Incorporation of Ge in ferrihydrite: Implications for the structure of ferrihydrite

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ABSTRACT

Ferrihydrite is the main form of ferric iron in surficial environments and a key reactive nanoparticle that regulates nutrient availability and the mobility of metal(loid) contaminants, yet its structure is not completely elucidated. Two models exist to date: the "f-phase" in which Fe is fully octahedral and the "akdalaite-model" possessing 20% of the Fe atoms in tetrahedral coordination. In this study, germanium was used as a structural probe to re-examine the validity of the latter model. Germaniumbearing ferrihydrites containing 0.2, 0.6, 1.4, 2.2, 2.9, 3.8, 12, and 15 wt% Ge were synthesized in the laboratory at 25 and 65 °C. X-ray diffraction analyses showed all the precipitates to be six-line ferrihydrite. Semi-quantitative energy-dispersive X-ray microanalyses (TEM) indicate that the precipitates made from solutions having Fe/Ge molar ratios of two and four have Fe/Ge atomic ratios of 3.8–3.9 and 4.4–5.1, respectively, which suggest a limit of Ge uptake in ferrihydrite of about 20 at% relative to total cations. Based on TEM examinations, these high Ge-bearing ferrihydrites are homogenous and consist of equant and plate-like crystallites about 5-6 nm in size. Furthermore, it appears that higher Ge concentrations in solution have no significant effect on the crystallite size, supporting the incorporation of Ge in the ferrihydrite structure. Extended X-ray absorption fine structure (EXAFS) spectroscopy indicated that the Fe atoms in both the low and high Ge-bearing ferrihydrites are in octahedral coordination and that Ge occurs in the ferrihydrite structure by filling the empty tetrahedral sites and coordinating to 4 edge-sharing FeO₆ trimers through sharing a common oxygen (Ge-O-Fe linkage). Incorporation of the Ge tetrahedra in the ferrihydrite structure requires redistribution of Fe occupancy along the alternating O/OH layers while forming an ordered distribution of octahedral Fe and tetrahedral Ge. The local structure around Ge mimics a Keggin-like motif in two different, yet equivalent, orientations. It appears that the split diffraction peak at 1.46 and 1.51 Å is a characteristic feature of Ge-rich ferrihydrite and suggests that it is a fingerprint of increased order due to significant Ge incorporation in the tetrahedral sites. The findings can be rationalized in terms of the incorporation of Ge in the so-called "f-phase" of the classical ferrihydrite model, and demonstrate the flexibility of the model in terms of accommodating a Keggin-like cluster without the need of imposing unrealistic constraints as in the akdalaite model. Direct comparison of the imaginary parts of the Fourier transforms for ferrihydrite and maghemite further confirms the absence of tetrahedral Fe in ferrihydrite. The absence of tetrahedral Fe substantiates the use of goethite-like or akaganeite-like models to describe the polyhedral structure of ferrihydrite used in modeling sorption reactions at the ferrihydrite-water interface.

Keywords: Ferrihydrite, structure, germanium, iron, tetrahedral iron, EXAFS

INTRODUCTION

Ferrihydrite is a poorly crystalline and metastable nano-sized ferric oxyhydroxide. It is widespread in soils, iron-rich oxidized sediments, acid mine drainage settings, mine wastes, and Fe-rich hydrometallurgical process waters (Jambor and Dutrizac 1998). Because of its small size [i.e., 2–3.5 nm, Eggleton and Fitzpatrick (1988); 1–6 nm, Janney et al. (2000)], its abundance, and the geochemical reactivity of the contained ferric ion, ferrihydrite plays an important role in iron cycling and in controlling nutrient and toxic element mobility and bioavailability in the near-surface environment.

Ferrihydrite has long been considered to be a mixture of defective and defect-free varieties, the so-called "d-phase" and

"f-phase" (Drits et al. 1993a; Marchand and Rancourt 2009; Manceau 2009, 2011). More recently, Michel et al. (2007, 2010) proposed a new structural model for ferrihydrite which is singlephase, has a low density of defects, and is isostructural with the mineral akdalaite $[Al_{10}O_{14}(OH)_2]$. Unlike the conventional model (Drits et al. 1993a; Manceau 2011), 20% of the Fe atoms are in tetrahedral coordination in the new model, and octahedra share corners and edges only, without a face-sharing arrangement. The new model received criticism because of its shortcomings in adequately describing the X-ray diffraction, X-ray absorption spectroscopy, and Mössbauer data, and not being in accordance with fundamental crystal-chemical principles (Rancourt and Meunier 2008; Hiemstra and van Riemsdijk 2009; Manceau 2009, 2010, 2011, 2012a).

Recently Song et al. (2010) reported incorporation of Ge in

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the ferrihydrite structure. In their synthesis experiments using dilute solutions, Ge was coprecipitated with Fe at a Fe/Ge molar ratio of 2 and pH 2, 5, 10, and 13, followed by aging at 95 °C for 5 days. The final products were characterized by a combination of techniques and the authors interpreted the results as being supportive of the new structural model of Michel et al. (2007, 2010).

More than a decade ago, we synthesized Ge-bearing ferrihydrite from ferric sulfate and germanium tetrachloride solutions. The motivation was to test the ability and capacity of ferrihydrite to control impurities such as Ge in Fe-rich hydrometallurgical solutions. In the metallurgical industry, Ge is commonly concentrated from process solutions by ferrihydrite precipitation. Germanium-bearing ferrihydrite is later dissolved in acid media and is further upgraded to produce a germanium product. To test the incorporation of Ge in the ferrihydrite structure as a surrogate of the tetrahedrally coordinated Fe3+ and to provide further insights to the ferrihydrite structural models, we reanalyzed our old samples and performed additional synthesis experiments using a protocol similar to that of Song et al. (2010) but much expanded in terms of solution compositions and synthesis temperatures. In this contribution, we report our findings on the nature of Ge coprecipitated with Fe under conditions promoting the formation of six-line ferrihydrite.

METHODOLOGY

Our earlier synthesis experiments were performed at 65 °C from 0.1 M $Fe(SO_4)_{1.5}$ and dilute GeCl₄ solutions at pH 2.5 to 3.2. Germanium concentrations in the starting solutions were 0.2, 0.5, 1.0, 1.4, 1.9, and 2.4 mM with corresponding Fe/Ge molar ratios of 435, 213, 105, 71, 54, and 43. The solution pH was adjusted to the desired value by the slow addition of 0.3 M NaOH at 4.8 mL/min. The final products were filtered and washed with deionized water. The extent of Ge precipitation ranged from 43 to 435 and final products ranging from 3.8 to 0.2% Ge.

Our more recent synthesis experiments followed a protocol similar to that reported by Song et al. (2010). The experiments were performed at room temperature using solutions containing 0.002 M Fe(NO₃)₃.9H₂O and 0.001 M Ge(IV) ethoxide [GeO₄(C₂O₃)₄] at pH 2, 5, 10, and 13. The ferric nitrate solution in the reactor was continuously stirred at high speed during the drop-wise addition of Ge(IV) ethoxide. The solution pH was subsequently adjusted to 2, 5, 10, and 13 by the addition of 1 M NaOH at a rate of 0.5 mL/min, and then the solution pH was rapidly decreased to about 1.5 by adding 20% HNO₃. The resulting slurries were stirred for an additional hour at room temperature before they were aged in an oven at 95 °C for 5 days. The products were centrifuged, washed several times with dionized water and ethanol, dialyzed, and freeze dried. The synthesis experiments were performed at a Fe/Ge molar ratio of two as in Song et al. (2010), and also at four to test the effect of Ge concentration in the starting solution. As a control, synthesis experiments were also performed at pH 2 without the addition of Ge following the same protocol.

X-ray diffraction analyses were performed by a Rigaku D/MAX 2500 rotating anode X-ray powder diffractometer using CuK α radiation at 50 kV and 260 mA with a step size of 0.02° and scan rate of 1°/min in 20. The samples were placed on zero-background plates and disseminated by acetone for the X-ray powder diffraction analysis. For monitoring purposes and very small samples in capillary tubes and small zero-background holders, a rotating anode Rigaku Rapid-2-R micro-XRD with a curved image plate was also used.

Extended X-ray absorption fine structure (EXAFS) spectroscopy measurements were made at the PNC-CAT bending magnet beamline of the Advanced Photon Source. The samples were prepared separately for Fe K-edge and Ge K-edge EXAFS by diluting with boron nitride and homogenizing to achieve a sample thickness of 1 absorption length. The monochromator crystals were detuned to 20% to eliminate harmonic contributions. The EXAFS spectra were collected at room temperature in both the transmission and fluorescence modes. Only the transmission measurements were used in the analysis with the exception of the Ge EXAFS pectra of the dilute Ge precipitates. Each sample was analyzed 10 to 12 times and the spectra were averaged. Data reduction and analysis were

accomplished by ATHENA and IFFEFIT/ARTEMIS (Ravel and Newville 2005).

TEM samples were prepared from nine samples, listed on Table 1, by placing a drop of the dilute precipitate in solution after ultrasonication in ethanol onto a Lacey Carbon Film on a copper TEM grid. TEM examination was performed using a JEOL 2010 STEM operated at 200 kV. Semi-quantitative Fe and Ge microanalyses were performed using a Link (Oxford) PentaFET energy-dispersive X-ray spectrometer.

RESULTS

X-ray diffraction

XRD patterns of the precipitates indicate that they are six-line ferrihydrite (Fig. 1). The peaks of the samples synthesized from solutions with Fe/Ge molar ratios of 2 and 4 are at 2.525, 2.232, 1.972, 1721, 1.509, and 1.461 Å, coinciding with the *d*-spacing values of the Ge-bearing ferrihydrite reported by Song et al. (2010) and corresponding to six-line ferrihydrite (e.g., Childs et al. 1982; Eggleton and Fitzpatrick 1988; Drits et al. 1993a). Two characteristic features of these Ge-bearing ferrihydrites are the hump at about 2.50 Å from the 101 reflection, and the presence of the split peak at 1.51 and 1.46 Å from the 105 and 110 reflections. Better resolution of these peaks indicates that the Ge-bearing ferrihydrite crystals have a higher crystallinity in the *c* direction and *a-b* plane. The split peak is a characteristic feature of the Ge-ferrihydrite and suggests that it is a fingerprint of increased order due to Ge incorporation. Germanium-bearing ferrihydrites synthesized at higher Fe/Ge molar ratios (i.e., ratios \geq 43) do not display the split peak and they appear to be less ordered. The split peak at 1.51 Å is not detected in many of the XRD patterns reported for six-line ferrihydrite. A subtle peak at the *d*-spacing value of 4.2 Å ($2\theta = 21.1^{\circ}$) indicates the presence of minor goethite in some of the samples (Fig. 1).

The precipitates formed from solutions without Ge (i.e., control experiments) yielded goethite and hematite indicating that the presence of Ge stabilized ferrihydrite preventing its transformation to hematite and goethite.

Transmission electron microscopy

The synthesis products formed at pH 2, 5, 10, and 13 from solutions with Fe/Ge molar ratios of 2 and 4 were characterized by TEM. All the synthesis products are homogenous and consist of equant and plate-like crystallites. They often display faceted hexagonal outlines with sub rounded corners (Fig. 2). Crystallite sizes of the precipitates are relatively uniform at 5.2 ± 1.0 and 6.2 ± 1.6 nm for pH 2; 5.5 ± 1.0 and 5.7 ± 1.2 nm for pH 5; 5.6 ± 1.1 and 6.0 ± 1.5 nm for pH 10; and 6.2 ± 1.6 and 6.7 ± 1.7 nm for pH 13 for precipitates having Fe/Ge molar ratios of 2 and 4, respectively. The data presented in Table 1 suggest little pH or

 TABLE 1.
 Particle sizes of the precipitates formed from solutions with Fe/Ge molar ratios of 2 and 4

Sample no.	Solution	рΗ	Particle size (nm)					
	Fe/Ge		average	St. dev.	min	max	n	
2-r2	2	2	5.2	1.0	3.1	8.3	96	
5-r2	2	5	5.5	1.0	3.1	8.1	135	
10-r2	2	10	5.6	1.1	2.3	8.4	128	
13-r2	2	13	6.2	1.3	2.6	8.7	91	
2-r4	4	2	6.2	1.6	2.9	12.2	141	
5-r4	4	5	5.7	1.2	2.3	8.7	177	
10-r4	4	10	6.0	1.5	2.9	10.5	86	
13b-r4	4	13	6.7	1.7	3.6	11.3	97	
13t-r4	4	13	5.8	1.6	2.6	10.9	127	

Notes: Fe/Ge is molar ratio; St.dev. = standard deviation; min = minimum; max = maximum; n = number of particles measured.

3.1 105 2.8 71 54 2.7 43 2.5 2.5 •2θ (Cu-Kα) 20 30 60 70 FIGURE 1. XRD patterns of the precipitates made from solutions having various Fe/Ge molar ratios. Italic numbers above the patterns are d-spacings in Å. Corresponding hkl reflections of ferrihydrite (f-phase) are given in parentheses. Small peaks at ~21° in the precipitates with Fe/Ge ratios of 4 (pH 13), 71, 105, 213, and 435 are indicative of the

compositional control on the crystallite sizes. This conclusion is different than the findings of Song et al. (2010) for Ge-bearing ferrihydrites precipitated from solutions with Fe/Ge molar ratios of 2 (i.e., 10 nm for pH 13 and 40 nm for pH 5). Our crystallite sizes are comparable to the reported size ranges for Ge-free six-line ferrihydrite [e.g., 5–10 nm by Childs et al. (1982); 4–5 nm by Saleh and Jones (1984); 4–5 nm by Eggleton and Fitzpatrick (1988); 5–6 nm by Janney et al. (2000)]. Furthermore, Dyer et al. (2010) reported crystallite sizes of less than 10 nm for Si-bearing ferrihydrite.

presence of minor goethite.

The size variation is small for the particles formed from

solutions with higher Ge concentrations; that is, higher Ge concentrations in the solution have a negligible effect on the crystallite size. This suggests that the excess Ge in solution is controlling the particle growth by occupying the surface sites of the Fe oligomers during hydrolysis.

Selected-area electron diffraction (SAED) patterns display 2 to 5 diffuse rings with uniform *d*-spacings averaging at 2.57, 2.26, 1.98, 1.74, and 1.50 Å for the samples with Fe/Ge molar ratios of 2 and 4. The average values are based on 22 SAED patterns. These values are comparable to the more precise *d*-spacings obtained from the powder XRD patterns. High-resolution TEM (HRTEM) images display well-developed lattice fringes with two to three sets of lattice fringes (Fig. 3).

Semi-quantitative energy-dispersive X-ray microanalyses of Fe and Ge indicate that the synthesis products have Fe/Ge atomic ratios in the 3.8 to 3.9 range for the Fe/Ge = 2 precipitates and in the 4.4 to 5.1 range for the Fe/Ge = 4 samples. It appears that the amount of Ge in the precipitate is limited to about 20 at% of the total cations (Fe+Ge) for the Fe/Ge = 2 precipitates and to 17 at% of the total cations for the Fe/Ge = 4 precipitates. In other words, the precipitated with ferrihydrite) was between 79 and 91% for the Fe/Ge = 4 experiments, but only 51–53% for the Fe/Ge = 2 tests. This would indicate a limit of Ge uptake of about 20 at% Ge at the cation sites in ferrihydrite. Because the ferrihydrite precipitates typically contain ~45 wt% Fe, the products can incorporate up to ~15 wt% Ge in their structure.

X-ray absorption spectroscopy

The Ge *K*-edge position remained unchanged with pH and solution composition. The XANES spectra and post edge features are similar to the tetrahedrally coordinated quartz polymorph of GeO_2 rather than the octahedrally coordinated rutile-like GeO_2 (Bull et al. 2004).

Ge K-edge EXAFS spectra of the precipitates formed at different pH values for Fe/Ge molar ratios of 2 and 4 are identical (Fig. 4) indicating that the local structural environments around the Ge atoms are not influenced by pH. Accordingly, for use in EXAFS fitting and further comparisons, the spectra were averaged to obtain one spectrum for each solution composition (i.e., r2 and r4). The spectra of the precipitates formed from solutions with Fe/Ge molar ratios of 43 and 54 are broadly similar although noisy above the k value of about 11 Å⁻¹. These spectra were also averaged to obtain one spectrum representing the dilute samples (r43+). As illustrated in Figure 5, the Ge-dilute average spectrum displays close similarities to the two Ge-concentrated average spectra, and this suggests that solution composition has little, if any, influence on the local structure of Ge. The spectra are different than those reported by Pokrovsky et al. (2006) for GeO₄ adsorbed onto goethite, suggesting differences in the local coordination environments of the different samples. Pokrovsky et al. (2006) also reported two co-precipitate samples showing some similarity in Fourier transforms to our samples, but their corresponding EXAFS spectra were not available and their longrange identities were shown as "undetermined."

Our EXAFS fitting strategy involved fitting the first peak in the radial distribution function (RDF) in the $R+\Delta R$ -range from 1 to 2 Å (values uncorrected for phase-shift) followed





FIGURE 2. TEM photomicrographs showing equant and platy ferrihydrite crystallites. Top left = r2 pH 5; top right = r2 pH 10; bottom left = r4 pH 5; bottom right = r4 pH 10.



FIGURE 3. HRTEM photomicrographs of ferrihydrite crystallites with rounded to hexagonal outlines and showing well-developed lattice fringes. Top left: r2 pH 10; top right: r2 pH 13; bottom left: r4 pH 2; bottom right: r4 pH 10.

by the sequential addition of Ge and/or Fe shells to simulate the first and second RDF peaks. EXAFS fitting resulted with coordination numbers of 4.8 ± 0.4 for the first shell of O atoms at distances of 1.76-1.77 Å indicating that the Ge atoms are tetrahedrally coordinated to O atoms (Table 2). These values are identical within precision to the Ge-O distances of 1.764 Å reported by Song et al. (2010) for Ge-Fe co-precipitated sixline ferrihydrite, 1.76 ± 0.01 Å in GeO₄ tetrahedra adsorbed onto goethite and a co-precipitate (Pokrovsky et al. 2006), and 1.76 ± 0.01 Å in synthetic talc (Martin et al. 1996). Other Ge-O distances based on tetrahedral crystal structures include 1.772 Å in brunogeierite, a Fe₂GeO₄ spinel (Welch et al. 2001), 1.76 \pm 0.04 Å in a diopside-like structure (Hattori et al. 2000), 1.77 ± 0.04 Å in Fe₃Ge₂O₈ (Kato et al. 1983a), and 1.76 ± 0.02 Å in Fe₁₅Ge₈O₃₆ (Kato et al. 1983b). Calculated Ge-O distances from the first-principles density functional theory include 1.77-1.81 Å for GeO₄ tetrahedra adsorbed onto FeO₆ octahedra as bidentate corner-sharing surface complexes (Li and Liu 2010). Other Ge-O distances include somewhat shorter values at 1.73 ± 0.03 Å (Price et al. 1998), 1.74 Å (Lu et al. 1985), 1.73 and 1.74 Å (Drewitt et al. 2010), and 1.72-1.74 Å (Micoulaut et al. 2006a,



FIGURE 4. *k*³-weighted Ge *K*-edge EXAFS spectra of the precipitates. Spectra identified by the Fe/Ge molar ratio (number preceding dash) and synthesis pH (number following dash).



2006b) in Ge-oxide glasses.

The second shell fitting considered four possible structural occurrences of GeO₄ tetrahedra in natural and synthetic materials: (1) as framework tetrahedra; (2) as tetrahedral sheets (doublechains or rings); (3) as single chains of tetrahedra including very short chains such as dimers; and (4) as isolated tetrahedra. The first three models involve Ge-O-Ge linkages. In the first case for framework tetrahedra, there are four Ge atoms around a central Ge at a distance of 3.16-3.32 Å, as observed in the GeO₂ glass structure where GeO4 tetrahedra are connected through corner O atoms and no-edge sharing tetrahedra exist (Lu et al. 1985; Price et al. 1998; Micoulaut et al. 2006a, 2006b). In the second case, GeO₄ tetrahedra form layers through corner-linkages, resulting in Ge-Ge distances of 3.13-3.18 Å and Ge coordination numbers of 2–3, as observed in synthetic talc (Martin et al. 1996). In the third model, there are two Ge atoms around a central Ge at a distance of 3.10 Å, observed in the high-P clinopyroxene (FeGeO₃) structure of Hattori et al. (2000) or one Ge at 3.09 Å as in Fe₃Ge₂O₈ and Fe₁₅Ge₈O₃₆ (Kato et al. 1983a, 1983b).

Simulations involving Ge as the second shell to test the presence of Ge-O-Ge linkages in the precipitate formed from a solution with the highest Ge (i.e., r2 or molar Fe/Ge = 2) resulted in a Ge-Ge distance of 3.27 ± 0.02 Å for 4 Ge. This fit

TABLE 2. Local structural parameters determined from Ge-EXAFS

		Ν	R	σ^2	$\Delta E0$	rf	rX2
r2	0	4.8 ± 0.4	1.76 ± 0.00	0.0043	1.0	0.0078	768
	MS21	12*	3.16 ± 0.05	0.0023			
	Fe1	6.3 ± 1.4	3.38 ± 0.03	0.0109			
	Fe2	1.7†	3.54 ± 0.08	"			
r4	0	4.8 ± 0.3	1.77 ± 0.00	0.0042	1.6	0.0065	487
	MS21	12*	3.15 ± 0.04	0.0020			
	Fe1	6.0 ± 1.1	3.38 ± 0.02	0.0102			
	Fe2	2.0†	3.54 ± 0.06	"			
r43+	0	4.8 ± 0.4	1.76 ± 0.00	0.0031	2.3	0.0080	29
	MS21	12*	3.14 ± 0.05	0.0013			
	Fe1	6.2 ± 0.8	3.38 ± 0.01	0.0090			
	Fe2	1.8†	3.56 ± 0.05	"			

Notes: Fit performed in *R*-space (R = 1-3.5 Å; k = 3-15 Å⁻¹); amplitude reduction factor (S_0^2) is constrained to 0.9; N = coordination number; R = interatomic distance (Å); $\sigma^2 = \text{Debye-Waller parameter } (Å^2)$; $\Delta E0 = \text{energy offset } (eV)$; rf = r-factor and rX^2 reduced chi square as the goodness-of-fit parameters. Multiple scattering path, MS21, refers to Ge-O1-O2.

* Fixed value.

+ Constrained to 8 as total Fe; Debye-Waller parameters of Fe2 were constrained to be identical with Fe1.

r43+

r4

r2

5 6

FIGURE 5. k^3 -weighted Ge K-edge EXAFS spectra and their Fourier transforms. Experimental spectra shown in black solid lines and simulations in red circle lines.

required a third shell of 4.4 Fe atoms at 3.42 ± 0.02 Å with the corresponding fitting parameters of the first shell of 4.8 ± 0.4 O at 1.76 Å. The Ge-Ge distance is too long in comparison with the Ge-Ge distances reported for dimers (3.09 Å), single chains (3.10 Å), and sheets (3.13 and 3.18 Å), but it is within the limit of the range of GeO₂ glasses. However, the second cation shell parameters (i.e., 4.4 Fe atoms at 3.42 ± 0.02 Å) are incompatible with an infinite framework of corner-linked GeO4 tetrahedra. The other possibility of small clusters of corner-linked GeO₄ tetrahedra attached to ferrihydrite is also unlikely because it would require Ge coordination numbers of 2 and smaller. Furthermore, simulation of the dilute sample where the likelihood of a Ge-O-Ge linkage is very low resulted in Ge-Ge distances that are similar to those of the concentrated samples. In support of the TEM observations that the precipitates are composed of uniform ferrihydrite crystallites, the EXAFS data suggest that there are no Ge-O-Ge linkages in the precipitates and that the GeO₄ tetrahedra are isolated and attached to Fe octahedra as in the fourth structural model which can be represented by brunogeierite, a Fe_2GeO_4 spinel (Welch et al. 2001).



FIGURE 6. *k*³-weighted Fe *K*-edge EXAFS spectra of the precipitates. Spectra identified by the Fe/Ge molar ratio (number preceding dash) and synthesis pH (number following dash).

Our next set of simulations of the Ge K-edge spectra involved Fe as the second shell and Ge or Fe as the third shell of atoms. The position of the second RDF peak was reproduced for both the Fe+Fe and Fe+Ge models; however, the qualities of the fits were not adequate. Contribution of the multiple scattering paths, as in AsO₄ tetrahedra, was tested by sequentially adding the Ge-O1-O2, Ge-O1-Ge-O2, Ge-O1-Ge-O1, and Ge-O-Fe paths derived from FEFF calculations (Ankudinov et al. 1998) based on the crystal structures of Hattori et al. (2000) and Welch et al. (2001). These multiple scattering paths are labeled MS21 (Ge-O1-O2), MS31 (Ge-O1-Ge-O2), MS32 (Ge-O1-Ge-O1), and MS22 (Ge-O-Fe) following the designations of Manceau et al. (2007). The quality of the fit improved with the inclusion of MS21 and reproduced both the shape and magnitude of the second RDF peak. As listed on Table 2, there are about 6 and 2 Fe atoms at distances of 3.38 ± 0.03 and 3.54 ± 0.08 Å. Floating both Fe shells during the fit resulted in large uncertainties (e.g., 7.8 ± 11.6 Fe at 3.38 ± 0.03 Å and 1.7 ± 2.9 Fe at 3.57 ± 0.20 Å for r2); therefore, they were constrained and optimized to 8 as the total number of Fe atoms. The resulting fit was marginally better than the fits obtained by constraining the combined Fe coordination numbers to 10, 12, and 16 (Fig. 5). The use of Ge, instead of Fe as the second metal shell at about 3.5-3.6 Å, was equally plausible when the fits were performed with the same set of parameters and constraints. This suggests that the amplitude and phase-shift functions of Ge and Fe are too close to distinguish the two types of backscattering waves by EXAFS. These local structural parameters are different than those reported by Pokrovsky et al. (2006) for a Ge-adsorbed goethite (i.e., 1 Ge at 3.30 Å) and an unknown co-precipitate with a Fe/Ge ratio of 3.6 (i.e., 1 Ge at 2.87 ± 0.04 Å and 2 Ge at 3.38 ± 0.02 Å).

Like the Ge *K*-edge EXAFS spectra, the Fe *K*-edge EXAFS spectra of the precipitates synthesized at different pH values from solutions with Fe/Ge molar ratios of 2 are identical (Fig. 6); therefore, they were averaged and presented as r2 (Fig. 7). Similarly, the spectra representing precipitates from solutions having a Fe/Ge molar ratio of 4 were averaged and presented as r4. The precipitate formed from the solution with a Fe/Ge molar ratio of 54 was presented as r54 and the precipitates formed from very dilute Ge solutions (i.e., Fe/Ge = 105 and 213) were



FIGURE 7. *k*³-weighted Fe *K*-edge EXAFS spectra and their Fourier transforms. Experimental spectra shown in black solid lines and simulations in red circle lines.

TABLE 3. Local structural parameters determined from Fe-EXAFS

		Ν	R	σ^2	$\Delta E0$	rf	rX ²
r2	01	5.4 ± 1.4	1.96 ± 0.02	0.0103	-3.1	0.0118	751
	02	0.6†	2.11 ± 0.02	и			
	Fe1	1.2 ± 0.3	3.00 ± 0.02	0.0077			
	Fe2	2.1 ± 0.6	3.43 ± 0.02	"			
r4	01	3.8 ± 0.6	1.93 ± 0.02	0.0077	-2.9	0.0103	439
	02	2.2†	2.06 ± 0.03	"			
	Fe1	0.8 ± 0.5	2.93 ± 0.05	0.0065			
	Fe2	1.1 ± 0.4	3.04 ± 0.04	и			
	Fe3	1.7 ± 0.8	3.42 ± 0.01	"			
r54	01	4.1 ± 0.9	1.95 ± 0.03	0.0085	-1.8	0.0107	252
	02	1.9†	2.08 ± 0.05	и			
	Fe1	1.6 ± 1.4	3.03 ± 0.03	0.0096			
	Fe2	1.7 ± 1.4	3.41 ± 0.03	"			
r105+	01	5.4 ± 0.9	1.98 ± 0.02	0.0105	-1.2	0.0108	488
	02	0.6†	2.16 ± 0.10	"			
	Fe1	1.5 ± 0.7	3.03 ± 0.02	0.0076			
	Fe2	1.1 ± 0.5	3.43 ± 0.02	и			
Fh6L	01	3.4 ± 0.9	1.92 ± 0.03	0.0073	-2.7	0.0128	1054
	02	2.6†	2.05 ± 0.04	"			
	Fe1	2.5 ± 2.9	3.04 ± 0.04	0.0129			
	Fe2	3.4 ± 3.9	3.43 ± 0.03	и			

Notes: Fit performed in *R*-space (R = 1.1-3.8 Å; k = 2.5-15 Å⁻¹ for r2 and r4; k = 3-13 Å⁻¹ for r54, r105+ and Fh6L]; amplitude reduction factor (S_0^2) is constrained to 0.8; N = coordination number; R = interatomic distance (Å); $\sigma^2 =$ Debye-Waller parameter (Å²); $\Delta E0 =$ energy offset (eV); rf = r-factor and rX^2 reduced chi square as the goodness-of-fit parameters.

+ Constrained to 6 as total O. Debye-Waller parameters of subsequent O and Fe shells were constrained to be identical with the first shell values.

averaged and presented as r105+. The spectra representing the different synthesis concentrations display subtle differences at high *k* but there is no trend or pattern as a function of the solution concentration. For instance, the r2 spectrum is more similar to that of the Ge-free six-line ferrihydrite (Fh6L) than to r4. If a trend existed, the r4 spectrum should have displayed more similarity to Fh6h.

EXAFS analysis of r2 indicates that the Fe-O radial distances are 1.96 ± 0.02 Å for 5.4 ± 1.4 O atoms and 2.11 ± 0.02 Å for 0.6O atoms (Table 3). The asymmetric nature of the Fe-O bonding can be explained by the large variety of bonding environments that exist in the structure, such as Fe-O-Ge, Fe-O-Fe, Fe-OH-Fe, and Fe-H₂O. Following the O shell, 1.2 ± 0.3 and 2.1 ± 0.6 Fe atoms are detected at distances of 3.00 ± 0.02 and 3.43 ± 0.02 Å. The r4 spectrum is described by two O shells having 3.8 ± 0.6 and 2.2 O atoms at 1.93 ± 0.02 and 2.06 ± 0.03 Å. The Fe shell as the next-nearest neighbors is split into 3 sub-shells at 2.93 ± 0.05 . 3.04 ± 0.04 , and 3.42 ± 0.01 Å with coordination numbers of 0.8 ± 0.5 , 1.1 ± 0.4 , and 1.7 ± 0.8 . The short Fe-Fe distance is similar to the face-sharing Fe-Fe distance in hematite. The longer Fe-Fe distances are similar to those of r2 and are typical of edge-sharing and corner-sharing arrangements observed in Fe oxyhydroxides (Manceau and Drits 1993). The Fe-Fe distance of 3.42-3.43 Å is similar to the Ge-Fe distance (i.e., 3.38 ± 0.03 Å), and Fe and Ge have similar scattering amplitudes and phase shifts, suggesting that the detection of Fe-Ge pairs at this distance would be difficult at the Fe K-edge (see supplementary materials¹). In essence, these measured local structural parameters of r2 and r4 are consistent with the classical ferrihydrite structure. The small spectral differences between r2 and r4 reflect changes imposed by the presence of Ge and other bonding constraints (Fig. 7).

EXAFS fitting of the spectra belonging to the dilute samples (r54 and r105+) also resulted in local structural parameters that are consistent with the classical ferrihydrite structure. The differences in the local structural parameters between the Ge-rich and dilute ferrihydrite precipitates are insignificant as they lie within the estimated uncertainty values.

DISCUSSION

Fitting of the Ge-EXAFS spectra indicated that Ge occurs as isolated tetrahedra surrounded by Fe atoms at nearly 3.38 Å and then by Fe or Ge atoms at nearly 3.54 Å distance for Ge-bearing ferrihydrites precipitated from both concentrated and dilute Ge solutions. These local structural parameters along with the similarity of the Ge-EXAFS spectra of the precipitates formed over a wide pH range from 2 to 13 imply that Ge is incorporated in the ferrihydrite structure. It appears based on the semi-quantitative TEM microanalyses that the incorporation is limited to about 17-20% of the total cations (Fe+Ge). The local structural data derived from Ge-EXAFS can also be explained by the adsorption of Ge onto very small ferrihydrite crystallites (i.e., 1–2 nm) and their aggregation aided by the highly reactive surface Ge. However, there are no indications for the presence of subgrains within the ferrihydrite crystallites, which measure about 5-6 nm. In addition, the uniformity of the ferrihydrite crystallite size and shape across the wide pH and compositional ranges, and the continuity of the lattice fringes across the particles would dictate against the occurrence of Ge as an adsorbed species.

In the new ferrihydrite structure (Fhyd6) of Michel et al. (2010), 20% of the total iron occurs in tetrahedral coordination. Maillot et al. (2011), Guyodo et al. (2012), and Peak and Regier (2012) claimed to have found evidences for the presence of 15 to 40% tetrahedral iron (^{IV}Fe) in ferrihydrite. We disagree with the EXAFS interpretation of Maillot et al. (2011) (20–30% ^{IV}Fe) because it suffers from unconstrained fitting of Fe-O pairs (Manceau 2011; Figs. S2 and S4 in the Supplementary materials¹).

As demonstrated in the supplementary materials¹, the uncertainties in the determination of the Fe-O distances (i.e., ±0.01 Å) and the coordination numbers (i.e., 20% on each O shell) reported by Maillot et al. (2011) to calculate the amounts of ^{IV}Fe are overly optimistic. Our estimated minimum uncertainty levels associated with unconstrained fitting are ± 0.02 Å for the Fe-O distances and 30% for the coordination numbers (Table S2). These uncertainties would be compounded by the experimental error, including statistical noise and systematic errors resulting from measurement and data reduction such as the shell-by-shell Fourier filtering strategy of Maillot et al. (2011). Uncertainties in the calculation of ^{IV}Fe would be 29-50% at best and as high as 52–116% (Fig. S4¹) suggesting that the amounts of ^{IV}Fe in ferrihydrite reported by Maillot et al. (2011) are not statistically different from those in maghemite (37.5%) and akaganeite (0%). Maillot et al. (2011) also determined the average Fe-O distance by the Landweber iterative method of Rossberg and Funke (2010). This calculation is not convincing either because there is limited information with respect to the total number of iterations. In the

¹ Deposit item AM-13-053, Supplementary Material including table and figures. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www. minsocam.org, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

Landweber approach, fit improvement is continuous, increasing with the number of iterations; however, there is a limit to the total number of iterations for producing statistically meaningful data, which requires an independent knowledge of the experimental errors associated with each data set. In summary, the fits performed by Maillot et al. (2011) at an extended *k*-range are inconclusive in terms of providing the needed finesses for determining the Fe-O distances in ferrihydrite in support of the tetrahedral Fe hypothesis.

To further elaborate on the claimed presence of 20 to 30% ^{IV}Fe in ferrihydrite, we compared the Fe-EXAFS spectra of nano- and micro-scale maghemite samples (Corrias et al. 2000) to our Ge-free Fh6L (Figs. 8A-8H). First of all, Fourier transform magnitudes of the nano- and micro-sized maghemite clearly show that the Fe coordination numbers of the micro-scale maghemite are expectedly greater than those of the nano-scale counterpart while the oxygen coordination numbers remain unchanged, in agreement with the observations of Maillot et al. (2011). In addition, there are remarkable similarities between the long-range structures of the ferrihydrite with tetrahedral Fe (akdalaite model) and maghemite (Manceau 2011). Similarities also exist in the short-range structures as depicted by Michel et al. (2007, 2010). Furthermore, a reevaluation of the data presented by Maillot et al. (2011) indicates that the amount of ^{IV}Fe in ferrihydrite is not very different from that of maghemite (Supplementary materials1). These observations rationalize the use of the Fe-EXAFS spectrum of nano-scale maghemite of Corrias et al. (2000) in our comparative evaluation. A clear shift to lower distances of the imaginary part corresponding to the O shell is seen in the Fourier transform of maghemite relative to six-line ferrihydrite

data, consistent with the presence of ^{IV}Fe in maghemite (Fig. 8F). The shift is present regardless of the integration range (i.e., k = 2.3-14.2 Å⁻¹ or 2.3–16.1 Å⁻¹). This is a definite point in that six-line ferrihydrite and maghemite have different Fe-O bonding environments and it argues strongly against the findings of Maillot et al. (2011) about the occupation of tetrahedral sites by Fe in ferrihydrite.

The other statement put forward by Maillot et al. (2011) from data fitting of the O shell is that the detection of ^{IV}Fe would require EXAFS measurements at extended *k* ranges of 17 Å⁻¹ and cryogenic temperatures. We tested this hypothesis by comparing our six-line ferrihydrite data recorded at room temperature to that of Manceau (2011) measured at liquid He temperature at *k* values of up to 16.1 and 14.2 Å⁻¹. Figure 8b shows that the peak maximum of the Fe-O distribution is shifted to higher distances at low temperature, because the distribution of the Fe-O distances is wide and asymmetric, as discussed by Manceau (2011). At room temperature, this effect manifests itself by a broadening of the Fe-O peak of six-line ferrihydrite to higher *R* values relative to maghemite (Fig. 8F). Thus, the displacement of the Fe-O distance the need for low-temperature measurements for the detection of ^{IV}Fe.

The argument of Peak and Regier (2012a) based on Fe *L*-edge XANES spectra is questionable as discussed in Manceau's (2012b) rebuttal because Peak and Regier (2012b) failed to acknowledge that the same spectral feature, interpreted as evidence for tetrahedral Fe, has been reported for cobalt and interpreted as a disorder effect (distribution of crystal field splitting). The claim of Guyodo et al. (2012) for the presence of tetrahedral



FIGURE 8. Comparison of k^3 -weighted Fe K-edge EXAFS spectra of ferrihydrite and maghemite and their Fourier transforms superimposed with imaginary parts. (**A** and **B**) six-line ferrihydrite at room (black) vs. liquid He (blue) temperatures; (**C** and **D**) nano- (red) vs. micro-sized (purple) maghemite; (**E** and **F**) six-line ferrihydrite at room temperature vs. nano-sized maghemite with integrations to k values of 16.1 (black and red); (**G** and **H**) six-line ferrihydrite at liquid He (blue) temperature vs. nano-sized maghemite (red). Six-line ferrihydrite spectrum collected at liquid He temperatures are from Manceau (2011) and maghemite spectra from Corrias et al. (2000). The y-scales are identical for all spectra and Fourier transforms.

iron in a synthetic six-line ferrihydrite sample based on X-ray magnetic circular dichroism measurements performed at Fe *K*- and *L*-edges is not convincing: first for the reasons outlined in the rebuttal papers by Manceau (2012b) and Hocking et al. (2012), and second because of the mistaken attribution of the antiferromagnetic properties to tetrahedral and octahedral Fe (Francombe and Rooksby 1959) instead of face-sharing Fe octahedra (Pernet et al. 1984; Drits et al. 1993b).

The ratio of octahedral Fe (VIFe) to tetrahedral Fe (IVFe) in the akdalaite model (i.e., VIFe/IVFe=4) would be analogous to our r2 and r4 samples with Fe/Ge \approx 4 if we assume that Ge substitutes for ^{IV}Fe, as proposed by Song et al. (2010). In this case, our Ge-EXAFS should produce data similar to the local structure around ^{IV}Fe in Fhyd6 and our Fe-O coordination numbers and distances should reflect only the octahedral Fe in Fhyd6. In Fhyd6, ^{IV}Fe is bonded to 10 VIFe at about 3.38 Å, whereas our Ge-EXAFS spectra indicate that there are only six Fe atoms at that distance. On average, each VIFe sees 7.5 VIFe at distances between 2.91 and 3.49 Å. Based on the Fe-EXAFS of Ge-bearing ferrihydrites, there are only 1 to 2 Fe at 2.93-3.04 Å and ~2 Fe at 3.42-3.43 Å, and this accounts for less than half of the VIFe of Fhyd6 in the 2.91-3.49 Å range. However, this difference is marginal as it can be explained by disorder. The Ge-O distances (1.76 ± 0.01) Å) are much smaller than the ^{IV}Fe-O distances of Fhyd6 (1.91 \pm 0.08 Å). A Ge for ^{TV}Fe substitution would require the Ge-Fe dis-



FIGURE 9. Polyhedral representation of ferrihydrite (f-phase) using a $2 \times 2 \times 1$ supercell with 50% Fe (brown) occupancy (**a**) and with Ge tetrahedra (violet) occupying 25% of tetrahedral sites in the BA and CA anion layers (**b**) or the AB and AC layers (**c**). Total tetrahedral site occupancy of the supercell is 12.5%. Note the changes in Fe occupancy and O (red) and OH (gray) distribution among the anion layers due to Ge incorporation. With Ge corner-linked to four edge-sharing FeO₆ trimers, the f-phase possesses Keggin-like clusters in two different orientations (**b** and **c**) that are symmetrically equivalent. Also shown is the unit cell of the Fhyd6 structure (**d**) for its similarity to the f-phase with Ge occurring along BA and CA layers (**b**). Fhyd6 structure (Fe1 = light brown; Fe2 = pink; Fe3 = yellow) is based on Michel et al. (2007).

tances to be shorter than the ^{IV}Fe-^{VI}Fe distances of Fhyd6 because our Fe-O distances $(1.98 \pm 0.06 \text{ Å})$ are comparable, within the limits of error, to the ^{VI}Fe-O distance $(2.01 \pm 0.08 \text{ Å})$ of Fhyd6. However, this is not the case. The Ge-Fe distances of 3.38 ± 0.03 and 3.54 ± 0.08 Å are similar to the ^{IV}Fe-^{VI}Fe distances of $3.38 \pm$ 0.01 and 3.56 ± 0.07 Å of Fhyd6. In addition, our EXAFS data indicate that the local structures of Ge and VIFe do not change with increased Ge substitution, and this casts serious doubts on the presence of ^{IV}Fe in the ferrihydrite structure. If ^{IV}Fe existed in the ferrihydrite structure, then the measured Fe-O distances would have been longer in the Ge-rich precipitates (r2 and r4) than those in the Ge-free Fh6L precipitate. The similarity of the average Fe-O distances calculated from the data of Table 3, which are 1.98 Å for r2, 1.98 Å for r4, and 1.99 Å for Fh6L, does not support the presence of ^{IV}Fe in the ferrihydrite structure. Furthermore, the similarity of the Fe-EXAFS spectra of r2, r4, r105+, and Fh6L, representing the high, low and no Ge-bearing ferrihydrite precipitates, indicates that the local structure of Fe is not affected by the presence of Ge. This observation dictates against the presence of ^{IV}Fe.

The local structure of Ge can be conceptualized in the defectfree phase (i.e., "f-phase") of the classical ferrihydrite structure through the use of a $2 \times 2 \times 1$ supercell of the f-phase (Fig. 9). The f-phase is composed of O atoms and hydroxyls closely packed with ABACA stacking and Fe randomly occupying 50% of the octahedral sites in each anion layer (Drits et al. 1993a; Manceau 2009, 2011). Distribution of Fe across the anion layers is such that there are no face-sharing arrangements between Fe octahedra along the B and C planes of the structure and that hydroxyls are confined to the A and oxygen to the B and C layers (Fig. 9a). The observed Fe-Fe distances of 3.00 to 3.04 Å in the Ge-bearing ferrihydrite precipitates would correspond to the 2.96 Å distance of the f-phase representing first nearest pairs of edge-sharing octahedra. In contrast, the 3.41–3.43 Å distances correspond to the 3.30-3.50 Å distances representing the average of the second nearest pairs of edge-sharing and the bridging or double corner-sharing octahedra. This distribution partly explains why the effective coordination numbers for the second metal shell reported in Table 2 are greatly reduced.

Using EXAFS-derived local structural data. Ge can be distributed in the f-phase with the following constraints: (1) Ge occupies tetrahedral sites in the structure; (2) there are no Ge-O-Ge linkages between the tetrahedra; and (3) no face-sharing between the Ge tetrahedra and Fe octahedra is allowed. The resulting long-range configuration is of Ge filling empty tetrahedral sites by occupying every other tetrahedral site along the a and b directions in alternating octahedral layers (i.e., BA and CA or AB and AC layers of the close-packing O/OH framework) (Figs. 9b and 9c). This corresponds to 25% occupancy of the tetrahedral sites along the layers with Ge, or 12.5% of the total tetrahedral sites. Three adjacent octahedral sites in the same laver surrounding the tetrahedra must be vacant to avoid face-sharing arrangement between the Ge tetrahedra and Fe octahedra, which would mean equal number of tetrahedra and octahedra in these layers. This results in a 75% octahedral vacancy along the layers with Ge and 25% along the adjacent layers without Ge (Fig. 10). Although this configuration differs from the 50% occupancy of each anion layer in the f-phase, the bulk occupancy remains similar at 50%.



FIGURE 10. Polyhedral representation of Ge (violet) occupying tetrahedral sites along the BA and CA layers of ferrihydrite (f-phase).

The "apical O atoms" of the tetrahedral sites are located along the B or C layers of the f-phase; therefore, the B and C layers will have Ge-O-Fe and Fe-OH-Fe linkages with Fe-OH-Fe being three times as many as the Ge-O-Fe linkages. The A layer, on the other hand, will have three times as many Ge-O-Fe linkages as the Fe-OH-Fe linkages. The protons, confined to the A layers in the Ge-free f-phase, will have to be redistributed to prevent Ge-OH-Fe linkages because this O atom is already saturated, being bonded to three edge-sharing Fe octahedra. Thus, in addition to reordering of the Fe occupancy, three-quarters of the OH sites would have to move from the A to B and C layers. Like the Fe redistribution, this does not change the bulk or average proportions of OH and O in the f-phase, and a stoichiometry close to FeOOH is maintained in agreement with Hiemstra and van Riemsdijk (2009). In addition, each Fe octahedron contains three O atoms and three hydroxyls, as for the Ge-free f-phase and all iron oxyhydroxides. With the incorporation of Ge in the structure occupying 12.5% of the total tetrahedral sites and accompanying redistribution of the Fe occupancy across the layers, Ge tetrahedra form 20% of the total Ge+Fe cation sites, which is consistent with the constant Ge content of the r2 and r4 precipitates.

Occurrences or motifs of Ge in the BA+CA and AB+AC anion layers are identical within the limits of the symmetry elements (Figs. 9b and 9c). Rotating the supercell around the *c*-axis and flipping it across the *a-b* plane is sufficient to demonstrate that the two motifs are indistinguishable. This is also confirmed by the close-packing notations as illustrated on Figure 11 with sequences that are equivalent through the lattice symmetry. The two motifs have the same XRD pattern and can coexist in the same crystal. This means that it would be possible to maintain 50% Fe occupancy along individual layers as in the f-phase. In this case the mosaic Ge-Fe crystals would be short-range ordered, but long-range disordered with antiphase boundaries between the BA+CA and AB+AC Ge domains.

The local structure of Ge as illustrated on Figure 9 is such that a Ge tetrahedron is coordinated to 4 edge-sharing FeO₆ trimers or 12 FeO₆ octahedra through sharing of a common oxygen. This means that the local arrangement of ^{IV}Fe in Fhyd6 or the Kegginlike motif is possible in the f-phase of the classical ferrihydrite structure. The Fe1 octahedra of Fhyd6 (Fig. 9d; Michel et al. 2007) would then correspond to the octahedral layers defined by the AB and AC (Fig. 9b) or BA and CA (Fig. 9c) anion layers



FIGURE 11. Sketch of atomic positions in a $2 \times 2 \times 1$ supercell of the f-phase demonstrating the identical nature of the two motifs arising from the incorporation of Ge in BA+CA and AB+AC anion layers with close-packing notations. Fe = light brown; Ge = violet; O/OH = red.

of the f-phase. It is possible that the flexibility of the f-phase in terms of accommodating tetrahedral ions with a Keggin-like motif may have contributed to some of the disagreements in the literature. What is needed is a justification for the coordination change from ^{VI}Fe to ^{IV}Fe during the hydrolysis of Fe(H₂O)₆ leading to the nucleation of ferrihydrite. The evidence suggests that Fe³⁺ is present in octahedral coordination in oxygenated ionic solutions and that initial polymerization of Fe(O,OH)₆ octahedra proceeds through the formation of dimers, trimers, and tetramers (e.g., Bottero et al. 1994; Rose et al. 1997). In contrast, tetrahedral coordination of Fe³⁺, as observed in maghemite, appears to require the presence of organic compounds such as citric acid and/or Fe²⁺ in the starting solution.

In conclusion, the findings of the present study indicate that there is no compelling evidence for the presence of tetrahedrally coordinated iron in the ferrihydrite structure. Furthermore, the classical model does not require the transition of octahedrally coordinated Fe in solution into a tetrahedral coordination in the ferrihydrite precipitate. Incorporation of Ge tetrahedra in the ferrihydrite structure is possible through the redistribution of octahedral Fe site occupancies and protonated O atoms in the f-phase. The flexibility of the classical ferrihydrite model in terms of accommodating a Keggin-like arrangement, possibly with two distinct orientations within the same crystal, allows tetrahedrally coordinated ions, such as Ge and possibly Si, to be incorporated in an octahedrally coordinated Fe structure. That is, there is no need to invoke Keggin-like clustering of tetrahedrally coordinated Fe in the akdalaite model of the ferrihydrite structure (e.g., Michel et al. 2010; Harrington et al. 2011; Xu et al. 2011) as the structure of Ge-free or Ge-bearing ferrihydrite can be readily rationalized using the existing f-phase.

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