

Ferrosilicate stabilization controls the anomalously high Fe(III) concentration at alkaline pH

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Abstract

Elevated concentrations of dissolved Fe(III) in silicon-rich, alkaline cementitious pore solutions deviate strongly from the solubility limits controlled by the precipitation of ferric (hydr)oxides. This behavior is commonly attributed to the formation of metastable iron-bearing phases, yet growing experimental and modelling evidence challenges this interpretation. In the study presented here, we analyze the aqueous speciation and solid phase evolution in the Fe(III) – Si(IV) – H₂O system. We demonstrate that the solubility of dissolved Fe(III) is governed by the stabilization of siliceous ferrihydrite, a hitherto uncharacterized amorphous corrosion product forming a solid solution with pure 2-line ferrihydrite at increasing levels of silicon incorporation. Spectroscopic investigations into the local electronic structure of siliceous ferrihydrite reveal a mixed tetrahedral/octahedral coordination environment, where both the emergence of structural Fe – Si motifs as well as fraction of tetracoordinated Fe(III) are mutually consistent with the phase composition derived from mass balance calculations. We further assign the elevated solubility of iron at pH 12.5 to 13.0 to the stabilization of Fe(OH)₃SiO(OH)₃[–] in equilibrium with siliceous ferrihydrite, conflicting its conventional assignment to the formation of γ -FeOOH(s). Together, these findings corroborate a coherent picture, identifying aqueous ferrosilicate complex formation as the key factor, controlling the anomalously high concentration of Fe(III) in alkaline, silicon-bearing environments.

Keywords

iron, silicon, XAS, quantum chemical calculations, thermodynamic modelling

Introduction

Iron (hydr)oxides are ubiquitous in natural and engineered systems, acting as key regulators of contaminant transport in soils, groundwaters and nuclear processing environments [1–3], driving corrosion processes that influence the durability and degradation of cementitious materials [4–7], while also enabling applications in wastewater treatment, protective coatings [8], and electrochemical energy conversion [9]. Their formation proceeds via metastable intermediates, most notably, 2-line ferrihydrite, a highly reactive and thermodynamically unstable Fe(III) hydroxide that serves as a precursor to more crystalline phases such as hematite and goethite [10, 11]. In the presence of silicon, however, these transformation pathways are accompanied by a pronounced increase in the aqueous iron concentration [12, 13]. This departure from classical solubility constraints is commonly assigned to the formation of metastable intermediates that buffer the aqueous concentration of Fe(III) far above the theoretical solubility limit imposed by the formation of thermodynamically stable Fe (hydr)oxides. Yet, this conventional picture has recently been called into question by a number of experimental and modelling observations [5, 14], instead pointing towards a strong complexation between dissolved Si(IV) and Fe(III) at alkaline pH.

It is well established that Si(IV) forms a striking variety of aqueous complexes in the presence of the trivalent aluminium cation, with no fewer than 10 aqueous aluminosilicate complexes of varying degrees of polymerization characterized to date [15–21]. In contrast to the extensive work on the speciation of aluminium in silicon-bearing solutions, the corresponding coordination chemistry of the ferric cation in the Fe(III) – Si(IV) – H₂O has received far less attention. Absorbance measurements on the solubility of amorphous silica in ferric nitrate solutions provide qualitative evidence for the formation of the aqueous ferrosilicate cation from Fe³⁺ and Si(OH)₄(aq) at pH < 4.0 [22, 23]. Despite a number of thermodynamic reviews attributing the increase in aqueous Fe(III) solubility in dilute acidic electrolytes to the formation of FeSiO(OH)₂²⁺ [24, 25], no conclusion can be drawn with regard to the speciation of Fe(III) and Si(IV), either at high pH, or in analogy to the complexation of other metal cations [25]. Pokrovski et al. [26] investigate the influence of aqueous silica on the hydrolysis of Fe(III) nitrate and chloride salts at acidic to highly alkaline pH and observe significant changes to the local coordination environment of iron in the presence of 0.05 to 0.16 M Si. Although the authors derive coordination numbers in line with complex stoichiometries of Fe₂Si_{1–2} and Fe₃Si_{2–3}, the precise stoichiometry and thermodynamic stability regime of aqueous ferrosilicate complexes at alkaline pH remains subject to considerable uncertainty, primarily due to the limited experimental data available. In addition to the affinity of dissolved Fe(III) and Si(IV) in solution, silicon is also known to significantly inhibit Fe(III) polymerization and solid phase (trans)formation [12, 13, 26, 27]. Cismasu et al. [12] demonstrate that silicate oxoanions severely impede the degree of Fe(O,OH)₆ polymerization and particle growth. Precipitates formed at an iron to silicon ratio of [Fe]/[Si] < 1 lead to the formation of structurally disordered ferrihydrite and the co-precipitation of an amorphous Fe-bearing silica phase, featuring a homogeneous Si distribution at nanometer scale. Other studies on the formation of mineral precipitates in the Fe(III) – Si(IV) – H₂O system demonstrate that the degree of Fe polymerization is minimized at equimolar elemental concentrations of [Fe]/[Si] = 1 at pH 3.0 to 10.0, where 3-dimensional particle growth is favored in the excess of either mineral constituent [27]. Although the authors acknowledge substantial changes in the next-nearest coordination shell of iron [27], it has been reported that the addition of an Si shell did not significantly affect the quality of fits to the experimentally measured spectra. In a study regarding the influence of Si on the transformation of corrosion products at alkaline pH [13], it was shown that minor amounts of silicon (0.1 to 0.5 mM, equivalent to an [Fe]/[Si] of 200 to 40) retard the transformation of the amorphous corrosion product 2-line ferrihydrite (2l – Fe(OH)₃(s)) to the crystalline phase goethite (α – FeOOH(s)), with rates of solid phase transformation decreasing exponentially as a function of [Si]. In addition to the uptake of large amounts of silicon into the structure of the poorly-ordered initial corrosion product 2-line ferrihydrite [12, 27], the observed retardation was tentatively attributed to the stabilization of an aqueous ferrosilicate complex that elevates the total amount of aqueous Fe(III) at successively higher silicon concentrations. Taken together, these observations underscore that no study has yet examined the combined influence of iron and silicon on aqueous complex formation and the solid phase modification systematically.

This work elucidates the molecular mechanisms governing Fe – Si interactions by integrating bulk spectroscopic analyses, solubility measurements, quantum mechanical calculations and thermodynamic modelling

techniques. Fe and Si K-edge X-ray absorption spectroscopy (XAS) was employed to resolve the local coordination environment of Fe(III) and Si(IV) within solid mineral phases, enabling direct identification of structural Fe – O, Si – O and Fe – Si motifs within the first and second coordination shell of both absorber atoms. The observed changes in local coordination unambiguously indicate the formation of a hitherto uncharacterized Fe – Si hydroxide solid, hereafter referred to as siliceous ferrihydrite $((\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)(\text{H}_2\text{O})_y)$. Synchrotron XAS of aqueous samples revealed analogous modifications in the first and second coordination shell of Fe(III), consistent with the stabilization of polynuclear ferrosilicate complexes in Si-bearing alkaline solutions. Time- and composition-resolved solution analyses by inductively coupled plasma optical emission spectroscopy (ICP-OES) were used to quantify the partitioning of Fe and Si between aqueous and solid phases, thereby allowing the quantification of solubility products of siliceous ferrihydrite. These experimental datasets were integrated with thermodynamic modeling (TDM) to evaluate the stability of Fe(III) complexes and solid phases under highly alkaline conditions. Finally, the structure and stability of ferrosilicate complexes derived from solubility-based TDM were independently analyzed by density functional theory (DFT) calculations. Comparison of candidate Fe(III) – Si complex structures and spin states indicates that the high-spin $(\text{OH})_3\text{Fe} - \text{O} - \text{Si}(\text{OH})_3$ complex represents the most stable configuration, both in remarkable agreement with the speciation derived from TDM and consistent across all implicit solvent models considered. Together, these approaches establish a coherent picture linking the speciation of Fe and Si in solution with the structural and compositional evolution of the solid phases, thereby providing molecular-level insight into their chemical affinity across a wide range of natural and engineered systems.

Results and discussion

The elevated solubility of iron in the presence of silicon can be attributed to a number of interrelated phenomena, that become operative at different initial silicon concentrations and levels of alkalinity. These include the preferential adsorption of silicon on the metastable and crystalline mineral end-members of the Fe(III) – H_2O system, the emergence of a siliceous ferrihydrite, forming a solid solution with silicon-free ferrihydrite and the stabilization of aqueous ferrosilicate complexes that increase the Fe concentration far above the thermodynamically controlled solubility limit achieved in the absence of silicon. In the following subsections, these competing phenomena will be examined in turn.

Aqueous concentration measurements

In the presence of 2 mM Si ($[\text{Fe}]/[\text{Si}] = 10/1$), the equilibrium solubility of iron increases exponentially with increasing pH (Supporting Information, Figure S1a, slope = 1). The measured progression of $[\text{Fe}]$ is shifted in negative y-direction by 0.90 ± 0.05 log units, corresponding to an approximate excess Gibbs free energy of $\Delta G_{ex}^\circ = -4553 \pm 25 \text{ J mol}^{-1}$ w.r.t. the standard molar Gibbs free energy of formation of 2l – $\text{Fe}(\text{OH})_3(\text{s})$ ¹. In the presence of 20.0 mM Si ($[\text{Fe}]/[\text{Si}] = 1/1$), the total solubility of iron can be subdivided into two distinct regions (Supporting Information, Figure S1c). Across the first interval at $\text{pH} \geq 13.2$, the measured aqueous iron concentrations are in agreement with the thermodynamically predicted solubility limit, as controlled by the precipitation of 2l – $\text{Fe}(\text{OH})_3(\text{s})$ from $\text{Fe}(\text{OH})_4^-$ [28]. For $\text{pH} < 13.2$, the measured $[\text{Fe}]$ significantly exceed their theoretical counterparts by one order of magnitude, reaching equilibrium values of 8.7×10^{-6} M towards pH 12.5 after one month. Lastly, in the presence of 200.0 mM Si, i.e., at an initial $[\text{Fe}]/[\text{Si}]$ ratio of 1/10, the total aqueous iron concentration uniformly exceeds the solubility limit of 2-line ferrihydrite, approaching values of approx. 2.0×10^{-3} M at $\text{pH} \leq 13.0$ (Supporting Information, Figure S1e). Coinciding with the progression of dissolved iron, the aqueous silicon concentration increases as a function of the pH for both the 2.0 mM and 20.0 mM series, and decreases exponentially as a function of equilibration time, irrespective of the initial concentration (Supporting Information, Figure S1). As evident from $[\text{Si}]$ displayed in Figure S1b, the total dissolved silicon concentration increases from approx. 2.0×10^{-4} M at pH 12.3 to 1.0×10^{-3} M at pH 13.5. Likewise, the total aqueous silicon concentration emerging at equimolar Fe and Si amounts to 1.0×10^{-2} M at pH 12.6 and 1.3×10^{-2} M at pH 13.5, equivalent to 50 % and 65 % of

¹The standard equilibrium constant of 2-line ferrihydrite formation according to $\text{Fe}^{3+} + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{l} - \text{Fe}(\text{OH})_3(\text{s}) + 3\text{H}^+$ is $\log_{10}K^\circ = -3.50 \pm 0.40$ [25] in the absence of silicon and $\log_{10}K^\circ = -4.40 \pm 0.40$ the presence of 2 mM Si (compare Figure S1a).

the initial amount of Na_2SiO_3 dissolved. For a silicon concentration of 200.0 mM, the total dissolved $[\text{Si}]$ remains independent of the pH, plateauing at 65 % of the initial amount of Na_2SiO_3 dissolved. Note that the total aqueous silicon concentration remains undersaturated with respect to amorphous $\text{SiO}_2(\text{s})$ for all initial silicon concentrations considered.

Structural characterization of siliceous ferrihydrite

The stabilization of siliceous iron hydroxides at alkaline pH coincides with a rapid decrease in the aqueous silicon concentration by approx. 60 % w.r.t. the initial amount dissolved (Supporting Information, Figure S1). For small amounts of silicon (0.1 to 0.5 mM), the apparent decrease is caused by the initial uptake of Si by the amorphous corrosion products 2-line ferrihydrite and the preferential adsorption of silicon onto the terminal sites of goethite at later equilibration stages [29] (Supporting Information, Note E). In the presence of 20.0 mM Si, i.e., at equimolar initial amounts of $[\text{Fe}]$ and $[\text{Si}]$ (Figure S3d), phase transformation is prevented entirely. As the formation of goethite was not observed, the amount of silicon scavenged from solution must conversely have been either adsorbed or structurally incorporated into its amorphous precursor 2-line ferrihydrite, forming siliceous ferrihydrite.

In conjugation with the measured initial amounts of iron and silicon dissolved, the equilibrium concentration of both solutes can be used to determine the molar ratios of Fe/Si in the precipitate as a function of the pH via mass-balance approaches (Supporting Information, Table S1). Siliceous iron (hydr)oxide samples equilibrated in the presence of 10 mM Si are both more rich in iron ($\text{Fe}_2\text{O}_3/\text{SiO}_2 = 1.92$) and structural water ($\text{H}_2\text{O}/\text{SiO}_2 = 4.25$) compared to those samples stabilized in the presence of 20.0 and 200.0 mM. Siliceous ferrihydrite compounds equilibrated in the presence of 20.0 mM Si feature increasingly higher Fe/Si ratios with increasing pH. Thermogravimetric measurements further highlight that the depletion of structural Fe coincides with progressively lower weight losses relative to 2-line ferrihydrite (Supporting information, Figure S4). Concomitant to the decrease in the solid Fe/Si ratio at successively lower pH, samples stabilized in the presence of 20.0 mM Si feature successively lower amounts of structural water (Table S1), resulting in a final wet molecular weight of $M_w = 334.6 \text{ g mol}^{-1}$ at pH 13.4 and $M_w = 230.5 \text{ g mol}^{-1}$ at pH 12.7, respectively. Samples equilibrated in the presence of 200.0 mM Si on the other hand do not feature a systematic change in their Fe/Si ratio as a function of the pH. As their formation yields a pH-independent solubility limit after one month of equilibration time, we derive an average stoichiometric ratio of $\text{Fe/Si} = 0.52 \pm 0.04$. Measured variations in the solid Fe/Si ratio translate into an average of 1.24 ± 0.08 equivalents of structural H_2O per unit SiO_2 , corresponding to a molecular weight of $M_w = 124 \pm 4 \text{ g mol}^{-1}$.

X-ray absorption spectroscopy at the Fe K-edge reveals that variations in the solid Fe and Si contents are accompanied by systematic changes in the local coordination environment of Fe at progressively higher Si. Correspondingly, Si K-edge spectra indicate that the local coordination environment of silicon evolves with increasing Fe/Si ratios, thus pointing towards the formation of siliceous ferrihydrite containing Si and Fe. Figure 1 illustrates the full normalized Fe K-edge XANES (a) and pre-edge (c) spectra, together with the k^3 -weighted radial distribution functions (b) and k^2 -weighted EXAFS spectra (d) of selected (siliceous) iron hydroxide compounds aged for 24 hours in the absence of dissolved silicon ($2\text{l} - \text{Fe}(\text{OH})_3(\text{s})$), in the presence of 10.0 mM and 20.0 mM Si as well as polynuclear aqueous Fe(III) stabilized in the presence of 200.0 mM Si. Equilibration at higher dissolved silicon concentrations introduces a systematic change to the integrated peak intensity and position of the pre-edge feature located at approx $7113.5 \pm 0.5 \text{ eV}$, due to $1\text{s} \rightarrow 3\text{d}$ (quadrupolar) and $1\text{s} \rightarrow 4\text{p}$ (dipolar) electronic transitions in Fe(III) [30, 31]. At $[\text{Si}] = 0.1 \text{ mM}$, XANES spectra recorded feature a significantly reduced pre-edge intensity compared to the spectra of samples aged in the presence of higher initial silicon concentrations. In agreement with theoretical predictions [32, 33], the normalized pre-edge spectrum (Figure 1c) can be fitted with two components centered at ~ 7112.9 and $\sim 7114.1 \text{ eV}$ as well as an additional centroid just above 7115.0 eV . In comparison to the pre-edge feature of 2-line ferrihydrite, the observed extra transition is significantly reduced in intensity, thereby indicating a higher degree of $\text{Fe}(\text{O}, \text{OH}, \text{H}_2\text{O})_6$ polymerization, characteristic to the octahedrally coordinated goethite ($\alpha - \text{FeOOH}(\text{s})$) [13, 34]. The observed enhancement pre-edge feature intensity and the successive transition towards a less centrosymmetric, tetrahedral coordination environment is in agreement with the XRD spectra of various siliceous iron hydroxides equilibrated in the presence of 0.1 mM to 20.0 mM Si (Figure

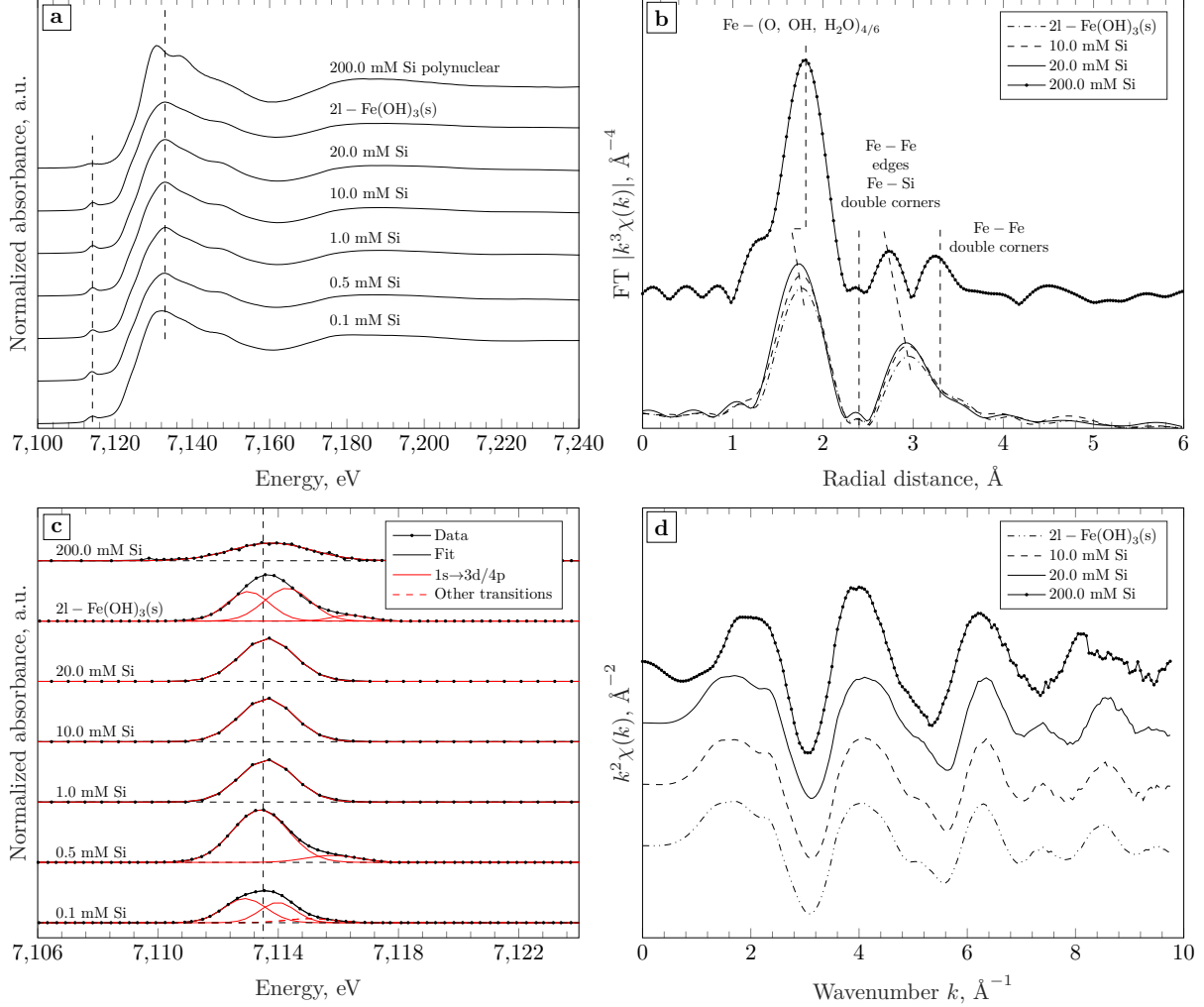


Figure 1: Normalized Fe K-edge XANES and EXAFS spectra of siliceous iron hydroxides at pH 13.4, containing varying amounts of Na₂SiO₃. Figures 1a and 1c display the normalized full XANES and pre-edge spectra of 2-line ferrihydrite aged for 24 hours in the absence of (2l-Fe(OH)₃(s)) and in the presence of 0.1 mM to 200.0 mM Si. Figures 1b and 1d show the Fourier transformed and k^3 -weighted Fe K-edge EXAFS spectra of 2-line ferrihydrite and the siliceous iron hydroxides formed in the presence of 10.0 mM and 200.0 mM Si.

S4). For silicon concentrations exceeding 0.5 mM, the recorded pre-edge feature rises and shifts towards successively higher energies and can be fitted by mostly one dominant component centered at ~ 7113.7 eV. This is indicative of a mixed tetrahedral and octahedral coordination of the ferric cation, resembling the local electronic structure of Fe-doped LiAlO₂, yoderite and other 5-coordinated Fe(III)-bearing minerals [34, 35]. Approaching an initial silicon concentration of $[\text{Si}] = 20.0$ mM, it is further evident that the extra transitions above 7115.0 eV, commonly assigned to long-range order, related to 3d orbitals of neighboring Fe [36], diminish, and the corresponding experimentally measured pre-edge can be fitted by one single component. For the polynuclear aqueous spectrum aged in the presence of 200.0 mM Si(III) on the other hand, the pre-edge feature is significantly broadened, indicating a shift towards a more centrosymmetric, octahedral coordination environment, together with minor amounts of four- and five-coordinated Fe(III) [34, 37]. Fourier-transformed k^3 -weighted EXAFS spectra (Figure 1b) reveal that the observed increase is directly associated with substantial changes in the local coordination environment of Fe(III). In comparison to the radial distribution function of pure 2-line ferrihydrite, compounds aged in the presence of 10.0 mM and 20.0

mM Si feature increasingly higher Fe – (O,OH,H₂O)_{4/6} and Fe – Fe edge contributions at approx. 2.0 Å and 2.4 to 2.9 Å, respectively [26]. No evidence was found for a simultaneous increase in the magnitude of Fe – Fe double corner contributions at 3.2 Å within the second coordination sphere of the ferric cation. Due to the topology of the unit cell of goethite, the thermodynamically stable variant of the FeOOH(s) polymorphs generally features Fe – Fe edge and double corner contributions of comparable magnitude [38]. By analogous reasoning, the metastable iron hydroxide lepidocrocite (γ – FeOOH(s)) features a pronounced Fe – Fe edge and a comparably negligible Fe – Fe double corner contribution. It can thus be ruled out that the observed increase of the first Fe – (O,OH,H₂O)_{4/6} contribution to the RDF recorded is due to the stabilization of either lepidocrocite or goethite. In comparison to the local coordination environment of Fe(III) in (Fe₂O₃)_x(SiO₂)_y(H₂O)_z(s), the obtained XANES spectrum of polynuclear Fe(III) aged in the presence of 200.0 mM Si features a significantly more pronounced main resonance peak at approx. 10 eV above the absorption edge (Figure 1) as well as a higher Fe – (O,OH,H₂O) contribution at 2.0 Å. Within the overlapping region of Fe – Fe and Fe – Si scattering paths at 2.4 to 2.9 Å, two distinct contributions of comparable magnitude are observed. Analogous to the observations of Pokrovski et al. [26] (pH 12.7), these features are indicative of a mixed tetrahedral/octahedral coordination environment of Fe(III) in solutions highly enriched in silicon due to the incorporation of Fe(III) in Si-polymer networks. Bearing resemblance to the observed increase in Fe – Fe contributions observed at the Fe K-edge, samples aged in the presence of 10.0 to 20.0 mM Si feature significantly higher Si – Fe contributions at interatomic distances of approx. 2.8 to 3.1 Å compared to the spectrum observed in the presence of 1.0 mM Si observed at the Si K-edge (Supporting Information, Figure S5). In addition, the siliceous ferrihydrite sample aged in the presence of the highest initial silicon concentration (20.0 mM) shows a reduction in the Si – O contribution within its first coordination shell. Whilst these changes in the local electronic structure of Si are significantly less well-pronounced compared to those observed at the Fe K-edge, their combined observation strongly suggests the incorporation of structural silicon into ferrihydrite, hence giving rise to the formation of an entirely new amorphous ferrosilicate compound.

To further investigate the changes introduced to the local structural environment of Fe due to the incorporation of silicon, we employ a series of EXAFS shell-by-shell fitting approaches. Structural parameters of synthetic 2-line ferrihydrite are determined by employing a single Fe – O scattering path for the first and two Fe – Fe paths for the next-nearest atomic shell. Table 1 summarizes the thereby obtained structural parameters, including the energy shift ΔE_0 , interatomic distances R , number of neighboring atoms N and Debye-Waller factors σ^2 , corresponding to the experimentally measured and fitted k^3 - weighted EXAFS spectra displayed in Figure 2. The resultant coordination numbers are in close agreement with the structural parameters obtained by Maillot et al. [39], employing an additional Fe – O contribution within the first atomic shell, resulting in an average interatomic distance of $R_{\text{Fe-O}} = 1.97$ Å. Changes to the structural parameters of the first and next-nearest atomic shell in the presence Si are investigated under the additional consideration of one Fe – Si scattering path, (i) allowing for the free adjustment of neighboring silicon atoms and (ii) restricting the number of silicon atoms to the Fe/Si ratio derived via mass balance calculations (compare Table S1). In both cases, the introduction of an additional Fe – Si scattering path leads to stable refinements (R-factor = 0.74 – 1.00 %), capturing the observed phase shifts and amplitude changes across the entire range of initial silicon concentrations investigated. Notably, restricting the Fe – Si coordination number to the Fe/Si ratio in (Fe₂O₃)_x(SiO₂)_y(H₂O)_z(s) yields structural parameters that are comparable to those obtained under the stoichiometrically unconstrained approach (Supporting Information, Table S2, Figure S5). Coinciding with a reduction in the interatomic Fe – O distance from $R = 1.96 \pm 0.01$ Å in the absence of Si to $R = 1.93 \pm 0.02$ Å, the number of neighboring oxygen atoms increases from $N_{\text{Fe-O}} = 3.52 \pm 0.34$ to $N_{\text{Fe-O}} = 4.12 \pm 0.46$. In the next-nearest coordination shell, the observed evolution within the overlapping region of Fe – Fe edge, Fe – Fe and Fe – Si double corner contributions is consistent with a linear decrease in the Fe(III) content at increasingly higher levels of silicon incorporation. The number of neighboring Fe atoms decreases from $N_{\text{Fe-Fe}_1} = 1.87 \pm 0.49$ and $N_{\text{Fe-Fe}_2} = 1.71 \pm 0.48$ to first $N_{\text{Fe-Fe}_1} = 1.70 \pm 0.18$ and $N_{\text{Fe-Fe}_2} = 1.40 \pm 0.18$ in the presence of 10 mM and then to $N_{\text{Fe-Fe}_1} = 1.55 \pm 0.16$ and $N_{\text{Fe-Fe}_2} = 1.20 \pm 0.13$ in the presence of 20.0 mM Si. Likewise, the number of neighboring silicon atoms increases to first 0.81 and then 1.01, corresponding to a solid silicon content of approx. 21 and 32 mol.%, respectively. Taken together, the restricted EXAFS shell-by-shell fitting and mass balance calculations performed produce a mutually consistent description of the composition of siliceous ferrihydrite.

Table 1: Structural parameters of the first and next-nearest atomic shell of iron, obtained from Fe K-edge EXAFS shell-by-shell fitting, accounting for one Fe – Si scattering path in addition to the atomic pairs presented in Supporting Information, Table S1. Various values in parentheses represent the uncertainty for each fitting parameter. ΔE_0 = energy shift, R = interatomic distance, N = number of neighboring atoms, σ^2 = Debye-Waller factor, R-factor = residual factor. Values of σ^2 were constrained for all scattering paths considered. The amplitude reduction factor S_0^2 was globally fixed to a value of 1.0 for all fits performed.

Sample	Solid Si(IV) (mol.%)	ΔE_0 eV	Atomic pair	R (Å)	N (atom)	σ^2 (Å ²)	R-factor %
2l – Fe(OH) ₃ (s)	0.00	–4.14(1.42)	Fe – O	1.96(0.01)	3.53(0.34)	0.0094(0.0023)	1.00
			Fe – Fe ₁	3.02(0.02)	1.87(0.49)	0.0135(0.0010)	
			Fe – Fe ₂	3.44(0.03)	1.71(0.48)	0.0103(0.0023)	
			Fe – Si ₁	/	/	/	
Fe(OH) ₃ (s) + 10.0 mM Si	20.56	–4.65(0.98)	Fe – O	1.95(0.02)	3.72(0.38)	0.0094(0.0023)	0.74
			Fe – Fe ₁	3.01(0.03)	1.70(0.18)	0.0199(0.0036)	
			Fe – Fe ₂	3.44(0.04)	1.40(0.18)	0.0106(0.0051)	
			Fe – Si ₁	3.20(0.00)	0.81 [†]	0.0110(0.0010)	
Fe(OH) ₃ (s) + 20.0 mM Si	32.71	–5.28(1.54)	Fe – O	1.93(0.02)	4.12(0.46)	0.0094(0.0023)	1.00
			Fe – Fe ₁	3.01(0.03)	1.55(0.16)	0.0095(0.0028)	
			Fe – Fe ₂	3.42(0.05)	1.20(0.13)	0.0097(0.0010)	
			Fe – Si ₁	3.18(0.00)	1.01 [†]	0.0130(0.0010)	
Fe(OH) ₃ (s) + 200.0 mM Si polynuclear	/	–3.63(1.10)	Fe – O	1.98(0.01)	5.55(0.65)	0.0080(0.0014)	0.49
			Fe – Si ₁	3.11(0.03)	4.10(1.00)	0.0100(0.0018)	
			Fe – Si ₂	3.34(0.03)	1.61(0.28)	0.0040(0.0061)	

[†]Fixed to the molar ratios derived by ICP mass balance calculations.

The stoichiometrically restricted fitting approach was performed under free adjustment of the Debye-Waller factor σ^2 , where the best fitting results were globally achieved using disorder parameters ranging from 0.009 to 0.013 for all Fe – Fe and Fe – Si scattering paths, although comparable fitting qualities (R-factor = 1 – 2 %) can be achieved under restriction of σ^2 in the range of 0.005 to 0.008 (compare Supporting Information, Table S2). These results are well in line with the reported σ^2 of disordered crystalline solids [40] as well as a range of other ferrous [41, 42] and ferric [43] silicon-bearing compounds.

Structural parameters derived from EXAFS shell-by-shell fitting of Si K-edge spectra (Supporting Information, Figure S6-S7 and Table S3) yield satisfactory agreement with their counterparts at the Fe K-edge. Samples aged in the presence of 10.0 to 20.0 mM Si feature an interatomic distance of $R_{\text{Si-O}} = 1.63 \pm 0.01$ Å within the first coordination shell of silicon, with the number of neighboring oxygen atoms varying from approx. $N_{\text{Si-O}} = 3.48 \pm 0.22$ to $N_{\text{Si-O}} = 3.39 \pm 0.20$. In line with the increased silicon content of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$, the number of neighboring silicon atoms in the second coordination shell increases from $N_{\text{Si-Si}} = 0.59 \pm 0.24$ to $N_{\text{Si-Si}} = 0.71 \pm 0.25$ in the presence of 10.0 and 20.0 mM Si, where the corresponding interatomic distance remains constant at approx. $R_{\text{Si-Si}} = 2.51 \pm 0.03$ to $R_{\text{Si-Si}} = 2.53 \pm 0.03$ Å. Under restriction of the respective contributions of various Fe – Fe and Fe – Si paths to the bulk molar ratio of iron and silicon in $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$, i.e., by fixing $N_{\text{Si-Fe}} = (2x/y) \times N_{\text{Si-Si}}$, the computed interatomic distances of Si – Fe paths, $R_{\text{Si-Fe}} = 3.20 \pm 0.04$ to $R_{\text{Si-Fe}} = 3.18 \pm 0.04$ Å, fall within the uncertainty of the corresponding distances to the Fe-centered Fe – Si contributions obtained (Table 1). From the Fourier-transformed Si K-edge EXAFS spectra displayed in Figure S5 and the observed increase in the number of neighboring silicon atoms, it is evident that, despite the remarkable agreement of both

fitting approaches employed, the proposed stoichiometry of siliceous ferrihydrite does not entirely capture the observed changes in the local coordination structure of Si. Analogous to the observations of Cismasu et al. [12], it is likely that these discrepancies stem from the additional presence of poorly crystalline SiO_2 that co-precipitated together with siliceous ferrihydrite at higher initial silicon concentrations. Although several attempts have been made to include a complementary Si – Si contribution to the fits performed, the quality and energy range of the spectra observed do not permit the refinement under consideration of an additional three fitting parameters.

EXAFS analysis of polynuclear iron provides further evidence for the incorporation of Fe(III) into siliceous polymer networks under conditions of excess silicon (200.0 mM). Figures 2g and 2h display the k^3 -weighted FT-RDF and corresponding $k^3\chi(k)$. Under consideration of one Fe – O contribution in the first and two Fe – Si scattering paths in the second coordination shell, the number of best fitting neighbors is found to be $N_{\text{Fe-O}} = 5.55 \pm 0.65$, $N_{\text{Fe-Si}_1} = 4.10 \pm 1.00$ and $N_{\text{Fe-Si}_2} = 1.61 \pm 0.28$, i.e., equivalent to polynuclear stoichiometries of FeSi_{4-5} that have previously been hypothesized to form at alkaline pH [26]. The corresponding interatomic distances of $R_{\text{Fe-O}} = 1.98 \pm 0.01$, $R_{\text{Fe-Si}_1} = 3.11 \pm 0.03$ and $R_{\text{Fe-Si}_2} = 3.34 \pm 0.03$ Å are comparable to those observed in the presence of 50 to 160 mM Si [26]. As previously discussed, both the increase in the number of neighboring oxygen atoms as well as the observed shift in the mean Fe – O distance are indicative of a mixed tetrahedral/octahedral coordination environment, where the fraction of tetracoordinated Fe(III) is expected to be lower in comparison to the amorphous Fe hydroxide 2-line ferrihydrite stabilized in the absence of silicon. Figure 3 displays the fraction of tetracoordinated Fe(III) in $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ and polynuclear Fe(III) versus the mean Fe – O distance $R_{\text{Fe-O}}$ in Å estimated via EXAFS shell-by-shell fitting, together with a schematic illustration of the structure of siliceous ferrihydrite. In comparison to $\text{Fe}(\text{OH})_3(\text{s})$ of varying degrees of long-range order [39], siliceous ferrihydrite features a significantly higher degree of tetracoordination, reaching approx. 41 % in the presence of 10.0 and 49 % in the presence of 20.0 mM Si, respectively (Figure 3a).

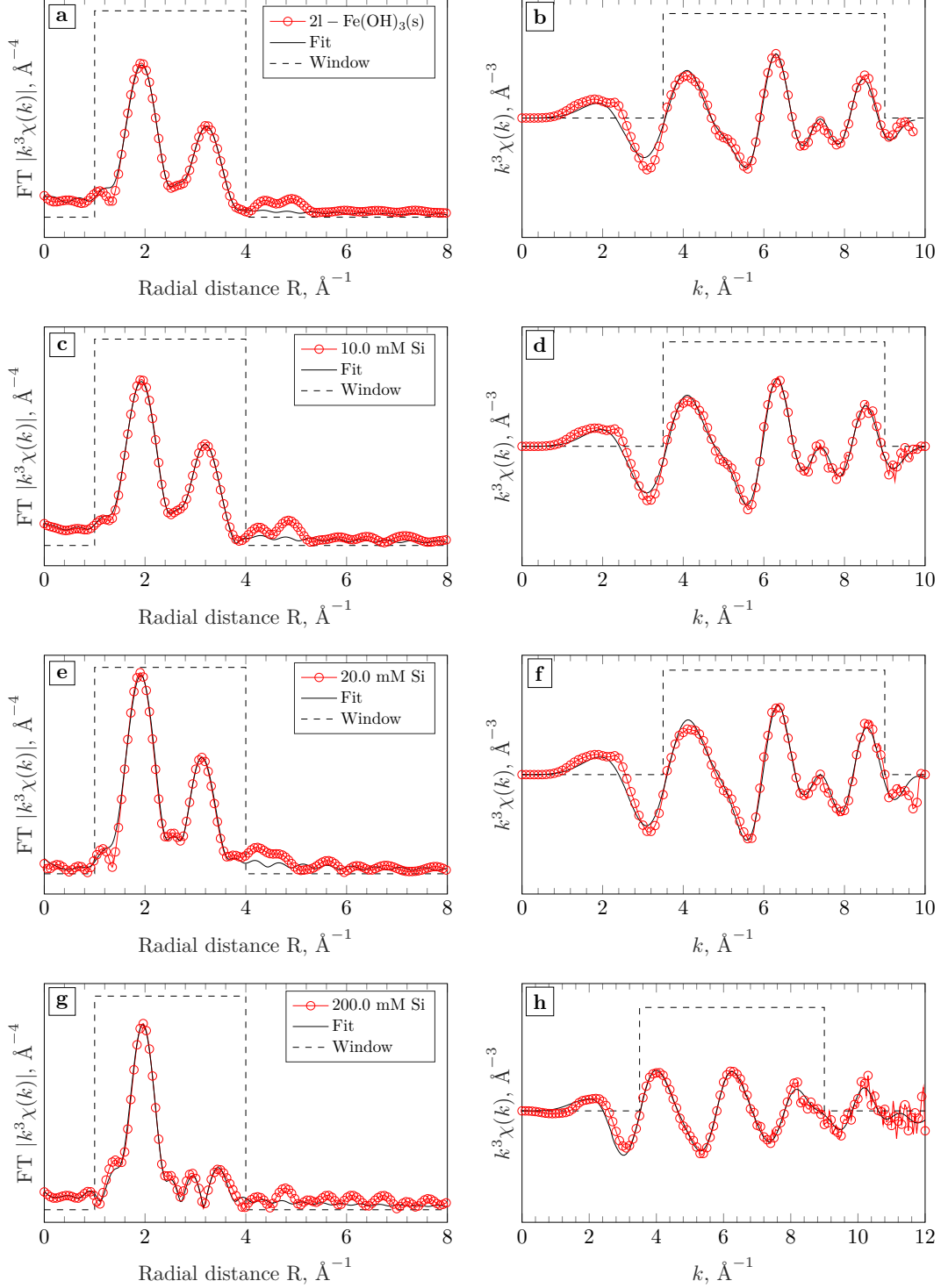


Figure 2: Fourier-transformed Fe K-edge EXAFS spectra of selected silicon-containing iron hydroxide powders (a, c and e) and polynuclear Fe(III) (g), together with their corresponding $k^3\chi(k)$ (b, d, f and h). Fits are obtained from Fe K-edge EXAFS shell-by-shell fitting, accounting for one Fe – O, two Fe – Fe and one Fe – Si scattering path. The number of neighboring atoms N for the Fe – Si scattering path was restricted, matching the molar ratios derived by ICP mass balance calculations (compare Table S1). Fits of polynuclear Fe(III) in the presence of 200.0 mM Si are obtained, accounting for one Fe – O and two Fe – Si contribution. The window for the forward Fourier transformation is indicated by the dashed black lines. All corresponding structural parameters are summarized in Table 1.

As $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ formed in the presence of 10 mM Si is significantly more rich in octacoordinated Fe(III) ($\text{Fe}_2\text{O}_3/\text{SiO}_2 = 1.92$) compared to its counterpart formed at 20.0 mM ($\text{Fe}_2\text{O}_3/\text{SiO}_2 = 1.36$), the apparent shift towards lower Fe – O distances, i.e., away from the mean interatomic distance of pure $\alpha - \text{Fe}_2\text{O}_3(\text{s})$, is in keeping with the bulk stoichiometry of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ previously derived. Figure 3c illustrates the effect of Si on the structure of pure and siliceous ferrihydrites for increasingly higher

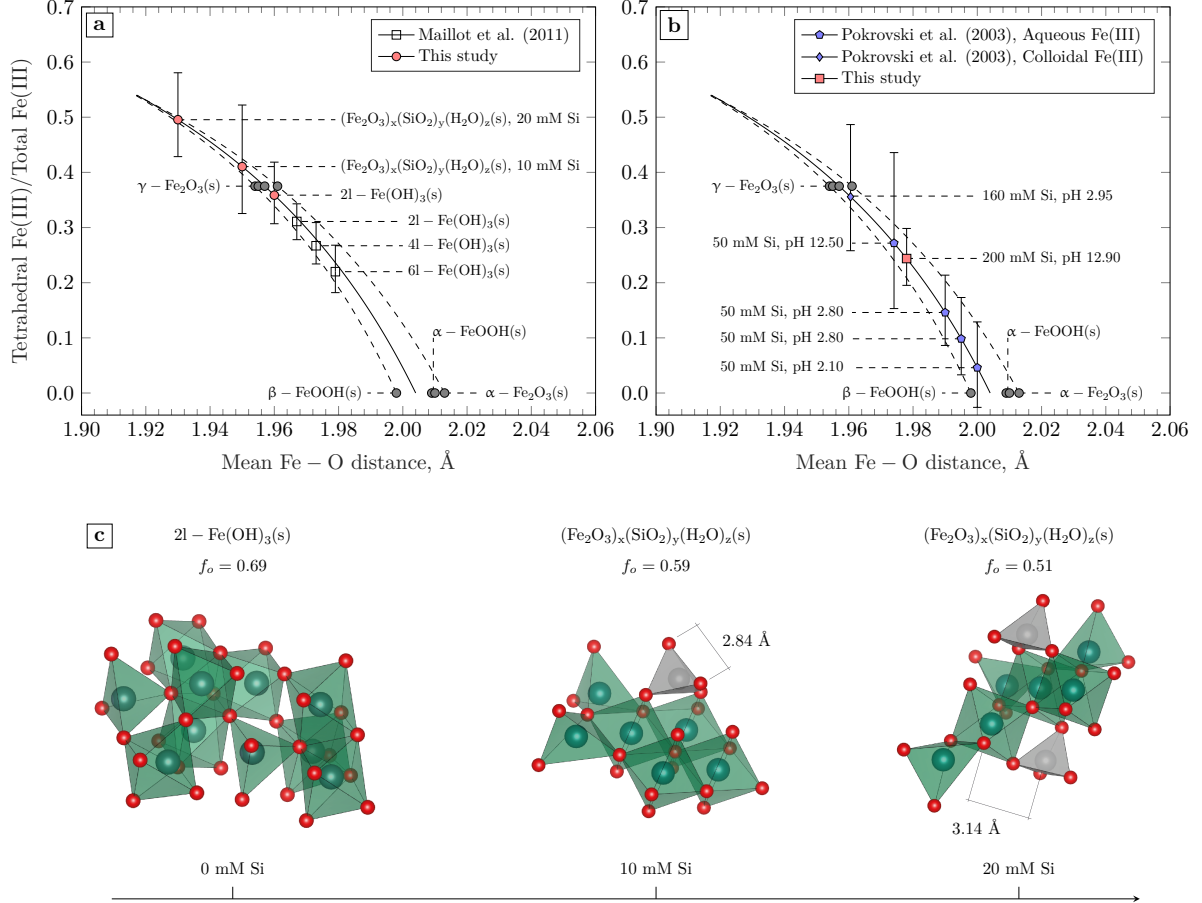


Figure 3: The fraction of tetraordinated Fe(III) in $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ (a) and aqueous and polynuclear Fe(III) (b) as a function of the mean Fe–O distance $R_{\text{Fe-O}}$ in Å, as determined by EXAFS shell-by-shell fitting, together with a schematic illustration of the influence of Si on the structure of 2-line and siliceous ferrihydrites (c). Silicon binding across the free oxygens of two adjacent edge-sharing $\text{Fe}(\text{O}, \text{OH}, \text{H}_2\text{O})_6$ effectively suppresses Fe(III) polymerization, thereby leading to a reduction in the fraction of octacoordinated Fe(III) (f_o) in $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ with respect to silicon-free 2-line ferrihydrite. The central regression lines relating the amount of tetraordinated Fe(III) to $R_{\text{Fe-O}}$ were adapted from Maillot et al. [39], together with the crystallographically determined percentage of tetrahedral Fe(III) for the reference compounds goethite ($\alpha - \text{FeOOH}(\text{s})$), akaganéite ($\beta - \text{FeOOH}(\text{s})$), hematite ($\alpha - \text{Fe}_2\text{O}_3(\text{s})$) and maghemite ($\gamma - \text{Fe}_2\text{O}_3(\text{s})$). For a detailed description of the computation of the regression line, the reader is referred to Supporting Information, Note G.

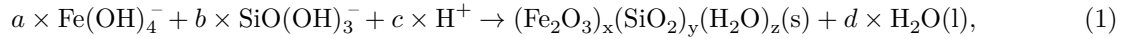
levels of silicon loading. Analogous to the influence of silicon on aqueous Fe(III) [26], it is evident that the suppression of Fe(III) polymerization must proceed via silicon binding to the free oxygens of two adjacent edge-sharing $\text{Fe}(\text{O}, \text{OH}, \text{H}_2\text{O})_6$. The resultant interatomic distance of $R_{\text{Fe-Si}} = 3.14 \text{ Å}$ is in good agreement with the structural parameters obtained from XAS shell-by-shell fitting at the Fe and Si K-edge (compare Tables 1 and S1). Si binding to one of the free $\text{Fe}(\text{O}, \text{OH}, \text{H}_2\text{O})_6$ edges on the other hand results in an approximate $R_{\text{Fe-Si}} = 2.26 \text{ Å}$, i.e., significantly closer than the experimentally predicted interatomic distance.

Coinciding with the successive incorporation of tetracoordinated Si into the $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ solid solution, the fraction of octacoordinated Fe(III) is reduced from $f_o = 0.69$ in 2-line to $f_o = 0.51$ in siliceous ferrihydrite aged in the presence of 20 mM Si.

Analysis of the mean Fe – O distance of aqueous Fe(III) in the presence of 50 mM Si [26] further shows that the fraction of tetrahedrally coordinated Fe(III) increases from pH 2.10 to 12.5, successively approaching the degree of tetracoordination in maghemite (Figure 3b). Polynuclear Fe(III) features a mixed tetrahedral/octahedral coordination environment, where degree of tetracoordination appears to decrease, both with increasing pH and [Si]. Whilst at pH 2.95 in the presence of 160 mM Si [26], the mean interatomic distance approaches that of maghemite, polynuclear Fe(III) formed at pH 12.9 and [Si] = 200.0 mM is determined to have a lower degree of tetracoordination, equivalent to approx 24 %. We hypothesize that this reconfiguration is related to the pH-dependent speciation of silicon, specifically, the preferential stabilization of polysilicate complexes in mildly alkaline conditions compared to the predominant monoatomic aqueous complexes at low pH. At present, this interpretation remains speculative, and systematic experimental investigations will be necessary to verify the coordination environment of aqueous and polynuclear Fe(III) across a broader interval of silicon concentrations and pH values.

The solubility of siliceous ferrihydrite

In addition to the derived atomic formulae (Table S1), experimentally measured aqueous iron and silicon concentrations allow for the direct computation of the solubility products of siliceous ferrihydrite under full consideration of the pH-dependent speciation of iron and silicon in alkaline conditions. Assuming a generic precipitation reaction under the consumption of the predominant negatively charged Fe(III) and Si(IV) hydrolysis products $\text{Fe}(\text{OH})_4^-$ and $\text{SiO}(\text{OH})_3^-$,



the solubility product (K) of siliceous ferrihydrite is evaluated according to

$$K = \{\text{Fe}(\text{OH})_4^-\}^{-a} \{\text{SiO}(\text{OH})_3^-\}^{-b} \{\text{H}^+\}^{-c} \{\text{H}_2\text{O}(\text{l})\}^d, \quad (2)$$

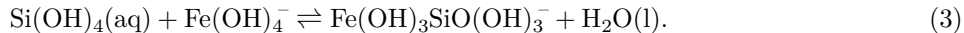
where $\{\}$ denotes the activity of all reactive species involved. Table 2 summarizes the resultant solubility products, calculated based on the experimentally measured aqueous Fe(III) and Si(IV) concentrations with varying solid phase compositions for the samples equilibrated in the presence of 20.0 mM Si at pH values > 13.0 . Note that no solubility product for the 200.0 mM Si series was calculated, as those values are affected by the strong formation of polynuclear aqueous Si complexes. At increasingly lower pH, the gradual reduction in structural iron and water in siliceous ferrihydrite coincides with (i) a reduction in aqueous Fe and Si with respect to $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ at pH 13.4 and (ii) with an increase in the solubility limit of Fe compared to 2-line ferrihydrite at pH 13.1 to 12.7 [14]. Across the pH interval investigated, the computed $\log_{10} K^\circ$ reduces from 76.09 ± 0.44 (pH 13.4) to 52.20 ± 0.31 (pH 12.7).

Table 2: Measured total aqueous iron and silicon concentrations in equilibrium with siliceous ferrihydrite, aged in the presence of 20.0 mM Si, together with the solubility products $\log_{10} K^\circ$ (compare Equation 2) at $T = 298.15$ K as a function of the pH-dependent composition of $(\text{Fe}_2\text{O}_3)_x\text{SiO}_2(\text{H}_2\text{O})_y$. The estimated uncertainty of various computationally predicted $\log_{10} K^\circ$ obeys the standard rules of error propagation [44] (compare Supporting Information, Note C).

	Phase	[Fe], μM	[Si], mM	pH	$\log_{10} K^\circ$
[Si] = 20.0, mM	$(\text{Fe}_2\text{O}_3)_{1.36}\text{SiO}_2(\text{H}_2\text{O})_{3.21}$	17.63 ± 0.25	13.42 ± 0.13	13.4	77.86 ± 0.44
	$(\text{Fe}_2\text{O}_3)_{0.97}\text{SiO}_2(\text{H}_2\text{O})_{2.81}$	9.71 ± 0.21	11.62 ± 0.20	13.2	59.74 ± 0.35
	$(\text{Fe}_2\text{O}_3)_{0.92}\text{SiO}_2(\text{H}_2\text{O})_{2.50}$	8.56 ± 0.01	10.87 ± 0.23	13.1	57.58 ± 0.33
	$(\text{Fe}_2\text{O}_3)_{0.82}\text{SiO}_2(\text{H}_2\text{O})_{2.25}$	8.72 ± 0.59	10.56 ± 0.03	13.0	53.48 ± 0.40
	$(\text{Fe}_2\text{O}_3)_{0.81}\text{SiO}_2(\text{H}_2\text{O})_{2.25}$	8.75 ± 1.60	8.51 ± 0.12	12.7	53.01 ± 0.31

Aqueous ferrosilicate complexes at alkaline pH

The observed departure from the theoretical solubility limit controlled by the precipitation of 2-line ferrihydrite can be attributed to the formation of an aqueous ferrosilicate complex that competes with the stabilization of the Fe(III) hydrolysis product $\text{Fe}(\text{OH})_4^-$ at high pH. Analogous to the coordination of Al(III) in alkaline environments [19], the stabilisation of ferrosilicate complexes can be formulated according to the thermodynamically predominant monomeric aqueous iron and silicon complexes $\text{Fe}(\text{OH})_4^-$ and $\text{Si}(\text{OH})_4(\text{aq})$ according to



To account for the deviation in the experimentally measured and computationally predicted total solubility of Fe(III), a number of aqueous complexes have been considered. These were independently validated using (i) thermodynamic analysis of their pH-dependent solubility increase at higher [Si] and (ii) quantum chemical calculations. Across the range of initial silicon concentrations and pH values investigated in this study, the sole contender that satisfies the observed departure from the theoretical solubility limit of 2-line ferrihydrite is the negatively charged ferrosilicate complex $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$. The corresponding Gibbs free energy change estimated by thermodynamic modelling techniques and quantum chemical calculations performed across a range of implicit solvent models is $\Delta G_{r,TDM}^\circ = -41.2 \pm 1.0 \text{ kJ mol}^{-1}$ and $\Delta G_{r,DFT}^\circ = -41.1 \pm 4.3 \text{ kJ mol}^{-1}$, respectively. Figure 4 displays the solubility limit of Fe(III) and Si(IV) in the presence of 2.0 mM (a) and 20.0 mM (b) Si, together with the aqueous molar fractions of $\text{Fe}(\text{OH})_4^-$ and $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ (c) and the geometry-optimized high- and low-spin structure of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$. It can be recognized that the additional consideration of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ produces a satisfactory agreement between the experimentally measured and computationally predicted solubility of Fe(III) in the presence of both 2.0 and 20.0 mM Si, using a stability constant of $\log_{10} K^\circ = 7.21 \pm 0.20$ (Equation 3). Across both concentrations, the total solubility of Fe(III) is controlled by the formation of $\text{Fe}(\text{OH})_4^-$ towards pH 14.0 and the preferential stabilization of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ towards pH 12.0. The respective predominance region of both complexes depends on the aqueous silicon concentration (Figure 4c) and, by extension, on the pH-dependent composition of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$. Accounting for the formation of an ideal solid solution between $(\text{Fe}_2\text{O}_3)_{1.36}\text{SiO}_2(\text{H}_2\text{O})_{3.21}$ and $(\text{Fe}_2\text{O}_3)_{0.81}\text{SiO}_2(\text{H}_2\text{O})_{2.25}$, i.e., the variants of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)_y(\text{H}_2\text{O})_z(\text{s})$ stabilized at pH 13.4 and 12.7, captures the progression of both elemental concentrations in line with the previously derived stoichiometry of siliceous ferrihydrite. Geometry optimization and vibrational frequency calculations performed on Fe(III) – Si complex structures and spin states indicates that the high-spin $(\text{OH})_3\text{Fe} - \text{O} - \text{Si}(\text{OH})_3$ complex represents the most stable configuration among the tested models (Supporting Information, Table S4). The Gibbs free energy of Reaction 3 was evaluated for a range of implicit solvent models (Supporting Information, Table S5). The resultant Gibbs free energy of $\Delta G_r^\circ = -41.1 \pm 4.3 \text{ kJ mol}^{-1}$ is in remarkable agreement with the corresponding value derived from thermodynamic modelling computations. Calculations using different implicit solvent models (i.e., PCM [45], CPCM [46] and SMD [47]) gave reaction free energies of -41.1 , -45.3 , $-43.1 \text{ kJ mol}^{-1}$, respectively. The small variation among the tested solvation models, approximately 4.3 kJ mol^{-1} , suggests that the qualitative conclusion is not strongly affected by the choice of implicit solvation model (Supporting Information, Table S5-S8). Corresponding Fe – O and Si – O bridging distances of 1.92 and 1.65 Å (Supplementary Information, Table S9) are in good agreement with the EXAFS-derived interatomic distances of siliceous ferrihydrite aged in the presence of 20 mM Si as well as polynuclear Fe(III) stabilized in the presence of 200 mM Si (Table 1). Thus, the quantum-chemical results independently support the thermodynamic findings by showing that Fe – O – Si bond formation can act as an energetically favorable initial step toward aqueous ferrosilicate stabilization and subsequent siliceous ferrihydrite formation. It is further remarked that the here proposed identity and stability constant of the ferrosilicate complex $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ fails to account for the observed increase in aqueous Fe(III) in the presence of 200.0 mM Si (Supporting information, Figure S10). An increase of the initial silicon concentration from 2.0 to 20.0 mM produces a corresponding increase in the total aqueous Fe(III) concentration across the predominance region of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$. Extrapolation from 20.0 to 200.0 mM falls short of the experimentally measured aqueous Fe by a factor of 10, likely due to the replacement of Fe(III) in silicon-rich polymer networks or polynuclear silicon species [26]. The preferential stabilization of polynuclear complexes at increasing [Si] is further evident from the pH-dependent speciation of silicon within the alkaline pH regime (Supporting Information, Note H). Based on the here presented analysis of the coordination environment of polynuclear Fe(III), the pH-dependent speciation of

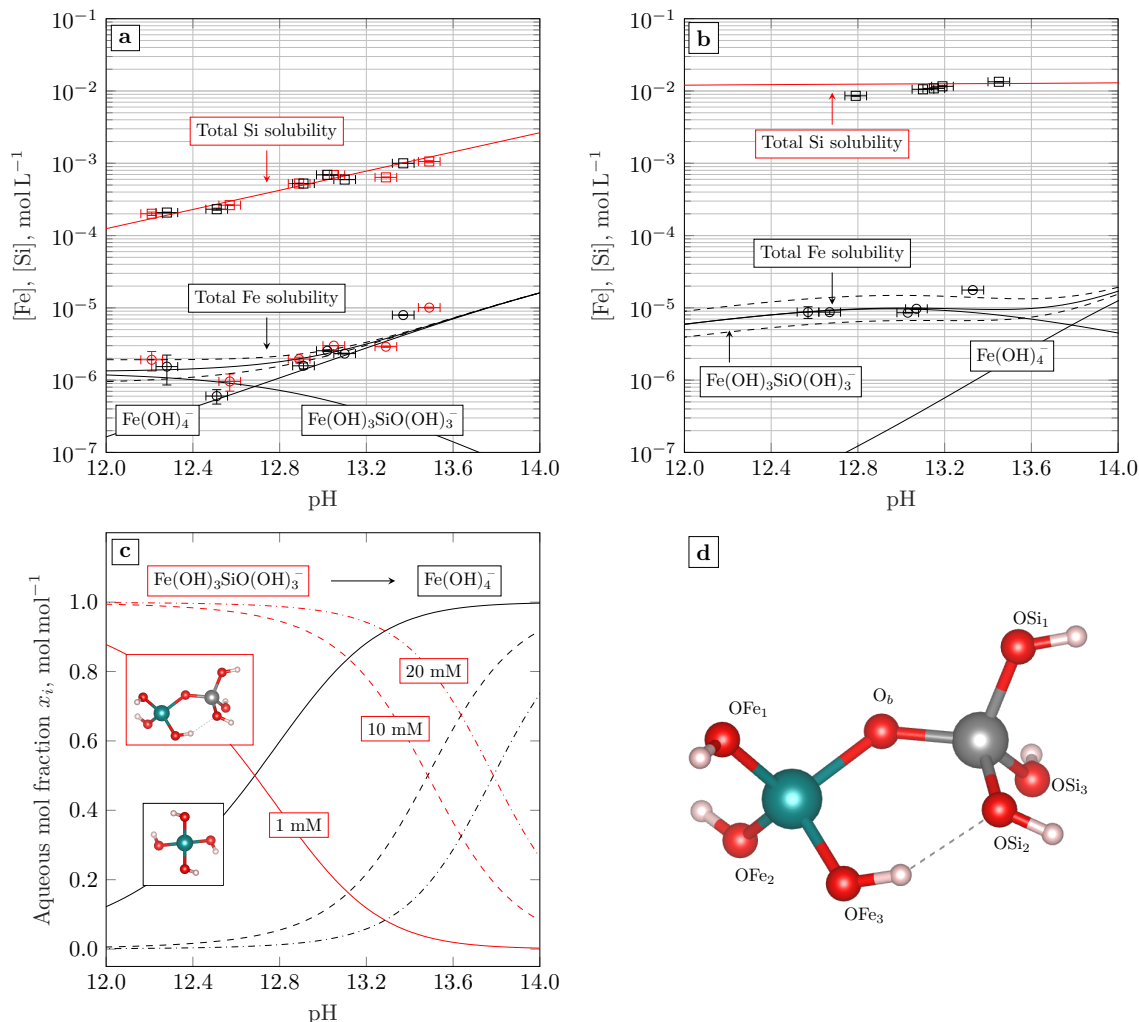


Figure 4: The solubility of iron and silicon at alkaline pH, as controlled by the precipitation of siliceous ferrihydrite from Fe(OH)_4^- and $\text{Fe(OH)}_3\text{SiO(OH)}_3^-$ in the presence of 2 mM Si (a) and 20.0 mM Si (b), together with the aqueous molar fractions of both solubility-controlling aqueous complexes (c) and the geometry-optimized high spin configuration of $\text{Fe(OH)}_3\text{SiO(OH)}_3^-$ (d). The computationally predicted solubility of both solutes are fitted to the respective experimentally measured equilibrium concentrations in the presence of 2.0 and 20.0 mM Si after 1 week (red) and 1 month (black), by adjusting the Gibbs free energy of formation of $\text{Fe(OH)}_3\text{SiO(OH)}_3^-$. Changes in the composition of siliceous ferrihydrite are accounted for, by assuming the formation of an ideal solid solution between $(\text{Fe}_2\text{O}_3)_{1.36}\text{SiO}_2(\text{H}_2\text{O})_{3.21}$ and $(\text{Fe}_2\text{O}_3)_{0.81}\text{SiO}_2(\text{H}_2\text{O})_{2.25}$, i.e., the variants of siliceous ferrihydrite stabilized at pH 13.4 and 12.7, respectively.

Si(IV) (Figure S7) as well as the observations of Pokrovski et al. [26], it can be reasonably concluded that the observed discrepancy in experimentally measured and computed $[\text{Fe}]$ is due to the incorporation of Fe(III) into polynuclear silicon complexes, where resulting in stoichiometries feature significantly higher Si/Fe ratios than the solubility controlling ferrosilicate complex stabilized at low to moderate Si.

Conclusions

We have presented a comprehensive investigation into the interactions of iron and silicon at alkaline pH, demonstrating how the local electronic structure of iron in poorly crystalline siliceous ferrihydrite varies systematically in the presence of Si. These results are supported by a tightly coupled experimental and computational approach. Mass balance calculations derived from solution measurements allow, for the first time, to determine the structure and bulk composition of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)(\text{H}_2\text{O})_y$ as a function of the electrolyte pH. Synchrotron-based investigations at the Fe and Si K-edge reveal a local electronic structure that is mutually consistent with the bulk stoichiometry derived from mass balance calculations.

In accordance with the thermodynamic stability regime of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)(\text{H}_2\text{O})_y$, it is further shown that the affinity of Fe(III) and Si(IV) stabilizes the aqueous ferrosilicate complex $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ in solution. Analogous to the formation of aluminosilicate complexes at alkaline pH, the stability regime of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ features a large overlap with the otherwise predominant aqueous Fe(III) hydrolysis complex $\text{Fe}(\text{OH})_4^-$, thereby significantly altering the speciation of iron in the Fe(III) – Si(IV) – H_2O , compared to the Fe(III) – H_2O system. A tentatively assigned stability constant of $\log_{10} K^\circ = 7.21 \pm 0.20$ yields satisfactory agreement between the experimentally measured and computationally predicted total solubility of Fe(III) in the presence of 2 to 20.0 mM Si on the basis of thermodynamic modelling and quantum mechanical calculations. In the presence of 200.0 mM Si, thermodynamically predicted Fe(III) concentrations fall short of their experimental counterparts. Analysis of the local coordination environment of polynuclear Fe(III) and the speciation of Si(IV) in the presence of 200.0 mM Si suggest that Fe(III) can be incorporated into silicon-rich polymer networks, further elevating the solubility limit of iron controlled by the formation of $(\text{Fe}_2\text{O}_3)_x(\text{SiO}_2)(\text{H}_2\text{O})_y$ and the competing stabilization of $\text{Fe}(\text{OH})_3\text{SiO}(\text{OH})_3^-$ and $\text{Fe}(\text{OH})_4^-$ in solution.

Although these results provide a quantitative basis towards a more holistic understanding of the solubility and speciation of iron within the pore solution of cementitious systems, we highlight that the derived composition and thermodynamic stability regime of Si-bearing solids and aqueous complexes must be further augmented. Comparative follow up studies, involving investigations into the solubility of Fe(III) across a broader levels of alkalinity, aqueous silicon concentrations and ionic strengths, complemented by spectroscopic techniques capable of probing the coordination environment of Fe(III) in solution can provide further insights into the stabilization of ferrosilicate complexes at alkaline pH.

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Contributions

F.E.F., B.L., S.M. and U.M.A conceived the study, F.E.F., B.L., S.M., N.C.P., K.D., C.N.B. and T.H. designed the experiments. F.E.F., S.M., C.N.B, N.C.P. and K.D. carried out the experimental work. F.E.F., B.L., S.M., C.N.B., T.H., K.D. and X.G. analyzed the data. F.E.F., C.N.B, T.H. and K.D. analyzed the XAS data. F.E.F. and B.L. developed the thermodynamic framework. R.Y. and S.C. performed the quantum mechanical calculations. F.E.F. wrote the paper with inputs from all other authors. U.M.A. supervised the study.

Notes

The authors declare no competing interests.

Supporting information

The following files are available free of charge.

- Experimental and computational methods, including material additional characterization techniques, XRD patterns, TGA/DTG curves, XAS shell-by-shell fitting details, time-dependent aqueous concentration measurements and a detailed account of the thermodynamic and quantum mechanical modelling approaches.

References

- (1) Peak, D.; Sparks, D. Mechanisms of selenate adsorption on iron oxides and hydroxides. *Environmental Science & Technology* **2002**, *36*, 1460–1466.
- (2) Dixit, S.; Hering, J. G. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environmental Science & Technology* **2003**, *37*, 4182–4189.
- (3) Dodge, C.; Francis, A.; Gillow, J.; Halada, G.; Eng, C.; Clayton, C. Association of uranium with iron oxides typically formed on corroding steel surfaces. *Environmental Science & Technology* **2002**, *36*, 3504–3511.
- (4) Whitman, W. G.; Russell, R.; Davis, G. The solubility of ferrous hydroxide and its effect upon corrosion. *Journal of the American Chemical Society* **1925**, *47*, 70–79.
- (5) Wieland, E.; Miron, G. D.; Ma, B.; Geng, G.; Lothenbach, B. Speciation of iron (II/III) at the iron-cement interface: A review. *Materials and Structures* **2023**, *56*, 31.
- (6) Dilnesa, B. Z.; Lothenbach, B.; Renaudin, G.; Wichser, A.; Kulik, D. Synthesis and characterization of hydrogarnet $\text{Ca}_3(\text{Al}_x\text{Fe}_{1-x})_2(\text{SiO}_4)_y(\text{OH})_{4(3-y)}$. *Cement and Concrete Research* **2014**, *59*, 96–111.
- (7) Mancini, A.; Wieland, E.; Geng, G.; Dähn, R.; Skibsted, J.; Wehrli, B.; Lothenbach, B. Fe(III) uptake by calcium silicate hydrates. *Applied Geochemistry* **2020**, *113*, 104460.
- (8) Bozorth, R. M. Structure of a protective coating of iron oxides. *Journal of the American Chemical Society* **1927**, *49*, 969–976.
- (9) Indra, A.; Menezes, P. W.; Sahraie, N. R.; Bergmann, A.; Das, C.; Tallarida, M.; SchmeiSSer, D.; Strasser, P.; Driess, M. Unification of catalytic water oxidation and oxygen reduction reactions: amorphous beat crystalline cobalt iron oxides. *Journal of the American Chemical Society* **2014**, *136*, 17530–17536.
- (10) Furcas, F. E.; Lothenbach, B.; Mundra, S.; Borca, C. N.; Albert, C. C.; Isgor, O. B.; Huthwelker, T.; Angst, U. M. Transformation of 2-line ferrihydrite to goethite at alkaline pH. *Environmental Science & Technology* **2023**, *57*, 16097–16108.
- (11) Das, S.; Hendry, M. J.; Essilfie-Dughan, J. Transformation of two-line ferrihydrite to goethite and hematite as a function of pH and temperature. *Environmental Science & Technology* **2011**, *45*, 268–275.
- (12) Cismasu, A. C.; Michel, F. M.; Tcacu, A. P.; Brown Jr, G. E. Properties of impurity-bearing ferrihydrite III. Effects of Si on the structure of 2-line ferrihydrite. *Geochimica et Cosmochimica Acta* **2014**, *133*, 168–185.
- (13) Furcas, F. E.; Mundra, S.; Lothenbach, B.; Borca, C. N.; Huthwelker, T.; Angst, U. M. The influence of silicon on the formation and transformation of corrosion products. *Cement and Concrete Research* **2024**, *182*, 107554.
- (14) Furcas, F. E.; Lothenbach, B.; Isgor, O. B.; Mundra, S.; Zhang, Z.; Angst, U. M. Solubility and speciation of iron in cementitious systems. *Cement and Concrete Research* **2022**, *151*, 106620.

- (15) Yokoyama, T.; Yamanaka, C.; Tarutani, T. Formation of silicato complexes of aluminium in aqueous solution. *Journal of Chromatography A* **1987**, *403*, 151–157.
- (16) Exley, C.; Birchall, J. Hydroxyaluminosilicate formation in solutions of low total aluminum concentration. *Polyhedron* **1992**, *11*, 1901–1907.
- (17) Gout, R.; Pokrovski, G.; Schott, J.; Zwick, A. Raman spectroscopic study of aluminum silicate complexation in acidic solutions from 25 to 150 C. *Journal of Solution Chemistry* **1999**, *28*, 73–82.
- (18) Farmer, V.; Lumsdon, D. An assessment of complex formation between aluminium and silicic acid in acidic solutions. *Geochimica et Cosmochimica Acta* **1994**, *58*, 3331–3334.
- (19) Swaddle, T. W. Silicate complexes of aluminum (III) in aqueous systems. *Coordination Chemistry Reviews* **2001**, *219*, 665–686.
- (20) Kinrade, S. D.; Swaddle, T. W. Direct detection of aluminosilicate species in aqueous solution by silicon-29 and aluminum-27 NMR spectroscopy. *Inorganic Chemistry* **1989**, *28*, 1952–1954.
- (21) McCormick, A.; Bell, A.; Radke, C. Multinuclear NMR investigation of the formation of aluminosilicate anions. *The Journal of Physical Chemistry* **1989**, *93*, 1741–1744.
- (22) Weber Jr, W.; Stumm, W. Formation of a silicato-iron(III) complex in dilute aqueous solution. *Journal of Inorganic and Nuclear Chemistry* **1965**, *27*, 237–239.
- (23) Porter, R. A.; Weber Jr, W. J. The interaction of silicic acid with iron(III) and uranyl ions in dilute aqueous solution. *Journal of Inorganic and Nuclear Chemistry* **1971**, *33*, 2443–2449.
- (24) Hummel, W.; Berner, U.; Curti, E.; Pearson, F.; Thoenen, T. Nagra/PSI chemical thermodynamic data base 01/01. *Radiochimica Acta* **2002**, *90*, 805–813.
- (25) Thoenen, T.; Hummel, W. *The PSI Chemical Thermodynamic Database 2020, Technical Report 21-03*; Report; PSI, 2020.
- (26) Pokrovski, G. S.; Schott, J.; Farges, F.; Hazemann, J.-L. Iron (III)-silica interactions in aqueous solution: Insights from X-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta* **2003**, *67*, 3559–3573.
- (27) Doelsch, E.; Rose, J.; Masion, A.; Bottero, J. Y.; Nahon, D.; Bertsch, P. M. Speciation and crystal chemistry of iron (III) chloride hydrolyzed in the presence of SiO₄ ligands. 1. An Fe K-edge EXAFS study. *Langmuir* **2000**, *16*, 4726–4731.
- (28) Furcas, F. E.; Mundra, S.; Lothenbach, B.; Angst, U. M. Speciation Controls the Kinetics of Iron Hydroxide Precipitation and Transformation at Alkaline pH. *Environmental Science & Technology* **2024**, *58*, 19851–19860.
- (29) Schwertmann, U.; Cornell, R. M. *Iron Oxides in the Laboratory: Preparation and Characterization*, 2nd ed.; John Wiley & Sons: 2008.
- (30) Dräger, G.; Frahm, R.; Materlik, G.; Brümmer, O. On the multipole character of the X-ray transitions in the pre-edge structure of Fe K absorption spectra. An experimental study. *Physica Status Solidi (B)* **1988**, *146*, 287–294.
- (31) Apte, M.; Waychunas, G.; Brown, G. Structure and specification of iron complexes in aqueous solutions determined by X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* **1985**, *49*, 2081–2089.
- (32) Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. A multiplet analysis of Fe K-edge 1s→3d pre-edge features of iron complexes. *Journal of the American Chemical Society* **1997**, *119*, 6297–6314.
- (33) Arrio, M.-A.; Rossano, S.; Brouder, C.; Galois, L.; Calas, G. Calculation of multipole transitions at the Fe K pre-edge through p-d hybridization in the Ligand Field Multiplet model. *EPL (Europhysics Letters)* **2000**, *51*, 454–460.
- (34) Wilke, M.; Farges, F.; Petit, P.-E.; Brown Jr, G. E.; Martin, F. Oxidation state and coordination of Fe in minerals: An Fe K-XANES spectroscopic study. *American Mineralogist* **2001**, *86*, 714–730.

- (35) Waychunas, G.; Rossman, G. Spectroscopic standard for tetrahedrally coordinated ferric iron: $\gamma\text{LiAlO}_2\text{:Fe}^{3+}$. *Physics and Chemistry of Minerals* **1983**, *9*, 212–215.
- (36) Dräger, G.; Frahm, R.; Materlik, G.; Brümmer, O. On the multipole character of the X-ray transitions in the preedge structure of Fe K absorption spectra. An experimental study. *Physica Status Solidi (b)* **1988**, *146*, 287–294.
- (37) Combes, J.; Manceau, A.; Calas, G.; Bottero, J. Formation of ferric oxides from aqueous solutions: A polyhedral approach by X-ray absorption spectroscopy: I. Hydrolysis and formation of ferric gels. *Geochimica et Cosmochimica Acta* **1989**, *53*, 583–594.
- (38) Manceau, A.; Combes, J. Structure of Mn and Fe oxides and oxyhydroxides: A topological approach by EXAFS. *Physics and Chemistry of Minerals* **1988**, *15*, 283–295.
- (39) Maillot, F.; Morin, G.; Wang, Y.; Bonnin, D.; Ildefonse, P.; Chaneac, C.; Calas, G. New insight into the structure of nanocrystalline ferrihydrite: EXAFS evidence for tetrahedrally coordinated iron (III). *Geochimica et Cosmochimica Acta* **2011**, *75*, 2708–2720.
- (40) O’day, P.; Rehr, J.; Zabinsky, S.; Brown, G. J. Extended X-ray absorption fine structure (EXAFS) analysis of disorder and multiple-scattering in complex crystalline solids. *Journal of the American Chemical Society* **1994**, *116*, 2938–2949.
- (41) Francisco, P. C. M.; Mitsui, S.; Ishidera, T.; Tachi, Y.; Doi, R.; Shiwaku, H. Interaction of Fe^{II} and Si under anoxic and reducing conditions: Structural characteristics of ferrous silicate co-precipitates. *Geochimica et Cosmochimica Acta* **2020**, *270*, 1–20.
- (42) Chemtob, S. M.; Nickerson, R. D.; Morris, R. V.; Agresti, D. G.; Catalano, J. G. Synthesis and structural characterization of ferrous trioctahedral smectites: Implications for clay mineral genesis and detectability on Mars. *Journal of Geophysical Research: Planets* **2015**, *120*, 1119–1140.
- (43) Manceau, A.; Ildefonse, P.; Hazemann, J.-L.; Flank, A.; Gallup, D. Crystal chemistry of hydrous iron silicate scale deposits at the Salton Sea geothermal field. *Clays and Clay Minerals* **1995**, *43*, 304–317.
- (44) Bevington, P. R.; Robinson, D. K. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill, New York, 1969.
- (45) Scalmani, G.; Frisch, M. J. Continuous surface charge polarizable continuum models of solvation. I. General formalism. *The Journal of Chemical Physics* **2010**, *132*.
- (46) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. Energies, structures, and electronic properties of molecules in solution with the CPCM solvation model. *Journal of Computational Chemistry* **2003**, *24*, 669–681.
- (47) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *The Journal of Physical Chemistry B* **2009**, *113*, 6378–6396.

