll et al. 1991). The soils in Catchments 14 and 15 in the Arbutus watershed are Becket-Mundal associations. Previously determined, but unpublished X-ray diffraction data (Table 1) indicated that a major source of the elevated soil Ca in Catchment 14 was a higher abundance of pyroxene relative to that found in Catchment 15. The pyroxene in the Huntington Forest has been identified as augite ($(Ca(Mg,Fe)Si_2O_6$; Moore 1995). Catchments 14 and

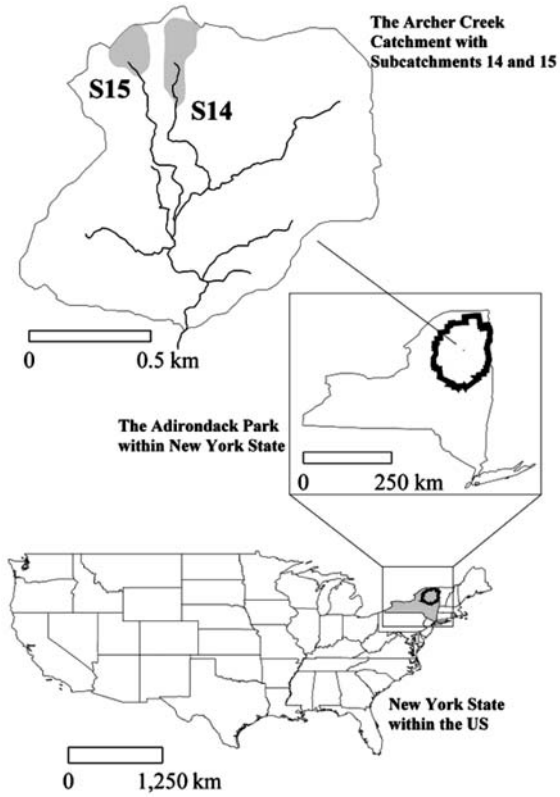

Fig. 1 Map of Catchments 14 and 15 within the Archer Creek Catchment of the Arbutus Lake watershed in the Central Adirondack Mountains, New York

15 are small (3.5 and 2.5 ha, respectively), relatively undisturbed sites with similar topography, aspect, elevation, and site history. Both catchments are dominated by northern hardwoods including sugar maple, American beech (hereafter, beech), white ash, American basswood (hereafter, basswood), and yellow birch (*Betula alleghaniensis*). Red spruce and white pine (*Pinus strobus*) were also present in lesser abundance in both catchments. Detailed descriptions of the physiography (Christopher et al. 2006) and hydrology (Christopher et al. 2007) of Catchments 14 and 15 have previously been reported.

Sampling

Vegetation surveys were conducted during summer 2002. Each catchment was divided into a grid of 20 × 20 m plots and six horizontal 20-m transects (two lower, two middle, two upper slope) were

Table 1 X-ray diffraction data from individual soil samples collected in 2002 from Catchments 14 and 15

Catchment	Depth (cm)	Quartz	Plagioclase	K-feldspar	Amphibole	Pyroxene	Di-clay	Chlorite	Total
14	15	33.7	12.8	18.2	3.4	15.0	7.7	4.0	94.8
14	50	22.0	14.4	24.1	4.8	22.2	4.1	7.9	99.5
15	15	20.9	16.0	15.5	6.2	5.0	2.5	–	66.1
15	50	18.8	16.4	13.7	4.9	4.9	0.5	–	59.2

Data are percentages (Watmough et al. 2005; Watmough, pers. commun.)

randomly selected for vegetation sampling. Within these transects, the species and diameter at 1.4 m above the ground (d.b.h.) were recorded for every tree ≥5 cm in diameter.

Leaf litter was collected from 10 2 × 2 m nets suspended approximately 2 m above the ground in each catchment during autumn 2003. Samples from five nets in the upper half and five nets in the lower half were pooled separately yielding two aggregate collections per catchment. After collection, leaves were air-dried, sorted by species, and sub-samples were ground in a Wiley Mill® using a #20 (0.85 mm) screen. Samples were analyzed for cation concentrations and Ca isotopes using the procedures given below.

Stemwood and root samples were collected from one canopy-dominant sugar maple and one dominant beech tree in each catchment during October 2005. Three stemwood cores (approximately 10 cm length, representing years 1980–2005) were collected from each tree using an increment borer at 1.4 m above the ground. Roots (approximately 0.5 cm diameter) from the same trees were collected by excavating soil near the base of the root crown. Aggregate samples of root tissue and stemwood tissue were analyzed separately for Ca concentrations and Ca isotopes using the procedures given below.

Mineral soil samples were collected in June 2002 from two pits excavated in each catchment at depths of 15 cm, 50 cm, and at the base of the pits ranging from 70 to 100 cm (designated as "deep"). Samples were air-dried and sieved to 2 mm prior to analysis for exchangeable and acid-leachable Ca. Forest floor samples (Oe and Oa horizons) were collected from three plots in both catchments, oven dried at 65°C and ground in a Wiley Mill® using a #20 (0.85 mm) screen. The forest floor samples were analyzed for exchangeable and acid-leachable Ca using the procedures given below.

Biomass and elemental content estimates

Mean biomass estimates for stemwood and foliage of sugar maple and beech were determined using equations from Ter-Mikaelian and Korzukhin (1997). Because foliar Ca generally has low mobility and little resorption during leaf senescence (Likens et al. 1998; McLaughlin and Wimmer 1999; Duchesne et al. 2001), it was assumed that Ca content in mature foliage and leaf litter was essentially equivalent, though concentrations could vary with mass. Biomass estimates for sugar maple and beech roots were determined using equations from Whittaker et al. (1974). Whole tree Ca isotope values were estimated as a mean value of the root, stem, and litter pools weighted by biomass Ca concentrations.

Chemical analysis

Concentrations of major cations from leaf litter, stemwood, and roots were analyzed by digesting 10–50 mg samples in 5 ml of concentrated Teflon®-distilled nitric acid (HNO_3) over 24 h. The HNO_3 solutions were evaporated on a hot plate, treated with a mixture of concentrated HNO_3 and Ultrex® hydrogen peroxide (H_2O_2) to oxidize any organic compounds, the residue was re-dissolved in 3 ml of 2% HNO_3 and the solution was retained for analysis.

For soil and forest floor samples, the exchangeable cation fractions were obtained from ~5 g of sieved (<2 mm fraction), oven-dried sample that was equilibrated with 50 ml of 1 N ammonium acetate (NH_4OAc) for several days. Each solution was filtered and the residue rinsed with 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 oxidize any organic compounds. The residue was re-dissolved in 3 ml of 2% HNO_3 and retained for analysis.

The soil acid-leachable fraction was obtained from 1 g of the soil remaining from the exchange procedure and was held in 10 ml of 1 N HNO_3 for 24 h on a hot plate at 30°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.

One-tenth of each 2% HNO_3 solution was used for determination of Ca concentrations on a Perkin Elmer Elan 6000® inductively coupled plasma mass spectrometer. Synthetic mixtures of pure element solutions were used as standards for analysis of the tree samples and exchangeable and 1 N acid-leachable soil fractions. Calcium concentrations were estimated with a precision of $\leq$3%. Because both exchangeable and acid-leachable fractions were obtained from individual soil samples, Ca concentration-weighted ([Ca]-weighted) means of the exchangeable and acid-leachable Ca isotope values were also determined.

Calcium isotope mass spectrometry

Calcium isotope measurements were conducted at the U.S. Geological Survey in Menlo Park, CA using thermal ionization mass spectrometry (TIMS) for isotope ratio determination. In order to avoid potential matrix effects associated with analysis of tree tissue and soil samples which can have widely varying chemical composition, we used the "double spike" mass spectrometry approach (Johnson et al. 1999; Bullen et al. 2004; Perakis et al. 2006). The double spike, an artificially prepared calcium standard containing a precisely known excess of ^{42}Ca and ^{48}Ca, was added to and allowed to equilibrate with each sample prior to chemical processing. The amount of spike added was adjusted to the calcium concentration of the sample so that a constant spike calcium: sample calcium ratio was maintained between samples. The double spike served as an internal standard. The spike and natural components of the mixed calcium sample were fractionated in exactly the same way by processing and TIMS analysis subsequent to spike addition. Thus at the end of the analysis it was possible to correct for any procedural or instrumental isotope fractionation that occurred after the spike was added, as well as any matrix effects, by comparing the measured ratio of the excess isotopes to the known value. Correction for fractionation and mathematical subtraction of the double spike component from the mixture was accomplished following Skulan et al. (1997) and Johnson et al. (1999).

Calcium in each sample-double spike mixture was purified using cation exchange column chromatography. Samples were processed through 2 ml of AG-50-X8 cation resin packed in 0.7 cm diameter glass columns, using 2 N HCl as the eluent. Purified samples were converted to nitrate form using concentrated HNO_3, dissolved in a small amount of H_3PO_4, loaded onto tantalum filaments and placed in a Finnigan MAT 261 thermal ionization mass spectrometer (TIMS) for isotopic analysis. Individual samples were analyzed once; the reported δ^{44}Ca values were based on a minimum of 60 isotope ratio measurements, with an internal precision of better than 0.15‰ (2σ,(95% confidence). External precision was assessed by running full procedural replicates on standard reference materials having δ^{44}Ca values largely bracketing those presented here. Results were: ±0.17‰ SD (standard deviation), ±0.06‰ 2σ (95% confidence), $n = 29$ for a seawater sample (δ^{44}Ca = 0‰); ±0.19‰ SD, ±0.04‰ 2σ, $n = 90$ for La Jolla Ca (δ^{44}Ca = −1.38‰); and ±0.18‰ SD, ±0.09‰ 2σ, $n = 15$ for NIST SRM915A (δ^{44}Ca = −2.01‰). These values suggest a reproducibility of ~0.18‰. In addition, 17 samples from the present dataset were run in duplicate, all of which agreed within 0.17‰ (mean difference = 0.09‰, ±0.04‰ SD), consistent with the reproducibility indicated by our multiple analyses of standard materials and demonstrated in previous Ca isotope studies performed in this laboratory (e.g., Skulan et al. 2007). Statistical comparisons of means were conducted using general linear model ANOVA procedures in SAS (1999).

Calcium isotope ratios are presented using the δ^{44}Ca notation calculated as:

$$‰\delta^{44}\mathrm{Ca} = \frac{\mathrm{sample}^{44}\mathrm{Ca}/^{40}\mathrm{Ca} - \mathrm{standard}^{44}\mathrm{Ca}/^{40}\mathrm{Ca}}{\mathrm{standard}^{44}\mathrm{Ca}/^{40}\mathrm{Ca}} \times 1{,}000$$

where the standard (sea water) ^{44}Ca/^{40}Ca ratio was 0.021713 on this mass spectrometer.

Results

Species composition and biomass

The species composition and total basal area of the two catchments were similar, with the major difference being the presence of basswood only in Catchment 14. The basal area of sugar maple was greater in Catchment 14 relative to Catchment 15 (17.1 and 9.8 m^2 ha^{-1}, respectively, $P = 0.01$), while beech (4.1 and 6.4 m^2 ha^{-1}, $P = 0.15$) and white ash (6.3 and 9.2 m^2 ha^{-1}, $P = 0.35$) had more similar basal areas in Catchments 14 and 15, respectively (Fig. 2). Biomass estimates similarly show that the dominance of sugar maple as compared to beech was more pronounced in Catchment 14 relative to Catchment 15 (Table 2).

Concentrations and content of calcium

Calcium concentrations in sugar maple and beech vegetation components were generally elevated in Catchment 14 relative to Catchment 15 (Table 2). Although not statistically significant given small sample sizes ($n = 2$ per catchment), calcium concentrations from soils sampled at depths of 15 cm, 50 cm, and deep (ranging from 70 to 100 cm) were elevated in Catchment 14 relative to Catchment 15 in acid-leachable ($P = 0.29$, 0.07, and 0.25, respectively; Table 3) and exchangeable fractions ($P = 0.25$, 0.21, and 0.18, respectively; Table 3). However, when the acid-leachable and exchangeable Ca concentrations were combined, differences between the two catchments were more apparent in the deeper soils ($P = 0.27$, 0.05, and 0.07 for 15 cm, 50 cm, and 70–100 cm depths, respectively). Estimates of stemwood, foliage, and root biomass from sugar maple and beech suggest that while foliage accounts for only 2–3% of the biomass, it represents 16–36% of the Ca content in the vegetation pools of these two catchments (Table 2).

Fig. 2 Basal area of tree species in Catchments 14 and 15 sampled during summer 2002. Species included as "Other" were yellow birch, red spruce, white pine, and eastern hophornbeam (*Ostrya virginiana*), the latter found only in Catchment 14

Calcium isotopes

Soil isotopic analysis revealed that acid-leachable δ^{44}Ca values in deep mineral soil were nearly identical in both catchments ($P = 0.96$; Table 4). Higher in the soil profile, mean acid-leachable δ^{44}Ca values were less similar at 50 and 15 cm depths, but still not significantly different ($P = 0.41$ and 0.09, respectively). Exchangeable δ^{44}Ca values were lower in Catchment 15 at 15 cm depth ($P = 0.05$), but differences between catchments were not significant at 50 cm or in deep (70–100 cm) soil ($P = 0.16$, 0.20, respectively). The combined acid-leachable and exchangeable isotopic values were similar to those from the acid-leachable pool alone ($P = 0.95$, 0.19, and 0.17 for deep, 50 cm, and 15 cm samples, respectively). Forest floor δ^{44}Ca values were more variable than those from the mineral soils (Fig. 3) and were not significantly different between catchments in either the exchangeable ($P = 0.51$) or acid-leachable fractions ($P = 0.47$).

A comparison of sugar maple and beech biomass pools indicated that roots generally had the least δ^{44}Ca values in individual trees followed by stems having similar (at Catchment 15) or greater (at Catchment 14) values, followed by leaf litter at both sites having the greatest values (Fig. 4). The estimated whole tree δ^{44}Ca values for both species were less than those of the forest floor and mineral soils in both catchments (Table 4).

In Catchment 14, there was a larger gradient of Ca concentrations in leaf litter among species as compared to Catchment 15 (Fig. 5). Additionally, as litter

Table 2 Biomass and Ca pools in sugar maple and beech stemwood, foliage and roots in Catchments 14 and 15 as estimated from vegetation sampling of tree dbh (diameter at 1.4 m) during summer 2002

	Catchment 14			Catchment 15		
	Roots	Stemwood	Foliage[a]	Roots	Stemwood	Foliage[a]
Dry biomass (kg ha^{-1})						
Sugar maple	27,600 (2,750)	137,000 (14,300)	2,840 (276)	17,000 (2,080)	83,200 (10,800)	1,760 (211)
Beech	4,990 (1,020)	16,700 (4,300)	602 (92)	8,540 (719)	27,200 (2,520)	1,070 (79)
Ca (μg g^{-1})						
Sugar maple	2,730 (N/A)	570 (N/A)	14,900 (1,400)	1,590 (N/A)	519 (N/A)	7,870 (674)
Beech	3,200 (N/A)	820 (N/A)	9,540 (975)	467 (N/A)	386 (N/A)	7,550 (441)
Ca (kg ha^{-1})						
Sugar maple	75 (39)	78 (40)	42 (22)	27 (32)	43 (51)	14 (16)
Beech	16 (45)	14 (39)	6 (16)	4 (18)	10 (47)	8 (36)

Values are means (1 SE) for dry biomass and Ca concentrations and means (%) of Ca (kg ha^{-1}) from the three biomass pools

[a] Foliage Ca concentrations were estimated from litter chemistry collected during autumn 2003

Table 3 Calcium concentrations from forest floor and soil collected at Catchments 14 and 15 in 2002

Sample	Type	Method	Catchment 14, mg kg^{-1}		Catchment 15, mg kg^{-1}	
			Mean	SE	Mean	SE
Forest floor	Oe, Oa horizons	Exchangeable	4,490	1,190	1,060	350
Soil	15 cm	Exchangeable	880	560	74	41
Soil	50 cm	Exchangeable	280	60	40	9
Soil	Deep (70–100 cm)	Exchangeable	120	70	14	4
Forest floor	Oe, Oa horizons	Acid-leachable	27,030	4,380	6,580	1,250
Soil	15 cm	Acid-leachable	570	230	180	50
Soil	50 cm	Acid-leachable	650	140	320	120
Soil	Deep (70–100 cm)	Acid-leachable	1,240	150	880	90
Forest floor	Oe, Oa horizons	Exch. + Acid-leach.	31,520	5,480	7,640	1,590
Soil	15 cm	Exch. + Acid-leach.	1,450	800	260	10
Soil	50 cm	Exch. + Acid-leach.	940	70	360	110
Soil	Deep (70–100 cm)	Exch. + Acid-leach.	1,370	90	890	100

Values for Exch. + Acid-leach. represent the sum of the exchangeable and acid-leachable fractions

Ca concentrations increased in Catchment 14, δ^{44}Ca values became progressively larger. A similar trend was not observed in litter from Catchment 15.

Discussion

Our data show that in both catchments, the δ^{44}Ca values of the combined exchangeable plus acid-leachable Ca fractions progressively increased with increasing depth through the soil profile. The increasing trend of δ^{44}Ca values with depth was persistent in Catchment 15, whereas in Catchment 14 there was a greater increase between the forest floor and upper mineral soil and a lesser increase within the mineral soil as compared to the same horizons in Catchment 15 (Fig. 3). While the differences in Ca isotope patterns for soil extracts between the catchments were not statistically significant, due in part to small sample sizes, the apparent trends are nonetheless intriguing and may reflect important process-level differences as discussed below.

The lesser δ^{44}Ca values observed in the upper soil horizons relative to those in the deeper soils mainly

Table 4 Calcium isotope values (‰) from forest floor ($n = 3$), soil ($n = 2$), leaf litter ($n = 2$), stem ($n = 1$), and root samples ($n = 1$) collected at Catchments 14 and 15

Sample	Type	Method	Catchment 14, δ^{44}Ca		Catchment 15, δ^{44}Ca	
			Mean	SE	Mean	SE
Forest floor	Oe, Oa horizons	Exchangeable	−2.35	0.39	−1.92	0.44
Soil	15 cm	Exchangeable	−1.50	0.03	−2.00	0.12
Soil	50 cm	Exchangeable	−1.20	0.18	−1.61	0.05
Soil	Deep (70–100 cm)	Exchangeable	−1.38	0.28	−1.91	0.03
Forest floor	Oe, Oa horizons	Acid-leachable	−2.53	0.19	−2.18	0.40
Soil	15 cm	Acid-leachable	−1.36	0.03	−1.89	0.23
Soil	50 cm	Acid-leachable	−1.06	0.37	−1.45	0.07
Soil	Deep (70–100 cm)	Acid-leachable	−0.88	0.41	−0.90	0.03
Forest floor	Oe, Oa horizons	[Ca] weighted mean	−2.51	0.43	−2.15	0.60
Soil	15 cm	[Ca] weighted mean	−1.44	0.03	−1.90	0.26
Soil	50 cm	[Ca] weighted mean	−1.05	0.41	−1.47	0.08
Soil	Deep (70–100 cm)	[Ca] weighted mean	−0.88	0.50	−0.91	0.03
Leaf litter	Sugar maple	Nitric acid digestion	−1.66	0.05	−1.34	0.18
Leaf litter	Beech	Nitric acid digestion	−1.80	0.05	−1.27	0.16
Leaf litter	White ash	Nitric acid digestion	−1.57	0.23	−1.17	0.12
Leaf litter	Basswood	Nitric acid digestion	−1.38	0.09	N/A	N/A
Stem	Sugar maple	Nitric acid digestion	−2.74	N/A	−3.57	N/A
Stem	Beech	Nitric acid digestion	−2.71	N/A	−3.07	N/A
Roots	Sugar maple	Nitric acid digestion	−4.08	N/A	−3.95	N/A
Roots	Beech	Nitric acid digestion	−3.99	N/A	−2.99	N/A
Whole tree	Sugar maple	Nitric acid digestion	−3.03	N/A	−3.30	N/A
Whole tree	Beech	Nitric acid digestion	−3.17	N/A	−2.47	N/A

Whole tree values are means weighted by Ca concentrations of roots, stems, and leaf litter

reflect the composition of litter deposited at each catchment. We note that the δ^{44}Ca values of the combined exchangeable and acid-leachable fractions in the forest floor were less than that of the leaf litter at each catchment, perhaps reflecting the incorporation of degrading wood biomass in addition to leaf litter in the forest floor. We point out that retention and accumulation of atmospherically derived Ca in the shallow soils probably had little influence on the Ca isotope composition of these soils. Based on a study of precipitation from a variety of locations, atmospherically derived Ca generally resembles carbonates and has δ^{44}Ca values ranging from −1.7 to −0.9‰ (Schmitt and Stille 2005). Silicate dust components in precipitation should have δ^{44}Ca values clustering around −1‰, close to the value for primary silicate minerals (DePaolo 2004) and intermediate to the range observed by Schmitt and Stille (2005). On average, then, atmospherically derived Ca should have δ^{44}Ca values close to −1.3‰, an average value for carbonates. Additionally, records from a NADP (National Atmospheric Deposition Program) site within 5 km of these catchments indicated that wet deposition contributed approximately 0.86 kg Ca ha^{-1} year^{-1} (range 0.14–1.7) from 1978 to 2006. This is a fairly small Ca influx relative to our combined estimates of Ca input from sugar maple and beech leaf litter alone ranging from 22 to 48 kg Ca ha^{-1} year^{-1}. Although we do not have data for dry Ca deposition for these sites, results from a nearby IFS site also located in the Huntington Forest found that dry deposition Ca was a relatively minor component compared to other Ca fluxes within this forest ecosystem (Mitchell et al. 1992; Shepard et al. 1989).

While our results indicated that soil δ^{44}Ca values generally decreased with increasing soil development from parent material to upper mineral horizons, Wiegand et al. (2005) reported increasing δ^{44}Ca

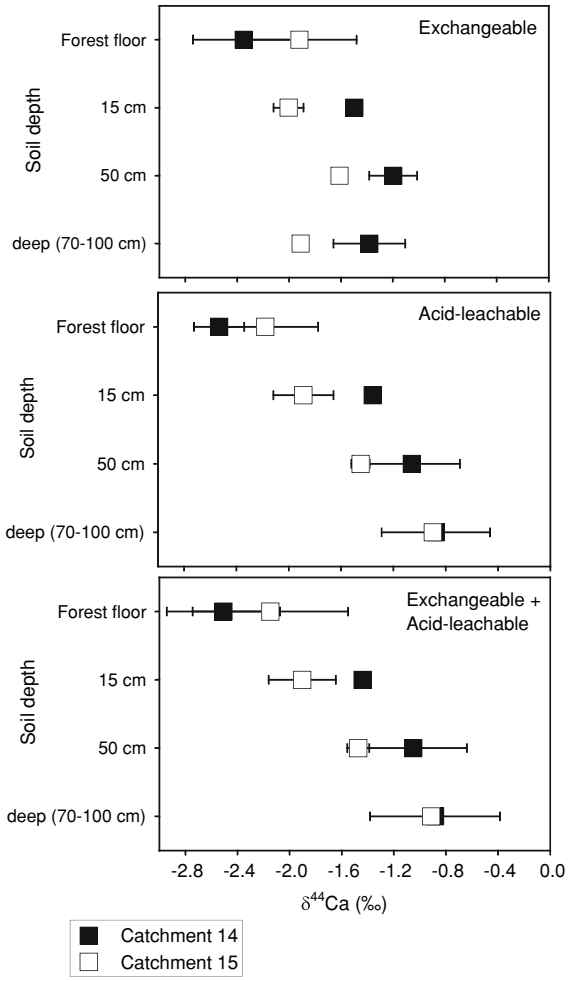

Fig. 3 δ^{44}Ca (‰) mean values from exchangeable and acid-leachable soil fractions from soil samples collected during summer 2002 in Catchment 14 and Catchment 15. Combined exchangeable and acid-leachable δ^{44}Ca (‰) values are calcium-concentration weighted means. Deep samples were from depths ranging from 70 to 100 cm. Error bars are 1 SE. Unseen error bars are smaller than the symbol

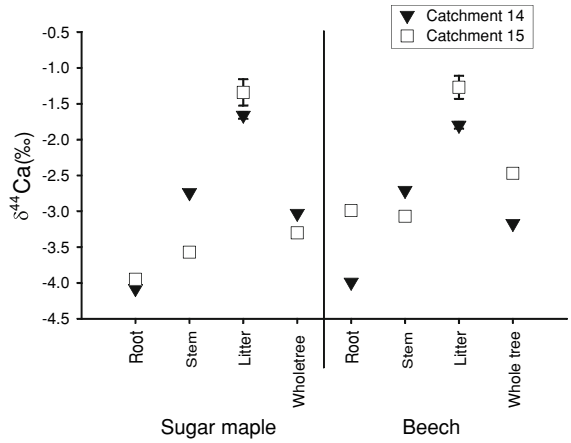

Fig. 4 δ^{44}Ca (‰) mean values from vegetation components from Catchments 14 and 15. Whole tree estimates are weighted by biomass Ca from root, stem, and litter pools. Error bars for leaf litter are 1 SE. Root and stem data are from single aggregate samples and therefore do not have SE bars. Unseen error bars for litter are smaller than the symbol, but SE values are presented in Table 4

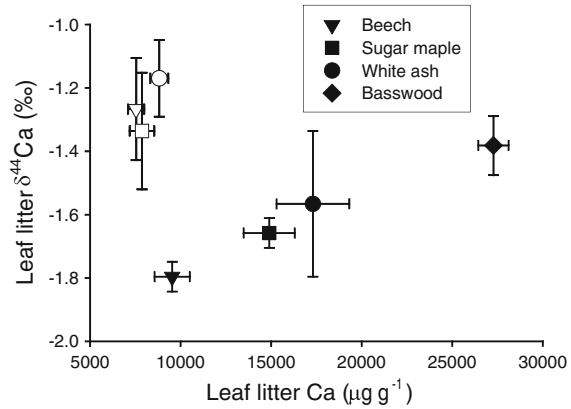

Fig. 5 Litter δ^{44}Ca (‰) values versus Ca concentrations (μg g^{-1}) from Catchment 14 (solid markers) and Catchment 15 (hollow markers) collected during autumn 2003. Error bars are 1 SE

values with increasing soil development over longer pedogenic time-frames in Hawaiian rainforests dominated by Ohia trees. Soils in three of their four sites ranged in age from 150 thousand years to 4.1 million years (Wiegand et al. 2005), whereas the soils in the Adirondacks have been developing more recently from the last glaciation, approximately 14,000 years ago. Mineral weathering over a longer time-frame coupled with the 2× factor increase in precipitation of the Hawaii sites (2,500 mm, Wiegand et al. 2005) relative to the Adirondack sites (1,080 mm) may have resulted in greater Ca leaching from the former. Additionally, the influence of marine aerosols having potentially greater δ^{44}Ca values (δ^{44}Ca of seawater = 0‰) could have been greater at the Hawaiian sites. Similar to our results, Perakis et al. (2006) found that upper mineral soils had lesser δ^{44}Ca values compared to those of deeper mineral soils in Douglas-fir stands in Oregon that receive annual precipitation ~1,700 mm. They suggested that the lesser δ^{44}Ca values within the upper soil horizons were attributable to recycling of biomass-derived Ca in the forest floor.

Our data also indicated that tree roots preferentially take up lighter Ca isotopes from soil pools. Indeed, the δ^{44}Ca values of three of four root samples reported here (−3.95 to −4.08‰) match (within analytical uncertainty) the lightest Ca isotope composition yet reported for a natural terrestrial material, a cougar bone having δ^{44}Ca of −4.1‰ relative to seawater (Skulan et al. 1997). Furthermore, as a result of Ca isotope fractionation at the roots, whole tree δ^{44}Ca estimates were lower than the soil δ^{44}Ca values. Wiegand et al. (2005) similarly reported that plants preferentially take up ^{40}Ca relative to ^{44}Ca, but that relatively greater uptake of the heavier Ca isotopes was observed in nutrient depleted soils relative to nutrient-rich sites. Also similar to Wiegand et al. (2005), we detected Ca fractionation along the transpiration stream within both sugar maple and beech trees (Fig. 4). While the exact mechanism for this internal fractionation is not known, Wiegand et al. (2005) suggested that cation exchange between xylem fluid and cell wall binding sites (McLaughlin and Wimmer 1999), coupled with preferential ^{40}Ca retention at those binding sites, may account for the increasing δ^{44}Ca values up the transpiration stream.

The combined influence of both soil Ca availability and tree species may have further implications for Ca isotope fractionation patterns observed at a given catchment. Our results (Fig. 5) showed that in a comparison of leaf litter from three species (beech, sugar maple, and white ash), that there was a broader gradient of δ^{44}Ca values and Ca concentrations when grown on a site with higher soil Ca concentrations (Catchment 14) as opposed to growth on a site with lower soil Ca concentrations (Catchment 15). In addition, at Catchment 14, the leaf litter of basswood, a relatively calciphilic species (Fujinuma et al. 2005), had the highest litter Ca concentrations and extended the trend of increasing δ^{44}Ca with increasing Ca concentrations of litter at this site. These differences in isotopic patterns, although generally not statistically significant, may suggest that with an increase in soil Ca availability relative to species demand, a greater proportion of light ^{40}Ca can reach the tree canopy through exchange reactions between the xylem fluid and cell wall binding sites. These differences could have further implications when trying to compare δ^{44}Ca values among various species.

Implications and future research

This is the first systematic study of Ca isotope distribution in paired catchments having contrasting Ca status and developed on crystalline bedrock. When we initiated this study, we hypothesized that we would see distinctive, measurable inter-catchment contrasts in Ca isotope distributions in soil extracts and tree tissues driven largely by the several-fold difference in Ca status of these catchments observed in previous studies. However, the inter-catchment differences we observed were not that striking, indicating that the results of our study may have broad transferability to studies of forest ecosystems in catchments developed on crystalline substrates elsewhere. We can conclude that (1) trees preferentially take up light Ca from soil pools; (2) Ca isotopes are fractionated up the transpiration stream of trees, such that roots have the lightest Ca and foliage the heaviest Ca within a tree; and (3) light Ca is concentrated and retained in the forest floor due to recycling of litter and woody biomass. Our results are broadly similar to and extend those of a previous study of Ca isotopes in trees and soils developed on a non-crystalline substrate (Wiegand et al. 2005) and confirm the important role that plants play in producing Ca isotope contrasts in the biosphere.

Initially we had hypothesized that Ca isotope distributions in soil extracts could be used to determine the depth from which Ca is taken up by tree roots. However, due to the similarity of δ^{44}Ca values between the soil and leaf litter pools in these catchments, Ca isotopic values alone would not be sufficient to distinguish Ca from these two sources in an end-member mixing analysis. On the other hand, tree root samples had lower δ^{44}Ca values than any soil pool, and therefore Ca isotopes may be useful for distinguishing Ca uptake mechanisms within the rhizosphere. Furthermore, the evidence of Ca fractionation along the transpiration stream suggests that δ^{44}Ca values may prove useful in evaluating internal Ca cycling processes within trees. At sites where Ca leaching and export to surface water can be monitored, sufficient differences in δ^{44}Ca values among mineral, soil, biotic, and atmospheric sources may enable the identification of specific pathways of Ca loss.

In our study, we observed several inter-catchment differences in Ca isotope distributions, in both

biomass and soil pools, for which we have no definitive explanations but consider worthy of further discussion to suggest directions for future research. For example, as shown in Fig. 4 we observed that δ^{44}Ca values of stemwood in sugar maple and beech at Catchment 15 were similar to that of their roots, while δ^{44}Ca values of stemwood of these trees at Catchment 14 were notably greater than that of their roots. On the other hand, δ^{44}Ca values of foliage of these trees at Catchment 15 were greater than those in Catchment 14. If the cation exchange mechanism for Ca isotope fractionation along the transpiration stream suggested by Wiegand et al. (2005) holds true, then differences in Ca concentration of the transpired fluid in these trees could account for the observed differences in Ca isotope distribution. Specifically, one might predict a greater ratio of dissolved Ca to bound Ca with increasing Ca concentrations in transpired fluid. Thus for Catchment 14, there would be greater chance for Ca isotope equilibration between binding sites and fluid than for Catchment 15, and thus the stemwood in trees at Catchment 14 would evolve to having greater δ^{44}Ca than stemwood in similar trees at Catchment 15. As a result, Ca reaching the foliage would have lesser δ^{44}Ca values at Catchment 14 than foliage at Catchment 15, consistent with our observations. In future studies, careful sampling of transpiration fluid in addition to tree tissue materials in a larger sample set would help to confirm and understand this observed difference in Ca isotope distribution in the trees.

Another observation for which we do not have a definitive explanation relates to the difference in Ca isotope distribution in the exchangeable plus acid-leachable pools in soils from these two catchments, as shown in Fig. 3. Again in the interest of guiding future research approaches, we suggest two possible explanations for these apparent differences in Ca isotope distribution. On one hand, there may be greater leaching and downward transport of Ca from the forest floor at Catchment 15 relative to that at Catchment 14, which would tend to make δ^{44}Ca values of labile Ca in the mineral soil at Catchment 15 appear similar to forest floor values. Alternatively, there may be similar leaching and downward transport of Ca from the organic soils at these sites, but simply more mineral-derived Ca remaining in the labile pool of the mineral soils at Catchment 14 as compared to Catchment 15.

Additional influences on Ca isotope distributions in soils could include differences in mineral weathering rates and tree rooting depths, though we have no specific information on their relative importance within these catchments. Moreover, forest age can also affect Ca cycling within forest floor and mineral soils (Yanai et al. 2005), although the similar structure and history of these two catchments suggest that age is unlikely to be a major factor in the observed differences. Clearly, however, our observations underscore the usefulness of comprehensive lysimetry networks where feasible, in order to chemically and isotopically characterize drainage waters as an input term to soil mass balance calculations.

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