Mineralogy of iron microbial mats from Loihi Seamount

Brandy M. Toner1*, Thelma S. Berquó2,3, F. Marc Michel4, Jeffry V. Sorensen1, Alexis S. Templeton5 and Katrina J. Edwards6,7

INTRODUCTION

Iron (Fe) microbial mats form in opposing iron and oxygen gradients in a wide variety of settings (Emerson and Revsbech, 1994; Chan et al., 2004; Rentz et al., 2007; Druschel et al., 2008; Edwards et al., 2011). The physical and chemical properties of the Fe-bearing phases will determine the biogeochemical reactivity of the minerals within the mats (Ekstrom et al., 2010; Boland et al., 2011; Hansel et al., 2011). Yet the crystallinity, local Fe coordination environment, and available reactive sites of the minerals are difficult to measure, and the structure or continuum of structures that compose one of the most common Fe oxyhydroxides, ferrihydrite (Fh), is an active topic of research and scientific controversy today (Michel et al., 2007a, 2010; Penn, 2007; Manceau, 2009, 2011; Pinney et al., 2009; Maillot et al., 2011), as it has been for more than two decades (Campbell, 1991; Drits et al., 1993; Manceau and Drits, 1993; Waychunas et al., 1996; Jambor and Dutrizac, 1998; Janney et al., 2000; Schwertmann et al., 2004). Poorly crystalline iron oxyhydroxides are often difficult to characterize due to nanometer particle dimensions (Michel et al., 2007a; Hochella Jr. et al., 2008) and a large number of polymorphs (Navrotsky et al., 2008). In addition, structural and compositional variability and complexity is intrinsic to Fe oxyhydroxides formed in settings such as microbial biofilms (Edwards et al., 2003; Chan et al., 2004; Toner et al., 2009) or in the presence of strongly sorbing inorganic and organic ligands (Cornell and Schwertmann, 1979; Waychunas et al., 1996; Rose et al., 1997; Vilge-Ritter et al., 1999; Doelsch et al., 2003; Mikutta, 2011). Considering that the gold standard measurement for mineralogy – powder X-ray diffraction (XSD) – relies on long-range structural order, it is not surprising that Fe mineralogy of microbial mats, often formed in the presence of abundant inorganic ligands and microbial cell surfaces and exudates, remains elusive. One viable strategy for describing Fe microbial mat mineralogy is to measure a suite of fundamental properties: (1) short-range structural order and valence state; (2) degree of structural defects relative to standard synthetic minerals; (3) degree of particle interaction and aggregation;
(4) distribution of particle dimensions and extent of structural
cohesion; and (5) stability and recrystallization as a function of
time and temperature.

In this context, the mineralogy of Loihi Seamount Fe microbial
mats was examined as a function of temperature, water depth, and
bulk aqueous geochemistry. Loihi Seamount is a seismically active
submarine volcano and emerging Hawaiian Island (Klein, 1982;
DeCarlo et al., 1983). Hydrothermal venting at Loihi produces
opposing Fe and oxygen gradients (Glazer and Rouxel, 2009) and
supports abundant microbial life including Fe-oxidizing bacteria
(Emerson and Moyer, 2002). Iron mat formation at Loihi is per-
vasive, occurring at a range of temperatures (0–60˚C), in diverse
settings (ultra-diffuse regional venting at 5000 m to focused vent-
ing as shallow as 1116 m), and microbial activity in the mats has
been demonstrated (Moyer et al., 1994, 1995; Emerson and Moyer,
2002; Edwards et al., 2011). Filamentous, non-filamentous, tubu-
lar, and branching microbial structures in the mats that form near
venting are encrusted with Fe minerals, and biological Fe oxidation
contributes approximately 60% of total Fe oxidation (Karl et al.,
1988, 1989; Emerson and Moyer, 2002). Vent fluids near the sum-
mit of Loihi are enriched in carbon dioxide, ammonium, silicon
(Si), Fe, and manganese (Mn) (Sedwick et al., 1992; Wheat et al.,
2000). The goal of this research is to describe the physical and
chemical properties of the minerals formed in Loihi Fe microbial
mats. To accomplish this, we used synchrotron radiation X-ray
absorption spectroscopy, X-ray fluorescence microspectroscopy,
and X-ray total scattering, as well as Mössbauer spectroscopy and
absorption spectroscopy, X-ray fluorescence microspectroscopy.

MATERIALS AND METHODS
LOIHI MAT COLLECTION AND STORAGE
Iron microbial mats at the Loihi Seamount were collected during
research cruises in 2006 (R/V Melville), 2007 (R/V Kilo Moana),
and 2008 (R/V Thompson) as part of a National Science Founda-
tion Fe Microbial Observatory (FeMO) project. General charac-
teristics of each site are summarized in Table 1. Sites represent the
range of naturally occurring characteristics of the vents that occur
at Loihi.

The remotely operated vehicle JASON2 was used to collect mats
with scoops and suction samplers. Typically the samples collected
by slurry suction sampling experience a vigorous mixing of a large
volume (several liters) of mat material, whereas consolidated mats
collected in polycarbonate scoops retain some of their structural
cohesiveness. Once shipboard, the loosely aggregated, well-mixed
mat “flocs” were sub-sampled into 15 mL sterile tubes and either:
(1) stored at 4˚C and referred to as “fresh” or “aged” mat samples;
or (2) frozen at −20˚C and referred to as “frozen” mat samples.
In the laboratory, a subset of these floculent mat samples were
defrosted, rinsed with purified water to remove sea salts, and dried
at 40˚C: these samples are referred to as (3) “dry” mat samples.
At the deepest, very low-temperature diffuse venting site Ula Nui,
approxi mately the top 5–10 cm of layered Fe–Mn microbial mats
were collected in scoop-samplers and were stored fresh and frozen
as fully (4) “intact” map samples. All of the mat samples exam-
ined for this study are reported in Table 1. The term “fresh” mat
is applied to samples that were stored at 4˚C and analyzed within
1 month of seafloor recovery. The term “aged” mat is applied to
samples stored at 4˚C and analyzed after 0.5 to greater than 1 year
after seafloor recovery.

X-RAY ABSORPTION SPECTROSCOPY
Iron K-edge X-ray absorption microspectroscopy
X-ray microprobe measurements were performed for three types
of Loihi mat samples: (a) intact surface crust from Ula Nui; (b)
fresh mat flocs; and (c) 4˚C aged mat flocs.

One intact surface crust of an Fe–Mn layered mat from Ula
Nui was prepared for X-ray microprobe element mapping by slic-
ing a 3-mm thick by 8 cm wide by 4 cm tall section of a sample
frozen at −20˚C. The slice was then positioned into an anaer-
obic aluminum sample holder with thin mylar windows that was

| Area       | Description                        | Depth (m) | $T_{\text{max}}$ (˚C)$^a$ | $pH_{\text{max}}$ | $[\text{Si}]_{\text{max}}$$^b$ | $[\text{P}]_{\text{max}}$ | $[\text{Fe}]_{\text{max}}$ |
|------------|------------------------------------|-----------|---------------------------|------------------|-------------------------------|--------------------------|--------------------------|
| Ula Nui    | Ultra-diffuse, cold, base of seamount | 4988      | 1.75                      | -                | -                             | -                        | 127                      |
| Naha       | Extinct, rim of Pele’s Pit          | 1325      | <2.8                      | -                | -                             | -                        | -                        |
| Spillway   | Active, warm, rim of Pele’s Pit     | 1272      | 54.0                      | 55.0             | 6.37                          | 6.72                     | 4664                     |
| Tower      | Active, warm, Pele’s Pit            | 1304      | 51.0                      | 50.0             | 6.01                          | 6.29                     | 2966                     |
| Hiilo      | Active, warm, Pele’s Pit            | 1302      | 51.0                      | 52.0             | 5.94                          | 6.69                     | 3830                     |
| Lohiau     | Active, cool, Pele’s Pit site, frequently sampled | 1174 | 22.0 | 24.5 | 6.21 | 6.94 | 1558 | 675 | 2.5 | 1.2 | 234.7 | 68.3 |
| Hiilo Ridge| Active, warm, rim of Pele’s Pit     | 1116      | 14.6                      | -                | -                             | -                        | 224                      |
| Pohaku     | Active, warm, rim of Pele’s pit, not previously sampled | 1180 | - | 26.5 | - | 732 | - | 2210 | - | 4.5 | - | 796.4 |

$^a$ Data from Glazer and Rouxel (2009).
$^b$ All concentrations in micro molar.
$^c$ Data from Edwards et al. (2011).
continuously purged with helium at room temperature. Three different regions of the slice were then mapped – "R1," a 200-μm × 200-μm region at the very top surface of the mat, "R2," a 1600-μm × 200-μm region located 400 μm below the surface of the mat, and then "R3," a final 200 μm × 200 μm region in the middle of the mat. Each map area was sequentially raster scanned at three energies across the Mn K-edge (6545, 6550, and 6560 eV) and then three energies across the Fe K-edge (7120, 7126, and 7133 eV) at BL 2-3 at the Stanford Synchrotron Radiation Lightsource using a Si 220 phi = 0 monochromator detuned 30% and a focused spot size of 2 μm × 2 μm. Full X-ray fluorescence spectra were collected for each pixel with a 100-ms dwell time using a three-element germanium detector. A matrix of predicted Fe(II) versus Fe(III) and Mn(II) versus Mn(IV) fluorescence yields at each incident energy was generated from the Fe X-ray absorption near-edge structure (XANES) spectra of a reduced basalt glass [88% Fe(II)] versus the 100% Fe(III)-oxide standard, and the Mn XANES spectra of MnO²⁺ [100% Mn(II)] and 8-MnO₂ [100% Mn(IV)] standards (e.g., Templeton et al., 2009). The resulting I₀-normalized, dead time-corrected element distribution, and oxidation–reduction maps were generated using Microanalysis Toolkit (Webb, 2006). Iron and Mn K-edge XANES spectra were also collected from specific spots in each map and analyzed using SixPack to confirm the oxidation states of Fe and Mn by comparison to our model compound library.

X-ray microprobe measurements were also conducted among a random assortment of disseminated mat particle aggregates (flocs) to determine Fe speciation. These fresh and aged Loihi mat flocs (Loihiau, Pohaku, Naha, and Ula Nui) were deposited on polycarbonate membranes (0.2 μm pore size) and rinsed with purified water using a glass filtration tower (MilliPore) and hand vacuum pump. Mat samples were analyzed at room temperature on the membrane with no further processing using a published method (Toner et al., 2009). Briefly, microprobe Fe extended X-ray absorption fine structure (EXAFS) spectra were collected at the Advanced Light Source on beamline 10.3.2 with a 7120-μm × 7126-μm region at the very top surface of the mat, "R2, " a 200-μm × 200-μm region located 400 μm below the surface of the mat, and then "R3," a final 200 μm × 200 μm region in the middle of the mat. Each map area was sequentially raster scanned at three energies across the Mn K-edge (6545, 6550, and 6560 eV) and then three energies across the Fe K-edge (7120, 7126, and 7133 eV) at BL 2-3 at the Stanford Synchrotron Radiation Lightsource using a Si 220 phi = 0 monochromator detuned 30% and a focused spot size of 2 μm × 2 μm. Full X-ray fluorescence spectra were collected for each pixel with a 100-ms dwell time using a three-element germanium detector. A matrix of predicted Fe(II) versus Fe(III) and Mn(II) versus Mn(IV) fluorescence yields at each incident energy was generated from the Fe X-ray absorption near-edge structure (XANES) spectra of a reduced basalt glass [88% Fe(II)] versus the 100% Fe(III)-oxide standard, and the Mn XANES spectra of MnO²⁺ [100% Mn(II)] and 8-MnO₂ [100% Mn(IV)] standards (e.g., Templeton et al., 2009). The resulting I₀-normalized, dead time-corrected element distribution, and oxidation–reduction maps were generated using Microanalysis Toolkit (Webb, 2006). Iron and Mn K-edge XANES spectra were also collected from specific spots in each map and analyzed using SixPack to confirm the oxidation states of Fe and Mn by comparison to our model compound library.

Bulk iron K-edge X-ray absorption spectroscopy
Bulk Fe EXAFS spectra were collected for two types of Loihi mats: (1) frozen samples stored and analyzed under inert gas; and (2) "dry" samples that were frozen shipboard, and defrosted, rinsed, dried, and analyzed in ambient atmosphere.

Synchrotron-based Fe K-edge EXAFS spectra for two bulk mat flocs (Spillway and Hiilo mats) were collected from 7000 to 8000 eV on beamline 11-ID-B of the Advanced Photon Source, Argonne National Laboratory. Selected dry mat samples (Ula Nui-A/B, Loihiau A, Spillway A, and BT37) were packed into ~1 mm O.D. polyimide (Kapton) capillaries and the scattered intensity from the samples was collected at ambient temperature with an amorphous-silicon-based flat-panel detector system (Perkin Elmer) mounted orthogonal to the incident beam path. For synchrotron radiation X-ray diffraction (XRD; SR-XRD) measurements the X-ray energy was fixed at ~58 keV (λ = 0.2128 Å) and the sample-to-detector distance was optimized to cover d-spacings ranging from ~0.5 to 8.5 Å. For pair distribution function (PDF) experiments the X-ray energy was fixed at ~90.5 keV (λ = 0.13702 Å) and a sample-to-detector distance of ~21.5 cm was chosen. This experimental geometry yielded scattering data with a maximum usable Q-range of 30 Å⁻¹ (where Q = 4πsinθ/λ⁻¹ is the magnitude of the scattering vector or momentum transfer). The total exposure time for the blank (i.e., empty capillary) was 3200 s and each sample was 1200 s. Fit2D (Hammersley et al., 1996) was used to fit the scattered intensities to the X-ray scattering form factors and calculate the theoretical scattering patterns.
used to convert two-dimensional data to one-dimensional intensity versus scattering angle (2θ). The experimental total scattering structure function $S(Q)$, reduced structure function $f(Q)$, and PDF were obtained using PDFgetX2 (Qiu et al., 2004). The data were corrected for parasitic background scattering and inelastic contributions (e.g., Compton scattering) as well as those corrections unique to image-plate geometry (Chupas et al., 2003). A Lorch modification function (Lorch, 1969) was applied.

The PDF, or $G(r)$, is the Fourier transform of the reduced structure function and has been described in detail elsewhere (Guinier, 1963; Egami and Billinge, 2003). In general, peaks in the PDF occur at characteristic distances separating pairs of atoms, and thus the PDF is an averaged representation of structure. As discussed below, additional information such as the scattering domain size can be extracted from the attenuation in peak intensities with increasing $r$ (see Gilbert, 2008 for review). In this study, the maximum coherent scattering domain (CSD) size for the samples and references is estimated from the PDFs and is reported with an error of ±3 Å (Hall et al., 2000). Structural information was extracted directly from the experimental PDFs by fitting the features with Gaussian functions (PeakFit v4.12). At shorter length scales (<~2.5 Å) the peak positions yield actual average bond lengths (e.g., Si-O, Fe-O). At longer length scales the PDF becomes more complicated because peaks from different origins overlap. As such, the full width at half maximum (FWHM) of the Gaussian functions were varied together in order to minimize the number of free parameters. In addition, the positions of peaks at 3.03 and 3.44 Å (representing edge- and corner-sharing Fe polyhedra, respectively, as described below) were fixed during fitting of the natural samples in order to further constrain the number of degrees of freedom. As discussed below, the presence of at least edge-sharing Fe polyhedra is further justified by the EXAFS results for these samples.

Synthetic two-line Fh and amorphous silica were used as references. Ferrihydrite was precipitated at room temperature by the rapid hydrolysis of 0.1 M Fe(NO$_3$)$_3$ to pH 7 with 2 M NaOH. Amorphous SiO$_2$ (am-SiO$_2$) was precipitated by hydrolysis of tetraethyl orthosilicate [Si(OC$_2$H$_5$)$_4$ (Fisher Scientific)] with 12 M HCl according to the procedure described by Hirata et al. (2003).

**Magnetism**

A commercial SQUID magnetometer (MPMS-XL-Quantum Design) was used to measure induced magnetization curves [zero field cooling (ZFC) and field cooling (FC)], hysteresis loops, room temperature saturation isothermal remanent magnetization (RTSIRM), and AC susceptibility as a function of temperature, and frequency (Institute for Rock Magnetism, University of Minnesota). ZFC induced magnetization curves were obtained by cooling the samples in zero field from 300 to 2 K, then the magnetization was recorded as temperature increases in a small applied field ($B = 5$ mT). For field cooled induced magnetization curves, the sample is cooled to 2 K in a 5-mT applied field, and magnetization is measured as temperature increases. Hysteresis loops were obtained by using maximum applied fields up to 5 T at temperatures from 2 to 300 K. RTSIRM curves were obtained by applying a field of 2.5 T at room temperature, and measuring the remanent magnetization upon cooling to 10 K, and then warming back to 300 K. The AC susceptibility curves are measured for variable frequencies (1–1000 Hz) in the temperature range 2–300 K.

To estimate the particle size using ZFC data, the $T_P$ temperatures were identified directly from ZFC curves and the particle volume was obtained by the Néel–Arrhenius Law:

$$\tau = \tau_0 e^{\frac{KV}{T}}$$

where $T = T_P$, $\tau$ is the measuring time, $\tau_0$ is a constant characteristic of the material ($10^{-9}$–$10^{-11}$ s), $V$ is volume and $k_B$ is Boltzmann’s constant. After mathematical manipulation the above equation can be rewritten as

$$V = \frac{25k_B T}{K}$$

The volume was estimated considering particles with spherical geometry and Fh anisotropy constant of $K = 1.7 \times 10^5$ J/m$^3$ (Rodmacq, 1984). The values of constant of anisotropy $K$ of Fh available in the literature are still under debate and could be a source of uncertainty in this estimate. The range of $K$ values reported in the literature include: 3.6 $\times 10^5$ J/m$^3$ (Gilles et al., 2000); 3.12 $\times 10^5$ J/m$^3$ (Duarte et al., 2006); 1.0 $\times 10^5$ J/m$^3$ (Berquó et al., 2009); 4.7 $\times 10^5$–1.5 $\times 10^4$ J/m$^3$ (Silva et al., 2008); 1.7 $\times 10^5$ J/m$^3$ (Suzdalen et al., 1996). Another source of error is related to the fact that the model used to calculate particle size of natural Fh considered spherical particles. Previous work on synthetic Fh (Erbs et al., 2008) suggests that these particles may have an aspect ratio that is greater than 1. As such, the estimates obtained here are considered upper limits and are useful to identify particle size changes associated with the vents temperature.

**Mössbauer Spectroscopy**

A conventional constant-acceleration spectrometer (Institute for Rock Magnetism, University of Minnesota) was used in transmission geometry with a $^{57}$Co/Rh source, using α-Fe at room temperature to calibrate isomer shifts (ISs) and velocity scale. The magnetic hyperfine parameters such as magnetic hyperfine field ($B_{hf}$), IS, and quadrupole splitting (QS) were fitted using the NORMOS program (Brand, 1987).

**Heat Treatment of Hiolo Mat Flocs**

The Hiolo mat was subjected to heating experiments in an oven to determine the temperature at which the Fh-like minerals transformed to hematite. One mat sample (Hiolo) was dried and divided in five aliquots. One part was kept without thermal treatment and the other four aliquots were used for thermal treatment at different temperatures. The heating procedure started and finished always with samples at room temperature reaching a maximum temperature ($T_{max}$) of 400, 500, 600, or 800°C. After the oven reached $T_{max}$, the samples were maintained at that temperature for about 20 min, and then samples were cooled inside the oven. Powder XRD measurements were conducted for mat samples using a PANalytical X-Pert PRO MPD X-ray diffractometer equipped with a cobalt source and high speed detector (X-Clerator; Laboratory of R. Lee Penn, Department of Chemistry, University of Minnesota). The data were collected over the range of 10–90° 2θ, with a scan rate
of 0.6°/min, and data are compared to reference powder diffraction patterns. Mössbauer spectra were also collected for the heat treated mat, as described in Section “Mössbauer Spectroscopy.”

**ELEMENTAL ANALYSES**

Thawed Loihi Fe mat samples were prepared for elemental analysis (Aqueous Geochemistry Laboratory, Department of Earth Sciences, University of Minnesota) by 3× centrifugation and rinsing steps (18.2 Ω Milli-Q water), followed by drying for 24 h at 50°C. The dried samples were dissolved in 6 mL of a 50/50 mixture of Trace Grade HCl and HNO₃, and diluted with 18.2 Ω water to a total volume of 30 mL. Major elements (Al, B, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Si, Sr, Zn) were measured using a Thermo Scientific iCAP 6500 dual view Inductively Coupled Plasma-Optical Emission Spectrometer. The mat solutions were diluted for analysis with a cesium matrix modifier and yttrium as an internal standard. For trace metal analysis, the dissolved samples were diluted 40×, and 40 ppb of In internal standard was added. Trace elements (Be, Al, Sc, Ti, V, Ga, As, Se, Rb, Y, Zr, Mo, Ag, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Pb, Th, and U) were measured using a Thermo Scientific XSERIES 2 ICP-MS w/ESI PC3 Peltier cooled spray chamber, SC-FAST injection loop, and SC-4 autosampler. All elements except Li, Be, Al, were analyzed using Fe/H₂ collision–reaction mode.

To quantify organic carbon contents in several mats, 7–25 mg of material was leached in 0.1 N HCl, dried, reweighed, loaded into tin capsules, and analyzed using a Costech CHN 4010 elemental combustion system.

**RESULTS**

**IRON X-RAY ABSORPTION SPECTROSCOPY**

Microprobe Fe EXAFS spectra were collected for fresh and 4°C aged Loihi Fe microbial mats (Ula Nui, Loihau, Naha, and Pohaku; slurp samples; Table 1). The microprobe EXAFS data are presented in Figure 1 along with bulk EXAFS data and selected reference spectra of Fe oxyhydroxides (goethite, two-line Fh, and Juan de Fuca Ridge biogenic Fe oxyhydroxide). Iron EXAFS spectra for these mat flocs shows that the Fe speciation measured at the microscale is also representative of the bulk Fe speciation (Figure 1; Table 2).

Iron EXAFS spectra (Figure A1 in Appendix) for the Ula Nui mat were collected on samples with different storage (frozen under N₂, frozen in ambient atmosphere, and aged in ambient seawater at 4°C) and preparation (thawed under N₂, thawed/rinsed/dried in ambient atmosphere, and thawed/rinsed/dried at 40°C) on three different instruments (SSRL 2-3, ALS 10.3.2, and APS 20-8M). These spectra are very similar despite different storage, handling, and instruments. Although there is a perceptible line-shape difference in the EXAFS spectrum for the 4°C aged sample (Ula Nui C) at k = 7.5 Å⁻¹, the biggest difference among these Ula Nui spectra is observed in the amplitude of fluorescence versus transmission mode measurements. We interpret the lower amplitude in the fluorescence mode data to be over-absorption effects as the Loihi mats are up to 45.6% by weight Fe (Table 2). These observations hold true for other mats examined by replicate EXAFS measurements. Therefore, in Figure 1 only representative EXAFS spectra from Loihi mats are displayed while a full summary of spectra are available in Appendix A2 in Figure 1.

In Figure 1, several spectral features are highlighted for the Loihi mats and reference minerals. The Fe EXAFS spectra collected for the Loihi mats have similarities with two-line Fh in terms of line-shape, amplitude, and phase. In the Fourier transformed data, a corresponding reduction or absence of the longer peak (R + ΔR = 3.2 Å) in the second Fe–Fe shell is observed (except for Pohaku; Figure 1). For the Fe oxyhydroxide goethite, the spectral feature observed in k-range = 7–8 Å⁻¹ corresponds to corner-sharing Fe-O octahedra and the three-dimensional character of the structure (Toner et al., 2009). The EXAFS data indicate that the mats are composed primarily of Fe(III) oxyhydroxide phases with less three-dimensional ordering than two-line Fh. Therefore, these Fe(III) phases will be referred to as natural short-range ordered Fe oxyhydroxides (FhSR). Iron and Mn oxidation state maps, coupled with total Fe, Mn, Ca, and Ti distributions, were collected for an intact surface crust sample from the Ula Nui site (Figure 2). This sample was frozen shipboard under N₂ and analyzed at the synchrotron in the absence of O₂. Noticeable, discontinuous black banding can be observed visually in the laminated mats and these bands are represented in the X-ray fluorescence maps as regions of higher Mn fluorescence intensity [e.g., top of Region I (R1) and II (R2) in Figure 2]. XANES fitting of multiple energy maps collected across the Mn K-edge also indicates that these Mn-rich regions are Mn(IV)-oxides. The valence state is confirmed by analysis of Mn K-edge XANES spectra for this sample (data not shown). The majority of the map profile is then dominated by Fe(III) particles, although a zone dominated by reduced Fe(II) was mapped at the top of R2. Calcium is also enriched by more than an order of magnitude at the top of R2, and these Ca-rich zones envelop the particles in which Fe(II) is present. No micro-EXAFS spectra were collected on this sample and therefore the full speciation of the Fe in discrete regions is unknown, but possible candidate solid-phase Fe species include carbonates, sulfides, or basalt. The Fe(II)-rich particles are
The Fourier transform of these reduced structure functions results in the PDFs, which contain structural information in real-space for the Loihi mat Fe$_{RSO}$ (Figure 5). The first two major features in the PDFs for the BT37, Ula Nui-A, Ula Nui-B, Spillway A, and Loiha A mats correspond primarily to the average bond lengths for Si and Fe with oxygen. The peaks at $\sim$1.61 Å correspond to Si-O correlations in the first oxygen shell of Si in tetrahedral coordination. This bond length agrees well with that reported in the literature (e.g., Grimley et al., 1990; Poulsen et al., 1995) and for the am-SiO$_2$ reference compound (Table 3). The second major peaks at $\sim$1.98 Å correspond to Fe-O correlations in the first oxygen shell of Fe. Iron(III) in synthetic Fe$_3$O$_4$ is dominantly in octahedral coordination with oxygen (O and/or OH) although recent studies (Michel et al., 2007b, 2010; Maillot et al., 2011) support the presence of a minor amount (10–25%) of tetrahedrally coordinated Fe(III). As such, the Fe-O correlation for the natural samples may have bond length contributions from both types of coordination environments. The Fe-O peak is slightly asymmetric and also has a small shoulder peak centered at $\sim$2.13 Å. Similar Fe-O bond lengths were reported for synthetic Fe$_3$O$_4$ based on EXAFS spectroscopy data. The fitted Fe-O distances for the Loihi mat samples also correspond well with the Fe-O reference (Table 3), although the distances for the reference were slightly shorter at $\sim$1.96 and 2.11 Å, respectively. Note that although the Fe-O correlation, particularly in the case of the reference Fe$_3$O$_4$, is expected to have contributions from tetrahedrally coordinated Fe (average bond length $\sim$1.88 Å) only two Gaussian functions were used to avoid over fitting.

SYNCHROTRON X-RAY DIFFRACTION AND PAIR DISTRIBUTION FUNCTION ANALYSIS

Five Loihi mat samples (BT37, Ula Nui-A, Ula Nui-B, Spillway A, and Lohiau A) from the 2006 cruise were analyzed by SR-XRD, and all contain a Fe$_3$O$_4$-like phase based on the presence of diffuse scattering features similar to those observed for the synthetic Fe$_3$O$_4$ reference (Figure 3). With exception of sample Ula Nui-B, the most significant features occur at d-spacings of $\sim$1.5 and $\sim$2.55 Å and are indicative of Fe$_3$O$_4$ (e.g., Jambor and Dutrizac, 1998; Michel et al., 2007a). The specific crystalline phases attributable to the sharper peaks evident in samples Ula Nui-A, Spillway A, and Lohiau A (Figure 3) could not be positively identified due to uncertainty in the relative intensities and possibility of multiple phases. Sample Ula Nui-A contains an additional mineral phase with peaks at d-spacings $\sim$7.2, 3.5, 2.5, 1.4, and 1.2 Å, that can be indexed as Na-rich birnessite (e.g., ICSD 68916). The presence of birnessite in the Ula Nui mat is consistent with Mn EXAFS data for the Ula Nui site (Edwards et al., 2011). Consistent with the SR-XRD results, the total scattering data collected to higher Q-space values and presented as the reduced structure functions for these samples (Figure 4) are also dominated by features similar to those observed for the synthetic Fe$_3$O$_4$ reference.
Subsequent features in the PDFs correspond to second, third, and higher neighbors around Si and Fe, as well as oxygen pair correlations (i.e., O⋯O). For example, the small features at \( \sim 2.64 \text{ Å} \) (Figure 5) are due to the O⋯O distance in tetrahedral...
silicate (Figure 6) and are consistent with data for the *am*-SiO₂ reference. Also based on the PDF for the reference, a Si...Si distance corresponding to corner-sharing silica tetrahedra is expected at \( \sim 3.07 \text{ Å} \) (Figure 6) but is possibly obscured in the natural samples due, in part, to overlapping correlations resulting from the connectivity of FeO₄⁻/₆ polyhedra. The peak at \( \sim 3.03 \text{ Å} \) in synthetic Fh is dominated by Fe...Fe and O...O correlations for edge-sharing Fe octahedra and the next major peak at \( \sim 3.44 \text{ Å} \) has contributions from corner-sharing FeO₄⁻/₆ polyhedra (Michel et al., 2010). These edge- and corner-sharing Fe contributions are not clearly resolved in the mat samples due to the presence of additional features (Figure 5) the most significant of which occur at \( \sim 3.14, 3.31, \) and \( 3.6 \text{ Å} \) (Table 3). Previous work (Pokrovski et al., 2003) showed that in varying concentrations of Si solutions, the presence of one to two Si atoms was detected at \( 3.18 \pm 0.03 \text{ Å} \) in the second shell around Fe and was ascribed to SiO₄ linked bidentate to two neighboring Fe octahedra via corners (Figure 6). Other bonding motifs are also possible (Figure 6) and longer Si...Fe path lengths could explain the features at distances of \( \sim 3.3 \) and \( \sim 3.6 \text{ Å} \).

With exception of the degree of PDF decay, the most significant differences between the Loihi mat FhSRO and Fh reference are in the range \( 2.5 < r < 4 \text{ Å} \). As described above, differences in this region of the PDFs appear primarily due to Si...Fe pair correlations. Interestingly, the pair correlations beyond \( r \approx 4 \text{ Å} \) in BT37,
Toner et al. Mineralogy of iron microbial mats obtained down to 2 K show blocked particles and the presence of assumptions used is included in the Section “Magnetism.”

The PDF peaks decay at order and connectivity of Fe polyhedra are maintained over these length scales. The PDFs with increasing $r$ for the natural samples indicates smaller coherent scattering domain (CSD) sizes and increased disorder relative to synthetic Fh. Sample Ula Nui-B shows more structure at higher $r$ due to birnessite phase impurity. (B) Comparison of the short-range order for these samples. Similarities between natural samples and synthetic references for Fh and amorphous silica are highlighted.

Ula Nui-A, Spillway A, and Lohiau A closely resemble synthetic Fh (Figure A3 in Appendix) suggesting that the intermediate-range order and connectivity of Fe polyhedra are maintained over these length scales. The PDF peaks decay at $r \approx 16$ Å for BT37, Spillway A, and Lohiau A suggesting that these mat samples are more disordered and have smaller CSD sizes compared with synthetic two-line Fh which decays at $r \approx 23$ Å (Figure A3 in Appendix). Estimated CSD sizes for Ula Nui-A and Ula Nui-B (Table 3) are significantly larger ($\sim 23$ and 37 Å, respectively) however, the presence of relatively crystalline impurities in these samples prevents an accurate estimate for the Fh fractions, which are assumed to be less crystalline than the associated impurity phases. Shifts in peak positions for the natural samples relative to Fh at higher $r$ ($>4$ Å) may be attributable, in part, to increasing strain with decreasing CSD size, and this trend is consistent with previous studies of synthetic Fh in which the size and/or Fe(III) vacancy content varied significantly larger ($\approx 23$ Å) compared to experimental PDFs for Fh and amorphous SiO$_2$ in Appendix). The particle diameters calculated by this method range from 3.5 to 4.5 nm for the Loihi Seamount natural Fh$_{3RO}$ minerals.

**MÖSSBAUER SPECTROSCOPY**

Mössbauer spectra were obtained at room temperature and 4.2 K for selected Fe mat samples in order to confirm the valence state of Fe and the magnetic state of the Fh$_{3RO}$. Detailed chemical, structural, and magnetic information can be obtained with this method (Murad and Cashion, 2004), as the spectra depend on the mineralogy, lattice type, abundance of structural defects, and magnetic properties of the sample. The type of magnetic ordering (ferro-, ferri-, or antiferromagnetic) can be further tested by applying external magnetic fields, and effects related to thermal relaxation in nanoparticles (superparamagnetism) can be investigated by obtaining spectra at different temperatures.

The room temperature spectra for the Fe mat samples from the Spillway A, Tower, Hiolo A, Ula Nui-A, Ula Nui-B/C, Lohiau A, and BT37 areas of Loihi Seamount have a Fe$^{3+}$ doublet and magnetic hyperfine parameters corresponding to Fh (Table 5; Figure 8). The presence of a doublet in a Mössbauer spectrum is a feature associated with paramagnetism and/or superparamagnetism. A superparamagnetic phase has magnetic order below the blocking temperature. The Mössbauer spectra of Fe mats taken at 4.2 K have magnetic order and they exhibit a sextet. The magnetic hyperfine parameters of Loihi mat samples at 4.2 K agree with the ones found in the literature for Fh (Berqué et al., 2009). A decrease was observed in the magnetic hyperfine field ($B_{hf}$) as compared with synthetic Fh; this feature is associated with structural defects. Ferrihydrite, specifically two-line Fh, has significant defects in both the tetrahedral and octahedral Fe(III) sites (Michel et al., 2010), and these natural Fh$_{3RO}$ samples from Loihi Seamount seem to have extra Fe(III)-site lattice defects due perhaps to Fe substitution and vacancies.

**HEAT TREATMENT OF THE HIOLOA MAT**

A Loihi Seamount mat from the Hiolo area was thermally treated to determine the temperature at which the natural Fh$_{3RO}$ converts to hematite under oxic conditions. The temperature dependent conversion was monitored by powder XRD and room temperature Mössbauer spectroscopy. The XRD pattern obtained for the unheated Hiolo mat sample is presented in Figure 9. The pattern has the two broad lines characteristic of Fh and is in agreement with the SR-XRD data for Ula Nui-A, Ula Nui-B/C, BT37, Spillway A, and Lohiau A (Figure 3). In addition to the Fh pattern, several sharp diffraction lines are evident for the sample under different conditions: (1) no thermal treatment, halite, and Fh; (2) sample treated at 400°C, halite, Fh, and minor contribution of anhydrite (CaSO$_4$); (3) sample treated at 600°C, halite, hematite ($\alpha$-Fe$_2$O$_3$), and minor contribution of aegirine (NaFeSi$_2$O$_6$); and (4) sample treated at 800°C, halite, hematite, and minor contribution aegirine. The samples heated at 600 and 800°C have dominant, sharp diffraction lines consistent with the mineral hematite.
Table 3: Atom pair separations and coherent scattering domain sizes extracted from PDF analysis of references and selected mat samples.

| References | Pair assignments | CSD size (Å) |
|------------|------------------|--------------|
| Si-O       | Fe-O<sup>a</sup> | O...O        | Fe...Fe<sub>edge</sub> | Si...Si | Fe...Fe<sub>tern</sub> |
| Fh         | –                 | 2.11         | –                     | 3.03    | –                     | 3.437           | –     | 23 |
| am-SiO₂    | 1.608             | –            | 2.626                 | –       | 3.073                 | –                     | 3.47    | 8  |

Samples

| Correlation no. | 1 | 2   | 3   | 4   | 5   | 6<sup>*</sup> | 7   | 8   | 9<sup>*</sup> | 10  |
|-----------------|---|-----|-----|-----|-----|--------------|-----|-----|-------------|-----|
| BT37            | 1.616 | 1.986 | 2.206 | 2.653 | 2.944 | 3.03         | 3.147 | 3.307 | 3.44         | 3.605 | 16  |
| Ula Nui-A       | 1.604 | 1.979 | 2.125 | 2.624 | 2.996 | 3.03         | 3.140 | 3.295 | 3.44         | 3.605 | 23  |
| Ula Nui-B       | 1.594 | 1.963 | 2.132 | –     | 2.883 | 3.03         | 3.153 | 3.317 | 3.44         | 3.593 | 37  |
| Spillway A      | 1.612 | 1.974 | 2.121 | 2.648 | 2.955 | 3.03         | 3.142 | 3.306 | 3.44         | 3.606 | 16  |
| Lohiau A        | 1.618 | 1.977 | 2.131 | 2.648 | 2.898 | 3.03         | 3.146 | 3.309 | 3.44         | 3.600 | 16  |

Additional pair assignments

Si/O...O        Si/Fe<sup>1</sup> Si/Fe<sup>2</sup> Si/Fe<sup>3</sup>

<sup>a</sup>Two Gaussian functions were used to fit the correlation at ~2 Å.
<sup>b</sup>Si<sub>4</sub>O<sub>4</sub> linked bidentate to two neighboring Fe octahedra via corners.
<sup>c</sup>–(-) indicates feature is not applicable (references only) or not present (samples only).
<sup>d</sup>Si<sub>4</sub>O<sub>4</sub> linked monodentate to O doubly/triply coordinated with Fe.
<sup>e</sup>Peak position fixed.
<sup>f</sup>Si<sub>4</sub>O<sub>4</sub> linked monodentate to O singly coordinated with Fe (linear Si-O-Fe).

Mössbauer spectra tell a more detailed story of the mineral conversion (Figure 10). The Mössbauer spectra for the Hiolo mat, unheated, and after 400°C treatment, exhibit a doublet indicating a superparamagnetic phase. The Hiolo mat samples heated to 500°C showed the presence of at least two components, a sextet representing magnetic order at room temperature and a Fe<sup>3+</sup> doublet. The doublet represents the contribution of Fh that was not converted to a more stable phase, while the sextet does not have parameters that correspond to a specific Fe phase. The Fe phase(s) observed at 500°C are intermediates in the conversion process from natural Fb<sub>SRO</sub> to hematite. In contrast, the spectra at 600 and 800°C suggest the presence of hematite. At 600°C the B<sub>HF</sub> is reduced as compared with a stoichiometric hematite, indicating the presence of lattice defects in the conversion product. The data at 800°C show magnetic hyperfine parameters similar to stoichiometric hematite and suggest the thermal treatment completely converted Fb<sub>SRO</sub> to hematite at that temperature.

**DISCUSSION**

**MAT COMPOSITION AND STRUCTURE OF IRON-BEARING PHASES**

X-ray fluorescence mapping of major element distributions with depth show that spatial heterogeneity and geochemical zonation occur in layered mats such as at the Ula Nui site. The low-temperature (<2°C) Fe mats at Ula Nui are considered to be modern analogs to ancient umber deposits that form from Fe and Si-rich ultra-diffuse hydrothermal fluids (Edwards et al., 2011). Total cell densities reach values as high as 1.4 × 10<sup>9</sup> cells/g dry wt. in the Fe/Mn mats, and known Fe-oxidizing bacteria (e.g., Zeta-proteobacteria such as Mariprofundus ferrooxydans) that have been identified in these mats are likely supported by the advection of fluids containing 40–150 mM Fe (Glazer and Rouxel, 2009; Edwards et al., 2011). The reductive transformation of the Si-rich Fb<sub>SRO</sub> would not be predicted to occur substantially in superparamagnetic phase. The Hiolo mat samples heated to 500°C showed the presence of at least two components, a sextet representing magnetic order at room temperature and a Fe<sup>3+</sup> doublet. The doublet represents the contribution of Fh that was not converted to a more stable phase, while the sextet does not have parameters that correspond to a specific Fe phase. The Fe phase(s) observed at 500°C are intermediates in the conversion process from natural Fb<sub>SRO</sub> to hematite. In contrast, the spectra at 600 and 800°C suggest the presence of hematite. At 600°C the B<sub>HF</sub> is reduced as compared with a stoichiometric hematite, indicating the presence of lattice defects in the conversion product. The data at 800°C show magnetic hyperfine parameters similar to stoichiometric hematite and suggest the thermal treatment completely converted Fb<sub>SRO</sub> to hematite at that temperature.
FIGURE 7 | Induced magnetization curves, ZFC/FC and hysteresis loops. (A) ZFC/FC curves typical of Loihi Fe mat samples. Above peak temperature the material behaves as a paramagnetic phase. Below the peak temperature the material has magnetic order. (B) The Hysteresis loops at variable temperature show the antiferromagnetic character of ferrihydrite, that is the non-saturation at high fields. At 2 K the coercive force is different of zero (see inset) and indicates the sample has magnetic order. At 18 and 42 K HC is zero and indicates the sample is in the superparamagnetic state.

under these low Fe fluxes, and therefore the EXAFS signature of Fe(III) in the FhSRO dominates these samples. The Fe(II)-rich zones shown in R2 of Figure 2 occur several millimeters below the surface of the mat where oxygen concentrations drop to only a few micromolar; the Fe(II)-mineralization may represent regions of localized microbial Fe-reduction using fixed organic carbon (e.g., filaments and extracellular material) resulting in the precipitation of Fe(II)-rich phases such as carbonates or sulfides. Given the strong co-localization between Fe(II) and Ca in this region of the mat, carbonates are the most likely candidate phase, but Fe K-edge XANES were not collected in this region for quantitative analysis. Although 16S rRNA sequences of DNA extracted from Ula Nui mats has not been reported, and enrichments for Fe(III)-reducing bacteria from Ula Nui have been unsuccessful (D. Emerson, personal communication), the potential presence and activity of Fe-reducing bacteria is plausible given the isolation of Fe(III)-reducing bacteria from Fe mats at the Loihi summit (Bailey et al., 2009; Emerson, 2009) and the thermodynamic favorability of coupling organic matter oxidation to Fe(III)-reduction within interior anoxic portions of these mats. Reduction of biogenic Fe oxides has also been demonstrated at the Tonga–Kermadec Arc (Langley et al., 2009).

The local coordination environment of Fe(III) in the Loihi mats was compared to a reference library of Fe oxyhydroxide phases...
Toner et al. Mineralogy of iron microbial mats

FIGURE 9 | X-ray diffraction pattern of Loihi sample before and after thermal treatment. The pattern obtained with no heat treatment and treatment at 400˚C have only two broad lines similar to the pattern of material without treatment. In the 600 and 800˚C treatments, the sharp lines correspond to hematite and the broad lines of Fh are no longer present. Aegerine “a,” anhydrite “an,” hematite “ht,” and halite “h.”

(Figure 1), and found to be most similar to that of a deep-sea, biogenic Fe oxyhydroxide (seafloor incubation of sulfide minerals at Juan de Fuca Ridge; Toner et al., 2009). Within our dataset, the Fe mat from Pohaku hosts the only phase matching the standard two-line Fh. The most important difference between the Loihi mat spectra and that of the two-line Fh standard is in the $k$-range $= 7$–$8\,\text{Å}^{-1}$, where the peak at $k = 7.5\,\text{Å}^{-1}$ is greatly reduced in mat spectra relative to two-line Fh (except for Pohaku). Mikutta (2011) recently reported a similar observation for synthetic Fh formed in the presence of varying amounts of organic ligands and attributed the decrease in intensity of this feature with increasing L/Fe ratio to a reduced number of nearest Fe neighbors. Iron EXAFS spectra with characteristics similar to the Loihi FhSRO are reported in the presence of Si (Masion et al., 2001; Doelsch et al., 2003; Voegelin et al., 2010; Boland et al., 2011), and organic molecules (Vilge-Ritter et al., 1999; Mikutta, 2011). While the organic C content of the mats is low (~0.3 wt. %), the Si:Fe mole ratio for the Fe-rich mats is 0.107–0.298, and the P:Fe ratio is 0.0280–0.168 (Table 2). Based on these EXAFS observations, we hypothesize that Si, and perhaps P, is reducing the degree of structural order in Loihi Seamount natural FhSRO phases to an extent less than that typically observed for synthetic Fh. This is observed as a decrease in the magnetic hyperfine field ($B_{hf}$). Ferrihydrite, specifically two-line Fh, has significant defects in both the tetrahedral and octahedral Fe(III) sites (Michel et al., 2010), and these natural FhSRO samples from Loihi Seamount seem to have extra Fe(III)-site lattice defects due perhaps to Fe substitution and vacancies.

The SR-XRD (Figure 3) and total X-ray scattering data in the form of reduced structure functions (Figure 4) reveal that the high-Q (i.e., high angle) scattering maxima for the five natural mat samples are similar, but not identical, to the synthetic two-line Fh reference. In the case of BT37, Spillway A, and Lohiiau A (Tables 1 and 2), the samples with the most clearly resolvable fraction of natural FhSRO, the comparison to pure synthetic Fh suggests that these samples bear some structural similarities. Comparison of the PDFs for these samples confirms similarities in short- and intermediate-range structure and provides further insight as to the structural association of Si and Fe in the nanostructured matrix (Figures 5 and 6).

The Si:Fe mole ratio measured for the mats by ICP-OES are 0.245, 0.107, and 0.207, respectively. The total measured Si:Fe mole ratios for Ula Nui-A and Ula Nui-B/C mats are 0.289 and 0.227, respectively (Table 2). Assuming that these samples are primarily
single-phase, the differences in the region of the PDFs between 2.5 < r < 4 Å (Figure 5) suggest that Si is predominantly associated with the Fh$_{\text{SRO}}$ surfaces, perhaps in the form of a poorly ordered silica coating. Alternatively, in the case that these samples are multi-phase then the observed PDFs could also be explained by at least two phases; one comprised of a Fh-like core, perhaps with a Si-rich coating, and a second comprised of an Fe-bearing amorphous SiO$_2$ phase, similar to that observed by Pokrovski et al. (2003). Either scenario would also be consistent with the observation that features at higher r (>4 Å) in the PDFs show a return to Fh-like ordering, albeit with smaller CSD sizes. In addition, although the correlations attributable to edge- and corner-sharing Fe polyhedra at ~3.03 and 3.44 Å, respectively, are not clearly delineated in the PDFs for the mat samples it is possible that they exist but are obscured by other pair correlations involving Si. As discussed above, further evidence for the presence of edge-sharing Fe polyhedra is indicated by the EXAFS for all the Loihi mats. The presence of such polyhedral connectivity would be required in order to produce the intermediate-range Fh-like ordering observed in the region 4 < r < 12 Å (Figure A3 in Appendix). Structural information over these longer distances would not be available from previous (and present) EXAFS results since the range of inter-atomic distances measured, particularly in the case of Fh, are typically less than ~4–5 Å. In summary, the PDFs indicate the presence of limited intermediate-range Fh-like structural ordering, which suggests that silica is not structurally incorporated in ferrihydrite. Differences in short-range ordering of the natural samples relative to Si-free Fh suggest that the Fh particles are coated with Si.

**PARTICLE DIMENSIONS AND INTERACTIONS OF IRON-BEARING PHASES**

The magnetic behavior of the Loihi Seamount Fh$_{\text{SRO}}$ was evaluated since particle coatings such as Si or organic matter are expected to diminish or completely inhibit magnetic interactions of antiferromagnetic Fe oxyhydroxides. In a superparamagnetic system when particles are cooled without an applied field, the magnetic moments are randomly oriented and the resulting induced magnetization is around zero at 0 K. With increasing temperature of the system, the thermal energy of disorder is higher than the ordering energy and a superparamagnetic behavior results, leading to a decrease of the total magnetization with increasing temperature following the Curie–Weiss law. The presence of a maximum in the ZFC curve is therefore associated with the transition between magnetically relaxing superparamagnetic (unblocked state) and thermally stable magnetization (blocked state). The FC curve represents the superparamagnetic system cooled down in the presence of an external magnetic field.

Current models suggest that particle coatings prevent magnetic interactions for antiferromagnetic systems (Bervoët et al., 2009), although this may not prevent magnetic interactions for ferrimagnetic phases such as maghemite and magnetite. Since Fh particles are antiferromagnetic, we apply the antiferromagnetic model to understand Loihi ZFC/FC curves. Berquo et al. (2009) verified that synthetic agglomerated Fh particles, without coating and magnetically interacting, showed a $T_P$ shifted to higher temperatures as compared with the same particles coated, thus considered without magnetic interactions. The $T_P$ estimated from ZFC curves of Loihi samples are similar to the ones obtained by Berquo et al. (2009) for coated synthetic Fh, and this result strongly suggests that the natural Fh$_{\text{SRO}}$ particles are also individually wrapped in a way that prevents magnetic interactions. The coating agents that could create this magnetic masking include organic matter or Si in the environment where the particles precipitate. The Loihi Seamount Fh mats are enriched in Si, and Si bonding to the natural Fh$_{\text{SRO}}$ is well supported by our X-ray scattering data and analysis. In addition to agreeing with complementary data, this result makes it possible to obtain a better estimate of magnetic particle size (Table 4) considering that there is no shift in the peak temperature due to magnetic interaction. The ZFC peak reflects exclusively the changes in particle volume without undesired effects that may contribute to its shift.

Differences in the particle size estimates from low-temperature magnetic data and the CSD sizes from PDF analysis for samples Ula Nui-A, Ula Nui-B, Lohiau A, and Spillway A are evident (Table 4) and point toward the presence of structural disorder in the natural Fh$_{\text{SRO}}$. These two types of data can be considered as complementary in the sense that the low-temperature magnetic data indicate an upper limit for the maximum physical dimensions of the particles, while the PDF reveals the average dimensions over which the atoms in the structure scatter coherently. It is possible for the CSD to equal the particle size, but this is not always the case, in particular for Fh (e.g., Michel et al., 2008). In principal, for a monodisperse nanocrystalline material (i.e., with virtually no structural disorder), the PDF peaks decay as $r$ approaches the average maximum dimensions of the particle; therefore, particle size and CSD size are effectively equal. For highly disordered or amorphous structures, the CSD size can be substantially smaller than the physical size of the particles due to the effects of static/dynamic disorder, which attenuate the features in the PDF at higher $r$. It is worth noting that it becomes increasingly difficult to correlate CSD size with actual particle size, in particular for natural samples, from PDF data alone since the CSD size estimates become increasingly uncertain for polydisperse materials and/or if multiple structural phases are present, as is the case for natural samples Ula Nui-A and -B. However, for Lohiau A and Spillway A, natural samples that are dominantly Fh$_{\text{SRO}}$, the observed discrepancy between average particle size and CSD size suggests strongly that these samples have intrinsic static and dynamic forms of structural disorder. Past studies of pure synthetic Fh (Michel et al., 2010; Cismasu et al., 2011) have suggested that the bulk structure exhibits size-dependent lattice strain and defects in the form of vacancies. In addition, size- and defect-driven restructuring of the Fh surfaces is also possible, although poorly understood at present. Evidence for lattice strain and structural defects in natural Fh$_{\text{SRO}}$ is difficult to discern in the present case due, in part, to the presence of minor crystalline impurity phases such as birnessite. Additional complexity due to the presence of compositional impurities and/or adsorbed species such as silica or organic matter are also factors and may account...
for the discrepancies between average coherent scattering body size and particle size.

**PARTICLE STABILITY OF IRON-BEARING PHASES**

The local coordination of Fe in Loihi mats was remarkably insensitive to sample processing, storage, and handling procedures such as freezing, drying, and storage in seawater up to 1 year (Figure 1; Figures A1 and A2 in Appendix). The short-range order of the Naha and Loihau Fe mats (Figure A1 in Appendix; data not shown for Loihau) did not change after aging for 1 year at 4°C. Although the FhSRO phases might be expected to transform to more stable minerals such as goethite (Penn et al., 2006), no recrystallization was observed. The stability of the local structure of the FhSRO as a function of time and temperature is consistent with non-interacting particles. In addition, the Loihi Seamount Fe mats did not convert to the more stable hematite phase during a 400°C thermal treatment. Pure Fh is expected to rapidly convert to hematite between 300 and 400°C (Cornell and Schwertmann, 2003). However, surface coatings on Fh, such as adsorbed Si or organic molecules, are known to slow or inhibit its transformation to crystalline products (Cornell and Schwertmann, 1979; Anderson and Benjamin, 1985; Campbell et al., 2002). Stable Fe minerals such as goethite were not observed at any of the Loihi field sites or under any of the experimental conditions below 400°C. All EXAFS, PDF, and magnetism data from the present study point to Si particle coatings that limit chemical interactions among natural FhSRO particles in Loihi mats.

In addition to limited particle–particle interactions, chemical, and biological reactions involving Fe(II) may be limited in Loihi mats and contribute to stability of the FhSRO. The low activity of Fe-reducing bacteria in Loihi mats suggests that the FhSRO phases are not subject to intense biological reductive alteration (Emerson, 2009), although some Fe-reducing bacteria are known to solubilize Fe(II) from Si-enriched Fh (Percak-Dennett et al., 2011). Despite the constant source of Fe(II) to all but the “dead” Naha site, Fe(II) induced reduction of FhSRO may be negligible based on results from synthetic Si-enriched Fe studies (Jones et al., 2009; Boland et al., 2011). For example, Si:Fe ratios of 0.7 have been shown to inhibit Fe(II)-induced recrystallization of Fh to goethite at pH 6.5 (Boland et al., 2011). However, the data presented here does not address the potential for exchange between vent fluid Fe(II) and FeSROs, and there is evidence that Si-enriched Fh phases retain chemical reactivity. For example, Si:Fe mole ratios up to 0.5 can be achieved without blocking all reactive Fh surface sites due to surface-bound silicate oligomers (Swedlund et al., 2009). In addition, Si-enriched Fh phases are soluble in the presence of organic molecules, such as oxalate and acetate (Carlson and Schwertmann, 1981; Percak-Dennett et al., 2011). We speculate that the low organic carbon content of the Loihi mats may limit both biological and chemical reductive dissolution reactions. These factors combined suggest that the FeSRO signatures observed at Loihi may be resistant to diagenetic processes and persist over long periods of time.

**IRON MICROBIAL MATS AT DIFFUSE HYDROTHERMAL VENTS**

Iron and Si-rich microbial mats are observed in shallow and deep marine hydrothermal systems. The number of published observations of Fe microbial mats indicates that these deposits may be common features associated with diffuse venting. Diffuse hydrothermal vents at seamounts and submarine volcanoes associated with island arcs and mid-ocean ridge spreading centers host Fe (and Si) microbial mats, for example: Loihi Seamount (Karl et al., 1988; Edwards et al., 2011), Vailulu’u Seamount (Sudek et al., 2009); Giggenbach Volcano, Kermadec Arc (Jones et al., 2008); Axial Volcano, Juan de Fuca Ridge (Kennedy et al., 2003); South Tonga Arc volcanoes (Langley et al., 2009; Forget et al., 2010); Liliput vent field, Mid-Atlantic Ridge (Dekov et al., 2010). Among these studies, the Fe mineralogy, when reported, is resoundingly “amorphous” Fe oxyhydroxide, ferrihydrite, and occasionally goethite. A recent review of the microbiology of active seamount Fe microbial mats indicates that Zeta-proteobacteria and/or Epsilonproteobacteria are shared among sites (Emerson and Moyer, 2010), even though inter-site diversity is high (Davis and Moyer, 2008). A cultured representative of the Zeta-proteobacteria from Loihi Seamount (Emerson et al., 2007), *M. ferrooxydans*, is an Fe oxidizer that produces ferrihydrite-like phases in fresh filaments of twisted stalks (Chan et al., 2011). Frequent observations of extensive filamentous structures at diffuse vents, and the apparent ubiquity of Zeta-proteobacteria in the mats, suggest that Loihi Seamount mats may represent common depositional environments at the modern seafloor. The present study indicates that the presence of Si and organic templates are both primary geochemical factors in the structure of Fe-bearing phases as well as the preservation of the phases as a function of time and temperature.

**CONCLUSION**

Certain characteristics of Fe oxyhydroxide phases – particle size, crystallinity – are known to respond to solution conditions such as Si concentration, as well as factors that influence the rate of precipitation, such as temperature and pH (Cornell and Schwertmann, 2003). The overarching goal for this study is to determine whether Fe oxyhydroxide phases can be used to interpret the biogeochemical conditions of past depositional settings. In particular, we are concerned with whether the characteristics of fresh Fe oxyhydroxide phases are preserved over time. As a first step toward this goal, we examined the Fe-rich, flocculent microbial mats hosted by active (and recently active) vents of the Loihi Seamount. The mats are composed of nanoparticulate ferrihydrite (Fh)-like phases with short-range structural order (FhSRO) at all but one site (Pohaku) irrespective of depth or temperature. The Loihi FhSROs are primarily Fe(III) with little particle-to-particle variability in the local coordination environment of Fe within a single mat; although careful sampling of the Ula Nui site revealed isolated microzones of solid-phase Fe(II)-enrichment beneath the mat–seawater interface. For our entire sample set, maximum particle diameters of 3.5–4.6 nm (magnetism data) were found to be positively correlated with maximum vent fluid temperature, while CSD sizes (PDF analysis) as small as 1.6 nm were observed, and are inversely correlated with vent fluid temperature. These data indicate that the Loihi FhSRO phases have intrinsic static and dynamic forms of structural disorder, likely from lattice strain and vacancy or substitutional impurity defects. Magnetic data and PDF analysis both point to FhSRO particles coated by Si. The Loihi mat FhSRO phases did not transform to other Fe mineral phases in response to freezing, drying, aging in seawater for up to 1 year, or standard heat treatments under oxic conditions. We hypothesize that Si increases...
structural disorder and decreases CSD sizes in Loihi Seamount mats, and propose that the natural Fh SRO we detect is preserved from recrystallization to Fh, or other Fe oxyhydroxides such as goethite, by the presence of Si, although P and organic molecules could potentially contribute.

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APPENDIX

FIGURE A1 | Iron K-edge EXAFS spectra for the Ula Nui mats of Loihi Seamount having different sample handling and data collection conditions. The Ula Nui Crust was stored and analyzed frozen under N2 at an SSRL microprobe beamline in fluorescence mode. Ula Nui-A/B were stored frozen, thawed, rinsed, and dried at 40°C with analysis at the APS at a bulk beamline in transmission mode. Ula Nui C was stored in ambient seawater at 4°C for 6 months, and was analyzed as rinsed/air-dry particles at an ALS microprobe beamline in fluorescence mode.

FIGURE A2 | Summary of all Fe K-edge EXAFS data collected for this study. Samples described in Table 2.

FIGURE A3 | Comparison of PDFs for BT37, Spillway A, and Lohiau A to the Fh reference plotted as $G(r)^{2}r^{2}$ versus $r$ to amplify the features at higher $r$ values. Although subtle for the natural samples the features $>\sim 4$ Å are reasonable similar to those of synthetic Fh. Note that the PDF for Fh was also multiplied by 0.25 for comparison. Ula Nui-A and -B also showed similar features but due to impurities (e.g., birnessite) were excluded for clarity.

FIGURE A4 | The RTSIM shows the typical behavior associated with the presence of Ti-magnetite. The curves obtained on cooling (black circles) and on warming (red circles) are displayed. Due to its high magnetization, magnetite can be observed in the mats at very low concentrations.