An *in situ* XAS study of ferric iron hydrolysis and precipitation in the presence of perchlorate, nitrate, chloride and sulfate

Richard N. Collins^{a,*}, Kevin M. Rosso^b, Andrew L. Rose^c, Chris J. Glover^d and T. David Waite^a

^a *UNSW Water Research Centre, School of Civil and Environmental Engineering, UNSW Australia, Sydney, NSW 2052, Australia.*

^b *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99336, USA.*

^c *Southern Cross Geoscience, Southern Cross University, PO Box 157, Lismore, NSW 2480, Australia.*

^d *X-ray Absorption Spectroscopy Beamline, Australian Synchrotron Company Ltd, 800 Blackburn Rd, Clayton, VIC 3168, Australia.*

Revised and re-submitted to Geochimica et Cosmochimica Acta

21st January 2016

** Corresponding author, Tel: +61 2 9385 5082, Email: richard.collins@unsw.edu.au, Address: UNSW Water Research Centre, School of Civil and Environmental Engineering, UNSW Australia, Sydney, NSW 2052, Australia.*

Abstract

Using a novel combination of *in situ* potentiometric experiments and quick-scanning XAS we present Fe K-edge XAS spectra (to $k = 12 \text{ \AA}^{-1}$) during Fe^{III} hydrolysis and precipitation in 0.33 M $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{NO}_3)_3$, FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ solutions up to pH 4.8. Edge-sharing Fe^{III} polymers appeared almost immediately upon hydrolysis with strong evidence for a μ -oxo dimer species forming in the $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 solutions. The effects of SO_4 on hydrolysis and polymerization pathways included inhibition of both the formation of the μ -oxo dimer and double corner Fe^{III} bonding, ultimately resulting in the precipitation of schwertmannite. As such, under these experimental conditions, double corner Fe^{III} bonding appears to be critical to the formation of ferrihydrite. The spectral trends indicated that the decomposition/transformation of the dimer was sudden and broadly coincident with shortening average Fe-O bond distances, increased Fe neighbors at $\sim 3.43 \text{ \AA}$ and a pre-edge energy transformation suggestive of decreased ligand field strength as well as increasing proportions of tetrahedral Fe^{III} . This result suggests that the incorporation of tetrahedral Fe^{III} into ferrihydrite occurs only at the latter stages of extended polymerization.

1. INTRODUCTION

Due to its unique (redox) chemistry, iron is arguably the most important transition metal to life on earth. Although the aqueous chemistry of ferric iron (Fe^{III}) has been intensively studied for over 50 years, many aspects relating to hydrolysis and precipitation pathways (even to ubiquitous solid phases such as ferrihydrite) remain unresolved. Ferrihydrite is the natural nano-crystalline Fe^{III} oxyhydroxide that most often controls Fe^{III} solubility during forced hydrolysis (Cornell and Schwertmann, 2003). Its structure has been debated since the first detailed structural models of the mineral were proposed in 1967 (Harrison et al., 1967; Towe and Bradley, 1967) with much of the debate concerning the presence (or absence) of tetrahedrally-coordinated Fe^{III} (Cardile, 1988; Combes et al., 1989; Cowley et al., 2000; De Grave et al., 2005; Drits et al., 1993; Eggleton and Fitzpatrick, 1988, 1990; Gray, 1971; Harrison et al., 1967; Hiemstra and van Riemsdijk, 2009; Janney et al., 2000; Magini, 1977; Manceau, 2009, 2010; Manceau et al., 1990; Manceau and Drits, 1993; Manceau and Gates, 1997; Michel et al., 2010; Michel et al., 2007a; Michel et al., 2007b; Murad, 1988; Murad and Schwertmann, 1980; Pan et al., 2010; Pankhurst and Pollard, 1992; Rancourt and Meunier, 2008; Waychunas et al., 1996; Waychunas et al., 1993; Zhao et al., 1994; Zhao et al., 1993). Increasingly, evidence from a range of techniques has converged to support the presence of a tetrahedral component in ferrihydrite (Guyodo et al., 2012; Harrington et al., 2011; Maillot et al., 2011; Michel et al., 2007a; Xu et al., 2011). Nevertheless, uncertainty remains with regard to the forms of aqueous Fe^{III} hydrolysis and inorganically complexed species that arise prior to ferrihydrite precipitation and how tetrahedral Fe^{III} is structurally incorporated (Combes et al., 1989; de Abreu et al., 2006; Kubicki, 2001; Lopes et al., 2002; Magini and Caminiti, 1977; Martin et al., 1998; Mulay and Selwood, 1955; Perera and Hefter, 2003; Pham et al., 2006; Schwertmann et al., 1999; Yang et al., 2013; Zhu et al., 2016; Zhu et al., 2012; Zhu et al., 2013).

Iron K-edge X-ray absorption spectroscopy (XAS) has been one of the most popular analytical techniques to examine ferric iron complexation, hydrolysis and precipitation pathways since it is element specific and can be used to analyze both liquid and solid phases (Bottero et al., 1994; Combes et al., 1989; Doelsch et al., 2000; Drits et al., 1993; Maillot et al., 2011; Manceau and Drits, 1993; Manceau and Gates, 1997; Mikutta, 2011; Pokrovski et al., 2003; Rose et al., 1996; Rose et al., 1997; Waychunas et al., 1993; Westre et al., 1997; Zhu et al., 2016; Zhu et al., 2012; Zhu et al., 2013). Here we report on the application of quick-scanning XAS, which allowed for the collection of spectral data to ~1000 eV above the Fe K-edge in 22 seconds (Electronic Annex, Figure A1), thereby enabling the procurement of spectral data from *in situ* potentiometric experiments undertaken with the purpose of improving our understanding of the hydrolysis and precipitation pathways of Fe^{III} . These experiments have been undertaken in the presence of four inorganic anions

to compare how they may affect polymerization pathways as a result of strong complexation (e.g. between Cl and SO₄) relevant to oceanic, estuarine and acid sulfate environments (Rose and Waite, 2003; Zhu et al., 2012). Quick-scanning XAS has previously proven useful in studying the temporal speciation of Fe^{III} in partially-neutralized ferric nitrate solutions (Zhu et al., 2016; Zhu et al., 2013) as well as solid-state transformations of ferrihydrite to schwertmannite (Zhu et al., 2012) at acidic pH values. Thermodynamic equilibrium speciation and density functional theory (DFT) electronic structure calculations as well as reference to the literature have also been undertaken to aid interpretation of the Fe K-edge XAS data.

2. MATERIALS AND METHODS

2.1. Thermodynamic equilibrium speciation calculations

The dominant aqueous (and solid) Fe^{III} species expected to be present, at thermodynamic equilibrium, over the range of experimental conditions used in this study were determined using the computer speciation program Visual MINTEQ, version 3.1. The specific ion interaction model (SIT) was used for activity corrections, and the stability constants of the aqueous species and solubility products of ferrihydrite and schwertmannite used for these calculations are listed in Table A1.

2.2. Density functional theory (DFT) computations

Molecular orbital theory first principles calculations were performed with NWChem (Valiev et al., 2010) to determine the total energies and optimized structures of the most stable aqueous species of Fe^{III} that could occur during the potentiometric experiments. Ground-state geometry optimizations were undertaken using the open-shell Kohn-Sham DFT formalism and the B3LYP hybrid exchange-correlation functional (Becke, 1993). No symmetry restrictions were imposed on the geometry optimizations. Ahlrichs pVDZ was used as the Fe atom basis set and the 6-31G** basis set was used for H, N, O, S and Cl, which were obtained from the EMSL Basis Set library (Feller, 1996; Schuchardt et al., 2007). Concatenated fragment molecular orbitals were used to precondition the initial guess wavefunction with the desired initial spin structure, however, other than to fix the total spin multiplicity, no spin restrictions were imposed. Optimizations were first performed on the species *in vacuo* and these structures and converged wavefunctions were then used as a starting guess for optimizations performed with the COSMO dielectric continuum solvation model thereby enabling inclusion of the screening effects of surrounding bulk water in the final calculated structure and total energy (Klamt and Schuurmann, 1993). Vibrational frequencies of the optimized structures were then obtained for the solvated aqueous species, and the thermochemical contributions to

enthalpy and entropy were computed at 298.15 K and 1 atm to obtain the total Gibbs free energy at this standard condition. As discussed in Martin et al. (1998), this standard state, conventional in molecular orbital theory codes, includes a small error with respect to the condensed solution phase that must be corrected in absolute total energies of aqueous species, but cancels through total energy differences of species, such as exclusively used here. Only the results obtained for the optimized species in the aqueous phase are reported.

2.3. Solution/suspension conditions

Solutions (total $[\text{Fe}^{\text{III}}] = 0.33 \text{ M}$) made from $\text{Fe}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$, FeCl_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, Australia) dissolved in high-purity (18.2 M Ω .cm resistivity) water were potentiometrically titrated from their starting pH through to precipitation by the dropwise addition of 2 M KOH using a syringe pump. The solutions/suspensions were rapidly mixed using a magnetic stirrer and pH was measured in the solutions/suspensions using a pH probe calibrated using NIST-traceable buffers on the NBS scale. Throughout the experiments, sufficient KOH was added to increase pH through ~ 0.1 pH increments until it was evident that complete hydrolysis (and precipitation) of Fe^{III} had occurred (i.e., the solution provided no pH buffering to further KOH addition). The potentiometric experiments were conducted *in situ* at the XAS beamline of the Australian Synchrotron, Melbourne, Australia. The solution/suspensions were continuously (re)circulated through a 1.5 mm I.D. kapton tube using a peristaltic pump. After pH stabilization at each pH increment (~ 0.1 pH units), two to four transmission XAS spectra were collected through the kapton tube. The addition of KOH, and pH measurements, were facilitated remotely from outside the hutch and all experiments were completed within approximately 2.5 hours.

The high ionic strength of the solutions/suspensions used in these experiments required correction of measured pH values (on the National Bureau of Standards, NBS, scale) to obtain pH values on the free hydrogen ion scale, i.e. pH_{F} . This correction was achieved by the following methodology. A pH titration of a solution containing 0.9 M of the sodium salt (e.g. NaCl) and 0.1 M of the acid (e.g. HCl) or, in the case of sulfate, 0.45 M Na_2SO_4 + 0.05 M H_2SO_4 , with 1 M NaOH was undertaken using a Metrohm Titrando autotitrator equipped with the same pH probe as used for the *in situ* experiments at the Australian Synchrotron. From the titration data, theoretical pH values were derived based on the volume of 1 M NaOH added and the sum of squares of residuals (SSR) were calculated with comparison to the measured pH values. Microsoft Excel's solver was then used to minimize the SSR by adjusting the starting concentration of acid. This step was important in order to obtain a linear relationship between measured and theoretical pH values (as expected) since the

shape of the titration curve is very sensitive to small errors in the starting acid concentration. The calculated correction parameters ε and s were then used to correct the measured pH values by linearly relating the measured pH(NBS) with the theoretical pH_F per the equation $\text{pH}_F = \varepsilon + s \cdot \text{pH}(\text{NBS})$ (Table A2). Data are also presented as a function of the molar hydrolysis ratio (OH:Fe) which is the ratio of the total molar quantity of base added to the molar quantity of Fe^{III} present in the solution/suspension.

2.4. Additional solid- and solution phase characterization measurements

At the completion of the potentiometric experiments all of the resulting suspensions were centrifuged, to aid phase separation, and the solid phases were washed and centrifuged a further three times with high purity water. A subsample of the washed suspensions was analyzed by FTIR-ATR. The suspension was dried onto the ATR with N_{2(g)} and the spectrum was acquired at a resolution of 2 cm⁻¹ with a Perkin Elmer Frontier FTIR spectrometer. Default parameters were used to baseline correct the spectrum. The remaining solid phases were subsequently frozen and freeze-dried. Powder X-ray diffractograms were obtained from 10 to 85 degrees (2 θ) with a PANalytical Xpert XRD using a Cu-K α X-ray source and peak identification was performed using the software programme HighScore v4.1 (PANalytical).

Additional UV-vis spectra were recorded of the solutions before the addition of any base (i.e. OH:Fe = 0), over a 1-cm path length, using a Cary 50 UV-Vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA).

2.5. X-ray absorption spectroscopy measurements

X-ray absorption spectroscopy measurements across the Fe K-edge were undertaken at the Australian Synchrotron on the XAS beamline using an ‘on-the-fly’ approach which allowed the collection of transmission EXAFS spectra to ~1000 eV (~16 Å⁻¹ in k space) above the edge in 22 seconds. Comparison of ‘on-the-fly’ spectra obtained for Fe foil with that obtained with a traditional 45 minute step-by-step scan demonstrated no degradation in the quality of EXAFS data obtained (EA, Figure A1). The XAS beamline (and synchrotron) operational conditions were identical to those previously described (Boland et al., 2013) and the hutch was temperature-controlled to 20±1 °C.

2.6. X-ray absorption spectroscopy data processing

148 Processing of the XAS data was performed using the standard features of ATHENA (Ravel and
 149 Newville, 2005) including alignment and merging of multiple spectra and energy calibration to
 150 elemental Fe. All spectra were treated identically in terms of normalization and background removal.
 151 The E_0 value was fixed at 7125.935 eV, the first inflection point of the 1st derivative data for the
 152 initial spectrum collected on the solutions, for all spectra. The Autobk algorithm was used for
 153 background removal and an Rbkg value of 0.97 was applied to optimize high frequency background
 154 removal. ARTEMIS (Ravel and Newville, 2005) was used to generate theoretical phase and
 155 amplitude functions for single and multiple scattering pathways of Fe-O from monomeric $\text{Fe}(\text{H}_2\text{O})_{(6-x)}(\text{OH})_{(x)}$
 156 in octahedral or tetrahedral geometry. Single scattering pathways of Fe-Fe were generated
 157 from the crystallographic data of goethite (Gualtieri and Venturelli, 1999). EXAFS modelling of all
 158 coordination shells was undertaken simultaneously from 0.97 – 3.8 Å in R space, phase uncorrected,
 159 on forward Fourier-transformed k^3 -weighted $\chi(k)$ data from 2 – 12 Å⁻¹ (providing a distance
 160 resolution of ~0.13 Å). The amplitude reduction factor (S_0^2) was fixed at 0.80 based on modelling of
 161 the first data point of the $\text{Fe}_2(\text{SO}_4)_3$ solution. The coordination number (CN), average interatomic
 162 distance (R), and phase shift (ΔE_0) were used as adjustable fitting parameters during modelling of the
 163 spectra. Initial tests allowing the Debye-Waller factor (σ^2) to vary for the Fe-O and Fe-Fe
 164 coordination shells were undertaken on a goethite sample measured at the same time under identical
 165 beamline and experimental conditions (Boland et al., 2013). With the exception of the interatomic
 166 distance of the edge sharing Fe-Fe atoms (at 3.013 Å) which were overestimated by 0.021 Å, these
 167 tests showed that the Fe-O and Fe-Fe interatomic distances could be reproduced to crystallographic
 168 data to within 0.007 Å or better (Figure A2).
 169 Upon modelling of the data, however it was observed that this approach confounded the detection of
 170 the Fe shells when they first started appearing by producing large σ^2 values (which subsequently
 171 decreased during extended polymerization). To overcome this problem the data were subsequently
 172 modelled with σ^2 being fixed to 0.01 for the Fe-Fe shells. While this had little impact on the
 173 modelled Fe-O and Fe-Fe interatomic distances (e.g. < 0.01 Å, Figure A2), this modelling approach
 174 renders comparison of Fe shell CN results to previous literature difficult. Nevertheless, this still
 175 allows direct comparison between the Fe CN results for the data sets produced in this study.
 176 The F test (Downward et al., 2007) at a probability of $p < 0.05$ was used to test the statistical
 177 significance of 1) adding a second Fe-O/Cl phase and amplitude function to model the first
 178 coordination shell, 2) adding the Fe-Fe coordination shells to the fits, 3) allowing the CN of the first
 179 coordination shell to vary, and 4) adding higher order cumulants C_3 and C_4 to modelling the first
 180 coordination shell.

3. RESULTS

3.1. Thermodynamic equilibrium speciation calculations

Speciation calculations were undertaken over the pH range of the XAS experiments (total $\text{Fe}^{\text{III}} = 0.33$ M) to provide an initial basis for subsequent DFT structural optimizations of the major Fe^{III} species expected to be present during hydrolysis (Figure 1a). In all cases, Fe^{3+} (hexaquo water molecules ignored in the notation) was calculated to be a major aqueous species before precipitation of ferrihydrite or schwertmannite. Aqueous complexes with the respective counter-anions were also predicted to be major contributors to the speciation of Fe^{III} (Figure 1a). The dimer ($\text{Fe}_2(\text{OH})_2^{4+}$) and trimer ($\text{Fe}_3(\text{OH})_4^{5+}$) were the only hydrolysis species calculated to be present at significant concentrations, however, these two polymeric cations were not predicted to form in the $\text{Fe}_2(\text{SO}_4)_3$ solution (Figure 1a). It is acknowledged, however, that, of the polymeric species, compelling experimental evidence only exists for the dimer (Zhu et al., 2013). Neglecting the trimer from the calculations resulted in greater concentrations of the dimer during hydrolysis (by up to a factor of ~2, Figure 1b), but had very little influence on the concentrations of the monomeric species. In either case all other hydrolysis species (including the first, second and third monomeric hydrolysis species) contributed < 5 % to the speciation of Fe^{III} during hydrolysis.

3.2. Density functional theory computations

Density functional theory computations were undertaken to predict the most thermodynamically stable structures of the major aqueous Fe^{III} species shown in Figure 1a. For most of the species, multiple structural entities were optimized to examine the likelihood of two (or more) thermodynamically stable structures coexisting. Using the ratio of the Boltzmann distribution, given as,

$$\frac{\text{Structure 1}}{\text{Structure 2}} = e^{(E_2 - E_1)/kT}$$

the co-existence ratio of the first (*Structure 1*) and second (*Structure 2*) thermodynamically most favorable structures can be calculated, where E_1 and E_2 are the Gibbs free energy values (eV) of the two structural entities of the one species (or reaction products in Table 1), the Boltzmann constant (k) = 8.6173324×10^{-5} eV/K and $T = 298.15$ K (the Gibbs free energy values in Table 1 are provided as kJ/mol but can be converted to eV by dividing by 96.4853). For example, an energy difference of

213 ~7.4 kJ/mol between two structures (reaction products) results in a co-existence ratio of 20:1. The
 214 smallest energy difference between the first and second thermodynamically most favorable structures
 215 listed in Table 1 is 8.8 kJ/mol for the trimer, resulting in a ratio of 35:1. It is, therefore, apparent that
 216 the thermodynamically most favorable structures listed in Table 1 would be dominant.

217 The optimizations performed here resulted in an average Fe-OH₂ distance of 2.015 ± 0.002 Å for
 218 hexa-coordinated Fe(H₂O)₆³⁺ (Figure 2a, Table 2). The structures of the inner- and outer-sphere
 219 Fe(ClO₄)₂²⁺, Fe(NO₃)₂²⁺, Fe(SO₄)⁺ and FeCl₂⁺ complexes have been investigated rarely, if at all, with
 220 DFT (Hill and Schauble, 2008; Zakharov et al., 2001). The inner-sphere complexes were calculated
 221 to be thermodynamically more stable (Table 1) than outer-sphere ‘ion pairs’, as suggested by the
 222 thermodynamic equilibrium speciation calculations (Figure 1a). The common effects of
 223 complexation with ClO₄⁻, NO₃⁻ and SO₄²⁻ on the structure of the resultant complex included
 224 distortion in octahedral geometry with shorter Fe-O distances to the anion(s) (Figures 2b-e). For
 225 example, the Fe-O distances between Fe-O₄Cl, Fe-O₃N and Fe-O₄S were, respectively, 1.944 Å,
 226 1.940 Å and 1.986 ± 0.044 Å (Table 2). The average Fe-O distances for the Fe(H₂O)₅(ClO₄)₂²⁺ and
 227 Fe(H₂O)₅(NO₃)₂²⁺ complexes were extremely similar, 2.020 ± 0.044 Å and 2.023 ± 0.050 Å,
 228 respectively (Table 2), and therefore < 0.01 Å longer than that for Fe(H₂O)₆³⁺. These calculations
 229 suggest that it would be difficult to distinguish these two complexes from Fe(H₂O)₆³⁺ with XAS
 230 based on average Fe-O distances. The average Fe-O distance for Fe(H₂O)₄(SO₄)⁺ and the minor
 231 Fe(H₂O)₂(SO₄)₂⁻ species were ~0.03 - 0.05 Å longer at 2.045 ± 0.055 Å and 2.063 ± 0.059 Å,
 232 respectively (Table 2), suggesting that the presence of these complexes with Fe(H₂O)₆³⁺ would
 233 manifest in slighter longer Fe-O distances being measured by XAS.

234 The 1:1 and 1:2 ferric chloride complexes were rather different (Figures 2f-g) having much longer
 235 (average) Fe-Cl distances of, respectively, 2.215 and 2.263 ± 0.006 Å and average Fe-O bond
 236 distances to the remaining water molecules of 2.066 ± 0.030 and 2.124 ± 0.033 Å (Table 2). In
 237 these computations the *cis* isomer of the 1:2 complex was predicted to be thermodynamically more
 238 stable than the *trans* isomer.

239 Despite its classical hydroxy formula, the charge (4+) given to the dimeric species (Knight and
 240 Sylva, 1975; Milburn and Vosburgh, 1955; Sommer and Margerum, 1970) suggests Fe-O-Fe
 241 bonding could be either through two OH groups or one O atom. The latter (Figure 3a) was calculated
 242 here as the thermodynamically most stable structure (Table 1). The two Fe-O distances through the
 243 bridging O atom are almost identical at 1.831 ± 0.001 Å and the average Fe-O distance is $2.046 \pm$
 244 0.114 Å. The distance between the two Fe atoms is 3.495 Å with a resulting Fe-O-Fe bond angle of
 245 145° (Figure 3a). A reduction in the coordination of either or both Fe atoms resulted in structures

that were energetically less favorable indicating that hexa-coordination was thermodynamically preferred (Table 1).

A number of Fe-O-Fe bonding topologies can be consistent with the 5+ charge assigned to the speculative trimeric hydrolysis species (Arnek and Schlyter, 1968; Bottero et al., 1994). Some examples of the types of structures investigated are provided in Table 1. In contrast to the dimer, it was observed that a trimer consisting solely of Fe-OH-Fe bonding was thermodynamically most favorable (Table 1) with two hexa-coordinated Fe atoms edge sharing with the third hexa-coordinated Fe atom linked via double corner bonding (Figure 3b). As observed for the dimer, decreasing coordination to penta- or tetra-coordination was energetically unfavorable also suggesting that hexa-coordination for all Fe atoms was thermodynamically most favorable (Table 1). The Fe-Fe distance of 3.051 Å obtained for this structure is comparable to edge sharing Fe octahedra in Fe^{III} (oxyhydr)oxides, but the Fe-Fe distance at 3.595 ± 0.008 Å is more indicative of single corner sharing rather than double corner sharing in Fe^{III} (oxyhydr)oxides (Manceau and Drits, 1993). Nevertheless, these structural optimizations suggest that the simultaneous formation of the dimeric and the trimeric hydrolysis species (Figure 1) would manifest in XAS by the appearance of Fe neighbors at these distances and an increase in the average Fe-O distance might also be detectable by XAS (Table 2).

The interatomic distances listed in Table 2 for ferrihydrite and schwertmannite are those based on pair distribution function (PDF) refinements of high-energy X-ray total scattering data (Fernandez-Martinez et al., 2010; Michel et al., 2007a). The average Fe-O bond distance for (2-line) ferrihydrite is approximately 0.017 Å shorter than that calculated by DFT for Fe(H₂O)₆³⁺ whereas for schwertmannite it is almost identical at 2.020 Å (Table 2). A decrease in average Fe-O bond distances during ferrihydrite precipitation would be expected based on these results. Due to the overlapping backscattering distances it would be difficult to differentiate transformations from the dimer/trimer to ferrihydrite/schwertmannite based on Fe-Fe distances alone. However, the proposed structure for ferrihydrite (Michel et al. 2007a) includes Fe tetrahedra and, while the Fe-Fe distances are not directly indicative of tetrahedral geometry (Maillot et al., 2011), there are other features in XAS spectra which are sensitive to this type of geometry change (Maillot et al., 2011; Mikutta, 2011; Westre et al., 1997). In addition, it is also clear from the proposed ferrihydrite and schwertmannite structures that the magnitude of Fe-Fe backscattering between these two minerals should be noticeably different with relatively more intense backscattering occurring at > 3.4 Å in ferrihydrite (relative to that occurring from the edge sharing Fe atoms at ~ 3.0 Å, Table 2).

3.3. Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy

280

281 **3.3.1. General trends and single and multiple scattering at OH:Fe = 0**

282 Systematic changes are clearly evident in the Fourier-transformed EXAFS spectra during Fe^{III}
283 hydrolysis and precipitation in all the solutions (Figure 4; raw EXAFS data are presented in Figure
284 A3). Trends in spectral modifications are highlighted by the difference spectra also shown in Figure
285 4 which represent the difference between the initial (red) spectrum (OH:Fe = 0) and the other
286 spectra. It is important to note that Fourier-transformed difference EXAFS spectra appear positive in
287 magnitude regardless of whether the difference in magnitude in the Fourier-transformed EXAFS
288 spectra (of the data) is negative or positive. The reduction in the amplitude of the first intense peak
289 in the Fourier-transformed data, which is representative of the first coordination shell with oxygen
290 (and Cl for the FeCl₃ solution), can result from either a decrease in CN or an increase in variability of
291 the average bond length, i.e. bond distortion/disorder. Multiple scattering from the first coordination
292 shell is also evident in the spectra out to 4.0 Å (phase uncorrected) during the early stages of
293 hydrolysis and is similar for the Fe(ClO₄)₃ and Fe(NO₃)₃ solutions which, in turn, are dissimilar to
294 the FeCl₃ and Fe₂(SO₄)₃ solutions. Indeed, scattering between the latter two solutions is also visibly
295 dissimilar, particularly between 2 to 3 Å (phase uncorrected) and is suggestive of additional (or
296 different) Fe^{III} species being present (Figure 4). In general, multiple scattering decreases in
297 magnitude as hydrolysis progresses until single scattering from Fe backscatterers dominates in this
298 distance range. A noticeable contribution from Fe backscatterers between 2 to 3 Å, phase
299 uncorrected, in the solutions appears almost immediately upon hydrolysis (Figure 4) consistent with
300 thermodynamic equilibrium speciation calculations (Figure 1) - with the exception of the Fe₂(SO₄)₃
301 solution.

302 In order to gain further structural insights from the EXAFS spectral trends, modelling of the spectra
303 at OH:Fe = 0 with both single and multiple scattering pathways of the first coordination shell was
304 undertaken. The initial spectra of the Fe(ClO₄)₃ and Fe(NO₃)₃ solutions were easily modelled, based
305 on octahedral geometry, using one single scattering Fe-O pathway at ~2.01 Å, an orthogonal Fe-O-
306 O-Fe multiple scattering pathway at ~3.54 Å and three other (linear) multiple scattering pathways at
307 ~4.03 Å (full fitting results are provided in Table A3 and the model fits in Figure A4). The three
308 longer scattering pathways were fixed to the same interatomic distance as allowing these distances to
309 vary led to results where the differences were < 0.06 Å (which is below the resolution permitted with
310 the k range used here for modelling). The orthogonal Fe-O-O-Fe multiple scattering pathway at
311 ~3.54 Å is longer than that expected (~3.43 Å) for a symmetrical octahedral Fe(H₂O)₆³⁺ species with
312 an average Fe-O interatomic distance of ~2.01 Å but, as its magnitude decreases simultaneously with
313 distortion/disorder in the first coordination shell (Figure 4), it seems the most plausible scattering

314 pathway. Nevertheless, its contribution to the EXAFS signal is weak as its inclusion in modelling
315 only significantly improved ($p < 0.05$) the fit of the initial spectrum of the $\text{Fe}(\text{NO}_3)_3$ solution and not
316 that of the $\text{Fe}(\text{ClO}_4)_3$ solution. The thermodynamic equilibrium speciation calculations in Figure 1
317 indicate that the dimeric species would be present at significant concentrations at an OH:Fe ratio of 0
318 in the $\text{Fe}(\text{NO}_3)_3$ solution and, based on the DFT computations, a single scattering Fe-Fe pathway
319 around this interatomic distance could also explain this feature. Attempts to include a single
320 scattering Fe-Fe pathway between 3.5 - 3.6 Å, however, resulted in unrealistic CNs and Debye-
321 Waller factors.

322 Nevertheless, UV-vis spectra recorded for the OH:Fe = 0 solutions (Figure A5) showed that weak
323 bands at 447 and 497 nm, which have been suggested to arise from the presence of a μ -oxo dimer
324 species (Zhu et al., 2016; Zhu et al., 2013), were evident in the $\text{Fe}(\text{NO}_3)_3$ solution. These bands were
325 absent from the other three solution spectra and, in agreement with thermodynamic speciation
326 calculations (Figure 1), could suggest that this species was only present at significant concentrations
327 in the $\text{Fe}(\text{NO}_3)_3$ solution, though below the threshold amenable to detection by non-linear least
328 squares fitting.

329 Modelling of the spectrum obtained for the FeCl_3 solution at OH:Fe = 0 with the same single and
330 multiple scattering pathways used for the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ solutions resulted in a poor fit,
331 however, this was significantly ($p < 0.05$) improved by inclusion of a single scattering Fe-Cl
332 pathway at ~2.28 Å (Figure A6 with full fitting results in Table A3). The effect of this scattering
333 pathway is clearly evident in the Fourier-transformed data through destructive interference with the
334 Fe-O pathway around ~2.2 Å, phase uncorrected (Figure 4). The remaining multiple scattering
335 distances were similar (and statistically significant at $p < 0.05$) to those modelled for the $\text{Fe}(\text{ClO}_4)_3$
336 and $\text{Fe}(\text{NO}_3)_3$ solutions, suggesting that orthogonal multiple scattering involving Cl is extremely
337 weak compared to that from O. Nevertheless, evidence for multiple scattering involving Cl would
338 appear to exist beyond that modelled to 4.00 Å, phase uncorrected (Figure A6). Indeed, multiple
339 scattering between O and Cl and/or Cl and Cl could be included in the modelling with reasonable
340 parameters, but their inclusion either resulted in little improvement to, or actually decreased, the
341 quality of the fit (data not shown). As a result, neither multiple scattering pathway was included in
342 the modelling shown in Figure A6.

343 The distance of ~3.47 Å obtained for the orthogonal Fe-O-O-Fe multiple scattering pathway of the
344 first spectrum in $\text{Fe}_2(\text{SO}_4)_3$ solution is ~0.08 Å shorter than that modelled for the other solutions.
345 The inclusion of this pathway was significant ($p < 0.05$). Although the average Fe-O bond distance
346 measured was slightly shorter than in the other solutions at 2.002 Å, the shorter (average) distance
347 obtained for the orthogonal multiple scattering could also arise through complexation with SO_4^{2-} ,

resulting in a shorter average O-O interatomic distance. For example, based on the DFT computations described in section 3.2, the distance between the bridging O groups of the major $\text{Fe}(\text{H}_2\text{O})_4(\text{SO}_4)^+$ complex is significantly shorter (i.e. 2.356 Å compared to ~2.85 Å in $\text{Fe}(\text{H}_2\text{O})_6^{3+}$). A very weak single scattering pathway for Fe-S at ~2.62 Å could also be included in the modelling (Figure A6), but it did not significantly ($p < 0.05$) improve the fit. Due to its very weak contribution to the spectrum, it could therefore be purely coincidental that this Fe-S interatomic distance is remarkably similar to that calculated for the $\text{Fe}(\text{H}_2\text{O})_4(\text{SO}_4)^+$ complex (2.635 Å). Based on these results, the shell fitting described below only considered Cl as an additional single scattering pathway in the first coordination shell of Fe in the FeCl_3 solution. Furthermore, as there were generally monotonic increases or decreases around interatomic distances for both single and multiple scattering paths (Figure 4), no other additional scattering pathways were examined, except for Fe-Fe single scattering pathways arising from polymerization. Finally, as the contribution of multiple scattering to the EXAFS signal appeared to diminish with hydrolysis (Figure 4), these scattering pathways were omitted from further modelling, but are discussed in further detail when results for the Fe-Fe single scattering paths are presented in section 3.3.4.

3.3.2. Shell by shell fitting - modelling of the first coordination shell with one shell

Initially, modelling of the first coordination shell was restricted to one Fe-O phase and amplitude function and the statistical significance of varying the CN against maintaining a fixed CN at 6 (i.e. octahedral geometry) was determined. Model fits for the Fe-O coordination shell in the $\text{Fe}_2(\text{SO}_4)_3$ solution were not statistically ($p < 0.05$) improved when the CN was allowed to vary from 6 but fits were improved for all the other solutions at CNs < 5.4 (Tables A4-A7 with model fits, including Fe-Fe pathways, shown in Figures A6-A9). Modelling results with one Fe-O phase and amplitude function, allowing CN, R, σ^2 and ΔE_0 to vary, were then compared to results obtained with the inclusion of the higher order cumulants C_3 (related to interatomic distance) and C_4 (related to CN and, to a lesser extent, σ^2). Except in the case of one spectrum collected for the $\text{Fe}(\text{NO}_3)_3$ solution (Table A5), including these cumulants did not significantly ($p < 0.05$) improve the fitting results (Bunker, 1983; Dalba and Fornasini, 1997) and the same trends in the fitting parameters CN, R, σ^2 were maintained regardless of the inclusion of C_3 and C_4 (data not shown). These results demonstrate that the Fe-O coordination shell could almost always be adequately modelled by a Gaussian approximation such that use of the EXAFS equation provides valid modelling results when using only one Fe-O phase and amplitude function when the k range of data is limited to 12 Å⁻¹.

380 The fitting parameters CN, R and σ^2 are plotted in Figure 5 as a function of pH_F and (OH:Fe). In
381 Figure 5 it can be observed that the average Fe-O interatomic distance before the addition of any
382 base (i.e. OH:Fe = 0), for all solutions was 2.00 to 2.01 Å. Based on the calculations in Figure 1, the
383 $\text{Fe}(\text{H}_2\text{O})_5(\text{Cl})^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_4(\text{Cl})_2^+$ complexes would be expected to contribute to an increased Fe-O
384 bond distance in the FeCl_3 solution. This was observed, with the average Fe-O bond distance being
385 ~ 0.01 Å longer than that measured in the other solutions (at similar OH:Fe ratios), which is
386 qualitatively comparable to that expected from the DFT computations (Table 2) and thermodynamic
387 equilibrium calculations (Figure 1).

388 As hydrolysis progressed, the average Fe-O bond distance increased by a maximum of ~ 0.03 Å at an
389 OH:Fe ratio of ~ 1 , except in the $\text{Fe}_2(\text{SO}_4)_3$ solution. Although the inclusion of Fe backscatterers in
390 model fits did not become statistically significant until around this OH:Fe ratio, or later (discussed
391 further below), it is clear from the difference spectra shown in Figure 4 that there is an immediate
392 increase in magnitude around ~ 3.04 Å which is indicative of Fe backscatterers in edge-edge
393 coordination. The results, therefore, indicate that the mean Fe-O bond distances until this point are
394 already representative of both monomeric and polymeric species. Based on the DFT results, the
395 increase in Fe-O interatomic distances would be consistent with the formation of the dimer or trimer
396 (Table 2). The trend in Fe-O bond distances for the $\text{Fe}_2(\text{SO}_4)_3$ solution is clearly different to the
397 other solutions over this OH:Fe range, indicating the formation of different hydrolysis species.
398 While deprotonation of HSO_4^- might obfuscate the OH:Fe ratios measured during the titration of this
399 solution, this is unlikely given that the final OH:Fe ratios plateaued at ~ 3 and that the final five XAS
400 spectra were essentially identical - indicating complete Fe^{III} transformations (Table A7). This, in
401 turn, provides evidence that SO_4^{2-} does not suppress Fe^{III} hydrolysis over this OH:Fe range.

402 As the average Fe-O bond distances decrease from their maxima, the contribution of Fe
403 backscatterers to the spectra continue to increase (Figure 4). As noted in section 3.2, a decrease in
404 the Fe-O bond distance prior to, and concurrent with, polymerization would be consistent with the
405 formation of ferrihydrite. At (or near) complete hydrolysis the average Fe-O bond distances in the
406 polymers/precipitates cluster around ~ 1.985 Å for the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ solutions and ~ 1.990
407 Å for the $\text{Fe}(\text{Cl})_3$ and $\text{Fe}_2(\text{SO}_4)_3$ solutions.

408 Trends in the CN and Debye-Waller factor for the Fe-O coordination shell are also shown in Figure
409 5. The CN results are once again clearly different for the $\text{Fe}_2(\text{SO}_4)_3$ solution compared to the other
410 iron salt solutions. While there is a relatively large degree of uncertainty associated with the
411 determination of CNs, particularly in regards to the effects from disorder, the Debye-Waller factors
412 are essentially identical for all solutions when plotted as a function of the molar hydrolysis ratio

(Figure 5). When plotted against pH_F , the Debye-Waller factors for the $\text{Fe}_2(\text{SO}_4)_3$ solution are actually higher than for the other iron salt solutions. This observation suggests that the decreasing trend in CN for the Fe-O coordination shells of the other three solutions results from disorder rather than being classically expressed in the Debye-Waller factor. This is further supported by the statistical analyses described above which showed that allowing the CN to vary for the Fe-O coordination shell significantly improved ($p < 0.05$) fits when the CN was < 5.4 (Tables A4-A7). Overall, these results suggest that the formation of a common Fe^{III} specie in the $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{NO}_3)_3$ and FeCl_3 solutions is inhibited by sulfate, in agreement with thermodynamic equilibrium calculations (Figure 1).

3.3.3. Shell by shell fitting - modelling of the first coordination shell with two shells

A fitting approach invoking Fe-O and Fe-Cl scattering pathways significantly ($p < 0.05$) improved the fitting of the first six data points of the FeCl_3 solution (Table A6), but the destructive interference between the Fe-O and Fe-Cl pathways was observable to an OH:Fe ratio of 0.74. Despite differences in the experimental conditions of previous studies, the average interatomic distances obtained here for Fe-O and Fe-Cl, ~ 2.02 and $2.27 \text{ \AA}$ respectively, are remarkably similar to those previously reported (Bottero et al., 1994; Combes et al., 1989; Rose et al., 1996). There is also good agreement between these bond distances and those calculated by DFT, particularly for the $\text{Fe}(\text{H}_2\text{O})_4(\text{Cl})_2^+$ complex, but less so for $\text{Fe}(\text{H}_2\text{O})_5(\text{Cl})^{2+}$ (Table 2), indicating that the stability constant for the $\text{Fe}(\text{H}_2\text{O})_4(\text{Cl})_2^+$ complex could be higher than that used for the thermodynamic equilibrium speciation calculations shown in Figure 1.

A two shell approach to modelling the first coordination shell of Fe in Fe^{III} polymers/oxyhydroxides has recently gained attention (Maillot et al., 2011; Manceau, 2011; Zhu et al., 2016) whereby coordination pathways can be extracted from a coordination shell if the data permit a minimal spatial resolution (i.e. $\Delta R = \pi/(2\Delta k)$). To minimize correlations between the fitting parameters of the two Fe-O paths, investigators have either 1) fixed the Debye-Waller factors to be equal (Maillot et al., 2013); or 2) subjectively fixed CNs (Manceau, 2011; Toner et al., 2009; Zhu et al., 2016; Zhu et al., 2013). As it is difficult to compare previous studies due to significant differences between data quality and modelled k space regions, the three modelling approaches described above were used to examine their effect on detecting the expected shorter Fe-O interatomic distance in the dimeric species and/or ferrihydrite/schwertmannite from the first coordination shell in the $\text{Fe}(\text{ClO}_4)_3$ solution data (i.e. the cleanest data set). The $\text{Fe}_2(\text{SO}_4)_3$ solution was also modelled in the same manner to investigate further the differences in the results obtained based on the single shell Fe-O modelling

described in section 3.3.2. To obtain sufficient spatial resolution, the k range used for Fourier transformation was extended to $15.5 \text{ \AA}^{-1}$, providing a resolution of $0.101 \text{ \AA}$. Testing the modelling approaches on goethite revealed that fixing the Debye-Waller factors to be equal resulted in the most accurate determination of Fe-O interatomic distances, followed by fixing the CNs to be equal and finally allowing all of the fitting parameters to vary (Figure A2). To improve the spectral signal-to-noise ratio of the final precipitated phases, the final six spectra of the $\text{Fe}(\text{ClO}_4)_3$ and final four spectra of the $\text{Fe}_2(\text{SO}_4)_3$ solution were merged.

It can be seen in Figure A10 (fits shown in Figure A11) that the interatomic distances of the longer average Fe-O bond ($\sim 2.05 \text{ \AA}$) for the $\text{Fe}(\text{ClO}_4)_3$ solution were almost identical when either the CN or the Debye-Waller factor were fixed to be equal. While there was initially good agreement between the interatomic distances of the shorter average Fe-O bond ($\sim 1.95 \text{ \AA}$), the results significantly diverged between pH_F of 2.00 - 2.23 with Fe-O bond distances at $1.80 - 1.85 \text{ \AA}$ being fitted when the Debye-Waller factors were equal (Figure A10). These bond distances were also reproduced when all fitting parameters were allowed to vary at pH_F 2.00 and 2.11 which corresponds to the point at which the maximum concentrations of the dimer would be expected to be present (Figure 1). The fitting parameters of the final precipitated phase when either the Debye-Waller factor or CN were fixed to be equal were almost identical (Figure A10), while the third approach resulted in estimated average Fe-O interatomic distances of 1.885 and $2.002 \text{ \AA}$.

When the Debye-Waller factor and CN were fixed to be equal for the $\text{Fe}_2(\text{SO}_4)_3$ solution, almost identical Fe-O interatomic distances were obtained for all sample points (Figure A12, fits shown in Figure A13) clustering around 1.94 and $2.04 \text{ \AA}$. While the interatomic distances were significantly different at 1.98 and $2.07 \text{ \AA}$ (and thus below the minimal spatial resolution) when all fitting parameters were allowed to vary, the trends were similar; i.e. there was no change in Fe-O interatomic distances, except for the final solid phase where average interatomic distances shortened to 1.902 and $2.022 \text{ \AA}$.

Based on fitting the Fe-O coordination shell of goethite with the three modelling approaches, fixing the Debye-Waller factors to be equal provided the most accurate results for Fe-O interatomic distances (Figure A2). Here, fixing the Debye-Waller factors or CNs to be equal gave Fe-O interatomic distances having $< 0.01 \text{ \AA}$ difference for either of the solid phases precipitated from the two solutions (Figures A10 and A12). However, the fits were generally improved when allowing all of the parameters to vary. The respective shorter Fe-O interatomic distances obtained with this approach (1.885 and $1.902 \text{ \AA}$) would suggest that a certain proportion of Fe^{III} tetrahedra may exist in both solid phases, though it is acknowledged that the data quality here is inferior to that reported by Maillot et al. (2011, 2013).

While these results highlight some of the uncertainties in data interpretation introduced by modelling the Fe-O shell with two scattering pathways, two of the three approaches involved fitting a short Fe-O bond distance at 1.80 - 1.85 Å in the Fe(ClO₄)₃ solution when the corresponding one shell Fe-O average interatomic distances were at a maximum. These fitting results occur at the point when the concentration of the μ-oxo dimer would be expected to be at its maximum (Figure 1) and these short Fe-O interatomic distances are similar to those in the dimer's DFT-optimized structure (Table 2).

3.3.4. Full shell by shell fitting - modelling of the Fe-Fe coordination shells

EXAFS studies examining the structure of Fe polymers and the processes of polymerization following Fe^{III} hydrolysis have largely focused upon changes occurring in the Fe-Fe coordination shells (Bottero et al., 1994; Combes et al., 1989; Mikutta, 2011; Pokrovski et al., 2003; Rose et al., 1996; Rose et al., 1997). In general agreement with the studies of Bottero et al. (1994) and Combes et al. (1989), a monotonic increase in CN for Fe-Fe interatomic distances at ~3.04 and ~3.43 Å (~3.39 Å for the Fe₂(SO₄)₃ solution) was observed as hydrolysis progressed (Figure 6). The significance of orthogonal and linear multiple scattering from an octahedral Fe-O coordination shell in the Fe-Fe scattering region (when Fe-Fe scattering pathways became significant) was examined and, although both significantly ($p < 0.05$) improved fitting results, the effective radius for the orthogonal multiple scattering was centered at ~3.37 Å for all solutions (data not shown). This distance is too close to the longer Fe-Fe interatomic distances measured for this multiple scattering pathway to be resolved. In accord with a decrease in the average Fe-O bond distance, the linear multiple scattering pathways shortened in length to ~3.94 Å (data not shown). Ultimately, multiple scattering was not considered in the final fitting.

The shorter Fe-Fe scattering path significantly improved fitting before the longer Fe-Fe scattering pathway (Tables A4-A7), as observed previously (Bottero et al., 1994; Combes et al., 1989). However, the Fe-Fe contribution at ~3.04 Å is evident in the difference spectra before it became statistically significant to the fitting of the data (Figure 4). The range in OH:Fe values between which the two paths became statistically significant to the fit varied greatly between the solutions, ranging from 0.4 - 0.5 for the Fe(ClO₄)₃, Fe(NO₃)₃ and FeCl₃ solutions to 2 for the Fe₂(SO₄)₃ solution (Tables A4-A7). The Fe-Fe contribution at ~3.43 Å only became statistically significant at OH:Fe ≥ 2, but occurred much later for the Fe₂(SO₄)₃ solution (OH:Fe = 2.8).

The X-ray diffractograms of the final precipitates from the Fe(ClO₄)₃ and Fe(NO₃)₃ solutions indicated that the Fe^{III} minerals were extremely X-ray amorphous and showed two broad peaks characteristic of 2-line ferrihydrite (Figure A15a). The solid phases precipitated from the FeCl₃ and

Fe₂(SO₄)₃ solutions were also particularly X-ray amorphous, but were somewhat dissimilar from that formed from the other two solutions and both displayed a stronger peak centered at ~35 2θ (Figure A15a). Further FTIR-ATR analysis of the solid phase produced from the Fe₂(SO₄)₃ solution showed distinctive features (Figure A15b) which have been observed for schwertmannite precipitated at acidic pH values (Boily et al., 2010; Wang et al., 2015), indicating that schwertmannite precipitated from this solution. No peaks attributable to either goethite or lepidocrocite were detected in the spectra of all of the precipitated phases (Figure A15c).

3.4 X-ray Absorption Near-Edge Spectroscopy (XANES)

With the exception of the pre-edge region, changes in the XANES spectra of all the solutions were monotonic during Fe^{III} hydrolysis and precipitation (Figure 7a). Various regions of Fe K-edge XANES spectra, marked as A to E in Figure 7a, have been attributed to aspects of Fe^{III} geometry and coordination with the pre-edge features (enlarged in Figure 7b) perhaps receiving the most attention (Apted et al., 1985; Combes et al., 1989; Manceau and Gates, 1997; Mikutta, 2011; Westre et al., 1997).

3.4.1 (Multiple) Scattering Resonances

The (multiple scattering) resonance centered at ~7148 eV, which monotonically increases at A has either been attributed to increasing distortion in Fe^{III} octahedra (Pokrovski et al., 2003) or linked to an increase in Fe^{III} polymerization (Voegelin et al., 2010). The EXAFS results presented in sections 3.3.2 and 3.3.4 are, therefore, consistent with either of these interpretations. However, as Voegelin et al. (2010) observed this resonance in a range of Fe^{III} (oxyhydr)oxides (lepidocrocite, goethite, hematite and maghemite), it is difficult to assign this resonance to aspects of geometry, interatomic distance or bond angle, although all these minerals do contain edge-sharing Fe^{III} octahedra.

The (multiple scattering) resonance at ~7138 eV, marked as B in Figure 7a, has been related to Fe^{III} geometry, with an increase in absorption postulated to correspond to an increase in the proportion of tetrahedral Fe^{III} present (Katz et al., 2012; Pokrovski et al., 2003). Since this resonance decreased with Fe^{III} polymerization (also observed by Voegelin et al. (2010)), then the results presented here would indicate that the content of tetrahedral Fe^{III} decreases with hydrolysis and precipitation, if this interpretation were correct.

3.4.2 Edge region

545 For a number of 1st row divalent transition metals it has been shown that the peak of the white line,
546 corresponding to the 1s → 4p transition and marked as C in Figure 7a, decreases in intensity as
547 distortion increases within the first coordination shell (Chaboy et al., 2006; Collins et al., 2010;
548 Fernando et al., 2010). Such an interpretation would be valid for the results obtained here based on
549 the EXAFS modelling reported in section 3.3.2. It has also been theoretically demonstrated that the
550 maximum intensity of the peak of the white line and its energy position can vary as a function of
551 average bond distance within the first coordination shell (Katz et al., 2012), with an average increase
552 in bond distance resulting in a more intense peak at lower energy and vice versa. In all of the
553 solutions studied here, there is only a slight monotonic decrease in the energy position of the peak of
554 the white line. As such, this suggests that there is either very little change in the average Fe-O bond
555 distance or that simultaneous bond elongation and shortening (i.e. distortion) results in no net effect.
556 Alternatively, it has also been reported that the intensity of the peak of the white line decreases as the
557 covalency of first coordination shell bonding increases (Sarangi, 2013). As the process of oxolation
558 would also be expected to result in greater Fe-O bond covalency, it is therefore also possible that this
559 feature may reflect changes in Fe-O bonding during hydrolysis.

560 In Figure 7a it can also be observed that the edge energy monotonically decreases as a function of
561 hydrolysis and precipitation, particularly in the lower ‘half’ of the edge (marked as D in Figure 7a)
562 where a maximum downward shift of ~2 eV was measured in the Fe(ClO₄)₃ and Fe(NO₃)₃ solutions.
563 Photoreduction of Fe^{III} during the experiments is unlikely given that the solutions/suspensions were
564 only illuminated for 44 - 88 s approximately 18-20 times over a 2 ½ hr period. Indeed, the pre-edge
565 features provided confirmation that Fe existed solely in the Fe^{III} oxidation state (section 3.4.3). The
566 edge energy can also decrease with increasing (average) interatomic distances within the first
567 coordination shell but, as shown in section 3.3.2., this is inconsistent with the corresponding trends in
568 EXAFS data. As with the peak of the white line, it has also been suggested that an increase in bond
569 covalency within the first coordination shell can decrease the edge energy (DeWitt, 1992; Sarangi,
570 2013). For example, DeWitt (1992) observed a positive relationship between this feature and the
571 covalency of first coordination shell bonding in μ-oxo-bridged Fe^{III} molecules and noted that its
572 appearance also reflected greater distortion in this coordination shell. As noted in section 3.3.2.,
573 disorder increased in the first coordination shell as hydrolysis and precipitation progressed.
574 Furthermore, the process of oxolation, as mentioned above, would also be expected to result in
575 greater bond covalency. Therefore, the interpretation of DeWitt (1992) for this feature is consistent
576 with the results obtained here.

577

3.4.3 Pre-edge region

The pre-edge feature marked as E in Figure 7a is attributed to a forbidden $1s \rightarrow 3d$ transition that can be influenced by 4p mixing into the 3d state and so provide $1s \rightarrow 4p$ character to the transition (Shulman et al., 1976; Westre et al., 1997). It has been well established that the intensity of the pre-edge feature for high spin Fe^{III} increases as a result of symmetry distortion at the metal site while maintaining the same geometry, or as the local coordination environment changes from octahedral to tetrahedral geometry where there is also greater 4p mixing due to a reduction in symmetry (Westre et al., 1997). Expansion of the pre-edge features (Figure 7b) indicates that all solutions show similar trends during Fe^{III} hydrolysis and precipitation. For example, the pre-edge features of all the solutions at $\text{OH:Fe} = 0$ show two peaks split by ~ 1.4 eV, which has been observed for high-spin monomeric or dimeric Fe^{III} in octahedral geometry coordinated to oxygen atoms (Westre et al., 1997). As hydrolysis proceeds, the intensity of the higher energy peak increases more than that of the lower energy peak, but this is possibly obfuscated by the absorption of the rising edge also increasing in approximately equal intensity. As polymerization becomes statistically significant (in the EXAFS region, section 3.3.2), the split peaks are no longer apparent and the peak of maximum intensity shifts downwards in energy by ~ 0.4 eV for the FeCl_3 and $\text{Fe}_2(\text{SO}_4)_3$ solutions and by ~ 1 eV for the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ solutions.

To remove the confounding effects of the rising edge to the apparent absorption intensity of the pre-edge features, the data were ‘background subtracted’ by fitting an arc-tangent to the white line (Figure 8). It is clear from comparison of Figures 7b and 8 that removal of the rising edge absorption greatly reduces the intensity of the high energy peak (when observable). A number of other trends in the pre-edge features that are not obvious in the normalized-only data also become readily apparent in Figure 8. This is most clearly demonstrated for the $\text{Fe}(\text{NO}_3)_3$ solution data. For example, while the trend in increasing intensity of the higher energy peak during the early stages of hydrolysis to an OH:Fe ratio of 1.60 ($\text{pH}_\text{F} = 2.14$) is readily apparent (marked as trend 1b on Figure 8), a concomitant increase (maximum of ~ 0.5 eV) in the width of this peak also becomes obvious on its high energy side (marked as trend 1a). This would be expected given that peak width should increase with peak intensity.

After the maximum intensity of the higher energy peak was reached, two changes in the pre-edge features occurred simultaneously with the next increment in base addition ($\text{OH:Fe} = 1.97$, $\text{pH}_\text{F} = 2.23$). The apparent width of the higher energy peak reduced dramatically to be similar to, or less than, the spectrum at an OH:Fe ratio of 0 (trend 2a in Figure 8). At the same time, there was a downward shift in energy of the maximum peak intensity (~ 1 eV) but also a decrease in maximum

absorption intensity (trend 2b). The latter trend is not clearly evident in the normalized-only data. These changes occurred at the same time as single scattering from double corner-sharing Fe backscatterers significantly improved modelling of the EXAFS data (Table A5). Finally, there was a gradual increase in absorption with no further shifts in energy of the peak maxima and only minimal changes to peak width (trend 3). These trends are also apparent for the $\text{Fe}(\text{ClO}_4)_3$ solution and occur at similar OH:Fe ratios (where the significant presence of edge- and double corner-sharing Fe backscatterers occurs). The quality of the FeCl_3 solution data is insufficient to derive definitive conclusions. While the data for the $\text{Fe}_2(\text{SO}_4)_3$ solution showed similar trends, there are some marked differences from the other solutions. For example, while there is an increase in peak intensity of the higher energy peak during the early stages of hydrolysis (trend 1 in Figure 8), the maximum increase in intensity is less than half that observed for the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ solutions and there are also minimal changes to apparent peak widths. There is also a downwards shift in energy of the maximum peak intensity (trend 2a), which occurs well after edge-sharing Fe backscatterers significantly contributed to the EXAFS modelling (OH:Fe = 1.88, Table A7), and increased absorption (trend 2b), but both are also smaller than that observed in the other solutions.

4. DISCUSSION

4.1. The structure of aqueous Fe^{III} hydrolysis species and complexes

In this study, DFT structural optimizations were performed with the COSMO dielectric continuum solvation model to self-consistently include the influence of aqueous solvation (second hydration shell and beyond) on the structure and energy of the aqueous species. With one exception (Yamaguchi and Ohira, 2015), all previous studies have optimized structures *in vacuo* and then used these fixed coordinates to obtain solvation and vibrational energies in aqueous phase models (de Abreu et al., 2006; Kubicki, 2001; Martin et al., 1998; Ottonello and Zuccolini, 2009; Panina et al., 2010; Yang et al., 2013; Zhu et al., 2016; Zhu et al., 2013). The average Fe-OH₂ distance of 2.015 ± 0.002 Å obtained here for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ (Figure 2a, Table 2) is ~ 0.05 Å shorter than that generally reported for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ *in vacuo* (de Abreu et al., 2006; Kubicki, 2001; Li et al., 1996; Martin et al., 1998) and agrees extremely well with that determined experimentally for the OH:Fe = 0 solutions (Figure 5). The average Fe-OH₂ distances for the inner-sphere $\text{Fe}(\text{H}_2\text{O})_5(\text{ClO}_4)^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_5(\text{NO}_3)^{2+}$ complexes were extremely similar to that obtained for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and while the EXAFS modelling (Figure 5) does not provide definitive proof of their presence, the experimental results are in excellent agreement with the DFT optimized structures.

644 It was clear from modelling the first coordination shell of the FeCl_3 solution that there was inner-
 645 sphere bonding between Fe and Cl, in agreement with earlier work (Apted et al., 1985; Bottero et al.,
 646 1994; Combes et al., 1989; Pokrovski et al., 2003; Rose et al., 1996). In contrast to studies where it
 647 has been assumed that the Cl anions are in the *trans* position based on the crystallographic structure
 648 of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Combes et al., 1989; Hill and Schauble, 2008), the DFT computations indicated that
 649 the *cis* isomer of the 1:2 complex was thermodynamically more stable than the *trans* isomer.
 650 Although the average Fe-Cl bond distance of the *trans* isomer was approximately 0.04 Å longer (data
 651 not shown) than the *cis* form, the presence of a mixture of $\text{Fe}(\text{H}_2\text{O})_3\text{Cl}^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_3\text{Cl}_2^+$
 652 complexes makes it difficult to unequivocally confirm the theoretical result.
 653 The only relatively large discrepancy between modelled bond distances and the DFT optimized
 654 structures of the inner-sphere complexes was that obtained for the $\text{Fe}(\text{H}_2\text{O})_4(\text{SO}_4)^+$ complex. (Figure
 655 5 and Table 2). Although the thermodynamic equilibrium calculations in Figure 1 indicated that
 656 complexation of Fe^{III} by SO_4^{2-} should substantially affect Fe speciation, a slightly longer average Fe-
 657 O bond distance in this solution at $\text{OH}:\text{Fe} = 0$, as predicted by the DFT computations, was not
 658 observed. This difference raises the possibility that the complex optimized, $\text{Fe}(\text{H}_2\text{O})_4(\text{SO}_4)^+$, is not
 659 representative of the main species present. Although the number of bonding possibilities is restricted
 660 by the charge assigned to this complex, the pK_a of sulfate (pH 1.97) somewhat complicates matters
 661 as this anion will be present in varying proportions as SO_4^{2-} and HSO_4^- over the pH range examined.
 662 Nevertheless, the average Fe-O bond distance of a DFT optimized $\text{Fe}(\text{H}_2\text{O})_3\text{OH-HSO}_4$ complex was
 663 2.071 Å (data not shown) - even longer than the thermodynamically most stable complex (Table 2).
 664 Future use of alternative basis sets for S may eventually improve agreement with the experimental
 665 data obtained here as inhibition of the formation of the dimer in this solution supports the presence of
 666 strong inner-sphere bonding between Fe^{III} and SO_4^{2-} as has recently been suggested by Wang et al.
 667 (2015) during the formation of schwertmannite.
 668 A μ -oxo dimer (Figure 3a) was calculated here as the thermodynamically most stable structure
 669 (Table 1), in agreement with Yang et al. (2013) and Zhu et al. (2013) but contrasting to results
 670 obtained elsewhere (Lopes et al., 2002; Panina et al., 2010). Experimental evidence for bonding
 671 between a bridging O atom included: i) detection of a short Fe-O interatomic distance during two
 672 shell modelling of the first coordination shell of the $\text{Fe}(\text{ClO}_4)_3$ solution; ii) the trend in increasing
 673 average Fe-O interatomic distances during hydrolysis, as suggested by its DFT-optimized structure,
 674 and; iii) a concurrent increase in absorption of the high energy peak of the pre-edge region (Zhu et al.
 675 2013). An increase in absorption of the high energy peak has been related to μ -oxo bonding in
 676 octahedral Fe^{III} dimers (Westre et al., 1997) where it was postulated that the shorter Fe-O interatomic

distances in the Fe-O-Fe bonds allowed for greater 4p mixing into the 3d orbitals, and thus increased absorption intensity. Westre *et al.* (1997) also suggested that increasing bond covalency should manifest as an increase in intensity of the higher energy peak. Clearly Fe-OH or Fe-O bonding is more covalent than Fe-OH₂ and such an interpretation is, therefore, consistent with the trends observed in the XANES edge region (section 3.4.2).

These results strongly support the conclusions of Zhu *et al.* (2013) on the bonding topology of the Fe^{III} dimer species. However, one of the main differences between the DFT optimized structures of the dimer obtained here and elsewhere (Panina *et al.*, 2010; Yang *et al.*, 2013; Zhu *et al.*, 2013) is the Fe-O-Fe bond angle, and hence the Fe-Fe interatomic distance. Previously, it has been reported that this angle is approximately 180° in accord with the angle observed for our *in vacuo* calculations (data not shown) and those of Yamaguchi and Ohira (2015), whereas use of the COSMO dielectric continuum solvation model during structural optimizations resulted in a reduction of this angle to 145° (Figure 3a), similar to a dimer isolated from Nafion membranes (Pan *et al.*, 1983). Recent DFT calculations using a polarizable continuum model to account for solvation effects also reported an Fe-O-Fe angle of 157° (Yamaguchi and Ohira, 2015). As a neighboring Fe atom at ~3.50 Å (Table 2 and Yamaguchi and Ohira, 2015) or ~3.61 (Yang *et al.*, 2013; Zhu *et al.*, 2013) could not be modelled, confirmation of either angle was not obtained. A lack of XAS evidence for a neighboring Fe atom at ~3.60 also makes it difficult to experimentally confirm the formation of a trimer based on its DFT-optimized structure.

It should be noted, however, that Zhu *et al.* (2013) observed that the UV-vis spectrum of their solution containing dimers was blue shifted compared to literature presented on a linear Fe-O-Fe Fe-crown dimer (Junk *et al.*, 2002), suggestive that the dimer species may not have a linear Fe-O-Fe bond.

4.2. Effects of sulfate on polymerization pathways

For the Fe₂(SO₄)₃ solution it appears that double corner-sharing between Fe^{III} atoms is inhibited during hydrolysis, resulting in a CN at this interatomic distance that is approximately half that of the other solutions once precipitation was complete (Figure 6). Recently it has been shown that the sulfate inner-sphere complex in schwertmannite is likely to be bidendate-binuclear (Wang *et al.*, 2015) (i.e. double corner-bonded) and the results obtained here, therefore, support this conclusion.

Under the experimental conditions examined here, the complexation of Fe^{III} by the SO₄²⁻ anion also prevented the formation of the u-oxo dimer. It has recently been reported that the structural reconfiguration of this dimer is the rate-limiting step involved in the nucleation of ferrihydrite at high

710 Fe^{III} concentrations and acidic pH values (Zhu et al., 2016). If this were correct, then this
 711 thermodynamic barrier would be removed in the presence of sulfate and so ferrihydrite would be
 712 expected to precipitate. As this was not the case, it is more likely that the presence of sulfate favors
 713 the precipitation of schwertmannite due to double corner bonding with adjacent Fe^{III} atoms existing
 714 as either aqueous molecules or solid phase polymers. Given the important role of schwertmannite in
 715 the retention of many inorganic contaminants in acid mine drainage and acid sulfate environments
 716 (Regenspurg and Peiffer, 2005), insights into the pathways through which this mineral forms will
 717 further our understanding of how these elements can be structurally accommodated during
 718 schwertmannite precipitation. For example, in contrast to the study of Zhu et al. (2012), the
 719 experimental conditions of our potentiometric study did not result in the formation of ferrihydrite and
 720 its subsequent transformation to schwertmannite but, rather, resulted in the direct formation of
 721 schwertmannite, as originally proposed by Schwertmann et al. (1999).
 722 The inhibition of double corner-sharing between Fe^{III} atoms has also been previously observed
 723 during Fe^{III} hydrolysis and precipitation in the presence of other tetrahedral oxyanions, such as
 724 silicate (Doelsch et al., 2000; Jones et al., 2009; Pokrovski et al., 2003; Voegelin et al., 2010),
 725 phosphate (Rose et al., 1996; Voegelin et al., 2010) and arsenate (Maillot et al., 2013; Waychunas et
 726 al., 1993) where it has generally been proposed that these tetrahedral oxyanions block double corner
 727 bonding between Fe^{III} octahedra (Pokrovski et al., 2003). However, if this distance is also
 728 representative of tetrahedral Fe^{III} in ferrihydrite (Maillot et al., 2011; Michel et al., 2007a), then a
 729 decrease in the number of Fe backscatterers could also represent a loss of double corner bonding Fe^{III}
 730 tetrahedra.
 731 Although trends 2b and 3 in Figure 8 for the $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}(\text{ClO}_4)_3$ solutions have often been
 732 attributed to the presence of tetrahedral or pentahedral Fe^{III} within an octahedrally-dominated matrix
 733 (Mikutta, 2011; Pokrovski et al., 2003; Zhao et al., 1994; Zhao et al., 1993), for this to be the case in
 734 the present experiments, the related decrease in peak width of the high energy peak (trend 2a in
 735 Figure 8) can only be interpreted as octahedral Fe becoming less distorted (and thus losing
 736 absorption intensity) to a similar state as Fe^{III} at an OH:Fe ratio of 0. Westre *et al.* (1997) also noted
 737 that the energy difference between the two pre-edge peaks of monomeric Fe^{III} in octahedral geometry
 738 can vary by as much as 0.4 eV, depending on ligation, which they related to ligand field strength. As
 739 such, trends 2a and 2b observed for the $\text{Fe}(\text{ClO}_4)_3$ and $\text{Fe}(\text{NO}_3)_3$ solutions in Figure 8 also have a
 740 contribution from a decrease in ligand field strength in the first coordination shell bonding, which is
 741 coincident with the onset of significant polymerization. Indeed, we speculate that if polymerization
 742 is precursory to crystallization, and if long-range crystalline order moves the electronic structure of
 743 the system from molecule-like to crystal-like, then more continuous waves through the solid will

occur yielding more shared interactions that could decrease the local ligand field strength by “smearing out” electron density along a lattice. Therefore, the experimental evidence presented in Figure 8 indicates that the increase in pre-edge intensity observed for the solid phases (trend 3) most likely results from a combination of decreased ligand field strength and the presence of tetrahedral Fe^{III} in an octahedrally-dominated matrix where ferrihydrite precipitates. These results also provide experimental evidence for the recent suggestion of Zhu et al. (2016) that the assimilation of tetrahedral Fe^{III} into ferrihydrite occurs at the latter stages of polymerization.

5. CONCLUSIONS

The experimental conditions employed in this XAS study, principally the high Fe^{III} concentrations, are relevant to most studies that have examined the reactivity and structure of synthetically-prepared Fe^{III} oxyhydroxides, such as 2-line ferrihydrite and schwertmannite (Cornell and Schwertmann, 2003).

Thermodynamic equilibrium speciation calculations implied that the aqueous speciation of Fe^{III} would be relatively simple during the potentiometric experiments with Fe(H₂O)₆³⁺, the dimer/trimer and the inner-sphere complexes with the counter anions comprising > 95 % of the species present (section 3.1). This relative simplicity was expressed in the spectral trends of the XAS data.

Density functional theory calculations indicated that the μ -oxo dimer is thermodynamically most stable and XAS evidence for this species was obtained through one- and two-shell modelling of the Fe-O coordination shell as well as characteristic trends produced in the pre-edge region during hydrolysis. The DFT optimizations performed with the COSMO solvation model suggest that this species has an Fe-Fe interatomic distance at least 0.11 Å shorter than previously suggested. In addition, the thermodynamically most stable Fe(H₂O)₄(Cl)₂⁺ complex was calculated to have the Cl atoms in the *cis* position and there was good agreement between theoretically and experimentally determined Fe-Cl bond distances.

Multiple scattering pathways and trends in the average bond distance of the Fe-O coordination shell for the Fe₂(SO₄)₃ during the initial stages of hydrolysis support the presence of thermodynamically stable inner-sphere Fe^{III}-SO₄ aqueous complexes, as predicted from thermodynamic equilibrium calculations and Gibbs free energy differences calculated for DFT-optimized structures. The presence of sulfate inhibits the formation of the dimer species as well as double corner-bonding of octahedral/tetrahedral Fe^{III}. At the same time, edge-sharing Fe polymerization is promoted and the formation of schwertmannite becomes thermodynamically favorable.

The initial stages of polymerization were evident in Fe-Fe interatomic distances at ~3.04 Å. While this is similar to the interatomic distance for the edge-sharing Fe atoms in the trimer, no evidence

was obtained for the double corner Fe atom at ~ 3.60 Å. Though it would be expected to be more difficult to detect this distance through EXAFS modelling (due to its longer R), the structure of the trimer, unlike the dimer, does not have other unique XAS spectral features for which its presence could be confirmed. As such, the existence of this species remains speculative.

The decomposition/transformation of the dimer was broadly coincident with extended polymerization and, in particular, statistically significant proportions of Fe backscatters at ~ 3.43 Å and a pre-edge energy transformation suggestive of decreased ligand field strength and the incorporation of tetrahedral Fe^{III} into ferrihydrite.

ELECTRONIC ANNEX

Supplementary data (Tables A1-A7 and Figures A1-A15) associated with this article can be found in the Electronic Annex.

ACKNOWLEDGEMENTS

Richard Collins is a recipient of an Australian Research Council Future Fellowship (FT110100067) and also acknowledges the support of the Australian-American Fulbright Commission for a Senior Scholarship in Nuclear Science and Technology to work at Pacific Northwest National Laboratory. Kevin Rosso gratefully acknowledges the U.S. Department of Energy's (DOE) Office of Basic Energy Sciences, Chemical Sciences, Geosciences, & Biosciences (CSGB) Division for support through the Geosciences program at Pacific Northwest National Laboratory (PNNL). Andrew Rose is a recipient of an Australian Research Council QEII Fellowship (DP0987351). Funding support was also provided by the Australian Research Council project DP120103234. The DFT calculations were performed using either EMSL, a national scientific user facility sponsored by the U.S. DOE Office of Biological and Environmental Research and located at PNNL or the Leonardi Engineering Research Computing Cluster, UNSW Australia.

REFERENCES

- Apted, M.J., Waychunas, G.A. and Brown, G.E. (1985) Structure and specification of iron complexes in aqueous solutions determined by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 49, 2081-2089.
- Arnek, R. and Schlyter, K. (1968) Thermochemical studies of hydrolytic reactions 7. A recalculation of calorimeter data on iron(III) hydrolysis. *Acta Chemica Scandinavica* 22, 1327-1330.
- Becke, A.D. (1993) Density-functional thermochemistry .3. The role of exact exchange. *Journal of Chemical Physics* 98, 5648-5652.
- Boily, J.-F., Gassman, P.L., Peretyazhko, T., Szanyi, J. and Zachara, J.M. (2010) FTIR spectral components of schwertmannite. *Environ. Sci. Technol.* 44, 1185-1190.

815 Boland, D.D., Collins, R.N., Glover, C.J. and Waite, T.D. (2013) An *in situ* quick-EXAFS and redox
816 potential study of the Fe(II)-catalysed transformation of ferrihydrite. *Colloids and Surfaces A:*
817 *Physicochemical and Engineering Aspects* 435, 2-8.

818 Bottero, J.Y., Manceau, A., Villieras, F. and Tchoubar, D. (1994) Structure and mechanisms of
819 formation of FeOOH(Cl) polymers. *Langmuir* 10, 316-319.

820 Bunker, G. (1983) Application of the ratio method of EXAFS analysis to disordered systems.
821 *Nuclear Instruments and Methods* 207, 437-444.

822 Cardile, C.M. (1988) Tetrahedral Fe³⁺ in ferrihydrite: ⁵⁷Fe Mossbauer spectroscopic evidence. *Clays*
823 *Clay Mineral* 36, 537-539.

824 Chaboy, J., Munoz-Paez, A., Merklings, P.J. and Sanchez Marcos, E. (2006) The hydration of Cu²⁺:
825 can the Jahn-Teller effect be detected in liquid solution? *J. Chem. Phys.* 124, Article No. 064509.

826 Collins, R.N., Bakkaus, E., Carriere, M., Khodja, H., Proux, O., Morel, J.-L. and Gouget, B. (2010)
827 Uptake, localization, and speciation of cobalt in *Triticum aestivum* L. (wheat) and *Lycopersicon*
828 *esculentum* M. (tomato). *Environ. Sci. Technol.* 44, 2904-2910.

829 Combes, J.M., Manceau, A., Calas, G. and Bottero, J.Y. (1989) Formation of ferric oxides from
830 aqueous solutions: a polyhedral approach by X-ray absorption spectroscopy: I. Hydrolysis and
831 formation of ferric gels. *Geochim. Cosmochim. Acta* 53, 583-594.

832 Cornell, R.M. and Schwertmann, U. (2003) The iron oxides. Structures, properties, reactions,
833 occurrences and uses., 2nd Edition ed. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim,
834 Germany.

835 Cowley, J.M., Janney, D.E., Gerkin, R.C. and Buseck, P.R. (2000) The structure of ferritin cores
836 determined by electron nanodiffraction. *J. Structural Biol.* 131, 210-216.

837 Dalba, G. and Fornasini, P. (1997) EXAFS Debye-Waller factor and thermal vibrations of crystals.
838 *Journal of Synchrotron Radiation* 4, 243-255.

839 de Abreu, H.A., Guimaraes, L. and H.A., D. (2006) Density-functional theory study of iron(III)
840 hydrolysis in aqueous solution. *J. Phys. Chem. A* 110, 7713-7718.

841 De Grave, E., Vandenberghe, R.E. and Dauwe, C. (2005) ILEEMS: methodology and applications to
842 iron oxides. *Hyperfine Interactions* 161, 147-160.

843 DeWitt, J.G. (1992) X-ray absorption spectroscopic studies of the dinuclear iron center in methane
844 monooxygenase and the sulfur and chlorine centers in photographic materials. Stanford University,
845 CA, USA, Stanford.

846 Doelsch, E., Rose, J., Masion, A., Bottero, J.-Y., Nahon, D. and Bertsch, P.M. (2000) Speciation and
847 crystal chemistry of iron(III) chloride hydrolyzed in the presence of SiO₄ ligands. 1. An Fe K-edge
848 EXAFS study. *Langmuir* 16, 4726-4731.

849 Downward, L., Booth, C.H., Lukens, W.W. and Bridges, F. (2007) A variation of the F-test for
850 determining statistical relevance of particular parameters in EXAFS fits., in: Hedman, B., Pianetta, P.
851 (Eds.), *X-ray Absorbance Fine Structure - XAFS13: 13th International Conference*, Stanford, CA,
852 USA, pp. 129-131.

853 Drits, V.A., Sakharov, B.A., Salyn, A.L. and Manceau, A. (1993) Structural model for ferrihydrite.
854 *Clay Minerals* 28, 185-207.

855 Eggleton, R.A. and Fitzpatrick, R.W. (1988) New data and a revised structural model for
856 ferrihydrite. *Clays Clay Mineral* 36, 111-124.

857 Eggleton, R.A. and Fitzpatrick, R.W. (1990) New data and a revised structural model for
858 ferrihydrite: reply. *Clays Clay Mineral* 38, 335-336.

859 Feller, D.J. (1996) The role of databases in support of computational chemistry calculations. *Journal*
860 *of Computational Chemistry* 17, 1571-1586.

861 Fernandez-Martinez, A., Timon, V., Roman-Ross, G., Cuello, G.J., Daniels, J.E. and Ayora, C.
862 (2010) The structure of schwertmannite, a nanocrystalline iron oxyhydroxysulfate. *American*
863 *Mineralogist* 95, 1312-1322.

864 Fernando, D.R., Mizuno, T., Woodrow, I.E., Baker, A.J.M. and Collins, R.N. (2010)
 865 Characterisation of foliar Mn in Mn-(hyper)accumulators using X-ray absorption spectroscopy. *New*
 866 *Phytol.* 188, 1014-1027.
 867 Gray, H.B. (1971) Structural models for iron and copper proteins based on spectroscopic and
 868 magnetic properties. *Advances in Chemistry Series*, 365-389.
 869 Gualtieri, A. and Venturelli, P. (1999) In situ study of the goethite-hematite phase transformation by
 870 real time synchrotron powder diffraction. *Am. Mineral.* 84, 895-904.
 871 Guyodo, Y., Saintavit, P., Arrio, M.-A., Carvallo, C., Lee Penn, R., Erbs, J.J., Forsberg, B.S.,
 872 Morin, G., Maillot, F., Lagroix, F., Bonville, P., Wilhelm, F. and Rogalev, A. (2012) X-ray magnetic
 873 circular dichroism provides strong evidence for tetrahedral iron in ferrihydrite. *Geochem. Geophys.*
 874 *Geosyst.* 13, Q06Z44.
 875 Harrington, R., Hausner, D.B., Xu, W., Bhandari, N., Michel, F.M.M., Brown Jr, G.E., Strongin,
 876 D.R. and Parise, J.B. (2011) Neutron pair distribution function study of two-line ferrihydrite.
 877 *Environ. Sci. Technol.* 45, 9883-9890.
 878 Harrison, P.M., Fischbach, F.A., Hoy, T.G. and Haggis, G.H. (1967) Ferric oxyhydroxide core of
 879 ferritin. *Nature* 216, 1188-1190.
 880 Hiemstra, T. and van Riemsdijk, W.H. (2009) A surface structural model for ferrihydrite I: Sites
 881 related to primary charge, molar mass, and mass density. *Geochim. Cosmochim. Acta* 73, 4423-
 882 4436.
 883 Hill, P.S. and Schauble, E.A. (2008) Modeling the effects of bond environment on equilibrium iron
 884 isotope fractionation in ferric aquo-chloro complexes. *Geochim. Cosmochim. Acta* 72, 1939-1958.
 885 Janney, D.E., Cowley, J.M. and Buseck, P.R. (2000) Structure of synthetic 2-line ferrihydrite by
 886 electron nanodiffraction. *Am. Mineral.* 85, 1180-1187.
 887 Jones, A.M., Collins, R.N., Rose, J. and Waite, T.D. (2009) The effect of Si and NOM on the Fe(II)-
 888 catalysed transformation and reactivity of Fe(III) minerals. *Geochim. Cosmochim. Acta* 73, 4409-
 889 4422.
 890 Junk, P.C., McCool, B.J., Moubaraki, B., Murray, K.S., Spiccia, L., Cashion, J.D. and Steed, J.W.
 891 (2002) Utilization of crown ethers to stabilize the dinuclear u-oxo bridged iron(III) aqua ion,
 892 $[(H_2O)_5Fe(-O)Fe(OH_2)_5]^{4+}$. *J. Chem. Soc., Dalton Trans.*, 1024-1029.
 893 Katz, J.E., Zhang, X., Attenkofer, K., Chapman, K.W., Frandsen, C., Zarzycki, P., Rosso, K.M.,
 894 Falcone, R.W., Waychunas, G.A. and Gilbert, B. (2012) Electron small polarons and their mobility
 895 in iron (oxyhydr)oxide nanoparticles. *Science* 337, 1200-1203.
 896 Klamt, A. and Schuurmann, G. (1993) COSMO: a new approach to dielectric screening in solvents
 897 with explicit expressions for the screening energy and its gradient. *Journal of the Chemical Society,*
 898 *Perkin Transactions 2*, 799-805.
 899 Knight, R.J. and Sylva, R.N. (1975) Spectrophotometric investigation of iron(III) hydrolysis in light
 900 and heavy water at 25 °C. *Journal of Inorganic and Nuclear Chemistry* 37, 779-783.
 901 Kubicki, J.D. (2001) Self-consistent reaction field calculations of aqueous Al^{3+} , Fe^{3+} , and Si^{4+} :
 902 Calculated aqueous-phase deprotonation energies correlated with experimental $\ln(K_a)$ and pK_a . *J.*
 903 *Phys. Chem. A* 105, 8756-8762.
 904 Li, J., Fisher, C.L., J.L., C., Bashford, D. and Noodleman, L. (1996) Calculation of redox potentials
 905 and pK_a values of hydrated transition metal cations by a combined density functional and continuum
 906 dielectric theory. *Inorg. Chem.* 35, 4694-4702.
 907 Lopes, L., de Laat, J. and Legube, B. (2002) Charge transfer of iron(III) monomeric and oligomeric
 908 aqua hydroxo complexes: Semiempirical investigation into photoactivity. *Inorg. Chem.* 41, 2505-
 909 2517.
 910 Magini, M. (1977) Structural relationships between colloidal solutions and hydroxide gels of
 911 iron(III) nitrate. *J. Inorg. Nucl. Chem.* 39, 409-412.
 912 Magini, M. and Caminiti, R. (1977) On the structure of highly concentrated iron(III) salt solutions. *J.*
 913 *Inorg. Nucl. Chem.* 39, 91-94.

914 Maillot, F., Morin, G., Juillot, F., Bruneel, O., Casiot, C., Ona-Nguema, G., Wang, Y., Lebrun, S.,
 915 Aubry, E., Vlaic, G. and Brown Jr., G.E. (2013) Structure and reactivity of As(III)- and As(V)-rich
 916 schwertmannites and amorphous ferric arsenate sulfate from the Carnoules acid mine drainage,
 917 France: Comparison with biotic and abiotic model compounds and implications for As remediation.
 918 *Geochim. Cosmochim. Acta* 104, 310-329.
 919 Maillot, F., Morin, G., Wang, Y., Bonnin, D., Ildefonse, P., Chaneac, C. and Calas, G. (2011) New
 920 insight into the structure of nanocrystalline ferrihydrite: EXAFS evidence for tetrahedrally
 921 coordinated iron(III). *Geochimica et Cosmochimica Acta* 75, 2708-2720.
 922 Manceau, A. (2009) Evaluation of the structural model for ferrihydrite derived from real-space
 923 modelling of high-energy X-ray diffraction data. *Clay Minerals* 44, 19-34.
 924 Manceau, A. (2010) PDF analysis of ferrihydrite and the violation of Pauling's Principia. *Clay*
 925 *Minerals* 45, 225-228.
 926 Manceau, A. (2011) Critical evaluation of the revised akdalaite model for ferrihydrite. *Clay Minerals*
 927 45, 225-228.
 928 Manceau, A., Combes, J.M. and Calas, G. (1990) New data and a revised structural model for
 929 ferrihydrite: comment. *Clays Clay Mineral* 38, 331-334.
 930 Manceau, A. and Drits, V.A. (1993) Local structure of ferrihydrite and feroxyhite by EXAFS
 931 spectroscopy. *Clay Minerals* 28, 165-184.
 932 Manceau, A. and Gates, W.P. (1997) Surface structural model for ferrihydrite. *Clays Clay Mineral*
 933 45, 448-460.
 934 Martin, R.L., Hay, P.J. and Pratt, L.R. (1998) Hydrolysis of ferric ion in water and conformational
 935 equilibrium. *Journal of Physical Chemistry A* 102, 3565-3573.
 936 Michel, F.M., Barron, V., Torrent, J., Morales, M.P., Serna, C.J., Boily, J.-F., Liu, Q., Ambrosini, A.,
 937 Cismasu, A.C. and Brown Jr., G.E. (2010) Ordered ferrimagnetic form of ferrihydrite reveals links
 938 among structure, composition, and magnetism. *Proc. Natl. Ac. Sci. U.S.A.* 107, 2787-2792.
 939 Michel, F.M., Ehm, L., Antao, S.M., Lee, P.L., Chupas, P.J., Liu, G., Strongin, D.R., Schoonen,
 940 M.A.A., Phillips, B.L. and Parise, J.B. (2007a) The structure of ferrihydrite, a nanocrystalline
 941 material. *Science* 316, 1726-1729.
 942 Michel, F.M., Ehm, L., Liu, G., Han, W.Q., Antao, S.M., Chupas, P.J., Lee, P.L., Knorr, K., Eulert,
 943 H., Kim, J., Grey, C.P., Celestian, A.J., Gillow, J., Schoonen, M.A.A., Strongin, D.R. and Parise,
 944 J.B. (2007b) Similarities in 2- and 6-line ferrihydrite based on pair distribution function analysis of
 945 X-ray total scattering. *Chemistry of Materials* 19, 1489-1496.
 946 Mikutta, C. (2011) X-ray absorption spectroscopy study on the effect of hydroxybenzoic acids on the
 947 formation and structure of ferrihydrite. *Geochim. Cosmochim. Acta* 75, 5122-5139.
 948 Milburn, R.M. and Vosburgh, W.C. (1955) A spectrophotometric study of the hydrolysis of iron(III)
 949 ion. II. Polynuclear species. *Journal of the American Chemical Society* 77, 1352-1355.
 950 Mulay, L.N. and Selwood, P.W. (1955) Hydrolysis of Fe^{3+} : Magnetic and spectrophotometric studies
 951 on ferric perchlorate solutions. *Journal of the American Chemical Society* 77, 2693-2701.
 952 Murad, E. (1988) The Mossbauer spectrum of "well"-crystallized ferrihydrite. *J. Magnetism and*
 953 *Magnetic Materials* 74, 153-157.
 954 Murad, E. and Schwertmann, U. (1980) The Mossbauer spectrum of ferrihydrite and its relations to
 955 those of other iron oxides. *Am. Mineral.* 65, 1044-1049.
 956 Ottonello, G. and Zuccolini, M.V. (2009) Ab-initio structure, energy and stable Fe isotope
 957 equilibrium fractionation of some geochemically relevant H-O-Fe complexes. *Geochim. Cosmochim.*
 958 *Acta* 73, 6447-6469.
 959 Pan, H.K., Yarusso, D.J., Knapp, G.S., Pineri, M., Meagher, A., Coey, J.M.D. and Cooper, S.L.
 960 (1983) EXAFS and mossbauer studies of iron neutralized Nafion ionomers. *J. Chem. Phys.* 79, 4736.
 961 Pan, Y.-H., Vaughan, G., Brydson, R., Bleloch, A., Gass, M., Sader, K. and Brown, A. (2010)
 962 Electron-beam-induced reduction of Fe^{3+} in iron phosphate dihydrate, ferrihydrite, haemosiderin and
 963 ferritin as revealed by electron energy-loss spectroscopy. *Ultramicroscopy* 110, 1020-1032.

964 Panina, N.S., Belyaev, A.N., Eremin, A.V. and Davidovich, P.B. (2010) DFT quantum-chemical
 965 study of the hydrolysis products of Fe(II) and Fe(III) aqua-complexes. *Russian Journal of General*
 966 *Chemistry* 80, 889-894.
 967 Pankhurst, Q.A. and Pollard, R.J. (1992) Structural and magnetic properties of ferrihydrite. *Clays*
 968 *Clay Mineral* 40, 268-272.
 969 Perera, W.N. and Hefter, G. (2003) Mononuclear cyano- and hydroxo-complexes of iron(III). *Inorg.*
 970 *Chem.* 42, 5917-5923.
 971 Pham, A.N., Rose, A.L., Feitz, A.J. and Waite, T.D. (2006) Kinetics of Fe(III) precipitation in
 972 aqueous solutions at pH 6.0-9.5 and 25 °C. *Geochim. Cosmochim. Acta* 70, 640-650.
 973 Pokrovski, G.S., Schott, J., Farges, F. and Hazemann, J.-L. (2003) Iron (III)-silica interactions in
 974 aqueous solution: Insights from X-ray absorption fine structure spectroscopy. *Geochim. Cosmochim.*
 975 *Acta* 67, 3559-3573.
 976 Rancourt, D.G. and Meunier, J.-F. (2008) Constraints on structural models of ferrihydrite as a
 977 nanocrystalline material. *Am. Mineral.* 93, 1412-1417.
 978 Ravel, B. and Newville, M. (2005) ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray
 979 absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 12, 537-541.
 980 Regenspurg, S. and Peiffer, S. (2005) Arsenate and chromate incorporation in schwertmannite.
 981 *Applied Geochemistry* 20, 1226-1239.
 982 Rose, A.L. and Waite, T.D. (2003) Kinetics of hydrolysis and precipitation of ferric iron in seawater.
 983 *Environmental Science & Technology* 37, 3897-3903.
 984 Rose, J., Manceau, A., Bottero, J.-Y., Masion, A. and Garcia, F. (1996) Nucleation and growth
 985 mechanisms of Fe oxyhydroxide in the presence of PO₄ ions. 1. Fe K-edge EXAFS study. *Langmuir*
 986 12, 6701-6707.
 987 Rose, J., Manceau, A., Masion, A. and Bottero, J.Y. (1997) Structure and mechanisms of formation
 988 of FeOOH(NO₃) oligomers in the early stages of hydrolysis. *Langmuir* 13, 3240-3246.
 989 Sarangi, R. (2013) X-ray absorption near-edge spectroscopy in bioinorganic chemistry: Application
 990 to M-O₂ systems. *Coord. Chem. Rev.* 257, 459-472.
 991 Schuchardt, K.L., Didier, B.T., Elsethagen, T., Sun, L., Gurumoorthi, V., Chase, J., Li, J. and
 992 Windus, T.L. (2007) Basis set exchange: A community database for computational sciences. *Journal*
 993 *of Chemical Information and Modeling* 47, 1045-1052.
 994 Schwertmann, U., Friedl, J. and Stanjek, H. (1999) From Fe(III) ions to ferrihydrite and then to
 995 hematite. *J. Colloid Interf. Sci.* 209, 215-223.
 996 Shulman, R.G., Yafet, Y., Eisenberger, P. and Blumberg, W.E. (1976) Observation and interpretation
 997 of x-ray absorption edges in iron compounds and proteins. *Proc. Natl. Ac. Sci. U.S.A* 73, 1384-1388.
 998 Sommer, B.A. and Margerum, D.W. (1970) Kinetic study of the hydroxoiron(III) dimer. *Inorganic*
 999 *Chemistry* 9, 2517-2521.
 1000 Toner, B.M., Santelli, C.M., Marcus, M.A., Wirth, R., Chan, C.S., McCollom, T., Bach, W. and
 1001 Edwards, K.J. (2009) Biogenic iron oxyhydroxide formation at mid-ocean ridge hydrothermal vents:
 1002 Juan de Fuca Ridge. *Geochimica et Cosmochimica Acta* 73, 388-403.
 1003 Towe, K.M. and Bradley, W.F. (1967) Mineralogical constitution of colloidal hydrous ferric oxides.
 1004 *J. Colloid Interface Sci.* 24, 384-392.
 1005 Valiev, M., Bylaska, E.J., Govind, N., Kowalski, K., Straatsma, T.P., van Dam, H.J.J., Wang, D.,
 1006 Nieplocha, J., Apra, E., Windus, T.L. and de Jong, W.A. (2010) NWChem: a comprehensive and
 1007 scalable open-source solution for large scale molecular simulations. *Computer Physics*
 1008 *Communications* 181, 1477-1489.
 1009 Voegelin, A., Kaegi, R., Frommer, J., Vantelon, D. and Hug, S.J. (2010) Effect of phosphate,
 1010 silicate, and Ca on Fe(III)-precipitates formed in aerated Fe(II)- and As(III)-containing water studied
 1011 by X-ray absorption spectroscopy. *Geochim. Cosmochim. Acta* 74, 164-186.
 1012 Wang, X., Gu, C., Feng, X. and Zhu, M. (2015) Sulfate local coordination environment in
 1013 schwertmannite. *Environ. Sci. Technol.* 49, 10440-10448.

Waychunas, G.A., Fuller, C.C., Rea, B.A. and Davis, J.A. (1996) Wide angle X-ray scattering (WAXS) study of "two line"ferrihydrite structure: Effect of arsenate sorption and counterion variation and comparison with EXAFS results. *Geochim. Cosmochim. Acta* 60, 1765-1781.

Waychunas, G.A., Rea, B.A., Fuller, C.C. and Davis, J.A. (1993) Surface chemistry of ferrihydrite: Part 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* 57, 2251-2269.

Westre, T.E., Kennepohl, P., DeWitt, J.G., Hedman, B., Hodgson, K.O. and Solomon, E.I. (1997) A multiplet analysis of Fe K-edge 1s 3d pre-edge features of iron complexes. *Journal of the American Chemical Society* 119, 6297-6314.

Xu, W., Hausner, D.B., Harrington, R., Lee, P.L., Strongin, D.R. and Parise, J.B. (2011) Structural water in ferrihydrite and constraints this provides on possible structure models. *Am. Mineral.* 96, 513-520.

Yamaguchi, M. and Ohira, A. (2015) Density functional theory calculation of u-oxo and u-hydroxo bridged iron(III) aqua dimer complexes in perfluorinated sulfonic acid ionomer membranes. *Computational and Theoretical Chemistry* 1071, 61-67.

Yang, Y., Ratner, M.A. and Schatz, G.C. (2013) Computational modeling of octahedral iron oxide clusters: hexaaquairon(III) and its dimers. *J. Phys. Chem. C* 117, 21706-21717.

Zakharov, I.I., Kudjukov, K.Y., Bondar, V.V., Tyupalo, N.F. and Minaev, B.F. (2001) DFT-based thermodynamics of fento reactions rejects the 'pure' aquacomplex models. *Computational and Theoretical Chemistry* 964, 94-99.

Zhao, J., Huggins, F.E., Feng, Z. and Huffman, G.P. (1994) Ferrihydrite: Surface structure and its effects on phase transformation. *Clays Clay Mineral* 42, 737-746.

Zhao, J., Huggins, F.E., Feng, Z., Lu, F., Shah, N. and Huffman, G.P. (1993) Structure of a nanophase iron oxide catalyst. *Journal of Catalysis* 143, 499-509.

Zhu, M., Frandsen, C., Wallace, A.F., Legg, B., Khalid, S., Zhang, H., Morup, S., Banfield, J.F. and Waychunas, G.A. (2016) Precipitation pathways for ferrihydrite formation in acidic solutions. *Geochimica et Cosmochimica Acta* 172, 247-264.

Zhu, M., Legg, B., Zhang, H., Gilbert, B., Ren, Y., Banfield, J.F. and Waychunas, G.A. (2012) Early stage formation of iron oxyhydroxides during neutralization of simulated acid mine drainage solutions. *Environ. Sci. Technol.* 46, 8140-8147.

Zhu, M., Puls, B.W., Frandsen, C., Kubicki, J.D., Zhang, H. and Waychunas, G.A. (2013) In situ structural characterization of ferric iron dimers in aqueous solutions: identification of u-oxo species. *Inorganic Chemistry* 52, 6788-6797.

FIGURE CAPTIONS

Figure 1: Thermodynamic equilibrium speciation (25 °C, atm. pressure) of Fe^{III} as a function of pH for the various salt solutions with (a) inclusion and (b) exclusion of the trimer. Coordinated water molecules have been omitted for simplicity. Details on how these calculations were performed are provided in section 2.1.

Figure 2: DFT optimized structures and Fe-O/Cl bond distances (Å) of the thermodynamically most stable aqueous monomeric Fe^{III} species shown in Figure 1. a) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, b) $\text{Fe}(\text{ClO}_4)(\text{H}_2\text{O})_5^{2+}$, c) $\text{Fe}(\text{NO}_3)(\text{H}_2\text{O})_5^{2+}$, d) $\text{Fe}(\text{SO}_4)(\text{H}_2\text{O})_4^+$, e) $\text{Fe}(\text{SO}_4)_2(\text{H}_2\text{O})_2^-$, f) $\text{Fe}(\text{Cl})(\text{H}_2\text{O})_5^{2+}$ and g) *cis*- $\text{Fe}(\text{Cl})_2(\text{H}_2\text{O})_4^+$.

Figure 3: DFT optimized structures, and Fe-OH₂ bond distances (Å), of the thermodynamically most stable Fe^{III} dimeric (a) and trimeric (b) hydrolysis species.

Figure 4: Phase uncorrected Fourier-transformed EXAFS spectra (left) and difference spectra (right) during Fe^{III} hydrolysis and precipitation in the four solutions (k range = 2 - 12 Å⁻¹). Hydrolysis increases from the red spectrum through to the grey spectra. The difference spectra represent the difference to the first spectrum. The corresponding EXAFS spectra are provided in Figure A3.

Figure 5: Average Fe-O interatomic distance, coordination number (CN), and Debye-Waller factor (σ^2) as a function of pH_F and OH:Fe ratio ($\text{Fe}(\text{ClO}_4)_3$ = blue diamonds, $\text{Fe}(\text{NO}_3)_3$ = red squares, FeCl_3 = black circles and $\text{Fe}_2(\text{SO}_4)_3$ = green triangles). The CNs for the first four data points of the FeCl_3 solution are the sum of the CN for the Fe-O and Fe-Cl pathways. The other parameters shown are only those for the Fe-O pathway. The CNs shown for the $\text{Fe}_2(\text{SO}_4)_3$ solution were not significantly different from 6. Full modelling results and fits are provided in, respectively, Tables A4-A7 and Figures A6-A9.

Figure 6: Average Fe-Fe interatomic distance and coordination number (CN) as a function of pH_F and OH:Fe ratio ($\text{Fe}(\text{ClO}_4)_3$ = blue diamonds, $\text{Fe}(\text{NO}_3)_3$ = red squares, FeCl_3 = black circles and $\text{Fe}_2(\text{SO}_4)_3$ = green triangles). Full modelling results and fits are provided in, respectively, Tables A4-A7 and Figures A6-A9.

Figure 7: a) XANES spectra during Fe^{III} hydrolysis and precipitation in the four solutions. Hydrolysis increases from the red spectrum through to the grey spectra. The relevance of the energy

1082 regions marked from A to E is discussed in section 3.3.5; b) Pre-edge features, marked as E in Figure
1083 7a, enlarged for clarity.

1084

1085 Figure 8: Normalized and background (white-line) subtracted pre-edge features of the four solutions.

1086 The labelled arrows represent trends in the spectra which are discussed in section 3.4.3. Hydrolysis

1087 increases from the red spectrum through to the grey spectra.

Table 1: Calculated Gibbs free energy (kJ/mol) of Fe^{III} hydrolysis and complexation pathways in aqueous solution at $T = 298.15$ K and $p = 1$ atm. Reactions in bold highlight the thermodynamically most stable reaction products that form from hydrolysis or complexation and whose structures are shown in Figures 2 and 3. The Gibbs free energy of H^+ was sourced from (Zhan and Dixon, 2001).

Reaction	$\Delta G_{298.15(\text{aq})}$
<i>Inorganic complexation</i>	
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{ClO}_4^- \rightarrow \text{Fe}(\text{H}_2\text{O})_5(\text{ClO}_4)^{2+} + \text{H}_2\text{O}$	-23.4
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{ClO}_4^- \rightarrow \text{outersphere-Fe}(\text{H}_2\text{O})_6(\text{ClO}_4)^{2+}$	37.2
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{NO}_3^- \rightarrow \text{Fe}(\text{H}_2\text{O})_5(\text{NO}_3)^{2+} + \text{H}_2\text{O}$	-64.0
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{NO}_3^- \rightarrow \text{outersphere-Fe}(\text{H}_2\text{O})_5(\text{OH})(\text{HNO}_3)^{2+}$	25.9
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^- \rightarrow \text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+} + \text{H}_2\text{O}$	-116.6
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{Cl}^- \rightarrow \text{outersphere-Fe}(\text{H}_2\text{O})_6\text{Cl}^{2+}$	-29.7
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + 2\text{Cl}^- \rightarrow \text{cis-Fe}(\text{H}_2\text{O})_4(\text{Cl})_2^+ + 2\text{H}_2\text{O}$	-231.1
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + 2\text{Cl}^- \rightarrow \text{trans-Fe}(\text{H}_2\text{O})_4(\text{Cl})_2^+ + 2\text{H}_2\text{O}$	-220.4
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{SO}_4^{2-} \rightarrow \text{Fe}(\text{H}_2\text{O})_4(\text{SO}_4)^+ + 2\text{H}_2\text{O}$	-227.0
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{SO}_4^{2-} \rightarrow \text{Fe}(\text{H}_2\text{O})_4(\text{OH})(\text{HSO}_4)^+ + \text{H}_2\text{O}$	-193.6
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + \text{SO}_4^{2-} \rightarrow \text{outersphere-Fe}(\text{H}_2\text{O})_5(\text{OH})(\text{HSO}_4)^+$	-140.0
$\text{Fe}(\text{H}_2\text{O})_6^{3+} + 2\text{SO}_4^{2-} \rightarrow \text{Fe}(\text{H}_2\text{O})_2(\text{SO}_4)_2^- + 4\text{H}_2\text{O}$	-404.3
<i>Hydrolysis (dimeric species, total charge = +4)</i>	
$2 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{Fe}(\text{H}_2\text{O})_5\text{-O-Fe}(\text{H}_2\text{O})_5^{4+} + 2\text{H}^+ + \text{H}_2\text{O}$	6.1
$2 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{Fe}(\text{H}_2\text{O})_5\text{-O-Fe}(\text{H}_2\text{O})_4^{4+} + 2\text{H}^+ + 2\text{H}_2\text{O}$	23.0 ^a
$2 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{Fe}(\text{H}_2\text{O})_4\text{-2OH-Fe}(\text{H}_2\text{O})_4^{4+} + 2\text{H}^+ + 2\text{H}_2\text{O}$	26.9
<i>Hydrolysis (trimeric species, total charge = +5)</i>	
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{double corner-Fe}_3(\text{H}_2\text{O})_{10}(\text{OH})_4^{5+} + 4\text{H}^+ + 4\text{H}_2\text{O}$	-9.6
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_{14}(\text{O})_2^{5+} + 4\text{H}^+ + 2\text{H}_2\text{O}$	-0.8
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_{12}(\text{O})(\text{OH})_2^{5+} + 4\text{H}^+ + 3\text{H}_2\text{O}$	6.8
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{single corner-Fe}_3(\text{H}_2\text{O})_{14}(\text{O})_2^{5+} + 4\text{H}^+ + 2\text{H}_2\text{O}$	11.4
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_{10}(\text{OH})_4^{5+} + 4\text{H}^+ + 4\text{H}_2\text{O}$	18.6
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{single corner-Fe}_3(\text{H}_2\text{O})_{12}(\text{O})(\text{OH})_2^{5+} + 4\text{H}^+ + 3\text{H}_2\text{O}$	35.9
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_{12}(\text{O})_2^{5+} + 4\text{H}^+ + 4\text{H}_2\text{O}$	70.1 ^b
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_{12}(\text{O})_2^{5+} + 4\text{H}^+ + 4\text{H}_2\text{O}$	77.9 ^c
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{linear-Fe}_3(\text{H}_2\text{O})_8(\text{OH})_4^{5+} + 4\text{H}^+ + 6\text{H}_2\text{O}$	82.1 ^c
$3 \text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{double corner-Fe}_3(\text{H}_2\text{O})_8(\text{OH})_4^{5+} + 4\text{H}^+ + 6\text{H}_2\text{O}$	101.3 ^d

^a One Fe atom penta-coordinated.

^b End Fe atoms penta-coordinated.

^c Central Fe atom tetra-coordinated.

^d Double corner-bonded Fe atom tetra-coordinated.

Table 2

Table 2: Interatomic distances for the DFT-optimized structures of the thermodynamically most stable Fe^{III} aqueous species and for the ferrihydrite and schwertmannite structures proposed by, respectively, Michel et al. (2007a) and Fernandez-Martinez et al. (2010).

Species	Interatomic distances (Å)				
	Fe-OH ₂	Fe-OH/Anion	Fe-O	Average Fe-O	Fe-Fe
<i>Hydrolysis (monomeric species)</i>					
Fe(H ₂ O) ₆ ³⁺	2.015±0.002			2.015±0.002	
<i>Inorganic complexes</i>					
Fe(H ₂ O) ₅ (ClO ₄) ²⁺	2.035±0.026	1.944		2.020±0.044	
Fe(H ₂ O) ₅ (NO ₃) ²⁺	2.039±0.032	1.940		2.023±0.050	
Fe(H ₂ O) ₅ Cl ²⁺	2.066±0.030	2.215		2.091±0.067 ^a	
<i>cis</i> -Fe(H ₂ O) ₄ (Cl) ₂ ⁺	2.124±0.033	2.263±0.006		2.170±0.076 ^a	
Fe(H ₂ O) ₄ (SO ₄) ⁺	2.075±0.030	1.986±0.040		2.045±0.055	
Fe(H ₂ O) ₂ (SO ₄) ₂ ⁻	2.129±0.021	2.029±0.035		2.063±0.059	
<i>Hydrolysis (dimeric species)</i>					
Fe(H ₂ O) ₅ -O-Fe(H ₂ O) ₅ ⁴⁺	2.089±0.059		1.831±0.001	2.046±0.114	3.495
<i>Hydrolysis (trimeric species)</i>					
<i>double corner</i> -Fe ₃ (H ₂ O) ₁₀ (OH) ₄ ⁵⁺	2.064±0.014	1.979±0.033		2.026±0.050	3.051 3.595±0.008
<i>Minerals</i>					
‘Periodic’ ferrihydrite		2.052			2.941 (1.2) ^d
Octahedral Fe1			2.000±0.050 ^b		3.017 (1.2)
Octahedral Fe2			1.983±0.109	1.997 ^c	3.137 (1.2)
Tetrahedral Fe3			2.004±0.030		3.320 (1.2)
					3.396 (2.4)
					3.475 (1.2)
					3.504 (2.4)
					3.584 (2.4)
‘Periodic’ schwertmannite				2.020±0.106	3.004 (2)
					3.280 (1)
					3.388 (1)
					3.607 (1)
					3.668 (1)

^a Includes the Fe-Cl bonds.

^b Includes Fe-OH bond.

^c Average based on contribution of 64% Fe1-O bonds, 21% Fe2-O bonds and 14% Fe3-O bonds (i.e. 60 % Fe1, 20% Fe2 and 20% Fe3).

^d Values in parentheses indicate average number of Fe atoms in this position based on 60 % Fe1, 20% Fe2 and 20% Fe3.

Figure 1

Figure 2

Figure 3

a)

b)

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8