Structured Heterogeneity in a Marine Terrace Chronosequence: Upland Mottling

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Soil mottles generally are interpreted as a product of reducing conditions during periods of water saturation. The upland soils of the Santa Cruz, CA, marine terrace chronosequence display an evolving sequence of reticulate mottling from the youngest soil (65 ka) without mottles to the oldest soil (225 ka) with well-developed mottles. The mottles consist of an interconnected network of clay and C-enriched regions (gray, 2.5Y 6/1) bordered by leached parent material (white, 2.5Y 8/1) within a diminishing matrix of oxidized parent material (orange, 7.5YR 5/8). The mottles develop in soils that formed from relatively uniform nearshore sediments and occur below the depth of soil bioturbation. To explore how a presumably wetland feature occurs in an unsaturated upland soil, physical and chemical characteristics of mottle separates (orange, gray, and white) were compared through the deep time represented by the soil chronosequence. Mineralogical, isotopic, and surface-area differences among mottle separates indicate that rhizogenic centimeter-scale mass transfer acting across millennia is an integral part of weathering, pedogenesis, and C and nutrient transfer. Elemental analysis, electron microscopy, and Fe-isotope systematics indicate that mottle development is driven by deep roots together with their fungal and microbial symbionts. Taken together, these data suggest that deep soil horizons on old stable landforms can develop reticulate mottling as the long-term imprint of rhizospheric processes. The processes of rhizogenic mottle formation appear to regulate pedogenesis, nutrients, and C sequestration at depth in unsaturated zones.

Abbreviations: SEM, scanning electron microscope; XRD, X-ray diffraction.

Soils develop through complex interactions of climatic, biotic, and abiotic factors (Jenny, 1941). Soil formation in unconsolidated sediment proceeds uniformly, creating soil horizons that are generally parallel to the soil surface. The soils in a chronosequence near Santa Cruz, CA, occur in unconsolidated sediments where the older soils have at depth developed complex heterogeneity in the form of reticulate mottling (motting in a net or boxlike configuration). To understand the formation processes of heterogeneity, we must consider the complete network of soil-forming factors. Figure 1 illustrates interactions among the soil-forming factors, which when charted this way, illustrate soil moisture as the master variable through which other factors are regulated. Ecosystems are organized by water availability, and mineral dissolution and precipitation reactions are controlled by solutions. Soil moisture is important; even so, it is instructive to consider the time of soil development to understand profile heterogeneity.

Reticulate mottles are relatively unreported in the literature (which does not mean that they are rare). The objective of this study was to investigate these soil mottles and define the processes of formation. The mottles are most readily characterized by the observed orange presence or gray or white absence of Fe. Mottle formation is directly linked to the translocation of Fe in soils, and thus the processes controlling Fe mobility must be understood to adequately describe mottle formation. Ferric Fe is largely insoluble under the oxidizing
conditions of upland soils, but water-logging and high organic contents in wetland soils create reducing conditions under which soluble Fe$^{2+}$ moves readily by advection and diffusion in pore water (Richardson and Vepraskas, 2000). This process can create redoximorphic features (often referred to as mottles). Unlike the well-studied redoximorphic features of wetland soils, the marine terrace soils at Santa Cruz are relatively C-poor, upland soils, which are well oxygenated most of the year. The dissolved concentration of Fe in Santa Cruz soil waters is typically below detection in all seasons of the year (White et al., 2009), yet the Santa Cruz soils have well-developed mottling at depth, requiring the movement of Fe.

Given the present conditions, it seems unlikely that mottling in the Santa Cruz chronosequence resulted from the same pathway observed in wetland soils. We propose an alternative pathway, where the redistribution of Fe is driven by biotic processes. Iron is an essential micronutrient and, as a result, is relocated in soils through uptake by plants, bacteria, and fungi (Johnson et al., 2002; Graham and Stangoulis, 2003; Li et al., 2008; Porder and Chadwick, 2009; Lemanceau et al., 2009; Li and Richter, 2012). Solute concentrations of Fe in aerated soil are too low to support most biological growth. Therefore, plants and their symbionts have evolved strategies for rhizospheric Fe mobilization involving (Strategy I) acid-promoted dissolution and reduction followed by reductase-facilitated uptake through the cell membrane (Marschner, 1995; Marschner and Romheld, 1994) and (Strategy II) chelation by root-generated phytosiderophores (Guerinot and Yi, 1994; Lemanceau et al., 2009). Many Strategy I plant roots also exude phenolics and other Fe-binding ligands (Graham and Stangoulis, 2003; Colombo et al., 2014). The cumulative long-term effect of rhizospheric Fe uptake has an imprint on soil development, particularly for Fe distribution in older soils.

Plant exudates create steep localized gradients in soil moisture, pH, chemical concentrations, and redox potential (Marschner, 1995) and generate zones of high biologic activity immediately adjacent to growing roots with chemical conditions distinct from those of the bulk soil. Roots, and therefore rhizospheres, often extend well below the depth of bioturbation (Maeght et al., 2013; Laclau et al., 2013; Graham et al., 2010; Allen, 2007; McCulley et al., 2004; Egerton-Warburton et al., 2003). Rhizospheric features will persist in unmixed soil and can be further modified by the postmortem decomposition of decaying roots. As an additional feedback, new roots tend to follow existing fractures, burrows, and old root channels (Rasse and Smucker, 1998; Egerton-Warburton et al., 2003; White and Kirkegaard, 2010), meaning that root-driven exudates are repeatedly applied to the same materials. A relatively small portion of deep soil can be repeatedly subjected to chemical attack in the rhizosphere and become preferentially weathered (April and Keller, 1990).

Previous work has shown that reticulate mottling occurs in upland forest soils of the Appalachian Piedmont (Fimmen et al., 2008). This work interpreted mottles as the product of rhizospheric-driven Fe redox reactions coupled to weathering reactions involving the dissolution of primary minerals and precipitation of secondary
clays. The similarity of the deep Santa Cruz mottles in color, texture, and structure to those described by Fimmen et al. (2008) suggests that rhizospheric processes may be responsible for the development of structured heterogeneity in the Santa Cruz marine terrace sediments as well.

A literature search uncovered a few additional descriptions of deep reticulate mottling in upland soils. Johnson (1972) described “reticulate polygonal structures” in the B2 argillic horizon of an upland Green Mountain soil on San Miguel Island, off the southern coast of California. Stolt et al. (1994) described “strongly contrasting redoximorphic patterns” in upland soils of the Ridge and Valley Province in Virginia. Moody and Graham (1995) described “redoximorphic” mottling in coastal terraces in San Luis County, California. These consisted of gray mottles in the “basal regolith” that became progressively more prominent with increasing terrace age. MacEwan et al. (2012) described “tiger soils” containing mottles at depth on upland soils in low hills forming the southern rim of the Murray-Darling drainage basin in Victoria, Australia. Each of these studies proposed a different formation process for the mottles, perhaps due to the lack of a general model paradigm for deep soil upland mottling.

Stable Fe isotopic ratios are an increasingly useful tool for investigating Fe movement in soils. Recent work has improved understanding of Fe isotopic fractionation processes in porous solids and the solutions they contain (Brantley et al., 2001; Beard et al., 2003; Fantle and DePaolo, 2004; Emmanuel et al., 2005; Thompson et al., 2007; Moynier et al., 2013; Wiederhold et al., 2006, 2007a, 2007b). Relevant to the current study is the discovery that plants preferentially take up isotopically light Fe through their roots (Guelke and von Blanckenburg, 2007; Moynier et al., 2013). Preferential uptake and subsequent biocycling of light Fe by plants over the course of hundreds of thousands of years is expected to “enrich” shallow soil in isotopically light Fe. Isotopic profiles of old temperate soils indeed show isotopically light Fe accumulating at the surface (Fantle and DePaolo, 2004; Emmanuel et al., 2005).

Whereas previous studies looked at Fe isotope systematics in bulk soil, in this study we examined isotopic fraction of Fe in mottle separates as well as the bulk soil.

Biologically enhanced weathering of primary minerals for nutrient acquisition is important and has implications for soil formation, nutrient cycling, and C sequestration, but our understanding of the underlying processes is incomplete. The goal of the current study was to investigate the nature and development of heterogeneity (reticulate mottling) in the Santa Cruz terrace soils. Specific questions of the study included the following:

1. Do rhizospheric processes drive mottle formation?
2. How does mottling progress through time? Does the rate of mottle development change across the observational time frame of the chronosequence?

Mottle formation involves the movement and transformation of C in concert with the key weathering and nutrient elements Ca, K, Fe, and Al. Detailed study of mottles thus provides insight into the organization of deep C and nutrients in soils. By analyzing separates of the mottle zones for physical, chemical, and biological differences, we further explored and tested the ideas of Fimmen et al. (2008) to determine if these upland mottles are rhizogenic. Understanding upland mottle development will lead to a better understanding of deep soil processes and ecosystem function.

Materials and Methods

Site Description

Coastal marine terraces west and north of Santa Cruz, California (Fig. 2) consist of bedrock platforms covered by sediment. The bedrock platforms were carved into the Santa Cruz Mudstone and Santa Margarita Sandstone by wave action during high stands of sea level creating relatively flat surfaces that are blanketed with 1–10 m of sediment. Wave-cut platforms become terraces when they are stranded from further inundation by tectonic uplift (Bradley, 1957), and as near shore marine sediments over lain by fluvial, colluvial and aeolian deposits (Weber and Allwardt, 2001). Here the terraces are numbered sequentially starting at sea level, with terrace T0 representing current sea level, T1 the terrace adjacent to the present-day sea cliff, and so forth.

The soils of the Santa Cruz chronosequence are forming in shallow marine sediments. The youngest soil (65 ka) has an A horizon but no Bt horizon and no mottling. In this soil, orange-hued Fe oxides have formed a relatively uniform coating on primary mineral grains throughout the sediment deposit. Older members of the Santa Cruz chronosequence (90–226 ka, Terraces 2–5) display Bt horizons below the depth of bioturbation that contain mottles of high and low chroma (Fig. 3). The Bt horizons of the older terraces contrast strongly with the parent material with respect to bulk texture and other properties (White et al., 2008). The marine terraces near Santa Cruz have been dated using the cosmogenic isotopes $^{10}$Be and $^{26}$Al (Perg et al., 2001). The age determination has facilitated quantitative testing and development of reactive transport models for weathering and soil-profile development (White et al., 2009; Maher et al., 2009; Lawrence et al., 2014). Previous work on weathering and soil profile formation considered changes in bulk
mineralogy and pore-water chemistry with depth. This previous work treated the terrace soils as horizontally homogeneous as they evolved through time, and rhizospheric processes were not considered except through bulk chemical proxies.

The sediments of the terrace deposits are primarily granitic in composition and derive from the core of the Santa Cruz Mountains (White et al., 2008). Clay present in unweathered deep terrace sediments, noted by Bradley (1957) and identified by White et al. (2008) as Fe-rich smectite, constrains the depositional environment to shallow marine. This smectite, derived from local exposures of the Purisima Formation (Anima et al., 2002), is an important source of Fe in the weathering profile.

The studied soils are part of a coastal prairie ecosystem currently dominated by European annual grasses fringed by native shrubs. The non-native grasses have been present approximately 300 yr (Keeley, 2002). Pre-contact land use on coastal prairies included burn regimes imposed by Native Americans (Keeley, 2002). Detailed vegetational successions through glacial–interglacial cycles are unknown, although their cumulative pedogenic effects are present by proxy.

The current climate is Mediterranean, with cool wet winters and warm dry summers. The mean annual precipitation and temperature in Santa Cruz is ~730 mm and 13.4°C. The orographic influence of Ben Lomond Mountain causes the higher terraces to receive more rainfall than the lower (White et al., 2009), with the higher terrace sites of this study receiving approximately 20% more precipitation than the lower sites during a 1-yr monitoring period.

**Field and Sampling Methods**

Initial surveys for site establishment were conducted by hand auguring and field observations. Five sites, one per terrace, were selected from this survey for intensive characterization (White et al., 2008). Selection criteria included a lack of significant physical erosion based on lateral persistence of nearly flat topographic surfaces, ample distance from edges and toes of adjacent paleo sea cliffs, and lack of evidence of anthropogenic influences. Site selection also included sufficient sediment depth (3–9 m) to provide sampling into relatively unweathered parent material. One soil pit was excavated on each terrace for the data presented here. However, during the longer term study (White et al., 2008, 2009), each terrace had several soil pits opened, showing that the mottles...
described in detail here are laterally persistent across each terrace. Samples of the Purisima Formation were collected for Fe isotope analyses from an outcrop along the present-day sea cliff between Pigeon Point lighthouse and Natural Bridges State Beach. Grab samples of granite were collected from unweathered outcrops along streams within Wilder State Park.

To establish rooting depths, root density was measured on the wall of an open pit in Terrace 2 (T2). A 10-cm archeologic grid was hung vertically on the pit wall and three 10-cm squares counted at several depths. Roots were counted as they emerged from the wall of the pit within each sampled square. Root density increased sharply above 20 cm, becoming impractical to count due to abundance and wall sloughing. Vertical profiles of root density were qualitatively similar on all upland terraces.

**Chemical and Physical Characterization**

To characterize the physical characteristics of the mottles, we sampled from pit faces at two soil depths on Terraces 2, 3, and 5. Mottles were hand separated by color (gray, white, and orange). Each sample was a composite of mottles at the same soil depth. Two of the shallow samples (one each from T2 and T5) had only trace quantities of white mottling too small to separate; these samples were separated into only gray and orange. Splits of mottle separates were used for elemental analyses, quantitative X-ray diffraction (XRD), Na pyrophosphate extractions, measurement of specific surface areas, and Fe isotopic compositions. We were unable to separate enough of each mottle from each terrace to complete all the analyses. In addition to the analyses conducted across all sites, we were able to isolate enough of each mottle at T2 to measure organically bound metals through Na pyrophosphate extraction. The extraction was conducted on mottles from two depths at T2 as follows: 1 g of sample was weighed into a 50-mL centrifuge tube and 40 mL of sodium pyrophosphate reagent (0.1 mol L\(^{-1}\), pH = 10) was added. Samples were shaken for ~16 h and then centrifuged at room temperature for 20 min at approximately 20,000 × g. The supernatant was then decanted and syringe filtered through a 0.2-µm graduated membrane filter (Whatman GD/X). Concentrations of Al and Fe in the filtered solutions were measured by inductively coupled plasma mass spectrometry (ICPMS, PerkinElmer). Surface areas of unground mottle separates were measured with an 11-point BET method on a Micromeritics TriStar II. Elemental analyses were performed using ICPMS on splits that were brought into solution through HF–HCl dissolution. Mineral abundances were determined with RockJock (Eberl, 2003) based on non-oriented powder XRD data. Major element analyses had been previously determined by X-ray fluorescence on the <2-mm fraction of bulk soil samples (White et al., 2008).

Scanning electron microscopy used a Leo 982 digital field-emission scanning electron microscope (SEM). Samples were prepared by vacuum coating with Au. We imaged the mottle separates at several soil depths.

To establish mottle development through time, digital images of soil pit walls were classified by color using the open-source image-processing platform Fiji (Schindelin et al., 2012). Original images were cropped to exclude poorly illuminated areas and topographic divots. The cropped images were then split into red, green, and blue color channels. The blue band, which best revealed the contrast between the orange and gray soils, was used for binary classification using Fiji’s trainable-segmentation plug-in. Training was done separately for each image due to variations in the overall illumination from image to image. Image quality was such that the Fiji program was not able to reliably discriminate gray from white soil; thus, these two “mottled” (altered) regions (gray and white) were grouped together and differentiated from unaltered regions (orange). Limited additional processing was performed on some images to remove outlier noise. The percentages of pixels in each category were averaged for all images from a given terrace.
Iron Isotope Methods
We leveraged Fe isotope systematics to assess the movement of Fe as the result of soil development and biological processes. Splits of dissolved mottle separates were prepared for isotopic analysis following the methods of Balci et al. (2006) and run for Fe isotope analysis on a Neptune MC-ICPMS at the Bureau de Recherches Géologiques et Minières in Orléans, France. Samples were introduced using an Apex Q ultrasonic nebulizer with a membrane desolvator. Isotopic compositions were determined using the combined double-spike, standard–sample–standard bracketing approach. Isotope compositions of samples and the National Institute of Standards and Technology (NIST) 3126a Fe bracketing standards were corrected first for machine discrimination using a double-spike extraction algorithm based on the exponential power law. Double-spike-corrected ratios were further corrected by reference to the double-spike-corrected compositions of the adjacent bracketing standards using linear interpolation. The double-spike approach corrects for differing matrix effects among samples and subtle changes in machine sensitivity. The Neptune’s ‘hi resolution’ ion-beam edge resolution setting was used to resolve \(^{40}\text{Ar}^{14}\text{N}\) from \(^{54}\text{Fe}\) and \(^{40}\text{Ar}^{16}\text{O}\) from \(^{56}\text{Fe}\). Potential isobaric interference of \(^{54}\text{Cr}\) on \(^{54}\text{Fe}\) and \(^{58}\text{Ni}\) on \(^{56}\text{Fe}\) was assessed by monitoring \(^{52}\text{Cr}\) and \(^{60}\text{Ni}\), respectively, using \(\frac{^{54}/^{52}\text{Cr}}{^{58}/^{60}\text{Ni}}\) ratios measured on pure Cr and Ni solutions for the correction procedure when required.

All analyses are reported in the delta notation relative to the Institute for Reference Materials and Measurements (IRMM)-014 standard:

\[
\delta^{56}\text{Fe} = \left( \frac{\left( \frac{^{56}\text{Fe}}{^{54}\text{Fe}} \right)_{\text{sample}}}{\left( \frac{^{56}\text{Fe}}{^{54}\text{Fe}} \right)_{\text{IRMM-014}}} - 1 \right) \times 1000
\]

For each sample, two total procedural replicates were analyzed. For all reported samples, the determined \(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\) ratios of the two replicates agreed within 0.15% or better. Seventy double-spike determinations of \(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\) for the bracketing standard NIST 3126a during the course of this study had a standard deviation of 0.39% due in part to machine drift, indicating that the use of the standard–sample–standard approach in addition to double spiking improved replicate reproducibility. Results from standards analysis showed that the \(\frac{^{56}\text{Fe}}{^{54}\text{Fe}}\) ratio of NIST 3126a is 0.37‰ greater than that of the corresponding IRMM-014 Fe standard, as determined both by simple standard–sample–standard bracketing (20 repetitions) and combined double-spike, standard–sample–standard bracketing (10 repetitions). The overall precision obtained on these 30 measurements of IRMM-014 was 0.07‰ (2\(\sigma\)mean, 95% confidence level).

Determination of Elemental Loss and Gain
The movement of Fe and other elements in the soil–regolith system was examined using the approach of Brimhall and Dietrich (1987) and Chadwick et al. (1990). The mass transfer coefficient \(\tau\) for the \(j\)th element is

\[
\tau_j = \frac{C_{i,w} C_{j,p} - 1}{C_{j,p} C_{i,w}}
\]

where \(C_{i,p}\) is the concentration of the element of interest in the parent material and \(C_{j,w}\) is the concentration of the element in the weathered material. Likewise, \(C_{i,p}\) and \(C_{j,w}\) are the concentrations of an inert component in the parent and weathered material. A \(\tau\) value of zero indicates no gain or loss of an element, while \(\tau = -1\) indicates total loss of an element, and \(\tau > 0\) indicates the concentration or addition of an element.

The \(\tau\) calculation is sensitive to the choice of the inert component and the parent material composition. When applied to weathering of a relatively homogenous parent material (e.g., granite) the calculation typically uses the bulk composition of unweathered parent and an inert element such as Zr or Ti. These inert elements are commonly found in heavy minerals such as Zr and Ti. In a depositional sedimentary parent material like the Santa Cruz terraces, heavy minerals are not uniformly distributed. White et al. (2008) used quartz as the inert phase for bulk-soil \(\tau\) calculations. For the present study, the mottle separates being compared were in close proximity, and we used Ti as the inert element in the \(\tau\) calculations. Titanium is a valid element to use in this instance because mottle separates from the same depth (separated by only a few horizontal centimeters) will have been subjected to similar depositional hydrodynamic regimes and their heavy mineral concentrations would be similar. To account for variation in depositional dynamics, the parent material composition used was the average of the three deepest (unweathered) bulk samples from T1 as determined by White et al. (2008).

Results
Morphology and Development of Mottling
As described above, older soils of the chronosequence developed complex colorful mottling of the B horizon between the 0.5- and 1.5-m depths associated with textural, mineralogical, and chemical differences (Fig. 3). Mottled areas display three colors: orange (7.5YR 5/8), gray (2.5 Y 6/1), and white (2.5Y 8/1). Color and textural changes are generally gradational but can be sharp. When a white mottle is present, it occurs between orange and gray mottles. The soil on T1 has an organic-rich A horizon to a depth of 0.6 m, with a gradational lower boundary into the underlying sandy silt (Fig. 3a). The soil on T2 has an A horizon to a depth of 0.58 m with a wavy lower boundary (Fig. 3b). The T2 mottling consists of vertical and elongated sub-horizontal gray clay-rich zones bounded usually by white sandy silt. The gray and white zones break up the Fe-coated sand into reticulate mottles (Fig. 3b). The A horizon progressively thins from 0.58 m (T2) to 0.38 and 0.41 m at T3
and T5, respectively. Mottled argillic horizons thicken with age, occurring at shallower depth and extending deeper in T5.

Mottle development as quantified by Fiji analysis (Fig. 4; Supplemental Table S1) involves initiation between 65 and 90 ka, followed by rapid growth. Between 0 and 65 ka, no mottles formed but the parent material oxidized, with Fe oxides coating mineral grains. This is the matrix in which the mottles form. The growth in volume fraction of mottled (gray plus white) vs. unmottled (orange) sediment decreases nonlinearly with time from ~16% Ma⁻¹ shortly after initiation to ~0.7% Ma⁻¹ by 226 ka (Fig. 4).

**Roots and Mottles**

Roots were counted to establish rooting depth and root association with mottles. Roots of present-day vegetation were most abundant in the A horizon but extend well below it. Although root density decreased non-linearly with depth, roots appeared throughout the mottled zone (Supplemental Fig. S2 and S3). In the mottled soil between the 1.2- and 1.3-m depths, roots were found in gray mottles most of the time (data not shown), but the few countable roots at this depth resulted in poor statistics. Examples of root-mottle associations are illustrated in Supplemental Fig. S3. When dried, the gray clay-rich mottles fractured, allowing soil peds to pull easily off the pit wall (Supplemental Fig. S3c). Along these fractures, roots were revealed growing vertically within the gray clay. Root counts do not capture this association well. Incipient mottle features (Supplemental Fig. S3a and S3b) show fine clay filled fractures occupied by roots surrounded by white (bleached) sediment. Multiple lines of evidence demonstrate the intimate association of roots and motting. The most direct are visual and microscopic (optical and SEM) analysis of mottle samples.

**Chemistry and Mineralogy**

The chemical analyses of mottle separates show distinct major-element compositions in Fe and Al across the chronosequence (Fig. 5a; Supplemental Fig. S4; Supplemental Table S2). Iron is twice as concentrated in the orange mottles as it is in the gray and white mottles. Aluminum is more concentrated in the gray mottles. Although the C concentration of the soil at this depth is low in absolute terms (<0.3% by mass) there are large relative differences, with gray mottles containing almost twice as much C as orange mottles (Fig. 5b).

Concentrations of the essential nutrient elements Ca, K, and Na are also differentiated by mottle color. Within each terrace, gray mottles tend toward lower concentrations of these elements than orange or white mottles of the same terrace (Fig. 6; Supplemental Fig. S5; Supplemental Table S2). Calcium and K show a linear relation (Fig. 6a) that is differentiated by soil age (symbol shapes).
The youngest mottled soil (T2) has higher K and Ca than the oldest (T5). Sodium (not plotted) shows trends similar to Ca. The primary sources for Ca, Na, and K are plagioclase feldspar and K-feldspar, respectively, which both decline with increasing soil age (Fig. 6b) and decreasing soil depth.

X-ray diffraction mineralogy (Supplemental Table S3) generally supports the chemical analyses. Gray mottles are principally composed of the secondary clay minerals halloysite and kaolinite. Mineral trends in Fig. 6C show that the gray mottles have higher secondary clay contents and lower feldspar concentrations than the orange and white mottles.

A somewhat enigmatic result of the XRD data is the lack of goethite (or any other detectable Fe mineral phase) in several of the orange mottles (Supplemental Table S3). The Fe concentrations of these samples are substantial: T2 at 1.0 m, Fe = 6.5%; T3 at 1.1 m, Fe = 4.6%; and T5 at 1.4 m, Fe = 9.45%. The clear implication of this result is that Fe is present as colloidal or nanocrystalline phases that are amorphous and thus undetectable with XRD in the presence of large backgrounds of well-crystallized primary silicate minerals (Tsao et al., 2013).

Strong mottle-dependent correlations between pyrophosphate-extractable C, Al, and Fe suggest organic mobilization of the otherwise relatively immobile metals Al and Fe. Gray mottles have higher amounts of pyrophosphate-extractable C, Al, and Fe (Fig. 7; Supplemental Table S4). The gray mottles also contain more extractable C (Fig. 7). Extraction results are consistent with the gray clay-rich zones functioning as a relatively “active” rhizosphere soil, where Fe has been bound to organic compounds for increased solubility.

Gray mottles have relatively high surface areas (∼60–130 m² g⁻¹; Fig. 8; Supplemental Table S5), reflecting their high clay contents. White mottles from all terraces have similar surface areas (32.4 ± 2.6 m² g⁻¹). The specific surface areas of orange mottles are similar to the white (37.0 ± 7.5 m² g⁻¹). Initial attempts to determine the particle size of the gray-mottle separates by laser diffraction produced erratic results that did not reflect their clay composition, suggesting difficulties in achieving complete and reproducible dispersion. These attempts were abandoned due to a lack of remaining sample. Nevertheless, the XRD mineralogy, specific surface areas, and SEM images (Supplemental Fig. S7f) demonstrate that the gray mottles are composed primarily of particles much finer than the parent silty sand material.

Bulk soils and mottle color separations were analyzed for ⁵⁶Fe/⁵⁴Fe isotopic ratios. In addition, four bedrock samples were analyzed to establish the isotopic composition of the sediment source. The bulk soils show a progressively lighter Fe isotopic composition with soil age (Fig. 9a), with T5 being 0.2‰ lighter at the surface than T2 and about 0.4‰ lighter in the mottled zone. Age-related differences in ⁵⁶Fe/⁵⁴Fe isotopic ratios are significant at a p value of 0.002. Iron in mottle separates is clearly fractionated (Fig. 9b),
Elemental depletions and enrichments in mottles relative to the parent material, as expressed by mass-transfer coefficient $\tau$ values, were calculated using Ti as the inert phase (Fig. 10). Aluminum is enriched in the gray mottles but little changed in the white and orange mottles. In contrast, Fe is depleted in the white and gray mottles and enriched in the orange mottles. Sodium and Ca are nearly depleted in all mottle separates, with gray mottles the most depleted (Fig. 10; Na shown, Ca similar but not shown).

### Discussion

The Santa Cruz soil chronosequence displays a pedogenic evolution of mottling. The Fiji image analysis shows that the overall rate of mottle expansion drops quasi-exponentially from $\sim 16\%$ Ma$^{-1}$ initially to $\sim 0.7\%$ Ma$^{-1}$ by 226 ka. The formation of mottles in the 25-ka period between 65 and 90 ka may be due to nutrient depletion resulting in more intense extraction from deep sediment by roots but could also result from other factors such as a change in vegetation or ecosystem. Gray mottles increase in volume with soil age, while white and orange mottles decrease (Fig. 4; Supplemental Table S1). Mottle separates are chemically distinct. The chemistry and XRD mineralogy of mottle separates along with tau calculations show the gray mottles to be significantly more weathered than the orange or white mottles. Depletion of primary minerals (Fig. 6) and mobilization of Fe from gray mottles (Fig. 5) suggests root uptake of nutrients (rhizospheric transfer to plants).

Increased weathering of primary minerals in rhizospheres is well established (e.g., April and Keller, 1990; Belnap et al., 2003; Barre et al., 2007). Roots and their symbionts change the chemical, physical, mineralogical, and hydrological character of rhizosphere soil through biological processing and via exudates (Adamo et al., 2016; Philippot et al., 2013; Meheruna and Akagi, 2006; Adamo et al., 1998; Marschner, 1995). Steep geochemical gradients develop around roots over millimeter to centimeter distances in pH, cation exchange capacity, and essential elements (e.g., C, P, O, and N) (Turpault et al., 2008; Barre et al., 2007; Hinsinger et al., 2005; Marschner, 1995). The organic compounds in exudates create a biogeochemical hotspot (Supplemental Fig. S7) in the rhizosphere. In the shallow soil, rhizospheres are ephemeral due to bioturbation. The shallow soil horizons are generally well studied because they are of particular interest with respect to agricultural crops. In contrast, deep soil horizons have received less attention. Nevertheless, deep soils are important in sustaining ecosystems (Laclau et al., 2013; Maeght et al., 2013; Graham et al., 2010; Allen, 2007; McCulley et al., 2004; Egerton-Warburton et al., 2003). The A horizons of the Santa Cruz soils, which are
enriched in organic matter, are bioturbated and relatively homogeneous. Below the depth of bioturbation, there will be enduring zones of reacted soil that are the result of root exudates interacting with mineral soil.

Although sparse, roots do extend below the zone of bioturbation (Supplemental Fig. S2, S3, and S7). Roots that reach deep soil generally occupy pores or fractures (Rasse and Smucker, 1998; Egerton-Warburton et al., 2003; White and Kirkegaard 2010). Through months or years, roots die and new roots will reoccupy the same soil fractures; therefore, deep soil near fractures is repeatedly subjected to root exudates and becomes more weathered. Through plant-weathering feedbacks, fractures become self-sustaining passages for roots and for the preferential flow of soil pore water (Marin-Spiotta et al., 2011). Soils away from fractures are less affected by rhizospheric processes and thus remain less weathered. When this process is repeated for millennia, reticulate mottling develops.

An alternative explanation for the formation of clay-rich gray mottles entails translocation of clay particles from upper horizons to lower along fractures or other preferential flow paths (e.g., MacEwan et al., 2012). Some translocation undoubtedly occurs, as evidenced by clay films observed on some fracture surfaces in soil pits. However, translocation is not necessary to generate the clay-rich B horizons. Geochemical modeling of profile development at the Santa Cruz terrace sites accounted for the entire clay-rich B horizon through weathering of primary minerals coupled to in situ secondary clay precipitation (Maher et al., 2009; Lawrence et al., 2014). The horizontal orientation of many of the gray clay-rich mottles provides empirical evidence against translocation as a primary method of development (Fig. 3).

Other research supports clay formation along roots (Kodama et al., 1994; Arocena and Velde, 2009; Hinsinger, 2013). Clay precipitation near the root occurs by one of at least two mechanisms. In the first, water uptake by roots causes local oversaturation of mineral phases such as halloysite and kaolinite. In the second, degradation of organic–Al complexes causes Al oversaturation and precipitation of clays (Watt et al., 2006; Cheng et al., 2014; Lawrence et al., 2014; Keiluweit et al., 2015; Clarholm et al., 2015). The very fine-grained nature of the secondary clays in these soils supports an interpretation of short, quick periods of mineral precipitation (Supplemental Fig. S7f).

As discussed above, Fe is mobilized in soils through plant-exudate complexation (Marschner and Romheld, 1994; Colombo et al., 2014); therefore, we expect differences in pyrophosphate-extractable Fe between the rhizosphere and bulk soil. Several studies have documented Fe depletion in the soil around roots (Prietzel et al., 2007; Adano et al., 1998). Although there was insufficient sample size of the mottle separates to perform extractions on all of them, the two sets analyzed show that most Fe remaining in the gray mottle is in an organo–metal complex form. (The pyrophosphate extraction is intended to remove organo–metal complexes.) Pyrophosphate extraction provides an insight into the processes that create the chemical differences among the mottle separates (Fig. 7). The gray mottles have lower total Fe (Supplemental Table S2; Fig. 5); however, they have the highest pyrophosphate-extractable Fe (Fig. 7). Therefore, more of the Fe in the gray mottle is bound to organic matter (pyrophosphate extractable) than in the high-Fe orange zone. Extraction results are consistent with the gray clay-rich mottle being more like the rhizosphere soil than the white and orange mottles.

Iron isotopic data also support the idea of rhizosphere-driven weathering leading to mottle development. In general, older and
shallower samples are isotopically lighter; the cycling of light Fe through plants contributes to isotopically light Fe oxides in the surface soil. The white separate has the lowest concentrations of Fe. However, white mottles are more enriched in the heavier isotope $^{56}$Fe relative to the orange mottles, suggesting selective removal of the lighter $^{54}$Fe from the white regolith (Fig. 9b), consistent with preferential removal of light Fe through biologic processes. As discussed above, the movement of Fe can occur through biological processes that would fractionate the Fe (e.g., biochemically mediated reduction to Fe$^{2+}$ or complexation by organic compounds such as siderophores) or through transport processes (advection of colloids or nanoparticles) that would not fractionate the Fe. The bulk-soil isotopic results are consistent with previous studies in that lighter Fe was found in shallow soil (Fantle and DePaolo, 2004; Thompson et al., 2007; Wiederhold et al., 2007a, 2007b). However, ours is the first study of which we are aware to show that depth-dependent fractionation increases with age (Fig. 9).

The measurable difference in Fe isotopic values of adjacent mottle separates is the result of Fe cycling for millennia through the microscale processes of roots. We propose that root exudation of Fe siderophores is diurnal, beginning shortly after sunrise and lasting 4 to 6 h (Schenkeveld et al., 2014); this strategy solubilizes Fe early in the day, setting the stage for Fe uptake later in the day during the afternoon period of highest transpiration. Plant transpiration drives water movement during daylight hours toward roots and symbiotic fungi (Moradi et al., 2011; Quijano et al., 2013; Querejeta et al., 2003; Lucas 2001). During the night, shallow soil water is released by roots during periods of hydraulic redistribution (Allen, 2011; Prieto et al., 2012; Sardans and Penuelas, 2014), thus keeping the soil primed to receive exudates. In addition, soil water can move through the soil in any direction according to local potential-field gradients. We envision that the root-driven, diurnal push and pull of exudates and soil water is a process that can move solubilized Fe away from as well as toward the rhizosphere. As the isotopically light Fe–organo–metal complex breaks down, the solubilized Fe precipitates as Fe oxides in orange mottles.

The mobilization and transport of Fe is the result of complex rhizospheric processes that also govern weathering, ecosystem nutrient supply, and C accumulation in deep soils. A simplified diagram of mottle development shows the expansion of gray and white zones into orange zones as roots invade, grow, and die (Fig. 11). The diagram illustrates the process through the life cycle of one root. After this fundamental sequence, the dead root supplies a nutrient-rich preferential pathway for subsequent multiple cycles (over >60 ka) of invasion, growth, and death, which drive the expansion of mottling.

Rhizospheric processes occur wherever plants exist; however, the development and preservation of rhizogenic features depends on several factors. Reticulate mottling requires tens of thousands of years to develop. Therefore, a landscape position resulting in low rates of erosion and mass movement is a necessary requirement for the development and preservation of reticulate mottles. The 65-ka soil at Santa Cruz does not have reticulate mottles, but the soils older than 90 ka do. In addition, there appears to be a moisture-regime boundary for mottle formation. As mentioned above, soils with mottling similar to those in the Santa Cruz terrace soils (mean annual precipitation [MAP] ~730 mm) are found on the Channel Islands of southern California and along southern and central coastal California (Moody and Graham, 1995; Johnson, 1972), and on Santa Rosa Island (MAP ~350 mm; unpublished data, 2013). Precipitation increases from south to north along
coastal California. North of Mendocino (MAP ~1000 mm), mottles have not been found or reported, including a marine terrace chronosequence near Petrolia, CA (MAP ~1575 mm) that shows no reticulate mottling (personal observation, 2013). Drying and concurrent precipitation of secondary clays and Fe oxides are probably prerequisite for mottle preservation. Rhizogenic mottling will be more likely to be found on stable upland soils in arid to semi-humid areas, as suggested by similar upland mottles found in South Carolina and Australia. Finally, it is possible that mottle formation is ecosystem dependent. Santa Cruz terrace soils are currently coastal-prairie Mollisols. Soils forming on landforms older than 12 ka are polygenetic, having existed through one or more glacial–interglacial transitions and possible ecosystem shifts. Even though climate and ecosystems may transition, previously established soil properties may not be quickly overwritten. Preservation of cumulative effects is an important concept in understanding soils of old landforms. The extent to which reticulate mottling in the older soils of the Santa Cruz chronosequence formed under a different ecosystem is not yet known.

Conclusion

Differences in the physical and chemical characteristics among the various mottle separates are indicative of the rhizospheric processes by which the structures have formed. Separates of mottles by color have distinct differences in elemental abundances, Fe isotopes, mineralogy, and specific surface area. Isotopes, along with pyrophosphate-extractable C, Fe, and Al, indicate that biologic processes have solubilized and moved Fe. Long-term effects of root biogeochemistry can create rhizogenic mottles in deep soil horizons of old stable landforms and sequester C in deep unsaturated zones. Root–soil interactions acting over multi-millennial time frames involve a complex mix of processes that create rhizomorphic mottling. Our understanding of these processes is currently inadequate. It is important to understand deep soil (>50 cm) processes and functions and how they support ecosystem services. In addition, although the C concentration of deep soils is low compared with shallow soil, the volume of this deep C reservoir is large. Knowledge of the sources and sinks of deep soil C will assist in managing this reservoir through climate change.

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