Use of elemental and isotopic ratios to distinguish between lithogenic and biogenic sources of soil mineral nutrients

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Abstract
Although mineral nutrients such K, Ca, Mg and Si, are vital to plant growth and productivity, their sources and cycling in soils are difficult to characterize due to complex inorganic and biologic interactions. This paper investigates the use of major-trace element ratios Sr/Ca, Rb/K and Ge/Si, as well as the isotopic ratios $^{87}Sr/^{86}Sr$, $^{44}Ca/^{40}Ca$ and $^{24}Mg/^{22}Mg$ in deciphering temporal and spatial characteristics of mineral nutrients in pore waters, precipitation and vegetation associated with soils on a marine terrace chronosequence near Santa Cruz California. Seasonal plant growth patterns associated with the Mediterranean climate, along with strong soil permeability gradients, instill strong periodicities in elemental and isotopic cycling by the plants which are reflected in both selective extraction and passive litter decomposition.

Key Words
Isotopes, strontium, rubidium, germanium, chronosequence, mineral nutrients

Introduction
The physiological strategies by which plants utilize major mineral nutrients are generally well characterized. (Marschner 1995). However, the sources and fates of these nutrients in the soil environment are less understood due to complex interactions resulting from inputs from precipitation and weathering, as well as dynamic fluxes between pore water and soil organic and inorganic exchange complexes. Recent advances in analytical techniques, principally in mass spectroscopy, have provided access to an array of trace elements and isotopes that serve as important tracers for macronutrient behavior in the soil environment. In this paper, the use of the major-trace element pairs with similar chemical affinities, i. e., Sr/Ca, Rb/K and Ge/Si, in addition to isotopic ratios for $^{87}Sr/^{86}Sr$, $^{44}Ca/^{40}Ca$ and $^{24}Mg/^{22}Mg$, are investigated. The soils in this study comprise a chronosequence ranging in age from 65 to 225 kyrs, developed on marine terrace deposits along the coast of northern California. Vegetation consists primarily of annual European grasses whose growth cycle is controlled by a Mediterranean climate consisting of distinct wet and dry seasons. Detailed discussions of site climate, hydrology, geology and chemical weathering are contained in White *et al.* (2009).

Elemental Ratios
Small variations, such as in ionic radii and potentials of otherwise chemically similar elements, produce behavioral differences which are useful in tracing pathways in the soil environment (Tyler, 2004). These differences can be defined by a fractionation factor describing the concentration ratios in the plant and soil pore water

$$K_{trace/major} = \frac{\left[C_{trace} / C_{major} \right]_{plant}}{\left[C_{trace} / C_{major} \right]_{soil}}. \quad (1)$$

Sr/Ca fractionation
Numerous studies have addressed the partitioning of Ca and Sr between soil and vegetation, initially in terms of pathways for radioactive ^{90}Sr and more recently, in conjugation with $^{87}Sr/^{86}Sr$, for Ca availability, particularly in forest ecosystems. Results indicate complex interactions in which plants either concentrate or exclude Sr relative to Ca in the soil environment.
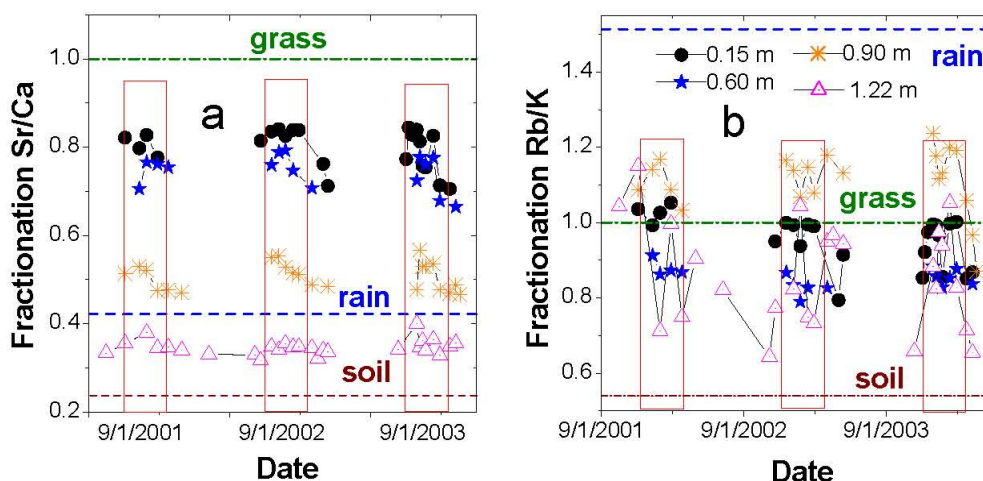
Figure 1. Seasonal variations in apparent fractionation factors (Eqn. 1) for (a) Sr/Ca and (b) Rb/K between plants and pore waters sampled at successively greater depths in the 92 kyr old Santa Cruz terrace. Horizontal lines correspond to zero fractionation of grass relative pore water ($K_{Sr/Ca}$), rain and bulk soil. Rectangular boxes define pore water variations during the growing season.

In the Santa Cruz soils, $K_{Sr/Ca}$ values are always less than unity, indicating the preferential uptake of plant Ca relative Sr (Figure 1a). However these $K_{Sr/Ca}$ values for shallow pore waters remain significantly higher than those for rain and soil weathering, suggesting Ca retention during closed system nutrient cycling. This effect is further elucidated by high, more plant-like $K_{Sr/Ca}$ values at the beginning of the growing season due to inputs to pore water from decaying plant litter. Later in the season, as plant growth intensifies, the $K_{Sr/Ca}$ values decline, indicating the exclusion of Sr relative to Ca in the biomass and consequent enrichment in the pore water. This seasonal cycling is diminished with depth and is nearly absent below the grass rooting depth of about 1 m where $K_{Sr/Ca}$ values approach that expected for plagioclase feldspar weathering (Figure 1a).
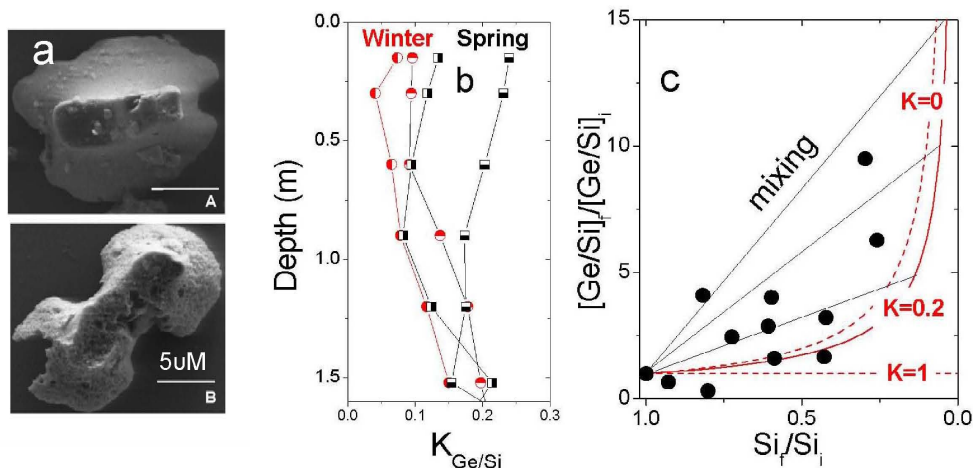
Rb/K fractionation
Recently, the partitioning of K and Rb has been investigated in terms of the contribution of biogenic K to watersheds and river systems (Chaudhuri *et al.* 2007). Shallow pore water K/Rb ratios at Santa Cruz are an order of magnitude lower than those of Sr/Ca, reflecting the strong retention of exchangeable Rb relative to K on clays. Although $K_{Rb/K}$ values differ between water samplers (Figure 1b), there is no consistent patterns with depth or seasonality. Average $K_{Rb/K}$ values cluster near unity, indicating that Santa Cruz grasses do not significantly distinguish between K and Rb during nutrient uptake. This conclusion is at odds with the literature consensus that Rb is preferentially excluded in biological material. These previous comparisons were most often made using bulk soils which contain relatively high and more tightly bound Rb compared more readily accessible soil pore water Rb considered in the present study. Unlike for Ca/Sr ratios, fractionation by vegetation is not a *a priori* requirement to explain K/Rb ratios in shallow pore waters which can be simple mixtures between high K/Rb ratios in precipitation and low K/Rb ratios produced by K-feldspar weathering (Figure 1b).

Ge/Si fractionation
Derry *et al*. (2005) suggested that high Ge/Si ratios in rivers reflect the exclusion of Ge and the high proportion of Si cycled by plants, principally in the form of phytoliths (Figure 2a). Such residual Ge increases are supported by low $K_{Ge/Si}$ values (Eqn. 1) for pore waters plotted as functions of depth in the 92 kyrs old Santa Cruz terrace (Figure 2b). The lowest $K_{Ge/Si}$ values occur in shallow pore water at the beginning of the growing season (early January) and increase to near the end of the growth season (April). Ideally, the Ge/Si fractionation factor should remain constant with the apparent seasonal variability in $K_{Ge/Si}$ reflecting the fact that the grass Ge/Si ratios are seasonally integrated values while the pore water ratios reflect changes in seasonal bioaccumulation.

One approach to describing Ge-Si cycling between the pore water and grasses is the Rayleigh relationship commonly used for isotopic fractionation. This can be written for Ge and Si as

Figure 2. (a) Fresh and partly weathered grass phytoliths isolated from the 92 kyr old Santa Cruz soil. (b) Ge/Si fractionation factors (Eqn. 1) at beginning and conclusion of growing season. (3) Comparison of measured Ge/Si ratos with predicted Rayleigh fractionation curves using different $K_{Ge/Si}$ values (Eqn. 2).

$$\frac{[Ge/Si]_f}{[Ge/Si]_i} = (Si_f/Si_i)^{(K_{Ge/Si}-1)}. \quad (2)$$

where $[Ge/Si]_i$ and $[Ge/Si]_f$ are the initial and final pore water ratios and Si_i and Si_f are the initial and final Si concentrations. The application of this Rayleigh relationship requires two conditions; the system is closed and that irreversible uptake occurs via a reactant, i. e., plant growth. The last condition is presumably met since Ge and Si are incorporated in the grass phytoliths (Figure 2a) and do not re-equilibrate with the pore waters. However the extend to which nutrient uptake occurs under closed system conditions is less well defined.

The model assumes that the initial pore waters at the start of growing season have high Si and low Ge/Si ratios reflecting dissolution of phyoliths in plant liter produced during the previous growing season (Figure 2c). With the onset of new plant grow, Si_f/Si_i decreases and $[Ge/Si]_f/[Ge/Si]_i$ increases. The extents of these changes will be dependent on the fractionation factor. If no fractionation occurs, i. e., $K_{Ge/Si} = 1$, Eqn. 2 results in a straight line in which $[Ge/Si]_f/[Ge/Si]_i = 1$ for all values of Si_f/Si_i. Concurrently, complete exclusion of Ge during Si uptake, i. e., $K_{Ge/Si} = 0$, produces a steep exponential increases in $[Ge/Si]_f/[Ge/Si]_i$. An intermediate exponential line is produced assuming that $K_{Ge/Si} = $ of 0.2, the approximate minimum fractionation shown in Figure 2b. The data points in Figure 2c, corresponding to measured Ge and Si in pore waters from several of the terraces, together exhibit an exponential trend of increasing Ge/Si with Si which is compatible with closed system Rayleigh distillation. However, this data trend suggests a more rapid increase in pore water Ge than expected based the range of possible fractionation factors in Eqn. 2, i. e., $K_{Ge/Si} = 0$ to 1.

The apparent anomaly most likely results from the assumption of sequential processes, i. e., pore water compositions are initially fixed by dissolution of the past seasons' plant litter phytoliths (high Si and low Ge in pore water) followed by the onset of selective extraction during the current seasons' growth (low Si and high Ge in pore water). A more accurate scenario, based on the relatively slow rates of phyotolith dissolution, is that of concurrent extraction and leaching. Schematically these processes are shown in Figure 2c by inclusion of linear mixing lines extending backward from biogenically fractioned pore waters toward initial pore water compositions dominated by phytolith dissolution at the initiation of seasonal plant growth. A two step process, involving various degrees of fractionation and mixing, are capable of reproducing the data field shown in Figure 2c

Isotopic Fractionation of Sr, Mg and Ca

The sensitivity of plants to uptake of different isotopes of the same elemental nutrient is dependent, in part, on their respective mass differences, i. e mass fractionation. Due to very small mass differences, plants do not exhibit measureable fractionation of $^{87}Sr/^{86}Sr$. This conclusion is supported by the data for the 95 kyr old soil (Figure 3a) which exhibit consistent trends in pore water and exchange $^{87}Sr/^{86}Sr$ extending between the

[87]Sr/[86]Sr composition of rain at shallow depths and toward more radiogenic plagioclase at greater depths. Grass [87]Sr/[86]Sr falls between shallow pore water and rain implying simple uptake of a mixture of these components with no fractionation.
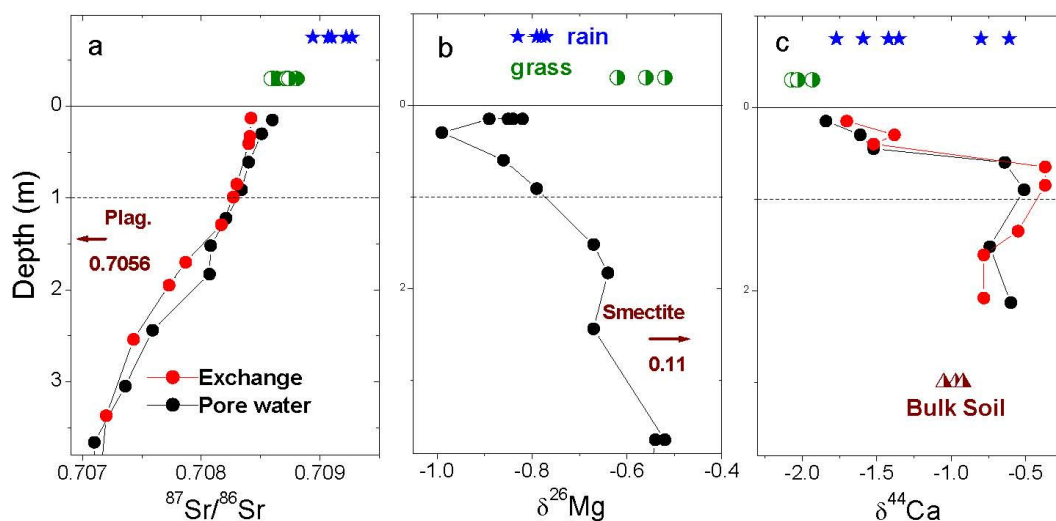
Figure 3. Distributions of selective isotopes of Sr, Mg and Ca in grasses pore waters, exchange sites and precipitation. Dashed line corresponds to maximum grass rotting depth.

Presently little information exists on the distribution of $^{26}Mg/^{24}Mg$ in soil environments with the data in Figure 3b representing the first direct comparison with Sr and Ca isotopes. Limited experimental data suggest that plants preferentially take up ^{26}Mg relative to ^{24}Mg, a conclusion supported by the Santa Cruz soils where plants are isotopically heavier than either rain or shallow pore waters (Figure 3b). At depth, $\delta^{26}Mg$ increases in pore waters due to increasing effects of smectite weathering. $^{44}Ca/^{40}Ca$ distributions exhibit the greatest biologic fractionation with $\delta^{44}Ca$ in grasses and shallow pore waters significantly lower than that of either rain or deeper pore waters reflecting soil weathering (Figure 3c).

Conclusions

The stable isotopes of major elements, in addition to trace-major element pairs of comparable chemical affinity, serve as importance tracers for nutrient cycling between plants and soils. Sr/Ca and Ge/Si fractionation factors are less than unity, indicating consistent discrimination of annual grasses against the heavier trace elements. Rb/K fraction factors are approximately unity, which, contrary to earlier work, indicates a lack of discrimination. A simple closed-system Rayleigh relationship can be used to explain fractionation between plants and pore waters, assuming simultaneous plant extraction and leaching. Isotopic fractionation of Sr, Mg and Ca exhibits a mass dependence, but the actual biologic dependence is determined by plant physiology which selectively enriches grasses with respect to isotopically heavy Mg but discriminate against isotopically heavy Ca.

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