Iron solid-phase differentiation along a redox gradient in basaltic soils

Aaron Thompson a,⇑, Denis G. Rancourt b, Oliver A. Chadwick c, Jon Chorover d

a Department of Crop and Soil Sciences, University of Georgia, Athens, GA 30602, USA
b Formerly at Department of Physics, University of Ottawa, Ottawa, Ont., Canada K1N 5N6
c Department of Geography, University of California, Santa Barbara, CA 93106, USA
d Department of Soil, Water & Environmental Science, University of Arizona, Tucson, AZ 85721, USA

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Abstract

Iron compounds in soil are multifunctional, providing physical structure, ion sorption sites, catalytic reaction-centers, and a sink for respiratory electrons. Basaltic soils contain large quantities of iron that reside in different mineral and organic phases depending on their age and redox status. We investigated changes in soil iron concentration and its solid-phase speciation across a single-aged (400 ky) lava flow subjected to a gradient in precipitation (2200–4200 mm yr⁻¹) and hence redox history. With increasing rainfall and decreasing Eh, total Fe decreased from about 25% to <1% of the soil mass. Quantitative speciation of soil solid-phase iron was constrained by combining ⁵⁷Fe Mössbauer spectroscopy (MBS) at 295 and 4.2 K with powder X-ray diffraction, selective chemical extractions, and magnetic susceptibility measurements. This approach allowed us to partition iron into (1) nanoparticulate and microcrystalline Fe³⁺-(oxy)hydroxides, (2) microcrystalline and bulk Fe³⁺-oxides, (3) organic/silicate bound Fe³⁺, and (4) ferrous iron. The Fe³⁺-(oxy)hydroxide fraction dominated solid-phase Fe, exhibiting a crystallinity continuum based on magnetic ordering temperature. The continuum extended from well-ordered microcrystalline goethite through nanocrystalline Fe³⁺-(oxy)hydroxides to a nano Fe³⁺-(oxy)hydroxide phase of extremely low crystallinity. Magnetic susceptibility was correlated (R² = 0.77) with Fe³⁺-oxide concentration, consistent with a contribution of maghemite to the otherwise hematite dominated Fe-oxide fraction. The Fe³⁺-(oxy)hydroxide fraction of total Fe decreased with increasing rainfall and was replaced by corresponding increase in the organic/silicate Fe³⁺ fraction. The crystallinity of the Fe³⁺-(oxy)hydroxides also decreased with increasing rainfall and leaching, with the most disordered members of the crystallinity continuum, the nano Fe³⁺-(oxy)hydroxides, gaining proportional abundance in the wetter sites. This finding runs counter to the conventional kinetic expectation of preferential removal of the most disordered minerals in a reductive dissolution-dominated environment. We suggest the persistence of highly disordered Fe phases reflects the dynamic redox conditions of these upland soils in which periods of anoxia are marked by high water-throughput and Fe²⁺(aq) removal, while periodic Fe oxidation events occur in the presence of high concentrations of organic matter. Our ⁵⁷Fe Mössbauer study shows basalt-derived nano-scale Fe³⁺ phases are more disordered than current synthetic analogs and have nano-structural characteristics that are linked to their formation environment.

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1. INTRODUCTION

Feedbacks between mineral weathering and ecosystem function affect the rate and trajectory of change in terrestrial biogeochemical systems (Lucas et al., 1993; Torn et al., 1997; Blum et al., 2002; Derry et al., 2005). The implications of this connectivity affect not only present-day contaminant/nutrient dynamics (Genin et al., 2001; Davidson et al., 2003) but can also inform paleoclimatic interpretations of geologic deposits (Yamaguchi et al., 2005). Iron plays a central role in ecosystem function throughout
pedogenesis. Iron oxidation during incongruent weathering of primary minerals results in the formation of secondary Fe phases whose interfacial reactivity exerts strong control over ecosystem cycling of nutrients, carbon, trace elements, and contaminants, including microbial mediation of these processes. The crystal size and bonding environment (collectively termed here “solid-phase speciation”) of Fe govern its influence on ecosystem biogeochemistry to a much larger extent than its total abundance. Short-range crystal order and small particle sizes distinguish the most reactive, high surface area Fe components from larger bulk Fe-oxides (Bonneville et al., 2004; Roden, 2006). Fe(III) species in these components are typically bonded to oxygen and/or hydroxide anions (i.e., Fe(III)-oxides vs. Fe(III)-(oxy)hydroxides) with various amounts of Al(III) substitution and structural water.

The trajectory of Fe-mineral differentiation depends on environmental redox conditions. Under persistent oxic conditions, the accumulation of secondary Fe(III) minerals is favoured thermodynamically, whereas under anoxic conditions, the accumulation of secondary Fe(III) minerals that are typically assessed by selective chemical extractions, infrared spectroscopy and electron microscopy, dull the layers and placed immediately on ice, according to procedures described in Bartlett and James (1993). For the wetter two sites, soil horizons were classified as either oxic or anoxic based on the presence/absence of redoximorphic features (mottles, gleys, standing water, hydrogen sulfide odor, etc.). Samples considered oxic were treated similarly to soils from the drier sites. Anoxic soils were doubled-bagged in a low O2-permeable, 3-mil Sarenex inner bag and a 4-mil polyethylene outer bag, flushed three times with ultra-pure N2 and packed on ice. All soils were transported to the lab on blue ice, homogenized in a 95%/5% N2:H2 glove box, frozen at 193 K and then freeze-dried before analysis.

2.2. Notation and definitions

Throughout this work we use the term crystallinity in a broad sense to denote the degree of long-range crystal order. Thus, our use of the terms, poorly-crystalline or nanocrystalline indicate chemical and/or structural deviations from the properties of a perfect bulk crystal structure having ideal end-member composition deriving from any one or combination of the following: a higher degree of vacancy defects, smaller particle size, increased cation substitutions, surface/defect-generated strain fields, electronic-instability defects, etc. A list of abbreviations used in the text is provided in Table 1.

2.3. Analytical approach

Our approach is to use the specificity of 57Fe MBS to expand our understanding of Fe phases that are difficult to detect by standard XRD and selective extraction analyses. To do so we draw on previously published 0.5 M HCl, acid-ammonium oxalate (AAO), and Na-pyrophosphate extractions for these soils (Thompson et al., 2007). In addition, we performed two consecutive citrate-dithionate bicarbonate extractions (Loeppert and Inskeep, 1996) on 0.5 g of dry soil with 30 ml of solution for each step in polypropylene co-polymer centrifuge tubes. Iron from the...
combined extract solutions was analyzed using inductively coupled plasma-mass spectrometry (Perkin Elmer DRC II ICPMS). Total soil carbon was measured by combustion coupled with CO2-detection using Shimadzu 5000A-SSM TOC analyzer (Columbia, MD). Fe 2+ was measured by a revised ferrozine method (Thompson et al., 2006b) following separate 0.5 M HCl extracts conducted on field moist soils at a 1:10 dry soil:solution ratio within a week after field collection.

Soils derived from weathering of basaltic parent materials in tropical environments contain mineral–organic complexes whose speciation and structure can be significantly altered through use of chemical pre-treatments commonly used prior to mineral analysis (Chorover et al., 2004; Mikutta et al., 2009b). We therefore avoided all such pre-treatments and conducted all spectroscopic and diffraction analyses on un-altered bulk samples. While the lack of pre-treatment diminishes the signal-to-noise obtainable by some of the analyses (e.g., XRD), it also better preserves sample integrity and avoids the introduction of artifacts.

2.4. X-ray diffraction (XRD)

2.4.1. XRD collection methods

XRD was conducted on a Philips X’pert MPD powder-sample diffractometer equipped with a spinning stage and X’Celerator multiple strip detector with Ni-filtered CuKα2 radiation at 45 kV and 40 mA. All samples were scanned from 5 to 75° 2θ, with a step size of 0.017° 2θ and step collection time of 7 s for a total run time of 8 h. Peaks at 2.03 Å are from the sample holder.

2.4.2. XRD interpretation

We identified the principal Fe minerals in the XRD as follows: well-crystallized hematite (Hm) via diffraction lines at d-spacings of 2.70, 2.52, and 1.70 Å; well-crystallized goethite (Gt) via diffraction lines at 4.18, 2.69, and 2.45 Å; and maghemite (Mh) based on a reflection at 2.95 Å (all other lines overlapped with hematite). The short-range ordered Fe III-(oxy)hydroxide phases, ferrihydrite (Fh) and nanocrystalline goethite (n-Gt), are harder to identify in XRD patterns. Both likely exhibit small particle sizes, Fh due to its intrinsic nature (Rancourt and Meunier, 2008; Marchand and Rancourt, 2009), and n-Gt because goethites in tropical basaltic soils are nearly always much smaller than typical synthetic analogs and often highly substituted by Al and other cations (e.g., Ti, Mn, etc.) (Norrish and Taylor, 1961; Langmuir, 1971; Wada and Wada, 1976; Golden et al., 1979; Fey and Dixon, 1981; Murad and Schwertmann, 1983; Fritsch et al., 2005; Waychunas et al., 2005; Otero et al., 2009). It is difficult to separate these two minerals on the basis of their XRD patterns alone. Both have broad reflections and many of those reflections are difficult to resolve from each other in complex mixtures such as soils. For instance, the main 2-line and 6-line Fh broad reflections (1 0 1) at 2.45 Å overlap with broad reflections from the (1 1 2) n-Gt (Cornell and Schwertmann, 2003). Broad (1 1 2) 6-line Fh reflections overlap with broad n-Gt reflections originating from the (4 0 1) and (2 1 1) orientations at 2.2 Å. Similarly, the broad (1 1 4) Fh reflection at 1.7 Å overlaps with the broad (2 1 2) reflection of n-Gt and in these soils may also be obscured by broad reflections from the kaolin-group minerals at 1.7 Å. Similarly the 1.5 Å (3 0 0) Fh line overlaps with these
kaolinite-group minerals, which are present in many samples. Thus, the best diagnostic peaks are the broad (101) peak of n-Gt at 4.18 Å and the broad 6-line Fh reflection (113) at 1.96 Å. Since the broad (101) n-Gt peak is the largest Gt reflection, we expect it in all samples containing goethite. Likewise, we expect samples with Fh to exhibit a main peak at ~2.45 Å, however since this overlaps with a prominent n-Gt reflection of only slightly smaller intensity than the 4.18 Å n-Gt reflection, we must further inspect the 1.96 Å region for the smaller (113) Fh reflections to establish an XRD signal for Fh.

2.5. Magnetic susceptibility

Mass-specific magnetic susceptibility (MS) measurements were collected on freeze-dried soils at 295 K in a custom-built AC-susceptibility bridge at the University of Georgia. Measurements were cross calibrated by Dr. Christoph Geiss (Trincoll University) on a KLY-4 Kappabridge susceptibility bridge (ASC Scientific).

2.6. 57Fe Mössbauer spectroscopy

2.6.1. MBS collection and analysis methods

All LHT and RT 57Fe Mössbauer spectra were collected in transmission mode using a 10–50 mCi 57Co-Rh source kept at RT. Freeze-dried powder samples were mounted in holders with 1.27 cm diameter windows and a thickness up to 0.64 cm (~100–500 mg per holder) based on the ideal absorber thickness calculated on the basis of bulk elemental composition to optimize signal-to-noise (Rancourt et al., 1993). The RT measurements had data accumulation times of 1–2 wks, whereas collection time was limited in the cryogenic measurements (by labor and cryogen costs) to approximately 1 day.

All measurements were performed with a velocity range of ±11 mm s\(^{-1}\) and achieved the typical detection limit of 0.1–1% of Fe. Velocity (i.e., gamma-ray energy) was calibrated using an enriched 57Fe foil at 298 K and all center shifts (CSs) and peak positions are reported with respect to this standard. The transducer was operated in constant acceleration mode and folding was performed to achieve a flat background. The spectra were not corrected for thickness effects (Rancourt et al., 1993). Cryogenic measurements were performed in a shielded, He gas flow type cryostat with temperature monitoring at the He gas outflow port and on the sample holder mount. The temperature during data collection did not rise above 4.5 K. Using this setup, temperature gradients across the absorber dimensions are typically less than 0.1 K per 1/2 inch. The entire setup is vibration isolated and calibration tests showed less than 0.001 mm s\(^{-1}\) peak-width broadening on standards.

2.6.2. MBS spectral analysis approach

Mössbauer spectral fitting of all the RT and LHT spectra was performed using the Voigt-based fitting (VBF) method of Rancourt and Ping (1991) for quadrupole splitting distributions (QSDs) and combined hyperfine field distributions (HFDs), as implemented in the Recoil™ software, developed by Rancourt in collaboration with ISA Inc. (http://www.isapps.ca/recoil). All VBF Mössbauer parameter definitions and a description of the relevant notation are given by Rancourt and Ping (1991). All errors in Mössbauer fitting parameters are two-standard deviation (2σ) errors, as calculated by Recoil™. In reporting quantitative phase abundances or site populations it is assumed that the Mössbauer recoilless fractions of all detected phases or Fe-bearing components are equal, such that subspectral areas (expressed as fractions of total spectral area) are equal to the amounts of Fe (expressed as fractions of total Fe) in the corresponding phases or components. This assumption is expected to be valid at cryogenic temperatures, and also to be a good approximation at RT with dry samples (Lalonde et al., 1998; Rancourt, 1998).

Details regarding the fitting approach and explanations of key MBS parameters are contained in Section EA-1 of the Electronic Annex. Briefly, we fit all paired 295 and 4.2 K spectra with a spectral component model in which the components could be assigned to four broad Fe bonding environments: (a) Fe\(^{17+}\)-oxyhydroxides (Fe\(^{3+}\)-OxHy); (b) Fe\(^{11+}\)-oxides (Fe\(^{3+}\)-Ox); (c) organic/silicate bound Fe\(^{3+}\); and (d) paramagnetic ferrous iron species (no magnetite octets were detected). We further divided the Fe\(^{3+}\)-OxHy assignment into three size/crystallinity categories based on the temperature of magnetic ordering (TN): (a1) <4.2 K (Fe\(^{11+}\)-OxHy\(_{<4.2\,K}\)); (a2) 4.2–295 K (Fe\(^{11+}\)-OxHy\(_{4.2–295\,K}\)); (a3) >295 K (Fe\(^{11+}\)-OxHy\(_{>295\,K}\)). While the fitting error is small between the four broad groups, there are trade-off uncertainties between the sub-groups of the Fe\(^{3+}\)-OxHy assignment.

3. RESULTS

Prior work (Miller et al., 2001; Schuur and Matson, 2001; Thompson et al., 2007) along the Maui climate gradient (MCG) gradient confirmed a negative correlation between total Fe and a greater frequency of “suboxic” and “anoxic” Eh values with increasing rainfall (Fig. 1). These data reveal that total Fe decreases from >25% of dry soil mass at low rainfall to <1% at the highest rainfall site (Table 2).

3.1. Selective chemical extractions

Prior chemical extraction data from Thompson et al. (2007) are summarized in Table 2 along with new data for CBD extractable Fe and total C. In the surface horizons the fraction of total Fe (\(f_{\text{tot-Fe}}\)) extracted by HCl oxalate (AAO), and Na-pyrophosphate (Na-Pyro) all increase with increasing rainfall, whereas the CBD-extractable \(f_{\text{tot-Fe}}\) (0.46 ± 0.06) is similar at all sites. In the subsurface horizons, increasing rainfall drives a decrease in the \(f_{\text{tot-Fe}}\) extracted by AAO, Na-Pyro, and CBD (Table 2). At the 3500 mm yr\(^{-1}\) site the \(f_{\text{tot-Fe}}\) extracted by all treatments decreased with depth. As a function of increasing rainfall, total carbon increased in the surface horizons and decreased in the subsurface horizons and with depth at the 3500 mm yr\(^{-1}\) site. Increasing rainfall also increases the HCl-extractable Fe\(^{2+}\)/\(f_{\text{tot-Fe}}\).
3.2. Analysis of X-ray diffraction data

Positive XRD peak identification has been made for the following minerals in various proportions throughout the sample set: quartz, muscovite, hematite, goethite, a short-range-ordered kaolin-group mineral (e.g., kaolinite/halloysite), anatase and illmenite. Well-crystallized hematite was identified in six samples: the surface and subsurface samples from 2200 to 2800 mm yr\(^{-1}\) site; the surface 3200 mm yr\(^{-1}\) site; and the 58–85 cm depth sample from the 3200 mm yr\(^{-1}\) site (Figs. EA-2, EA-3, and EA-4 of the Electronic Annex). Well-crystallized goethite was identified in three samples: the subsurface site 3200; and the surface and subsurface of site 2800 mm yr\(^{-1}\). Evidence for maghemite is present in five soils: all surface soils, except the 4200 mm yr\(^{-1}\) site; and at depth in the 2200 and 3500 mm yr\(^{-1}\) sites (Figs. EA-2, EA-3 and EA-4 of the Electronic Annex). Our XRD analysis yields supporting evidence for nano-goethite in all samples except the 4200 site and weak suggestions of ferrihydrite in all other samples except the 2200 mm yr\(^{-1}\) site and the surface of the 4200 mm yr\(^{-1}\) site.

3.3. Field variation in Mössbauer-assigned Fe phase abundance

Below we detail the change in Mössbauer-assigned abundance of Fe solid phases across the climate gradient. The molecular-level characteristics of these Fe solid phases revealed by Mössbauer spectroscopy are included in Section 4, immediately before the discussion section.

In both the surface and subsurface transects, increasing rainfall from 2800 to 4200 mm yr\(^{-1}\) results in a proportional decrease in the soil Fe\(^{III}\)-(oxy)hydroxide coincident with a proportional increase in ferrous and organic/silicate, while \(f_{\text{tot-Fe}}\) assigned to the Fe\(^{III}\)-oxides shows a variable climatic response (Fig. 2). Solid-phase ferrous iron, detectable only at the higher rainfall sites, never exceeds 5% of the total soil iron pool. Thus, Fe(III) is predominant even when mean Eh values would predict a prevalence of Fe(II) (see Fig. 1).

### Table 2

Fe concentrations from selective extractions, magnetic susceptibility and total organic carbon for the Maui climate gradient samples.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Total Fe(^a)</th>
<th>Fe from selective (non-sequential) extractions (g kg(^{-1}) soil)</th>
<th>Mag. Sus. (\chi) (10(^{-8}) m(^3) kg(^{-1}))</th>
<th>TOC (g kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HCl(^a)</td>
<td>Na-Pyro(^a)</td>
<td>Oxalate(^a)</td>
</tr>
<tr>
<td>Surface (10–20 cm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200 mm (A)</td>
<td>283.0 (198)(^b)</td>
<td>24.8 (14)</td>
<td>108.9 (83)</td>
<td>59.0 (34)</td>
</tr>
<tr>
<td>2800 mm (A)</td>
<td>156.0 (109)</td>
<td>16.0 (46)</td>
<td>64.2 (16)</td>
<td>38.6 (5)</td>
</tr>
<tr>
<td>3500 mm (Ag)</td>
<td>97.0 (68)</td>
<td>27.7 (16)</td>
<td>33.8 (26)</td>
<td>41.5 (25)</td>
</tr>
<tr>
<td>4200 mm (A)</td>
<td>6.2 (4)</td>
<td>1.8 (1)</td>
<td>3.9 (2)</td>
<td>5.3 (4)</td>
</tr>
<tr>
<td>Subsurface (50–70 cm)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200 mm (Bw3)</td>
<td>129.4 (91)</td>
<td>17.0 (26)</td>
<td>46.8 (5)</td>
<td>38.4 (5)</td>
</tr>
<tr>
<td>2800 mm (Bw3)</td>
<td>165.1 (116)</td>
<td>5.0 (5)</td>
<td>57.9 (41)</td>
<td>42.4 (72)</td>
</tr>
<tr>
<td>3500 mm (Bw3)</td>
<td>54.3 (38)</td>
<td>1.6 (1)</td>
<td>11.3 (10)</td>
<td>10.0 (14)</td>
</tr>
<tr>
<td>4200 mm (Bg3)</td>
<td>27.3 (19)</td>
<td>0.5 (0)</td>
<td>2.6 (12)</td>
<td>2.1 (0)</td>
</tr>
<tr>
<td>Depth profile (3500 mm MAP)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6–13 cm (Ag)</td>
<td>97.0 (68)</td>
<td>27.7 (16)</td>
<td>33.8 (26)</td>
<td>41.5 (25)</td>
</tr>
<tr>
<td>13–23 cm (Bw3)</td>
<td>76.0 (53)</td>
<td>8.3 (13)</td>
<td>41.8 (18)</td>
<td>34.5 (13)</td>
</tr>
<tr>
<td>40–58 cm (Bw3)</td>
<td>54.3 (38)</td>
<td>1.6 (1)</td>
<td>11.3 (10)</td>
<td>10.0 (14)</td>
</tr>
<tr>
<td>58–85 cm (Bw4)</td>
<td>66.5 (47)</td>
<td>1.6 (0)</td>
<td>3.0 (8)</td>
<td>6.0 (10)</td>
</tr>
</tbody>
</table>

\(^a\) Data reprinted from Thompson et al. (2007). Extractions done with soil:solution ratio of 1:60.

\(^b\) Errors are 1 standard deviation (1\(\sigma\)) based on: (a) triplicate analysis of a single sample for total Fe; (b) three replicates of the selective extractions and carbon data; (c) 15 replicates of the magnetic susceptibility data. Uncertainty is presented as the error in the last digit in concise notation (e.g., 5.0 (15) = 5.0 ± 1.5).

\(^c\) Data from a separate 0.5 M HCl extraction with a soil:solution ratio of 1:10.
microcrystalline goethite, while the majority ordered at 4.2 K (Fe$^{III}$-OxHy(4.2–295 K)) or below (Fe$^{III}$-OxHy(4.2 K)). The ordering-temperature based subdivision of the Fe$^{III}$-OxHy class suggests that the mean particle size/crystallinity decreases with increasing rainfall. The Fe$^{III}$-OxHy(4.2 K) sub-class increases as a fraction of the total Fe$^{III}$-OxHy with increasing rainfall in both the surface and subsurface horizon transects. This is most notable in the surface horizons in which at the highest rainfall site, none of the Fe$^{III}$-OxHy were ordered at room temperature (i.e., no Fe$^{III}$-OxHy(>295 K) detected).

With depth, the f$_{tot-Fe}$ of each phase was variable and did not exhibit significant trends with the exception that surface horizons contained proportionally more Fe$^{III}$-organic/silicate and nano-Fe$^{III}$-(oxy)hydroxides (Fe$^{III}$-OxHy(4.2 K)), while the subsurface horizons contained more Fe$^{III}$-oxides. These trends are evident within the four-sample depth profile at the 3500 mm yr$^{-1}$ site (Fig. 3) and also generally reflected in the surface and subsurface transects (Fig. 2).

4. MÖSSBAUER PHASE ANALYSIS

Details regarding the fitting of the spectral components and how these relate to the identified Fe phases are contained in Section 1 of the Electronic Annex. Below we provide an analysis of the four broad Fe populations.

4.1. Fe$^{III}$-(oxy)hydroxide populations

Synthesis of the RT and LHT MBS spectra suggests the Fe$^{III}$-(oxy)hydroxide solid phases in these soils exhibit a continuum of crystallinities. Those at the more crystalline end are recognized as microcrystalline-goethites that order at RT (Figs. 4 and EA-5, EA-6, and EA-7 of the Electronic Annex). These are best developed in the 2800 mm yr$^{-1}$ site, where strong XRD reflections of goethite are present at 4.18 Å along with lower intensity peaks at 2.69 and 2.45 Å d-spacing (Figs. EA-2 and EA-3 of the Electronic Annex). These phases (Fe$^{III}$-OxHy(295 K)) exhibit lower field strengths (Bhf RT/C24=35T vs. 38T for pure goethite), higher RT CS values (CS/C24=0.42 mm s$^{-1}$ vs. CS/C24=0.37 for pure goethite) and less negative quadrapole splitting ($\epsilon=0.06$ to $\epsilon=-0.14$ vs $\epsilon=-0.26$ for pure goethite) than pure goethite (Table 4). This is consistent with a lower crystalline character that likely derives from some combination of Al substitution and reduced particle size. Both factors have been shown to reduce Bhf by as much as 6T in synthetic samples (Goodman and Lewis, 1981); synthetic and natural Al-substituted goethites also typically have higher CS and less

![Fig. 2. $^{57}$Fe Mössbauer modeled Fe distribution for a surface (a) and subsurface (b) transect across the MCG. The fraction of four broad Fe-bearing group assignments was calculated from the proportional spectra area of the MBS-modeled components (see Tables 3 and 4, Fig. 4, and the Figs. EA-5 and EA-6 of the Electronic Annex) as follows: ferrous (green) = RT-F; organic/silicate-Fe (grey) = RT-Q; Fe$^{III}$-oxides (red) = RT-Ox; Fe$^{III}$-(oxy)hydroxides (orange) = LHT-OxHy + LHT-(b)OxHy. The Fe$^{III}$-(oxy)hydroxide (orange) assignment is split across a crystallinity continuum into three fractions based on MBS-ordering temperature with fraction of the most crystalline end-member (RT-HyOx) shown above the 295 K line and that of the least crystalline end-member (LHT-(b)OxHy) below the 4.2 K line. Errors are $\Delta r$, calculated using the covariance matrix in Recoil. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 3. $^{57}$Fe Mössbauer modeled Fe distribution along the depth gradient at the 3500 mm yr$^{-1}$ site. The fraction of four broad Fe-bearing group assignments was calculated from the proportional spectra area of the MBS-modeled components (see Tables 3 and 4, and Fig. EA-7 of the Electronic Annex) as described in Fig. 2. Errors are $\Delta r$, calculated using the covariance matrix in Recoil. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image2)
negative quadrupole splitting than pure goethites (Goodman and Lewis, 1981; Kukkadapu et al., 2001; Vandenbergh et al., 2000).

In the middle of the Fe$^{III}$-OxHy crystallinity continuum, are the LHT-ordered sextets (Fe$^{III}$-OxHy$_{<4.2\ K}$). A plot of the quadrupole splitting ($\epsilon$) vs. the most probable hyperfine field ($H_{\text{peak}}$) for these sextets illustrates they have lower $H_{\text{peak}}$ than typical nano-goethite (n-Gt) standards, yet more negative $\epsilon$ values than a set of un-substituted and As-substituted ferrihydrite (Fh) standards (Fig. 5). The quadrupole splitting parameter ($\epsilon$) is a sensitive measure of electron asymmetry, which is strongly influenced by lattice structure in ferric phases. Thus, Fh, which has inherent high structural disorder (Marchand and Rancourt, 2009) and very little mineral averaged asymmetry, will always exhibit $\epsilon$ values close to zero (Mikutta et al., 2008). In contrast, Gt with its needle-like character will have a higher degree of asymmetry and more negative $\epsilon$ values. In most of our samples, the more negative $\epsilon$ values suggest a strong n-Gt contribution (Fig. 5a). However, several of our samples have $\epsilon$ values that approach those of Fh, with one sample (surface 4200 mm yr$^{-1}$ site) containing high organic matter (48%) and low Fe (0.6%) in which $\epsilon$ is very poorly constrained and gives equally acceptable fits across the Fh to n-Gt parameter region (Fig. 5a). Variation in crystallinity within a mineral phase often produces co-variation in the sextet line broadening ($\sigma_{\text{HFD}}$) and hyperfine field strength ($B_{\text{hf}}$) along a phase specific slope as illustrated in Fig. 5b for n-Gt and Fh (Van Der Zee et al., 2003). Our samples generally have smaller line widths and/or lower $B_{\text{hf}}$ values than expected for the n-Gt slope in Fig. 5b. This also suggests an admixture of Fh within these soils or perhaps that certain types of disorder affect $B_{\text{hf}}$ and $\sigma_{\text{HFD}}$ differently. It is also plausible for most of the magnetic domains of individual Fe$^{III}$-OxHy minerals to exhibit lattice asymmetry consistent with typical n-Gt, while other domains within these minerals partially lose this asymmetry and exhibit $\epsilon$ values closer to synthetic, cation-substituted Fh.

At the most disordered end of the crystallinity continuum, are the collapsed sextets at 4.2 K (LHT-(b)OxHy), which are assigned to nano-Fe$^{III}$-(oxy)hydroxides (Fe$^{III}$-OxHy$_{<4.2\ K}$) near their ordering temperature ($T_N$). These phases represent a unique feature of these Hawaiian soils and are discussed more completely in the discussion.

Fig. 4. Fitted $^{57}$Fe Mössbauer spectra of (a) surface 2800 mm yr$^{-1}$ and (b) subsurface 4200 mm yr$^{-1}$ at 295 and 4.2 K. The black solid line is the total calculated fit, through the discrete data points (circles). The high and low velocity wings are shown as insets when possible. The resolved spectral components at 295 K are: (1) RT-Q, the dominant doublet (blue line); (2) RT-OxHy, a broadened sextet (red line); (3) RT-OxHy, a broadened sextet (purple line); and (4) RT-(b)OxHy, a highly broadened (collapsed sextet) central contribution (yellow line); (5) RT-F, a doublet corresponding to ferrous iron. The resolved spectral components at 4.2 K are: (1) LHT-Q, a doublet giving rise to the two shallow central peaks (blue line); (2) LHT-OxHy, a wide sextet contributing to the outermost peaks that is equal in area, within error, to RT-OxHy (red line); (3) LHT-OxHy, corresponding to the dominant (i.e., deepest peaks) sextet (purple line); and (4) LHT-(b)OxHy, a collapsed 'sextet' (yellow line); (5) RT-F, a doublet corresponding to ferrous iron. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4.2. Fe III-silicate/organic-bound Fe populations

Fe atoms in silicates and monomeric organic complexes are too distant from each other to order magnetically, and thus both site populations produce a doublet at LHT with CS (median 0.50 mm s $^{-1}$) and QS (median 0.75 mm s $^{-1}$) values consistent with octahedrally coordinated, trivalent Fe (Table 4). In most of our samples, the LHT doublet is a minor component of the spectra, however in the 4200 mm yr $^{-1}$ site samples it is the dominant feature (Figs. 4, EA-5 and EA-6 of the Electronic Annex). Here small differences in the LHT-Q components for the surface and subsurface 4200 mm yr $^{-1}$ site soils are consistent with an assignment of organic-Fe III complexes in the surface horizons and isomorphic substitution of Fe III in silicates in the subsurface soils. The carbon-rich (480 g kg $^{-1}$) surface soil has a CS value of 0.53 mm s $^{-1}$, which is close to LHT CS values of 0.54 mm s $^{-1}$ for organically-complexed Fe in peat soils reported by Schwertmann and Murad (1988). Whereas, the kaolinite/halloysite-rich subsurface soil has a CS of 0.48 mm s $^{-1}$, which is similar to that of 0.47–0.49 mm s $^{-1}$ reported for kaolin-group minerals by Fysh et al. (1983). The small size of the doublets at all other sites preclude extension of this analysis to the rest of the samples.

Table 3
Fe concentrations $^a$ (g kg $^{-1}$ dry soil) from Mössbauer spectroscopy (MBS).

<table>
<thead>
<tr>
<th>Horizon (10–20 cm)</th>
<th>Mössbauer-determined Fe concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-oxides</td>
<td>Fe-oxyhydroxides</td>
</tr>
<tr>
<td>RT ordered</td>
<td>LHT ordered</td>
</tr>
<tr>
<td>2200 mm (A)$^b$</td>
<td>53.5 (45)$^c$</td>
</tr>
<tr>
<td>2800 mm (A)</td>
<td>13.8 (10)</td>
</tr>
<tr>
<td>3500 mm (Ag)</td>
<td>9.3 (7)</td>
</tr>
<tr>
<td>4200 mm (A)</td>
<td>0.5 (1)</td>
</tr>
</tbody>
</table>

Table 4
Descriptions of the Mössbauer components and assignment to solid phases.

<table>
<thead>
<tr>
<th>Component label</th>
<th>Spectral shape</th>
<th>Assignment</th>
<th>MBS parameter ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temp. (RT) spectra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT-Q (blue)</td>
<td>Doublet (central)</td>
<td>Org./silicate Fe$^{III}$ and Fe$^{III}$-OxHy ($\sim$295 K)</td>
<td>CS (mm s $^{-1}$)$^a$</td>
</tr>
<tr>
<td>RT-F (green)</td>
<td>Doublet (high-energy)</td>
<td>Ferrous Fe</td>
<td>0.36 to 0.39</td>
</tr>
<tr>
<td>RT-Ox (red)</td>
<td>Sextet (widest)</td>
<td>Fe$^{III}$-oxides (Hm/Mh)</td>
<td>0.33 to 0.38</td>
</tr>
<tr>
<td>RT-(b)OxHy (yellow)</td>
<td>Sextet (collapsed)</td>
<td>Fe$^{III}$-OxHy ($\sim$295 K)</td>
<td>0.32 to 0.69</td>
</tr>
<tr>
<td>Liq. He Temp. (LHT) spectra</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LHT-Q (blue)</td>
<td>Doublet (central)</td>
<td>Org./silicate Fe$^{III}$</td>
<td>0.47 to 0.54</td>
</tr>
<tr>
<td>LHT-F (green)</td>
<td>Doublet (high)</td>
<td>Ferrous Fe</td>
<td>1.15 to 1.51</td>
</tr>
<tr>
<td>LHT-Ox (red)</td>
<td>Sextet (widest)</td>
<td>Fe$^{III}$-oxides (Hm/Mh)</td>
<td>0.44 to 0.53</td>
</tr>
<tr>
<td>LHT-OxHy (purple)</td>
<td>Sextet (middle)</td>
<td>Fe$^{III}$-OxHy (4.2–295 K)</td>
<td>0.37 to 0.50</td>
</tr>
<tr>
<td>LHT-(b)OxHy (yellow)</td>
<td>Sextet (collapsed)</td>
<td>Fe$^{III}$-OxHy ($\sim$295 K)</td>
<td>0.41 to 0.94</td>
</tr>
</tbody>
</table>

$^a$ All CS values are given relative to $\alpha$-Fe at 295 K.
4.3. Paramagnetic ferrous populations

The ferrous doublet components in our samples are best resolved in the higher resolution RT spectra. We observe paramagnetic ferrous contributions in four samples at the higher end of the rainfall gradient with RT QSD’s falling into three distinct identity groups consistent with (1) ilmenite (surface 3500 mm yr$^{-1}$), (2) pyroxenes (subsurface 3500 mm yr$^{-1}$), and (3) sheet silicates or sorbed Fe$^{2+}$ (both depths at 4200 mm yr$^{-1}$, see Fig. 4). No octets consistent with the presence of magnetite were observed in any of the spectra. The position of the high-energy line at 1.4 mm s$^{-1}$ is diagnostic for ilmenite. The high-energy lines (H$_{L}$) at 2.42 mm s$^{-1}$ in the 4200 mm yr$^{-1}$ site are much too high for ilmenite and are consistent with those commonly reported for alumino-silicate clays (Murad and Cashion, 2004), especially those of kaolinite for which H$_{L}$ averages 2.4 ± 0.1 mm s$^{-1}$ based on a compilation of eight studies reporting Fe$^{3+}$ in kaolinites (Murad and Cashion, 2004). XRD of the 4200 mm yr$^{-1}$ subsurface samples (Fig. EA-3) indicate a clear pattern of reflections for a poorly-ordered kaolin-group mineral. Sorbed Fe$^{2+}$ may also contribute to this peak, especially in the surface horizon, as Rancourt et al. (2005) have shown Fe$^{2+}$ sorbed to bacterial cells can yield H$_{L}$ lines even above 2.8 mm yr$^{-1}$. The H$_{L}$ line at 2.18 mm s$^{-1}$ matches well with pyroxene, but at this stage of weathering pyroxene is usually removed from the soil. We are the least confident of this ferrous assignment, although still highly confident that it is indeed a ferrous solid-phase.

4.4. Fe$^{3+}$-oxides

Strong hematite XRD reflections (Figs. EA-2 and EA-3) in the lower rainfall soils provide a strong-basis for assigning the wide RT Fe$^{3+}$-oxide sextets to hematite. The overall lower hyperfine fields (H$_{peak}$) of the MCG sextets than reference microcrystalline hematite (Fig. 5a) is consistent with smaller particle size (Dang et al., 1998) and/or cation substitution of Al or Ti within the Hm lattice (Degrave et al., 1988). However, the mass-specific magnetic susceptibility (MS) for these soils (χ up to 3.7 × 10$^{-5}$ m$^{3}$ kg$^{-1}$) is much higher than expected for the antiferromagnetic (AFM) and superparamagnetic (SP) Fe$^{3+}$ phases Hm, Gt and Fh (Table 2), which typically have χ values of $\sim$5.0 × 10$^{-7}$ m$^{3}$ kg$^{-1}$. This strongly suggests ferrimagnetic solid-phases, such are magnetite or maghemite are present in these soils—although we note recent reports of a ferrimagnetic ferrihydrite (Michel et al., 2010) that may be applicable here as well. Typical χ values for magnetite or maghemite are $\sim$4.5 × 10$^{-7}$ m$^{3}$ kg$^{-1}$, so even trace amounts can significantly alter the bulk χ value for the soil. In the MCG soils, a strong correlation between MS and the mass of Fe$^{3+}$-oxides (Fig. 6) suggests a ferrimagnetic solid-phase contributes to the Fe$^{3+}$-Ox spectral area. Since, no magnetite octets were observed in any of the MBS spectra, and we have XRD and MBS evidence for maghemite (Mh) in some of the samples (e.g., Figs. 5, EA-2, and EA-3), a common...
presence of Mh in these soils is more likely. If we assume all the MS in these soils results from Mh, we can estimate the mass of Mh using a typical y value of 4.0 \times 10^{-4} m^3 kg^{-1} Mh. By dividing this by the mass of Fe-oxides from the MBS spectra area (Table 3), we can roughly estimate the Mh contribution to the Fe-oxide fraction (Table EA-8 of the Electronic Annex). Comparing these values to the presence of either Hm or Mh related XRD peaks and the quadrupole splitting of the RT-Ox spectral component provides an interesting look at the Fe-oxides in these soils (Table EA-8 of the Electronic Annex). The Bhf values for Hm and Mh are very similar, but the two minerals have quite different y values (Murad and Cashion, 2004) with 

\[ \varepsilon_{mc,Hm} \approx -0.10 \text{ mm s}^{-1} \quad \text{and} \quad \varepsilon_{Mh} \approx -0.01 \text{ mm s}^{-1}. \]

In the two deepest samples at the 3500 mm yr^{-1} site, the estimated Mh mass matches or exceeds the mass of MBS-assigned Fe-oxides, and these samples have y values closest to zero. In the other samples, the Mh fraction of the Fe-oxide mass ranges from 0.1 to 0.7 with y values between -0.08 and -0.13 mm s^{-1}. XRD peaks were generally observed when estimated concentrations of Hm or Mh were above ~10 g Fe kg^{-1} soil. Thus, hematite likely represents the majority of Fe^{III}-Ox site populations (Figs. 2 and 3) with a sizable contribution of maghemite in the surface horizons and at depth in the 3500 mm yr^{-1} site. More detailed studies of the bulk magnetic properties of these soils are currently underway.

5. DISCUSSION

Fresh Hawaiian basalt has ~86 g kg^{-1} Fe primarily in divalent form residing in pyroxenes, olivine, ilmenite and basaltic glass (Burkhard, 2001). Initial weathering of volcanic glass proceeds rapidly (Shoji et al., 1993), releasing Fe and Al and Si faster than crystalline minerals can precipitate, leading to soil solutions that are over-saturated with respect to several nanocrystalline or short-range-ordered phases (allophane, ferrhydrite, and opaline silica). These metastable solids have smaller critical nuclei and are favoured initially over more crystalline forms (Steefel and Van Cappellen, 1990). As weathering proceeds and the volcanic glass fraction is removed, soil solution activities of Fe, Al and Si are decreased. Further transformations of these SRO phases to crystalline minerals (e.g., kaolinite, gibbsite, goethite, hematite or quartz) depend strongly on environmental conditions and aging time. Our interpretation of the present-day Fe-phase composition across the gradient emerges because of a dynamic interplay between fluctuating redox conditions and the presence of cat-ions and organic matter that alter the classic Ostwald ripening sequence (Ostwald, 1900). Mean Eh values for measurements logged weekly over a year illustrate sufficient Eh swings at all sites for both Fe reduction and re-oxidation of the released Fe^{3+}(aq) (Schuur and Matson, 2001) The sorption of Fe^{3+}(aq) onto Fe solid-phases has been shown to greatly accelerate mineral transformations that increase crystallinity via a process referred to as “atom exchange” (Charlet et al., 1998; Elsner et al., 2004; Fredrickson et al., 2004; Williams and Scherer, 2004; Crosby et al., 2005; Hansel et al., 2005; Pedersen et al., 2005; Larese-Casanova and Scherer, 2007; Gehin et al., 2007; Yanina and Rosso, 2008; Mikutta et al., 2009a). In fact, laboratory incubations with soils from this gradient indicate that oscillating redox conditions can produce large Fe^{3+}(aq) fluctuations that are superimposed on an overall increase in iron solid-phase crystallinity even on the time scale of weeks (Thompson et al., 2006b). Yet, low crystallinity Fe solids are abundant in these soils. We suggest this preservation of SRO solids is due to: (1) an open-system leaching environment that modulates the rise of Fe^{3+}(aq) concentrations during Fe reduction events and (2) the prevalence of organic matter (Table 2) in the surface horizons and Si and Ti in the subsurface horizons (Scribner et al., 2006) that retard the re-crystallization process. Retardation of Fe solid-phase transformation is well known to occur as a result of surface sorption of organic matter and Si, among other constituents (Schwertmann, 1966; Eusterhues et al., 2008; Mikutta et al., 2008; Jones et al., 2009). In fact, Jones et al. (2009) observed that the effects of Fe^{3+}-promoted atom exchange on Si-substituted ferrhydrite are different than on pure un-substituted Fh. Instead of the complete transformation to goethite observed for pure Fh, Fe^{3+} atom exchange on Si-substituted Fh preserves the Fh-structure, promoting Si release and the re-crystallization of a proportional increase of the most reactive and least crystalline Fe^{III}-OxHy components with increasing rainfall (and Fe removal via leaching) is unexpected. The conventional kinetic expectation in a dissolution-dominated environment (Sposito, 2008) is for the most reactive, soluble, and disordered (nanocrystalline) Fe solid-phases to be dissolved preferentially, resulting in selective retention of more kinetically stable, larger crystalline iron minerals, such as hematite (Stucki et al., 2007) and “bulk”, large-crystalline goethite (Jones et al., 2009; Postma, 1993). We observe the opposite. Labile phases such as the nano Fe^{III}(oxy)hydroxides (Fe^{III} OxHy_{<4.2 K}) maintain or increase their f_{ox}Fe abundance at higher rainfall sites (Fig. 4) while predictably recalcitrant phases such as Fe^{III}-Ox and Fe^{III}-OxHy_{(>295 K)} that are magnetically ordered at 295 K decrease as a f_{ox}Fe. This is particularly true for the surface soils, which have a greater abundance of OM than the subsurface soils (Table 2).

5.2. Controls on Fe solid-phase composition

Evidently, Fe solid-phase transformations occur concurrently with significant Fe loss (Fig. 1) across the gradient. We suggest that the observed Fe species distribution across the gradient emerges because of a dynamic interplay between fluctuating redox conditions and the presence of cat-ions and organic matter that alter the classic Ostwald ripening sequence (Ostwald, 1900). Mean Eh values for measurements logged weekly over a year illustrate sufficient Eh swings at all sites for both Fe reduction and re-oxidation of the released Fe^{3+}(aq) (Schuur and Matson, 2001) The sorption of Fe^{3+}(aq) onto Fe solid-phases has been shown to greatly accelerate mineral transformations that increase crystallinity via a process referred to as “atom exchange” (Charlet et al., 1998; Elsner et al., 2004; Fredrickson et al., 2004; Williams and Scherer, 2004; Crosby et al., 2005; Hansel et al., 2005; Pedersen et al., 2005; Larese-Casanova and Scherer, 2007; Gehin et al., 2007; Yanina and Rosso, 2008; Mikutta et al., 2009a). In fact, laboratory incubations with soils from this gradient indicate that oscillating redox conditions can produce large Fe^{3+}(aq) fluctuations that are superimposed on an overall increase in iron solid-phase crystallinity even on the time scale of weeks (Thompson et al., 2006b). Yet, low crystallinity Fe solids are abundant in these soils. We suggest this preservation of SRO solids is due to: (1) an open-system leaching environment that modulates the rise of Fe^{3+}(aq) concentrations during Fe reduction events and (2) the prevalence of organic matter (Table 2) in the surface horizons and Si and Ti in the subsurface horizons (Scribner et al., 2006) that retard the re-crystallization process. Retardation of Fe solid-phase transformation is well known to occur as a result of surface sorption of organic matter and Si, among other constituents (Schwertmann, 1966; Eusterhues et al., 2008; Mikutta et al., 2008; Jones et al., 2009). In fact, Jones et al. (2009) observed that the effects of Fe^{3+}-promoted atom exchange on Si-substituted ferrhydrite are different than on pure un-substituted Fh. Instead of the complete transformation to goethite observed for pure Fh, Fe^{3+} atom exchange on Si-substituted Fh preserves the Fh-structure, promoting Si release and the re-crystallization of
Si-free Fh particles. We hypothesize that this atom-exchange phenomenon also takes place in the MCG soils—which are intermittently exposed to Fe$^{2+}$(aq)—and likely exerts a pedogenic influence on the Fe solid-phase composition. We suggest that the resulting Fe solid-phase composition evolves in a leaching environment with consistent reductive dissolution forcing, intermittent oxidative-predissolution conditions, and processes that both accelerate (i.e., the presence of Fe$^{2+}$(aq)) and retard (i.e., the presence of sorbed OM and co-precipitated cations) solid-phase ripening.

5.3. Characteristics of short-range-ordered Fe on the MCG

Prior Fe solid-phase composition work in Hawaii has demonstrated these soils to be replete with short-range-ordered (SRO) or nanocrystalline Fe-solid-phases (Wada and Wada, 1976; Parfitt and Childs, 1988; Parfitt et al., 1988). Routinely, these SRO Fe phases are classified as ferrihydrite on the basis of selective extraction data, broad XRD peaks, or MBS at 77 K. With the exception of our previous work on the surface 3,500 mm yr$^{-1}$ site (Thompson et al., 2006b), the only prior low temperature (<77 K) MBS measurements on Hawaiian soils were on relatively young, dry, soils weathered via palagonitic or solfataric processes near the mouth of volcanoes that serve as Martian soil analogs (Bishop et al., 2007). Only at very low temperatures (e.g., 4.2 K) can one use MBS to distinguish between paramagnetic silicate/organic bound Fe and super-paramagnetic Fe$^{3+}$-(oxy)hydroxides such as ferrihydrite and nano-goethite (Stucki et al., 2007). While our data do provide some marginal MBS and XRD evidence for the presence of ferrihydrite sensu stricto in some samples (e.g., Fig. 5), the majority of SRO Fe-(oxy)hydroxides in these soils are better approximated by synthetic nano-goethites (e.g., Van Der Zee et al., 2003). In most precise terms, the SRO Fe phases in these soils carry no known synthetic analog, but can likely be accurately represented as Fe$^{3+}$-(oxy)hydroxides with nm particle sizes, high degrees of cation or OM substitution and/or other chemical/structural defects that decrease crystallinity.

This is especially true for the most disordered Fe$^{3+}$-OxHy solids, which produces a collapsed sextet at LHT (LHT-(b)OxHy) indicative of dynamic or homogeneous line-broadening of an Fe phase near its ordering temperature ($T_N$). Such solid-phases must have much lower crystallinity and/or much smaller magnetic domain sizes than currently studied synthetic analogs of authigenic Fe$^{3+}$-(oxy)hydroxides (e.g., ferrihydrite or nano-goethite with various degrees of cation substitution)—all of which, to our knowledge, are magnetically ordered at 4.2 K. A notable exception to this may be the DOM-Fe precipitate recently produced by Schwertmann et al. (2005), which in addition to an ordered Fh sextet, also includes a collapsed sextet feature at 4.2 K similar to our LHT-(b)OxHy sextet.

The association of Fe and organic matter may play an important role in determining the degree of disorder in soil Fe phases. Several recent studies have highlighted the effects of various organic components, organic matter and organic coatings on the magnetic properties of ferrihydrite (Schwertmann and Murad, 1988; Schwertmann et al., 2005; Eusterhues et al., 2008; Mikutta et al., 2008; Berquo et al., 2009; Michel et al., 2010). These studies illustrate that different carbon sources impact the Fh structure more substantially than others (Mikutta et al., 2008) decreasing Bhf between 1 and 3.5 T (Schwertmann et al., 2005; Eusterhues et al., 2008) and decreasing ordering temperature ($T_N$) up to 18 K. Even when changes to the Fh structure were minimal, Mikutta et al. (2008) found dramatic changes in the point of zero charge, surface area and mineral porosity for organic-Fh co-precipitates. However, when organic-compounds are surface-adsorbed rather than co-precipitated, reductions in Bhf are minimal (Berquo et al., 2009). Since cation substitution (Goodman and Lewis, 1981; Degrande et al., 1988; Vandenberghhe et al., 2000; Rancourt, 2001), small particle size, and lattice-defects can all substantially decrease $T_N$ individually, it is easy to see how precipitates formed in the multi-component soil environment would give rise to even greater suppression of $T_N$ to near or below 4.2 K as observed in the MCG soils.

These SRO Fe phases (Fe$^{3+}$-OxHy$_{4.2–295}$K) and Fe$^{3+}$-OxHy$_{4.2–295}$K) comprise a large majority of the Fe in these soils and are likely representative of the SRO components commonly cited as the reactive Fe in intermediate-aged Hawaiian soils (Crews et al., 1995; Kitayama et al., 1997; Torn et al., 1997; Vitousek et al., 1997; Chorover et al., 1999, 2004; Chadwick and Chorover, 2001; Miller et al., 2001; Chadwick et al., 2003; Mikutta et al., 2009b, 2010).

5.4. Comparison of selective wet-chemical extractions and MBS phases

There is good correlation (Fig. 7) between the AAO extraction and the MBS-assigned nano Fe$^{3+}$-(oxy)hydroxide phase (Fe-OxHy$_{4.2–295}$K; Table 3), but no apparent correlations between the MBS Fe site assignments and other selective extractions (Table 3). The concentrations of Fe extracted by Na-pyrophosphate are much larger than the MBS-assigned Fe silicate/organic phases, which would contain any Fe-coordinated with organic functionalities. In all but three samples from the wettest end of the gradient the moles of Fe extracted exceed estimates of the total ionisable surface functional groups on the organic matter (data not shown) assuming a mean 2 mol kg$^{-1}$ soil carbon (Essington, 2004). This suggests that most of the Na-pyrophosphate extractable Fe in these soils resides in nanocrystalline Fe$^{3+}$-(oxy)hydroxides (Fe$^{3+}$-OxHy$_{4.2–295}$K and Fe$^{3+}$-OxHy$_{4.2–295}$K), which are likely embedded in the organic matrix as observed previously (Chorover et al., 2004; Thompson et al., 2006a). The principal action of Na-pyrophosphate is to disperse aggregates of soil organic matter. When such a treatment is applied to volcanic soils with a high abundance of nano-sized mineral particles, these materials are measured along with the dispersed organic matter. Our observations are consistent those of Parfitt and Childs (1988) for a broader series of soils. It appears that in many cases Fe extracted by a standard Na-pyrophosphate extract does not resemble monomeric Fe-organic complexes, but rather includes nanocrystalline
Fe components. In addition, we obtained lower Fe recovery from CBD extractions than from Li-metaborate fusion (Table 2). This is consistent with prior observations by Parfitt et al. (1988), who found that some Hawaiian soil Fe-oxides were resistant to even multiple sequential CBD extractions, and Morris et al. (1993), who found hematite present in the CBD extract residue of Hawaiian palagonitic soils. These researchers attributed the apparent Fe phase recalcitrance to physical protection by a silicate matrix or large mineral particle sizes. We add that it could also be due to Fe co-precipitation.

5.5. Lack of significant solid-phase ferrous iron

The MCG soils do not contain significant quantities of ferrous iron despite low average Eh values in the wetter sites (Fig. 1). There is always a potential for Fe\textsuperscript{II} oxidation during sampling, transport and freeze-drying, but we were careful to N\textsubscript{2}-flush the samples immediately after sampling and to open them only in a N\textsubscript{2}/H\textsubscript{2} glove box until after they had been frozen at 193 K and freeze-dried. Hence, we believe low solid-phase ferrous abundances are a common feature of these variable-redox upland soils largely for two reasons: (1) low pH (<5) and low S and P content coupled with high leaching rates precludes solution oversaturation with respect to many common ferrous minerals (pyrite, siderite, vivianite, magnetite, green-rust); and (2) frequent fluctuations in dioxygen content (Fig. 1) that can rapidly oxidize ferrous to re-generate ferric iron phases. The combination of dynamic redox conditions and a high leaching rate likely separate these redox-affect ed upland soils from other redox-altered soils, such as those with fluctuating groundwater or soils in swales or wetlands.

6. CONCLUSION

The iron solid-phase composition along the Maui climate gradient develops within a context of leaching and dynamic redox conditions that vary as a function of rainfall. This results in extensive depletion of Fe with increasing rainfall. Concurrent with Fe depletion, is a coherent decrease in the fraction of total Fe (f\textsubscript{Fe\textperiodcentered}Fe) assigned to Fe-(oxy)hydroxide phases and corresponding increases in the f\textsubscript{Fe\textperiodcentered}Fe of silicate/organic Fe and ferrous Fe phases. Interestingly, the crystallinity of the Fe-(oxy)hydroxide phases decreases with increasing rainfall, suggesting that organic matter (OM) co-precipitation and cation substitutions retard mineral ripening.

Across all sites, most of the Fe was present as a continuum of Fe\textsuperscript{III}-(oxy)hydroxides. Those at the more crystalline end are recognized as microcrystalline-goethites on the basis of both MBS and XRD, progressively less crystalline components are still best described as goethite, in this case nano-goethites (Van Der Zee et al., 2003), but with MBS properties that in some soils suggest an admixture with ferrihydrite or at least enough structural disorder to partially remove the axial asymmetry that characterizes the crystal structure of the needle-forming goethite mineral. The least crystalline end-members are highly disordered with blocking or Néel temperatures (T\textsubscript{N}) suppressed near or below 4.2 K and are difficult to assign to goethite or ferrihydrite sensu stricto, but rather can be most appropriately described as nano-Fe\textsuperscript{III}-(oxy)hydroxides. The latter end-members suggest extremely low-crystallinity arising from substitutional and other defects and/or from nanometric particle or coherent-ordering domain sizes. In this regard, our results are consistent with previous statements by Murad and Schwertmann (1980), who write:

as particle sizes decrease the individual characteristics of the different iron oxides [and (oxy)hydroxides] gradually disappear, until finally only fundamental structural elements of short-range-order common to all, i.e., Fe\textsuperscript{III} surrounded by six O, OH, and/or OH\textsubscript{2}, remain. (p. 1048)

We would, however, broaden the statement to include substitutional and other defects affecting crystallinity, in addition to particle size (Rancourt et al., 2001, 2005; Thibault et al., 2009).

Our work suggests a need for future study on more appropriate synthetic analogs of co-precipitated Fe\textsuperscript{III}, (oxy)hydroxide solid phases. These reference solids would need to be co-precipitated with various cations and simple OM components under different precipitation kinetics to accumulate a broader range of nanocrystalline phases with low magnetic ordering temperatures. Such work, which is just beginning (e.g., Eusterhues et al., 2008; Mikutta et al., 2008; Thibault et al., 2009), is needed to further extend the interpretive power of Mössbauer spectroscopy.

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Iron phases along a redox gradient in basaltic soils

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