Ca cycling and isotopic fluxes in forested ecosystems in Hawaii

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[1] Biogeochemical processes fractionate Ca isotopes in plants and soils along a 4 million year developmental sequence in the Hawaiian Islands. We observed that plants preferentially take up 40Ca relative to 44Ca, and that biological fractionation and changes in the relative contributions from volcanic and marine sources produce a significant increase in 44Ca in soil exchangeable pools. Our results imply moderate fluxes enriched in 44Ca from strongly nutrient-depleted old soils, in contrast with high 40Ca fluxes in young and little weathered environments. In addition, biological fractionation controls divergent geochemical pathways of Ca and Sr in the plant-soil system. While Ca depletes progressively with increasing soil age, Sr/Ca ratios increase systematically. Sr isotope ratios provide a valuable tracer for provenance studies of alkaline earth elements in forested ecosystems, but its usefulness is limited when deciphering biogeochemical processes involved in the terrestrial Ca cycle. Ca isotopes in combination with Sr/Ca ratios reveal more complex processes involved in the biogeochemistry of Ca and Sr.


1. Introduction

[2] Ca supply helps to determine plant productivity and soil fertility in many ecosystems [McLaughlin and Wimmer, 1999]. Biogeochemical processes involving plant physiology, soil microbial communities, nutrient sources, and water flux control the cycling of Ca in terrestrial environments. Anthropogenic developments of the last century have depleted Ca in many soils worldwide [Lawrence et al., 1995; Likens et al., 1996; Driscoll et al., 2001]. The consequences are decreases in pH with lasting effects on poorly buffered soils and hydrological systems [Reuss and Johnson, 1986; Cronan et al., 1986; Mulder and Stein, 1994]. The weathering of soil minerals can buffer these changes - but in geologically old soils, primary minerals may be exhausted as a source of Ca and other cations [Chadwick et al., 1999; Richter and Markewitz, 2001]. Replenishment of Ca may then be dominated by atmospheric inputs of mineral dust and marine aerosols [Kurtz et al., 2001; Kennedy et al., 1998], and the maintenance of ecosystem functioning may depend primarily on recycling from internal sources.

[3] In order to assess the factors involved in long-term Ca cycling in terrestrial environments, we evaluated pools and isotopic compositions of Ca and Sr in soils and plants in four ecosystems arrayed on a soil chronosequence across the Hawaiian archipelago [Crews et al., 1995; Vitousek, 2004]. Sources of Ca in Hawaiian soils include weathering of volcanic rocks, and atmospheric inputs of marine aerosol and continental mineral dust [Kennedy et al., 1998; Vitousek et al., 1999; Kurtz et al., 2001]. Under tropical high rainfall conditions, rock weathering results in rapid breakdown of minerals. Because dissolved Ca2+ ions are weakly sorbed on soil colloids, they leach into ground and stream water, resulting in an irreversible loss from the soil pool [Juo and Franzluebbers, 2003]. Continued leaching depletes Ca sources in volcanic rock, leading to small pools dominated by Ca from atmospheric deposition of mineral dust and marine aerosols [Birkeland, 1999; Richter and Markewitz, 2001; Chadwick et al., 2003].

2. Methods

[4] The sites developed from volcanic parent rocks and cover 4 million years of soil and ecosystem development. Age differences among the sites are associated with strong variation in nutrient availability, with Ca most abundant in soils and plants in the youngest site. All sites support rainforests that are dominated (80–88%) by native Ohia trees (Metrosideros polymorpha). The understory is mainly composed of ferns, and a variety of woody plants. The forests have never been cleared or systematically altered by people. All sites have similar elevations and current climates with mean annual temperature near 16°C and 2,500 mm annual rainfall. The youngest site is located on tholeiitic flows of Kilauea Volcano on the Big Island of Hawaii, while the three older sites are developed on post-shield alkalic caps on Hawaii, Molokai, and Kauai.

[5] Ca and Sr were extracted from the soil exchange sites using 0.1N ammonium acetate. Bulk soil samples were digested in teflon vials using a mixture of conc. HNO3 and 40% HF (3:1). Leaves and tissues of Metrodiers trees were digested in conc. HNO3. Ca and Sr concentrations were analyzed by ICP-OES (Perkin Elmer Optima 3300 DV) at the Quat. Res. Center, Univ. of Washington, Seattle, WA. Analytical precisions are 5% for Ca and 10% for Sr.

[6] For Ca isotope analysis sample solutions were mixed with a 42Ca-48Ca double spike of known isotopic composition in order to calculate for mass dependent fractionation during chemical preparation and mass spectrometric measurement [e.g., Skulan et al., 1997; Zhu and MacDougall, 1998]. Two sample aliquots, one for Ca and one for Sr, were loaded onto cation exchange columns using Biorad AG50 ×
resin, and eluted with 2.5N HCl. All reagents were distilled.

Purified Sr and Ca fractions were measured on a Thermal Ionization Mass Spectrometer (Finnigan MAT262) at Stanford University using Ta single filaments and 0.25N H3PO4. Ratios of 40Ca, 42Ca, 44Ca, and 48Ca were scanned at least 80 times per sample; replicates were run for selected samples. Routine standard measurements yield a 44Ca/40Ca ratio of 0.021235 ± 0.000004 (2σ: n = 20) for seawater which was used as a standard, and 0.71026 ± 0.00002 (2σ: n = 32) for the NBS987 Sr standard. Variations in the 44Ca/40Ca are expressed in delta notation in % relative to the seawater 44Ca/40Ca ratio of 0.021235 (1):

\[ \delta^{44}\text{Ca} = \left( \frac{44\text{Ca}}{40\text{Ca}}_{\text{sample}} \right) / \left( \frac{44\text{Ca}}{40\text{Ca}}_{\text{awater}} \right) - 1 \times 1000 \]  

(1)

The analytical precision is 0.2‰ or less. Blanks are less than 1 ng for Ca, and less than 0.5 ng for Sr.

Mass-weighted \( \delta^{44}\text{Ca}_{w} \) values are integrated over the first 20 cm of soil profiles and are corrected for changes in thickness \( (d) \), density \( (p) \), and concentrations of Ca \( (Ca_i) \) of single soil horizons \( (h) \) according to equation (2):

\[ \delta^{44}\text{Ca}_{w} = \frac{\sum (\delta^{44}\text{Ca}_i \times d_i \times p_i \times Ca_{ih})}{\sum d_i \times p_i \times Ca_{ih}} \]  

(2)

3. Results and Discussion

Previous Sr isotope analyses by Kennedy et al. [1998] demonstrate changes in the provenance of Sr during ecosystem development in Hawaii. \(^{87}\text{Sr}^{86}\text{Sr} \) ratios of leaves from *Metrosideros* trees and soil exchangeable pools increase from 0.704 to 0.709 along the chronosequence, reflecting an increasing contribution of marine aerosols to plant-available pools (Figure 1a). The youngest site (0.3 ka) is little weathered and still contains most of its Sr in primary igneous minerals; about 90% of the plant-available Sr is derived from mineral weathering. The intermediate-aged site (150 ka) contains a highly weathered soil that has chemically active non-crystalline phases. Depletion of basalt-derived Sr in the soil is greater than 98%, and contributions of marine aerosols to the plant available Sr pool reach 70%. In the two oldest sites (1,400 ka and 4,100 ka) soils have undergone progressively greater transformation to relatively inert kaolin, and metal oxhydroxides. Few alkaline earth ions remain, and available Sr is almost exclusively (90–96%) supplied by atmospheric inputs [Kennedy et al., 1998; Chadwick et al., 1999].

![Figure 1](image-url)  
**Figure 1.** Avg. (a) \(^{87}\text{Sr}^{86}\text{Sr} \) and (b) Sr/Ca ratios in leaves of *Metrosideros* trees and soil pools across the age sequence: Thurston (0.3 ka), Kohala (150 ka), Molokai (1,400 ka), and Kauai (4,100 ka). End member values of the contributing sources are Hawaiian lava: \(^{86}\text{Sr}^{86}\text{Sr} 0.7035, \text{Sr/Ca} < 0.004\); marine aerosol (seawater: \(^{87}\text{Sr}^{86}\text{Sr} 0.7092, \text{Sr/Ca} 0.019\)).
shift to more $^{44}$Ca relative to $^{40}$Ca at the treetop can be explained by kinetic Ca isotope fractionation in the transpiration stream, driven by ion-exchange reactions within cell walls of the conducting xylem sapwood. Overall, $^{40}$Ca and Sr are preferentially incorporated in woody tissues, while Ca in xylem solution progressively enriches in $^{44}$Ca and depletes in Sr before reaching the canopy. Differences in Ca isotope ratios between leaves and other plant tissues were previously observed by [Platzer and Degani, 1990; Schmitt et al., 2003].

[12] Mass-weighted $^{44}$Ca$_{av}$ values from the exchange sites of the surface horizons are enriched in $^{44}$Ca by up to 1.4% $^{44}$Ca relative to total soil Ca in all but the youngest site (Figures 2a and 2b). Both exchangeable and total Ca pools decrease with soil age and increasing ecosystem development [Chadwick et al., 1999]. We interpret the increase in $^{44}$Ca in soil exchangeable pools as reflecting a combination of factors: (1) the dominance of marine aerosol-derived Ca (seawater has $^{44}$Ca of 0.0 ± 0.2‰) in small soil exchangeable pools, (2) the preferential plant uptake of $^{44}$Ca from those pools causing significant increases in $^{44}$Ca, and (3) the preferential partitioning of $^{40}$Ca in wood that turns over slowly, and hence relative enrichment of $^{44}$Ca in leaf litter. In the older sites exchangeable pools are small enough to develop a detectable enrichment in $^{44}$Ca by these processes, and Ca leached from these soils should be enriched in $^{44}$Ca. In contrast, in the young sites, rapid weathering of lava provides large plant-available Ca pools that dominate Ca cycling.

[13] $^{44}$Ca$_{av}$ values vary only little in total soil pools, except at the 1,400 ka Molokai site where $^{44}$Ca is enriched in all pools. Total Ca pools in the soil profiles are composed of mixtures from different sources that are distinct in their Ca isotopic compositions: volcanic rocks (avg. $^{44}$Ca = 1.1 ± 0.3‰; n = 3), continental dust (avg. $^{44}$Ca = 2.3 ± 0.2‰; n = 2), and soil organic matter (SOM) that has captured Ca from marine aerosols. While high amounts of continental dust would shift the Ca isotopic composition of soils towards enrichment in $^{40}$Ca, the accumulation of SOM that is enriched in $^{44}$Ca in old, Ca-depleted soil sites drives an opposite shift towards enrichment of $^{40}$Ca. Net primary productivity on this sequence peaks in the Molokai site (Figure 2c) [Herbert and Fownes, 1999], and there is a

Table 1. $^{44}$Ca (or $^{44}$Ca$_{av}$ for Soils), $^{87}$Sr/86Sr, and Sr/Ca in Leaves of Metrosideros Trees, Exchangeable and Total Soil Pools$^a$

<table>
<thead>
<tr>
<th>Location</th>
<th>Age, ka</th>
<th>$^{44}$Ca (1σ)</th>
<th>$^{87}$Sr/86Sr (1σ)</th>
<th>Sr/Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thurston</td>
<td>0.3</td>
<td>-1.29 (32)</td>
<td>0.70434 (15)</td>
<td>9.0032</td>
</tr>
<tr>
<td>Kohala</td>
<td>150</td>
<td>-1.01 (13)</td>
<td>0.70752 (2)</td>
<td>1.0137</td>
</tr>
<tr>
<td>Molokai</td>
<td>1,400</td>
<td>-0.22 (20)</td>
<td>0.70860 (2)</td>
<td>1.0080</td>
</tr>
<tr>
<td>Kauai</td>
<td>4,100</td>
<td>-0.45 (27)</td>
<td>0.70861 (8)</td>
<td>1.0102</td>
</tr>
</tbody>
</table>

$^a$Average values are followed by 1σ errors in the last digit(s) of the stated value (n = number of samples or soil horizons).

$^b$Analytical errors (2σ) apply to single data.

$^{44}$Ca and Sr/Ca of soils and plant tissues parallel the source-dependent shift of Sr isotopes from young to old sites (Figures 1a, 1b, and 2a and Table 1), but for those tracers both fractionation processes and differences in sources contribute to the overall pattern. For example, $^{44}$Ca and Sr/Ca ratios vary in different tissues of Metrosideros trees, in contrast to the conservative behavior of the Sr isotopes (Figure 3). Ca is abundant relative to Sr in leaves and roots of Metrosideros trees, while Sr concentrations are relatively greater in twigs and stem. During Ca uptake and xylem transport, Ca isotopes are fractionated in root and stem tissues by -1.0 to -2.0‰ $^{44}$Ca ($^{44}$Ca refers to the difference in $^{44}$Ca between two pools) relative to exchangeable pools, while twigs and leaves support isotopically heavier Ca pools of $^{44}$Ca: +0.5 to +0.7‰, relative to stem and roots. The results suggest a preferential absorption of $^{40}$Ca by roots. Ca uptake by roots follows electrochemical gradients and involves Ca channels (specialized transport proteins) that catalyze Ca$^{2+}$ flux across the plasma membrane [White, 2000; White et al., 2002]. This uptake process is likely to cause kinetic Ca isotope fractionation leading to preferred absorption of the lighter $^{40}$Ca isotope. Fractionation during uptake can enrich the remaining soil exchangeable pool in $^{44}$Ca where uptake is large relative to the pool size of Ca in soil. Within the tree, the

![Figure 3. $^{44}$Ca, Sr/Ca, and $^{87}$Sr/86Sr of Metrosideros trees from the 4,100 ka (triangles) and the 0.3 ka site (circles).](image-url)
significant linear correlation ($R^2 = 0.97$) between $\delta^{44}Ca_{w}$ of exchangeable pools and the abundance of SOM across the age sequence. The Molokai site has the highest concentrations of SOM in the surface soil horizon (Figure 2c), contributing to the pronounced enrichment in $^{44}Ca$ at this site.

Another important observation is that increases in Sr/Ca ratios in total soil pools parallel the increase in $\Delta^{44}Ca$ values across the soil chronosequence ($R^2 = 0.99$). The increase of Sr/Ca ratios reflects biological fractionation and progressive depletion of Ca relative to Sr with increasing substrate age. Long-lived plant pools (e.g., woody tissues of *Metrosideros*) preferentially preserve Sr while shorter-lived pools (leaves, fine roots) have higher abundances of Ca that tend to cycle more readily through the plant-soil system. As $Sr^{2+}$ ions are more strongly adsorbed to cation exchange sites in soils than $Ca^{2+}$ ions, Ca is leached more readily and in the long term losses will increase Sr in all pools [Capo et al., 1998].

### 4. Conclusions

The results of this study confirm considerable differences in the biogeochemical behavior of Ca and Sr that lead to divergent pathways of the two elements in the plant-soil system. In Hawaii, the strong decline in alkaline earth element concentrations from rapid weathering of volcanic rock allows us to attribute shifting proportions of Sr and Ca and their isotopes to particular ecosystem conditions. Whereas $^{87}Sr/^{86}Sr$ ratios provide a direct measure of Sr sources, $^{44}Ca$ values and Sr/Ca ratios provide signals that reflect both nutrient provenance and biological cycling. The processes causing shifts in the investigated tracers are not unique to Hawaii, but they are easier to document there.

The extent of detectable biological isotope effects on Ca in soils depends on the size of plant-available Ca pools and biomass productivity. The coupling of changes in biomass productivity and the evolution of Ca isotopes in Hawaiian ecosystems implies that intensely weathered and poorly buffered regions globally should have elevated $^{44}Ca$ values indicative of ecosystems dependent on internally cycled nutrient stores.

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### References


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