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## SPECIAL SECTION: STABILITY OF MINERAL-ORGANIC MATTER ASSOCIATIONS UNDER VARYING BIOGEOCHEMICAL CONDITIONS

## Fast redox switches lead to rapid transformation of goethite in humid tropical soils: A Mössbauer spectroscopy study

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**Abstract**

Humid tropical forest soils experience frequent rainfall, which limits oxygen diffusion and creates redox heterogeneity in upland soils. In this study we gauged the effect of short-term anoxic conditions on Fe mineralogy of relatively Fe- and C-rich surface soils (C/Fe mole ratio ~5) from a humid tropical forest in Puerto Rico. Soils subjected to 4-d oxic/anoxic oscillation were characterized by selective chemical extractions, Mössbauer spectroscopy (MBS), and X-ray diffraction. Chemical extraction data suggested that rapidly switching redox conditions had subtle effects on bulk Fe mineralogy. Mössbauer, on the other hand, indicated that (a) the soil Fe is a mixture of goethites of varying characteristics with minor contributions from ferrihydrite (<5%) and Fe(III)-organic matter (OM) phases (~10%), and (b) anoxic conditions rapidly transformed all forms of goethite to relatively stable Fe oxides. Such fast changes in goethite features could be due to rapid depletion and sorption of bio-released structural Al or sorbed OM onto residual soil components. The rapid temporal changes in MBS parameters and corresponding pore water nominal oxidation state of C values suggest that Fe-C transformations in these upland tropical soils are complex and intricately coupled. A comprehensive understanding of the fate of Fe, Al, and OM (Fe-organic moieties) during redox switches and concurrent changes in pore water chemistry is critical for development of robust transport models in humid tropical soils, which are subject to episodic low-redox events.

**Abbreviations:** MBS, Mössbauer spectroscopy; OM, organic matter; PP, pyrophosphate; SRO, short-range ordered; XRD, X-ray diffraction.

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## 1 | INTRODUCTION

Humid tropical forest soils experience frequent rainfall events that create temporary oxygen depletion and constrain both mineral-organic matter (OM) interactions and microbial metabolism that regulate soil C, Fe, and nutrient cycling (Cavaleri et al., 2015; Chorover et al., 2007; Ginn et al., 2017; O'Connell et al., 2018). Due to these periodic rain events, the ample supply of reduced OM, and fine-textured soils, frequent redox oscillations can occur, in parallel with changes in soil moisture, soil oxygen and solute diffusion, availability of terminal electron acceptors, and thus aerobic versus anaerobic respiratory processes (Conrad, 1996; Liptzin et al., 2011; Silver et al., 1999; Vasconcelos et al., 2004). Our study site, the Luquillo Experimental Forest in northeastern Puerto Rico, exists on upland ultisols with high redox-active Fe content ( $\sim 66 \text{ g kg}^{-1}$  soil), relatively high OM ( $66\text{--}100 \text{ g kg}^{-1}$  soil), and receives 3,000 mm annual precipitation (Beinroth, 1982; Scatena, 1989). When these Fe- and C-rich (OM/Fe mole ratio  $\sim 5$ ) tropical soils undergo periodic oxygen depletion, short-range ordered (SRO)-Fe oxides transform to micro-crystalline goethite and micro-hematite (depending on Fe(II) levels) via dissolution and re-precipitation processes (Thompson et al., 2006b). However, soil Fe oxides are often Al-substituted (Murad & Schwertmann, 1980) and carbon-coated (Lalonde et al., 2012). Laboratory-based studies with pure minerals have shown that, individually, both the extent of Al substitution and the amount of OM coating have pronounced effects on bioreduction/biotransformation of Fe oxides (Adhikari et al., 2018; Adhikari et al., 2017; Chen et al., 2015; Dahlgren, 1994; Dominik et al., 2002; Ekstrom et al., 2010). Because of this complexity, the precise nature of mineral-associated OM moieties, the combined effect of Al/(Al + Fe) stoichiometry, and the extent of OM coatings (or OM/Fe ratios) of mineral-associated OM moieties involved in reductive (bio)transformation of SRO-Fe oxides are not well understood.

Recent studies have indicated changes in soil SRO-Fe oxide crystallinity due to redox oscillations (Barcellos, Cyle, et al., 2018; Barcellos, O'Connell, et al., 2018; Bhattacharyya et al., 2018; Chen & Thompson, 2017, 2021; Chen et al., 2020; Chen et al., 2015; Chen et al., 2017; Chen et al., 2018; Chorover & Amistadi, 2001; Dubinsky et al., 2010; Hall & Silver, 2013; Thompson, Chadwick, Boman, et al., 2006; Thompson, Chadwick, Rancourt, et al., 2006; Winkler et al., 2018) based on ammonium-oxalate extractions and Mössbauer (MBS) measurements conducted below 77 K. Recent work from our group has shown that fast redox switches can cause changes in MBS spectra accompanied by simultaneous changes in amorphous or ammonium oxalate (AO)-extractable Fe, Al, dissolved Fe(II), and water-extractable dissolved organic carbon concentrations (Bhattacharyya et al., 2018). Our experimental data implied mineralogical changes of SRO-Fe oxides are

### Core Ideas

- Iron oxide crystallinity increases during rapid reduction events in humid tropical soils.
- Depletion of Al and redistribution of organic C on Fe-oxide surfaces lead to increased crystallinity of goethites.
- Mossbauer spectroscopy at 225 K is critical to identify molecular scale changes in mineralogy.

correlated to AO-soluble Fe and dissolved organic carbon. Together, these changes serve as the controlling factors behind the underlying molecular-scale reductive dissolution or oxidative transformation and precipitation processes in variable redox wet tropical soils.

In this study, we conducted an in-depth analysis of Fe speciation in surface (oxic) soils of the Luquillo Critical Zone Observatory that were sampled as quickly as 30 mins after switching from an oxic to an anoxic condition. Specifically, it probes: (a) the precise nature of Fe speciation of the "oxic" soil (types of Fe oxides, nature of Fe-containing clays/silicates, relative amounts of Fe-OM complexes); (b) mechanisms driving bulk changes to SRO-Fe oxide characteristics upon exposure to anoxic conditions; and (c) how well bulk SRO-Fe oxide speciation/crystallinity changes with redox shifts. Results from variable temperature  $^{57}\text{Fe}$  MBS were correlated with changes in AO- and pyrophosphate (PP)-soluble Fe, Al, and Si. To our knowledge, this is the first study that reports changes in SRO-Fe oxide characteristics within such a short time frame.

## 2 | MATERIALS AND METHODS

### 2.1 | Redox oscillation experiment

Soil samples for this experiment were collected from the Luquillo Experimental Forest, a National Science Foundation Critical Zone Observatory and Long-Term Ecological Research site in northeastern Puerto Rico ( $18^{\circ}18' \text{ N}$ ,  $65^{\circ}50' \text{ W}$ ). The site is characterized by steep topography with naturally dynamic soil redox regimes (Liptzin et al., 2011; Silver et al., 1999). Details of the study site and the redox oscillation experiment have been published previously (Bhattacharyya et al., 2018; Lin et al., 2021). Briefly, soils from the Luquillo Experimental Forest were subjected to redox oscillations during which the headspace was alternated to create shifts from oxic to anoxic conditions every few days. Microcosms were destructively harvested; soil samples were collected immediately prior to the headspace gas switch (switch\_0) at 30 min, 210 min, and 4 d post switch (labeled

switch\_30 min, switch\_210 min, and switch\_4d, respectively) to capture short-term geochemical responses that occurred as a function of the changing soil redox status. For our study, we focused on soils that were subjected to oxic-to-anoxic switches ('reduction' events). During harvest points, microcosm jars were opened and soils were lightly homogenized and then subsampled for microbial and chemical analyses. Sampling and extractions for anoxic headspace microcosms were performed within an anoxic chamber (5% H<sub>2</sub> and 95% N<sub>2</sub>). All chemical reagents used within this chamber were prepared in advance with degassed water to preserve the Fe oxidation state, and for samples harvested at anoxic sampling points, subsequent extractions were conducted under strict anoxic conditions.

## 2.2 | Iron speciation by Mössbauer spectroscopy

The Mössbauer spectroscopic method has advantages over X-ray-based techniques, most notably for characterization of metal substituted-Fe(III) oxides of varying Al content (Gorski & Scherer, 2010; Gorski et al., 2013; Handler et al., 2014; Kukkadapu et al., 2001). Our previous study showed that the differences in MBS data at 225 K between the variably redox-incubated tropical soils from the Luquillo Experimental Forest were more prominent than at any other measurement temperature (Figure SI in Bhattacharyya et al., 2018) and hence were used for this study, along with MBS data at 77 and 8K for an accurate interpretation of the mineralogical changes. To determine the changes in oxidation state, as well as structural environment of Fe due to redox incubation, Mössbauer spectra were collected at multiple temperatures (225, 77, and 8 K) on microcosms harvested before and after the reduction event during a redox oscillation cycle. Data were collected with a Web Research Company instrument at the Pacific Northwest National Laboratory that included a closed-cycle cryostat (SHI-850, Janis Research Company, Inc.), a Sumitomo CKW-21 He compressor unit and a Ritverc NaI detection system. A <sup>57</sup>Co/Rh source was used as the gamma energy source. Sample preparation was carried out in an anoxic chamber to prevent changes in Fe oxidation state. For MBS analysis, we also included a soil sample that had been under anoxic headspace for 4 d (switch\_4d). Data acquisition and data processing followed previously reported procedures (Peretyazhko et al., 2012). Additional details on Mössbauer analysis are provided in the Supplemental Material.

## 2.3 | X-ray diffraction

Powder x-ray diffraction (XRD) data were collected from the soil sample mounted in a zero-background holder using a Panalytical MPD Bragg-Brentano diffractometer. A Cu X-

ray tube ( $\lambda = 1.5418 \text{ \AA}$ ) and variable divergence slits were used, and data were collected at 0.04° 2 $\theta$  intervals between 5 and 100° 2 $\theta$ . Minerals were identified using JADE (Materials Data) by comparison with reference patterns in the International Center for Diffraction Data database.

## 2.4 | Iron and aluminum forms by selective chemical extractions

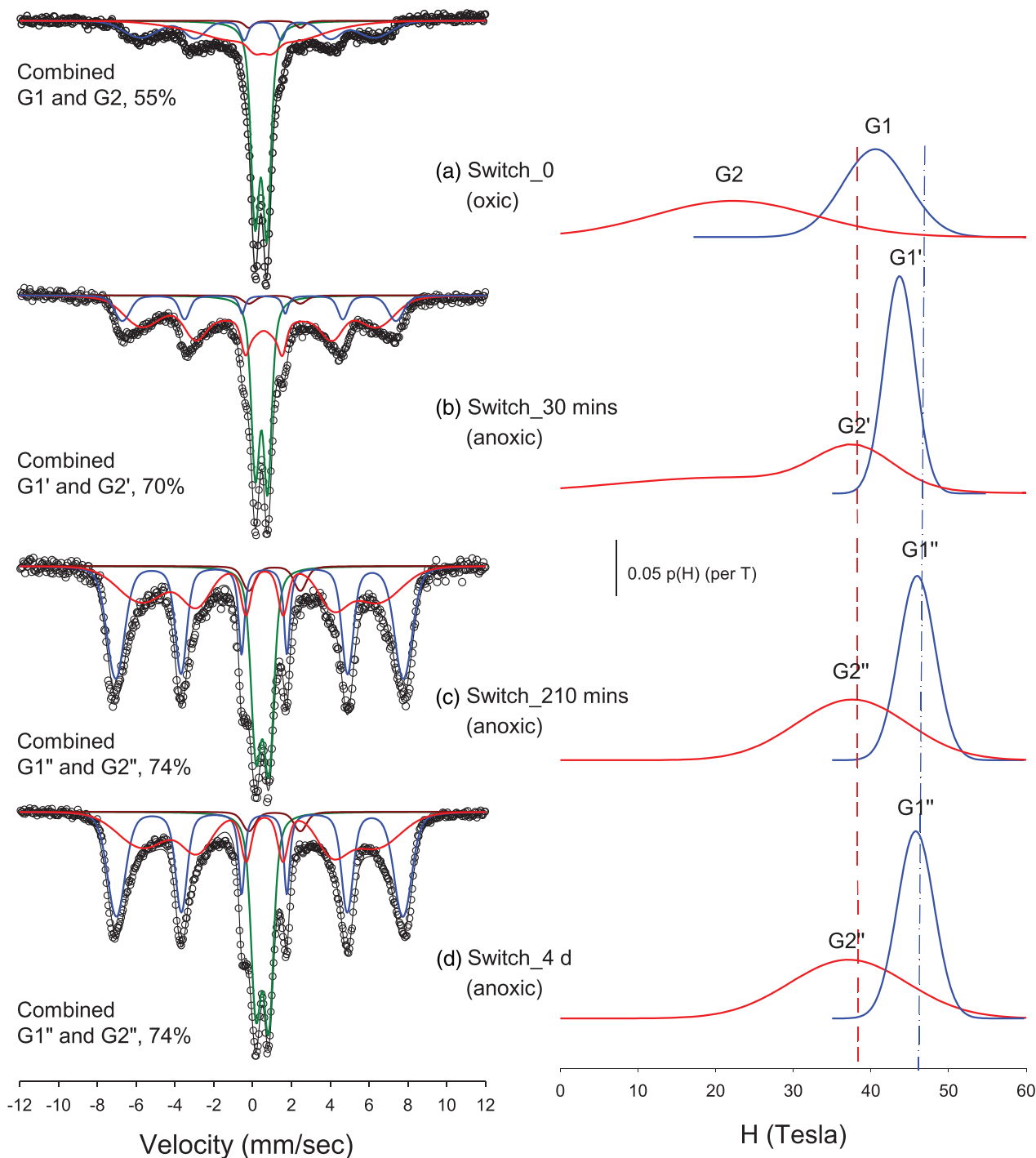
During the rapid redox switch, soil subsamples were analyzed for operationally defined Fe and Al forms using selective chemical extractions. The methods included treatment of the soil with PP (for "organically-bound" Fe and Al), 0.5 N hydrochloric acid (HCl; for weakly chelated Fe and Al), acid AO in the dark (for Fe in poorly-crystalline or "amorphous" phyllosilicates and Al-substituted in SRO-Fe oxides), dithionate-citrate (CD; for free, nonsilicate, reducible Fe(III) oxides with and without Al substitution) (USDA, 1972; McKeague, 1967; McKeague & Day, 1966). The extracts were analyzed for Fe and Al by inductively coupled plasma mass spectrometry. Total Fe and Al contents of the soil prior to incubation were also measured using microwave-assisted concentrated acid digestions of all samples (Element, 2007). Details of the chemical extractions are provided in the Supplemental Material.

# 3 | RESULTS AND DISCUSSION

## 3.1 | Effects of fast redox switches on iron mineral composition

### 3.1.1 | SRO-Fe oxides are primarily a mixture of various goethite forms

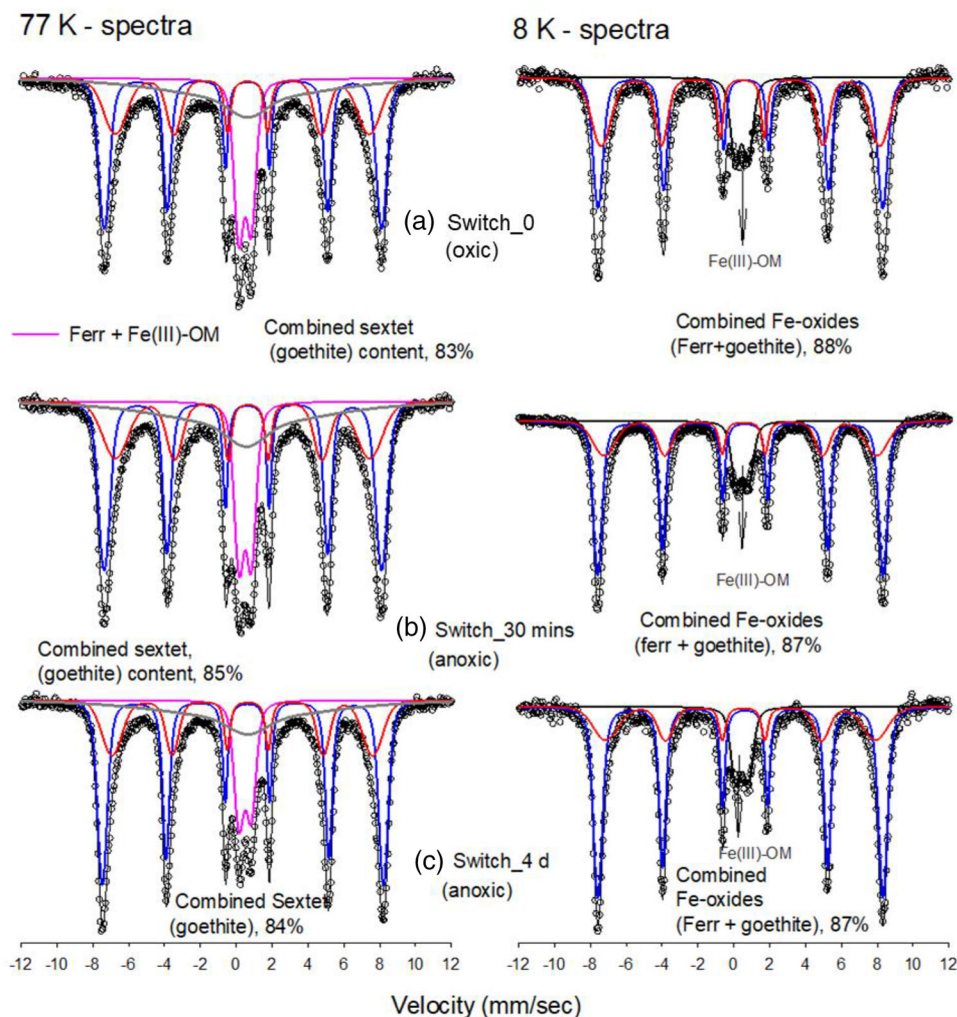
One oxic (switch\_0) and three anoxic incubated samples (switch\_30mins, switch\_210mins, and switch\_4d) were analyzed by MBS at room temperature, 225 K, 77 K, and 8 K. At room temperature, a minor broad feature with parameters similar to that of crystalline goethite was observed; sextet features due to other Fe oxides were not evident (Figure S1; Fysh & Clark, 1982; Murad & Cashion, 2004). At 225 K, all the samples showed the following features (Figures 1A–D): (a) two sextets: a well-defined sextet and a collapsed sextet in the switch\_0 min sample and two well-defined sextets in the switch\_30mins, switch\_210mins, and switch\_4d samples; (b) a Fe(III) doublet; and (c) a minor Fe(II) doublet. The sextets at 225 K were attributed to different forms of goethite, possibly of different particle size/Al substitution with or without organic coatings (G1 and G2 in switch\_0 min; G1' and G2' in switch\_30 mins; and G1'' and G2'' in switch\_210mins and switch\_4d). The central Fe(III) doublet was attributed to that



**FIGURE 1** Mössbauer spectra measurements at 225 K for wet tropical soils (Luquillo Experimental Forest, Puerto Rico) showing rapid changes (within 210 min) in (a) Mössbauer spectral features of the doublet and both the sextets upon switch to anoxic conditions (left panel) and (b) shifts in average magnetic hyperfine field ( $H$ ) of both the sextets to higher  $H$  values with incubation times (right panel), due to incongruent removal of more Al than Fe from soil Al-Fe-goethites with incubation time

of a mixture of ferrihydrite-like or a relatively Al-rich or OM-poor goethite (G3), Fe(III)-OM complexes, and Fe(III) in silicate minerals, and the Fe(II) doublet was attributed to Fe(II) in silicate minerals (Supplemental Table S1) (Coward et al., 2018; Fysh & Clark, 1982; Murad & Cashion, 2004).

At 77 K, three sextets comprising of two well-defined sextets and a collapsed sextet were observed in all the samples (G1a, G2a, and G3a in switch\_0 min; G1a', G2a', and G3a' in switch\_30 min; and G1a'', G2a'', and G3a'' in switch\_210 min and switch\_4d samples; Figure 2a–c, left

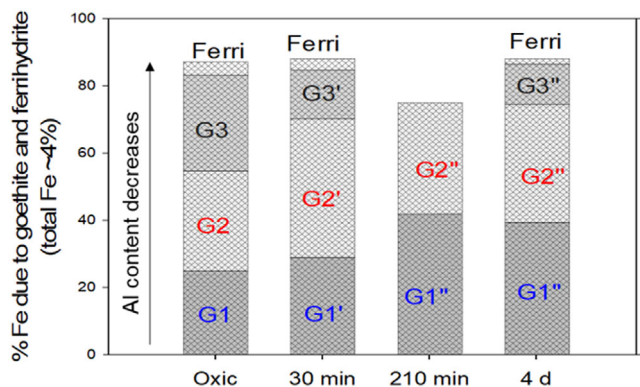


**FIGURE 2** Mössbauer spectra measurements at 77 and 8 K (left and right panels, respectively) of Luquillo Experimental Forest soils before and after varying periods of redox incubation showing relative contributions of combined goethite (3 sextets at 77 K) contents, tabulated ferrihydrite-like mineral (difference between 8 K and 77 K combined sextet spectral areas), and Fe(III)-organic matter (OM) contents

panel; Supplemental Table S2). The combined sextet spectral areas of the 77 K spectra in each of these samples were significantly higher than the combined sextet spectral areas of their 225 K counterparts, particularly in the switch\_0 min sample (Figures 1a–d, 2a–c; Supplemental Tables S1 and S2). All these sextets undoubtedly belonged to various forms of goethite because ferrihydrite with or without OM exists as a sextet only below 77 K (Chen et al., 2015) and Fe(III)-OM complexes occur as doublet even at liquid He temperature (Coward et al., 2018). Higher combined sextet areas suggested that a fraction of the 225 K Fe(III) doublet in each of these samples was transformed to a magnetic sextet that contributed to the 77 K combined sextet feature. We assigned the transformed fractions of 225 K Fe(III) doublet to a relatively Al-rich/OM-poor goethite G3 in switch\_0 min, G3' in switch\_30 min, and G3'' in the switch\_210 mins and switch\_4d samples (Supplemental Table S1). Their contents were estimated by subtracting spectral areas of the Fe(III)

doublet between 225 and 77 K (Figure 3). The relative spectral areas of the three goethite sextets in the 77 K spectra (G1a, G2a, and G3a in switch\_0 min; G1a', G2a', and G3a' in switch\_30 min; and G1a'', G2a'', and G3a'' in switch\_210 min and switch\_4d), however, differed considerably from the relative spectral areas of the G1, G2, and G3 in switch\_0 min; G1', G2', and G3' in switch\_30 min; and G1'', G2'', and G3'' switch\_210 min and switch\_4d of 225 K sextets, respectively (Supplemental Tables S1 and S2). More importantly, differences in combined sextet spectral areas among the samples were subtle at 77 K (Figure 2a–c, left panel; Supplemental Table S2) unlike that in the 225 K spectra. This observation further indicated the importance of 225 K measurements given rapid increases and coalescence of 225 K goethite hyperfine fields compared with somewhat similar fields at 77 K.

Cooling down to 8 K further affected the MBS spectral features. In all the samples, only two well-defined sextets with



**FIGURE 3** Relative contributions of various types of Fe minerals before a redox switch (switch\_0) and after 30-min, 210-min, and 4-d samples of anoxic incubation. The calculated Al contents from Mössbauer measurements are as follows:  $G1'' > G1' > G1$  and  $G2'' > G2' > G2$

combined spectral areas being ~4% greater than the combined spectral areas of their 77 K counterparts (Figure 2a–c, right panel; Supplemental Table S3) were evident. We assigned the outer sextet to G1 and G2 and the inner sextet to be predominantly G3 with minor ferrihydrite contribution (G3 + Ferr) (Golden et al., 1979). The differences among the samples, however, as observed in the 77 K spectra were subtle. The marginal difference in the combined spectral sextet areas between the 8 and 77 K spectra unambiguously indicated that only a minor fraction of the total Fe was ferrihydrite (<4%), the bulk of Fe oxides SRO-Fe minerals in these samples were goethites of varying composition (83–85% of the total Fe), and the rest of Fe (Fe(III) doublet feature) was primarily due to Fe(III) associated with organic matter (Fe-OM) (Coward et al., 2018). A small fraction of the Fe(III) doublet could also potentially originate from structural silicate/clay Fe(III). A disordered kaolinite was the only phyllosilicate mineral evident in XRD pattern of the switch\_0 min sample (Supplemental Figure S2). Contribution from amorphous materials appear to be relatively minor, based on semi-quantitative XRD pattern analysis.

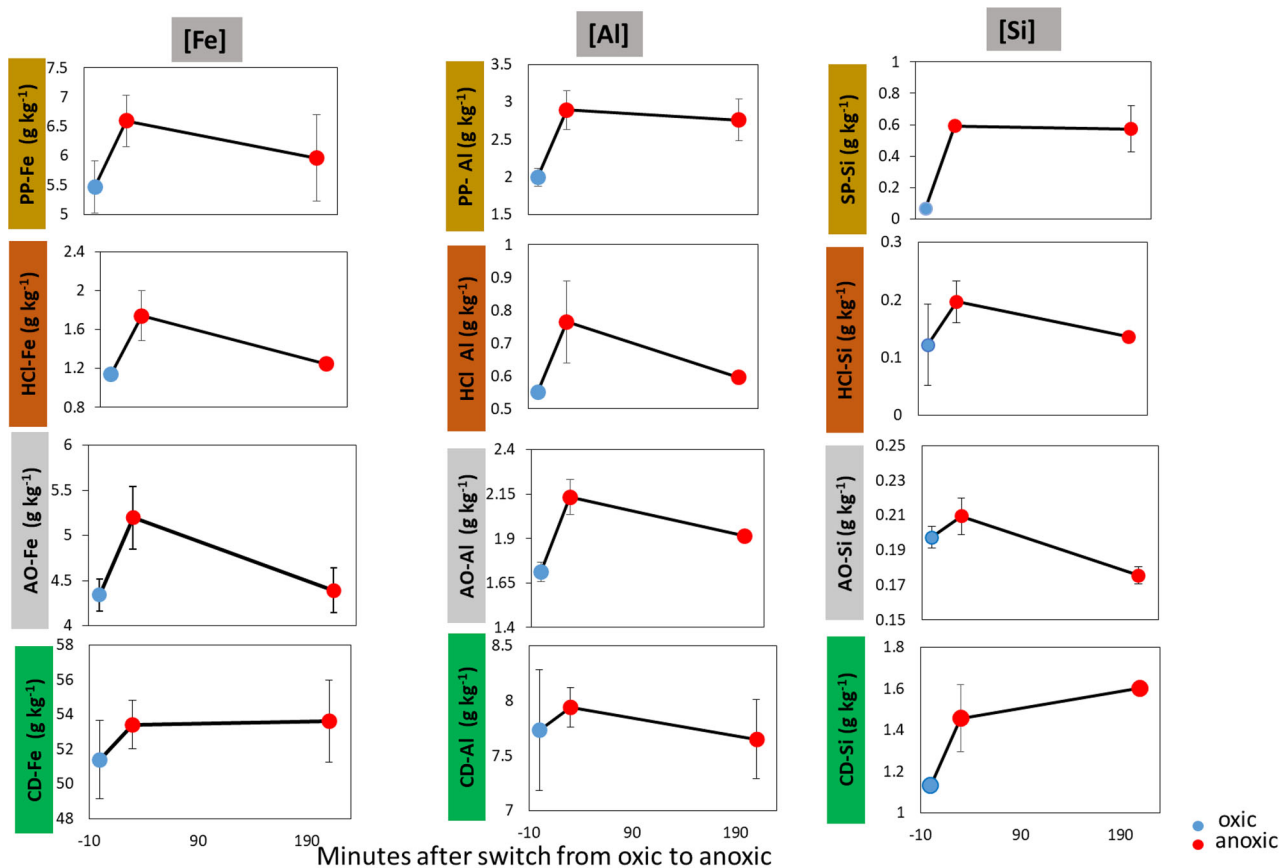
### 3.1.2 | A comparison of Mössbauer of 225 and 77 K spectra was critical to follow subtle differences in goethite characteristics during redox switch

Incubation time had a detectable effect on goethite characteristics. This was obvious from significant differences in 225 K sextet-MBS spectral parameters (average hyperfine field  $I_H$  and hyperfine field distribution ( $\sigma_{HFD}$ )), combined sextet spectral areas, and Fe(III) doublet areas between the switch\_0 min and the switch\_30 min samples (Figure 1, right panel; Supplemental Table S1). G1 and G2 sextets of the

switch\_0 min sample transitioned to G1' and G2' sextets in as quickly as 30 min of switching from oxic to anoxic conditions, with significant effect on their Fe(III) doublet areas. Combined sextet content increased from 55% (G1 and G2) of the total Fe to 70% (G1' and G2') in 30 min. The change was less between 30 and 210 min (the combined 225 K sextet areas of switch\_210 mins and switch\_4d samples was 74%), indicating that 30 min was sufficient to cause significant changes in goethite characteristics in these surface tropical soils. However, only subtle differences were observed among the samples in their 77 and 8 K MBS spectra, as noted earlier (Figure 2), which highlighted that a comparison between MBS measurements at 225 and 77 K is critical for identification of different types of goethite and estimation of G3–G3'–G3'' contents. Furthermore, a comparison between 77 K and near-liquid He temperature measurements is essential for estimation of ferrihydrite Fe(III)-OM and clay–silicate Fe contents.

### 3.1.3 | Redox incubation affects goethite characteristics (Al content and extent of C coating)

$B_{hf}$  values of synthetic Al goethite decrease with increase in Al loading (Fysh & Clark, 1982; Golden et al., 1979). Golden et al., 1979 used empirical equations based on temperatures at or below 77 K to estimate Al/(Al + Fe) ratios of soils with no or relatively free OM. To our knowledge, MBS spectra of OM-coated goethite have not been reported; however, previous MBS studies focusing on ferrihydrite-OM systems (Chen et al., 2015; Eusterhues et al., 2014) showed similar inverse relationships between OM loading and MBS  $B_{hf}$  magnitudes. Differences in spectral features and combined sextet area between 225 and 77 K spectra implied coexistence of three different goethite pools in the switch\_0 min sample with relative differences in Al or OM loadings as follows: G3 (part of the 225 K doublet) > G2 > G1. Furthermore, from our MBS data, it appears that Al or OM loading of the goethites rapidly and continuously decreased with incubation time up to 210 min. Relative distribution of the goethite phases (and ferrihydrite) and apparent decreases in Al and OM loadings (and ferrihydrite contents) with incubation time were as follows:  $G1 > G1' > G1''$  and  $G2 > G2' > G2''$  (Figure 3). Finally, our data also implied gradual increase in crystallinity of all forms of goethite with incubation time given an inverse relationship between Al content and crystallite sizes (Cornell & Schwertmann, 2003) and OM loadings (Chen et al., 2015; Eusterhues et al., 2014). Overall, MBS measurements show a much more detailed Fe speciation than the reported Fe extended X-ray absorption fine structure-derived Fe composition conducted in these soils in a previous study (Bhattacharyya et al., 2018).



**FIGURE 4** (Top to bottom) Changes in sodium pyrophosphate (PP), 0.5N hydrochloric acid (HCl), acid ammonium oxalate, and citrate-dithionite (CD) bottom-extractable Fe, Al, and Si concentrations (in  $\text{g kg}^{-1}$  soil) immediately before and after 30 and 210 min of switching from oxic to anoxic conditions. Blue and red circles indicate oxic and anoxic time points, respectively. Error bars indicate standard error for three replicate measurements

### 3.2 | Powder XRD and effects of fast redox switches on operationally defined Fe, Al, and Si fractions

Sharp features due to quartz (bulk of the sample) and gibbsite and somewhat broad peaks due to disordered kaolinite were conspicuous in the XRD pattern of the switch\_0 min sample (Supplemental Material). Minor peaks due to goethite were also evident. Broadness and cell parameters of goethite peaks suggest the presence of smaller particle sized or Al-substituted goethites (Kukkadapu et al., 2001). Characteristic peaks due to other common Fe oxides, such as hematite, lepidocrocite, and magnetite or any 2:1 phyllosilicate, on the other hand, were absent. Furthermore, the absence of a broad background hump around  $2\theta = 25^\circ$  in the XRD diffractogram implied the soil to be likely free of amorphous material.

Citrate dithionite-extractable Al/(Al + Fe) and Al/(Al + Si) mole ratios ( $\sim 0.24$  and  $\sim 0.8$ , respectively) for switch\_0 and incubated samples were remarkably similar (Figure 4; Table 1). We suspect that CD primarily extracted Fe from Fe-Al-goethite and ferrihydrite and little or none from kaolinite

dissolution, based on CD-Si contents, which were  $<0.02$  wt.% (Figure 4) of the soil weights (vs. 5 to 5.5 wt.% Fe and 0.8 wt.% Al). A portion of the CD-Fe/Al likely originated from extraction of Al and Fe from Al- and Fe-OM complexes (Dahlgren, 1994), but their maximum contribution to the total, if any, appears to be  $<10\%$  (Fe) and  $<3\%$  (Al), based on Na-PP extractions. Contribution of Al to the CD-Al pool from dissolution of crystalline gibbsite and kaolinite (Al/Si ratios of 33 to 45 vs. Al/Si ratio of 1 for kaolinite), however, appears unlikely or minor given the gentle extraction procedure (room temperature and overnight, Supplemental Material).

As anticipated, AO extracted significantly lower amounts of Fe and Al than that from CD ( $\sim 8$  and  $22\%$  from switch\_0 min;  $\sim 10$  and  $\sim 27\%$  from switch\_30 min, and  $\sim 8$  and  $\sim 25\%$  of CD-Fe and Al from switch\_210mins, respectively) as shown in Figure 4. The AO-extractable Fe amounts, however, were somewhat higher than anticipated based on ferrihydrite contents alone ( $<5\%$  of the total Fe; Supplemental Table S3b). Similar to CD, Fe extracted from Fe-OM complexes likely contributed to the AO-Fe pool (Dahlgren, 1994). Likewise, we suspect Al-ferrihydrite and Al-OM complexes



**TABLE 1** Al/(Fe+Al) and Al/(Si+Al) mole ratios calculated from Fe, Al, and Si concentrations from selective chemical extractions in surface soils of Luquillo Critical Zone Observatory

Sample	Citrate dithionite		Sodium pyrophosphate		Ammonium oxalate		0.5N HCl	
	Al/(Fe+Al)	Al/(Si+Al)	Al/(Fe+Al)	Al/(Si+Al)	Al/(Fe+Al)	Al/(Si+Al)	Al/(Fe+Al)	Al/(Si+Al)
Switch_0 (oxic)	0.24	0.88	0.43	0.97	0.45	0.90	0.5	0.82
Switch_30 min (anoxic)	0.24	0.85	0.48	0.84	0.45	0.91	0.47	0.8
Switch_210 min (anoxic)	0.23	0.83	0.49	0.83	0.48	0.92	0.5	0.82

Note. CD, citrate dithionite; PP, Na pyrophosphate; AO, ammonium oxalate; Switch\_0, soil sample harvested just before the redox switch from oxic to anoxic conditions; switch\_30 min, samples collected after 30 min of the redox switch; switch\_210 min, samples collected after 210 min of the redox switch.

contributed significantly to the AO-Al pool. Contribution from kaolinite is likely negligible given AO-extractable Al/Si ratios of ~22 to 24 (Supplemental Table S4). It is possible some of the soluble Al could be from dissolution of crystalline gibbsite. Lack of significant variation between AO- and PP-extractable Fe and Al contents (Figure 4) further implied that the bulk of AO-Fe and -Al content was due to dissolution of Al- and Fe-OM complexes. Qualitatively, the amount of PP-Fe extracted was in agreement with the MBS analysis-derived Fe(III)-OM from 8 K MBS doublet contents, suggesting that Fe bound to OM is predominantly Fe(III). The difference in  $Al_{AO}$  and  $Al_{PP}$  contents suggests only a small fraction of the AO-Al appeared to be mineral-associated (Dahlgren, 1994). Sodium pyrophosphate and 0.5 N HCl total Fe mirrored AO-Fe and -Al (Figure 4). However, total 0.5 N hydrochloric acid-Fe contents were only a small fraction of the total Fe (<3% of CD Fe) and semi-quantitatively in agreement with ferrihydrite contents. Subtraction of AO-Fe and Al contents (predominantly a composite of OM complexes and ferrihydrite-like phase) from CD-Fe and -Al suggests the approximate Al/(Al + Fe) ratio of the goethite in all the samples is ~0.22. These tabulated fractions, however, are questionable given the affinity of goethite surface to Al. Approximately one-tenth of the total Fe was Fe(II) or <0.3% of the CD-Fe. More importantly, Fe and Al concentrations from all the extractions (AO, PP, and 0.5 N HCl) increased by ~25% within 30 min of incubation and then tapered down back to switch\_0 min values after 210 min. The exact reason for this unusual upward and then downward trend is not clear. We hypothesize that heterogeneity in soil mineral composition could be responsible for this trend.

### 3.3 | Rapid transformation of goethite and the potential role of Al content and nature and loadings of OM

Variable-temperature MBS indicated coexistence of three goethite “pools” of varying  $B_{hf}$  values in the samples. These pools likely differed from each other either in their Al/(Al + Fe) mole ratios or in the OM/Fe ratios of mineral-associated OM moieties. If the differences in  $B_{hf}$  values among the samples were solely due to variation in Al/(Al + Fe) ratios, the

noted differences in 225 K MBS parameters (more sensitive than at 77 K) between oxic and anoxic samples would be due to incongruent removal of relatively more Al than Fe. However, such a scenario is unlikely because CD and AO-extractable Al/(Al + Fe) ratios (~0.24 and ~0.11 respectively) were similar for all the samples, implying congruent removal and the likely presence of OM-coated Fe oxides. If we assume that there is potentially little or no role of OM, one reason for this discrepancy between MBS and selective chemical extraction data could be due to sorption of the bio-released Al from Al-containing goethites onto residual Fe oxides and other soil components. This is in agreement with literature studies that show (bio)transformation of both laboratory-synthesized Al goethite (Dominik et al., 2002) and Al goethite-containing soil (Kukkadapu et al., 2001). More likely, the differences in spectral features could also be due to gradual OM depletion from the switch\_0 goethite, as observed in a pure ferrihydrite-OM transformation study (Chen et al., 2015). Such a scenario is probably predominant given that rapid depletion of Al from goethites is unlikely. The exact effect of Al or OM or how Al and OM compete, however, is not interpretable from MBS spectra alone. In our incubated soils the nominal oxidation state of C decreased significantly within 3 h of anoxic incubation, suggesting reduction of ferrihydrite and Al goethite (Bhattacharyya et al., 2018). Therefore, it is possible that the primary changes in MBS spectra were largely due to depletion of OM from Fe-oxide surfaces (as noted in Chen et al. [2015] in a ferrihydrite-OM reduction study), and any further changes past 210 min would be largely due to structural changes in Al and Fe stoichiometry of the oxide. We suspect that the lack of significant differences in MBS Fe(II) doublet content among the samples could be due to incorporation of the bulk of the biogenic Fe(II) (due to reductive dissolution of ferrihydrite) produced via electron and atom transfer (Latta et al., 2012) within goethite in symmetries similar to the bulk Fe(III) in goethite and not as typical Fe(II) species in phyllosilicates, Fe carbonates, Fe phosphates, etc. (Murad & Cashion, 2004). If the newly produced Fe(II) is sequestered in the goethite structure it would be fairly insoluble in 0.5 M HCl, which could be a reason for the reportedly low 0.5 M HCl extractable Fe concentrations (Bhattacharyya et al., 2018). Regardless, it is clear from this study that

in Luquillo soils, goethites of varying characteristics dominate Fe-oxide composition (combined ferrihydrite and Fe-OM complexes constitute around 10% of the total Fe) and these goethites rapidly transform to relatively “crystalline” phases or stable forms within 210 min, beyond which they are resistant to further rapid transformations. However, the marked differences among the chemical behavior of G1–G1’–G1” and G2–G2’–G2” forms (Figure 1) is puzzling and needs further evaluation. Resistance of G2–G2’–G2” sextets to transform to  $B_{hf}$  values akin to G1–G1’–G2” could be due to limited microbial access to these phases. From the present study it is clear that a robust comparison between MBS data, particularly above 77 K, and selective chemical extractions is essential. Finally, our study suggests that a library of MBS spectra of Al goethites with and without sorbed OM (pristine and (bio)reduced) would be helpful for interpretation of Fe-oxide transformation in OM-rich soils experiencing redox conditions. Coupling MBS and chemical extraction data to XRD, X-ray photoelectron spectroscopy, and carbon near edge X-ray absorption fine structure spectroscopy would further a greater understanding of the interplay between C and Fe in these systems. To our knowledge, this is the first study that documents such rapid changes in Fe oxide phase transformations due to fast redox switches. Findings from this study could be used in understanding the long-term fate of metal-OM transport in tropical ecosystems that can subsequently be incorporated into regional and global carbon cycling models.

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## AUTHOR CONTRIBUTIONS

Amrita Bhattacharyya: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Writing – original draft; Writing – review & editing. Ravi K. Kukkadapu: Data curation; Formal analysis; Software; Supervision; Writing – original draft; Writing – review & editing. Mark Bowden: Resources; Software. Jennifer Pett-Ridge: Conceptualization; Funding acquisition; Project administration; Supervision. Peter S. Nico: Conceptualization; Funding acquisition; Methodology; Supervision; Writing – review & editing.

## CONFLICT OF INTEREST

The authors declare no competing interests.

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