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Assessing the role of silicate polymerization on metal oxyhydroxide surfaces using X-ray photoelectron spectroscopy

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Abstract:

The iron oxide phases that precipitate in weathered environments can contain large amounts of adsorbed silicic acid (H_4SiO_4). This adsorbed silicate can be present as monomeric or oligomeric silicate species and affects many properties of iron oxides such as morphology, phase stability and surface charge. Therefore understanding the chemistry of H_4SiO_4 at iron oxide interfaces is important to describe the geochemistry of iron oxides and the elements that are associated with iron oxides. In this study we have measured the Si 2s and Si 2p binding energies (BE) in the XPS spectra of silicate adsorbed onto preformed ferrihydrite under conditions where the silicate surface chemistry is well defined. The positions of both the Si 2s and Si 2p peaks are indicative of the degree of polymerization of adsorbed silicate, but the Si 2p peaks overlap with an Fe 3p multiplet splitting peak. For ferrihydrite adsorbed H_4SiO_4 the Si 2s peak increased from 153.1 to 153.9 eV as the H_4SiO_4 surface concentrations (Γ_{Si} in mol Si (mol Fe)$^{-1}$) increased from 0.03 to 0.2. The low Γ_{Si} value is slightly lower than the Si 2s of the orthosilicate almandine (153.3 eV), while the high Γ_{Si} value lies midway between almandine and the tectosilicate quartz (154.6 eV). The positions of the Si 2s peaks correlate with the Si-O stretching bands (ν(Si-O)) in the FTIR spectra and are consistent with a model in which monomeric silicate species are present at low Γ_{Si} and one dimensional oligomers are formed at higher Γ_{Si}. The Si 2s BE and ν(Si-

24   O) for synthetic and natural ferrihydrites co-precipitated with silicates are substantially lower than those

25   for silicate adsorbed onto preformed ferrihydrite, clearly indicating a lower degree of silicate

26   polymerization for silicate adsorbed onto the internal surfaces between ferrihydrite domains. The Si 2s

27   and ν(Si-O) for co-precipitated ferrihydrites appear to be indicative of the age of the ferrihydrite and the

28   rate of ferric precipitation.

29

1. INTRODUCTION

31   Chemical weathering involves the leaching of soluble elements from primary minerals, ultimately

32   leaving the sparingly soluble oxides of multivalent cations such as Fe^{3+} and Al^{3+} (Chardon et al., 2006;

33   Wogelius et al., 2007). In weathered environments adsorption onto the surfaces of these oxide phases

34   can control the fate of many soluble cationic, anionic, and neutral species (Dzombak and Morel, 1990;

35   Jambor and Dutrizac, 1998). Anions such as nitrate and chloride which are the conjugate bases of

36   strong acids have a low affinity for metal oxides, while weak acids and their conjugate bases, such as

37   H_4SiO_4 and HPO_4^{2-}, have a high affinity for metal oxide surfaces. Typical concentrations of H_4SiO_4 in

38   aqueous systems ($\approx$ 0.1 to 1 mM) are higher than those of many other adsorbing ligands, and the iron

39   oxides in weathered systems can contain large amounts silicon (Carlson and Schwertmann, 1981). This

40   is especially true of the high surface area iron oxide phase ferrihydrite. The presence of adsorbed

41   H_4SiO_4 affects many aspects of the geochemistry of iron oxides such as the Point of Zero Charge

42   (Schwertmann and Fechter, 1982), mineralogy and morphology of transformation products (Cornell et

43   al., 1987; Kwon et al., 2007), colloid stability (Davis et al., 2001) and some biomineralization processes

44   (Fein et al., 2002). Understanding the chemistry of H_4SiO_4 on iron oxide surfaces is therefore important

45   to many areas of geochemistry.

46   Studies with magnetite (Yang et al., 2008), hydrolyzed ferric chloride (Doelsch et al., 2001), natural

47   and synthetic ferrihydrite (Carlson and Schwertmann, 1981) and goethite (Hiemstra et al., 2007) have all

48   shown that adsorbed H_4SiO_4 can be present in different chemical states. On ferrihydrite at low H_4SiO_4

49   surface concentrations (Γ_{Si} in mol Si (mol Fe)$^{-1}$) a monomeric Si species forms and a bidentate surface

50   complex in which two of the corners of an SiO_4 tetrahedron are bound to the ferrihydrite surface has

51   been proposed (Pokrovski et al., 2003; Swedlund et al., 2010b). At Γ_{Si} above ≈ 0.02 an oligomeric

52   surface Si species can be observed with siloxane linkages (Si-O-Si) formed by condensation reactions

53   between silanol groups.   ATR-IR spectra suggest that condensation produces a one dimensional

54   oligomeric species (Swedlund et al., 2010b) and a mechanism by which a solution H_4SiO_4 inserts

55   between two adjacent adsorbed monomers has been proposed. Figure 1 illustrates trimer formation and

56   one dimensional polymerization would occur by a continuation of this process. The oligomeric silicate

57   is the dominant ferrihydrite surface species at solution H_4SiO_4 concentrations (Si_{sol}) as low as 0.1 mM,

58   which contrasts with the H_4SiO_4 chemistry in solutions where only monomers are observed in solutions

59   at equilibrium with an $SiO_{2(am)}$ phase at pH < 9 with Si_{sol} of 1.8 mM (Sjoberg, 1996). Parameters to

60   describe the monomer and oligomer adsorption of H_4SiO_4 on ferrihydrite have been developed using the

61   Diffuse Layer Model (DLM) (Swedlund et al., 2010a).

62   The one dimensional oligomer model is based on ATR-IR spectra, and applying other techniques to

63   test this model is desirable. X-ray photoelectron spectroscopy (XPS) is an effective probe of the degree

64   of silicate polymerization in minerals (Seyama and Soma, 1985). The Si 2s binding energy (BE)

65   increases from ≈ 152.8 eV for minerals with isolated SiO_4^{4-} tetrahedra (e.g. olivine and almandine) to

66   154.4 eV for the fully polymerized quartz (Fig. 2a). The higher Si 2s BE for polymerized silicates

67   reflects the greater difficulty in removing Si electrons from SiO_4^{4-} units which are associated with next

68   nearest neighbors with a higher formal charge density. The formal charge density of Si^{4+} is substantially

69   larger than that of the other next nearest neighbors of the mineral phases in Figure 2, and therefore the

70   number of Si^{4+} linked to a given SiO_4^{4-} (i.e. the degree of silicate polymerization) is the main factor

71   influencing the Si 2s BE. For example, quartz has the highest Si 2s BE because each SiO_4^{4-} unit is

72   associated with four Si^{4+} next nearest neighbors. This line of reasoning also explains the difference in Si

73   2s BE for minerals with different cations but the same degree of silicate polymerization. For example,

74   the lower Si 2s BE of talc compared to kaolinite reflects the lower formal charge density of Mg^{2+}

75   compared to Al^{3+} (Figure 2b).

76   Two previous studies have used XPS to assess the chemical state of ferrihydrite-adsorbed H_4SiO_4 for

77   selected natural and synthetic samples. Soma et al. (1996) studied 5 natural ferrihydrites which had Si

78   2s BE's between 152.7 and 153.1 eV and surface Si/Fe ratios that were comparable to or smaller than

79   the bulk Si/Fe. These results were attributed to a predominantly monomeric species that was well

80   distributed throughout the primary particles by bonding at microcrystalline domains. Soma et al. (1996)

81   also prepared a synthetic ferrihydrite by mixing 0.1 M $FeSO_4$ and 15 mM Na_2SiO_3 at pH 7, and this

82   material had a Si enriched surface with a Si 2s BE of 154.1 eV. This indicates a polymerized silica-like

83   structure on the surface of the ferrihydrite which is expected given that the starting solution was $\approx$ 8

84   times oversaturated with respect to precipitation of an $SiO_{2(am)}$ phase. Vempati et al. (1990) measured Si

85   2p BE's of $\approx$100.8 eV for silicate that was adsorbed on a ferrihydrite with $\Gamma_{Si} < 0.05$. The Si 2p peaks

86   occur $\approx$ 51.0 eV lower than the Si 2s peaks so an Si 2p of 100.8 eV corresponds to an Si 2s BE of 151.8

87   eV which is 1 eV lower than the Si 2s BE's of Soma et al. (1990). Vempati et al. (1996) also measured

88   Si 2p BE's of 101.6 and 102.8 eV for ferrihydrites with $\Gamma_{Si} > 0.1$ and a Si 2p BE of 104.1 eV for a

89   separate silica rich phase that was present since some samples were prepared using H_4SiO_4

90   concentrations that were oversaturated with respect to an $SiO_{2(am)}$ phase. Of these peaks only the peak at

91   101.6 eV corresponded to the results of Soma et al. (1990) for ferrihydrite-sorbed Si. The Vempati et

92   al. (1996) Si 2p BE values of 102.8 and 104.1 eV corresponded to their measured values for biotite (a

93   phyllosilicate) and a silica gel (a tectosilicate) respectively.

94   The current paper uses XPS to probe the degree of oligomerization of silicates on ferrihydrite for

95   samples prepared with a range of Γ_{Si} in which the proportion of adsorbed silicate present as monomeric

96   and oligomeric species is known. Samples were prepared using solutions that were undersaturated with

97   respect to $SiO_{2(am)}$ so that only the silicate adsorption and oligomerization processes occurring on the

98   ferrihydrite surface are involved. The aim is to further probe the structures of adsorbed H_4SiO_4, resolve

99   the discrepancies in the XPS data of Vempati et al. (1990) and Soma et al (1996), and to provide a more

100   realistic model for silicates associated with ferrihydrite in natural surface aquatic systems.

2. METHODS

102   All solutions were made from 18.2 MΩ cm resistivity deionized water and pH adjustments were made

103   with HCl and NaOH solutions. A stock solution of 16.6 mM silicate in 0.1 M NaOH was prepared from

104   amorphous silica as previously described (Swedlund and Webster, 1999). Two-line ferrihydrite was

105   prepared by raising the pH of a ferric nitrate (5 mM) and HNO_3 (pH 2) solution to 8.5 and suspensions

106   were aged for 4-12 hours. The product was exclusively 2-line ferrihydrite as determined by X-ray

107   Diffraction of a freeze dried sample. After this time the H_4SiO_4 stock was added, the pH adjusted to 8.5

108   then the suspensions were equilibrated for 10 days. A pH of 8.5 was used as it is close to the pH of

109   maximum H_4SiO_4 adsorption and the change in surface silicate chemistry occurs at higher Γ_{Si} than at

110   lower pH which improves the spectra signal to noise ratio. During equilibration the pH of the

111   suspensions were manually adjusted to 8.5 every second day to correct for a general decrease in pH over

112   time by up to ≈ 0.5 pH units. After equilibration suspensions were centrifuged (4000 rpm) and

113   separated by filtration (0.45 μm cellulose acetate membrane) and rinsed quickly with water and the

114   solids freeze dried. Solution Si concentration (Si_{sol}) was measured with the molybdenum blue method

115   and the solid phase composition determined by ICP-MS after digestion in 1 M HCl. The molybdenum

116   blue method is suited to this work because all solution silicate is monomeric and there are no interfering

117   species in solution. The sum of the measured solution and adsorbed Si concentrations were within 10 %

118   of the added total Si. All reported surface concentrations (Γ_{Si}) are based on the analysis of the solid

119   phase.

120   The XPS data were collected on a Kratos Axis UltraDLD equipped with a hemispherical electron

121   energy analyser. Spectra were recorded using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray

122   source operating at 10 mA and 15 kV. The measurements were carried out in a normal emission

5

123   geometry at pressures of $\approx 10^{-9}$ torr. Survey scans were collected with an energy step of 1.0 eV and a

124   160 eV pass energy, whilst core level scans were collected with an energy step of 0.1 eV and a pass

125   energy of 20 eV. A charge neutralization system was used to alleviate sample charge buildup and

126   samples were pressed into an indium foil. The binding energy scale was corrected using the C 1s signal

127   from saturated hydrocarbon at 285.0 eV. Data analysis was performed using CasaXPS with Shirley

128   backgrounds and relative sensitivity factors supplied with the instrument. Where necessary the XPS

129   peaks were fitted with a single Gaussian/Lorentzian product peak with an 80 % Lorentzian component

130   termed GL(80). IR spectra of the dried ferrihydrites were measured using KBr pellets on a Perkin-Elmer

131   Spectrum 1000 FTIR spectrometer with a resolution of 4 cm^{-1}.

132   The DLM was used to describe the formation of monomeric and oligomeric surface silicate species on

133   surface hydroxyl groups ($\equiv$FeOH) using previously published reactions which are given in Table 1

134   (Swedlund et al.). The Dzombak and Morel (1990) values for the ferrihydrite surface area (600 m^2g^{-1}),

135   adsorption site densities (0.2 mol (mol Fe)$^{-1}$) and surface acidity constants were used. In the DLM

136   surface charge is located on one plane and the surface potential (Ψ) is related to surface charge by

137   electric double-layer theory. To account for the electrostatic work of adsorption the equilibrium

138   constants for the formation of a surface species with a charge of "n" include a columbic term $e^{nF\Psi/RT}$

139   (where F is Faraday's constant, R is the gas constant and T is temperature in Kelvin). The ionic strength

140   was 0.01 M and the Davies equation was used to calculate activity coefficients. Modeling used the

141   H_4SiO_4 pK_A values from Gustafsson (2006). The concentration of solution oligomeric species (Felmy et

142   al., 2001) were less than 0.03 % of the total Si concentration (Si_T) under all conditions in this work and

143   including or omitting these species in the model had a negligible effect on H_4SiO_4 speciation.

144   **3.0 RESULTS AND DISCUSSION**

145   Several general features of the data are initially discussed including the H_4SiO_4 adsorption isotherm, the

146   IR spectra and the Fe 2p and O 1s regions in the XPS. This is followed by a presentation of the Si 2p

147   regions of the spectra and finally the Si 2s regions of the spectra are discussed and compared with

6

148   previous studies. We conclude the discussion by presenting a model for the formation of adsorbed and

149   oligomerized silicate in natural and synthetic systems that is consistent with the data of this and previous

150   studies.

151   **3.1 Silicic acid adsorption isotherms on ferrihydrite and the IR spectra**
152   The measured and modeled ferrihydrite H_4SiO_4 adsorption isotherms are shown in Figure 3 along with

153   the modeled speciation of the adsorbed silicate (Si_{ads}). The conditions cover Si_{sol} from 2 to 1,200 µM

154   over which the adsorbed H_4SiO_4 goes from being 100 % monomeric to 93 % oligomeric based on the

155   DLM calculations. The ν(Si-O) regions of the IR spectra are presented in Figure 4 for ferrihydrite

156   samples with Γ_{Si} from 0.02 to 0.22 and for quartz and almandine. The IR spectrum of an isolated SiO_4^{4-}

157   tetrahedron would have one band being the triply degenerate antisymmetric ν(Si-O) (McIntosh et al.,

158   2011), however in the almandine crystal lattice the SiO_4^{4-} symmetry is lowered and the three ν(Si-O)

159   bands are clearly visible.   The individual ν(Si-O) bands are broader for adsorbed silicate and the

160   ferrihydrite samples with Γ_{Si} of 0.02 and 0.03 have a broad band with maximum absorbance at 940 cm$^-$

161   ^{1}(Swedlund et al., 2009) which indicates a monomeric adsorbed species. At a Γ_{Si} of 0.09 a shoulder at

162   1020 cm^{-1} becomes apparent indicating the development of an oligomeric phase, and this band grows to

163   be the dominant spectral feature at $\Gamma_{Si} \geq 0.17$.   The increase in ν(Si-O) frequency as the degree of

164   silicate polymerization increases can be considered as a consequence of bridging Si-O-Si bonds being

165   stiffer than terminal Si-O$^-$ bonds (Farmer, 1974) and the IR spectra are consistent with the fraction of

166   adsorbed silicate predicted to be present as monomeric species as shown in Figure 3 (Swedlund et al.,

167   2010b).

168   **3.2 XPS of silicic acid adsorbed on ferrihydrite**
169   *Wide scans and the Fe 2p and O 1s region*

170   The wide scan XPS spectrum of a typical ferrihydrite sample (Γ_{Si} = 0.33 and pH 8.5) illustrates the

171   main photoelectron and X-ray excited Auger electron peaks expected for the sample (Figure SI 1a). The

172 close proximity of the Fe 3s and Si 2p peaks is evident whereas the Si 2s peak is isolated from other

173 peaks. Vempati et al. (1990) report the Si 2p BE for ferrihydrite adsorbed silicate while Soma et al

174 (1996) report the Si 2s BE.   Vempati et al. (1990) did not justify the use of the Si 2p peak but, as can be

175 seen in the wide scan, it does have the attraction of having a greater intensity than that of the Si 2s peak.

176 The surface Si/Fe mole ratios in the present study were determined from the areas of the Si 2s and Fe 2p

177 peaks and were in reasonable agreement with the bulk Si/Fe ratios (Figure SI 1b). The samples were

178 prepared by adding H_4SiO_4 after ferrihydrite precipitation and the similarity between the surface and

179 bulk Si/Fe reflects the fact that the ferrihydrite primary particle has a radius of about 1 nm (Jambor and

180 Dutrizac, 1998) which is substantially less than the photoelectron escape depth. In addition the adsorbed

181 silicate is present in a single molecular layer, as evidenced from the absence of a three dimensional SiO_2

182 phase in the IR spectra, and does not attenuate the photoelectrons emitted from the underlying Fe.

183   The position of the O 1s peaks in silicate minerals depends on the protonation state of the oxygen (i.e.

184 O^{2-} , OH^- or H_2O) and on the degree of silicate polymerization (Seyama and Soma, 1985; Wagner et al.,

185 1982). The O 1s region of the ferrihydrite samples is complicated by the fact that the hydration state is

186 not defined and that a proportion of the surface oxygen is associated only with the ferric cations and this

187 proportion will decrease as Γ_{Si} increases. In general the O 1s region for the ferrihydrite samples

188 consisted of two overlapping peaks and the BE of each peak increases as Γ_{Si} increases (Figure SI 2).

189 The area of the high BE peak becomes proportionally larger as Γ_{Si} increases. Because of the various

190 compounding factors a detailed analysis of the O 1s region was not undertaken. The Fe 2p BE's were

191 all at $\approx$ 711.7 eV as expected for a ferric oxide (McIntyre and Zetaruk, 1977) and these values did not

192 vary with Γ_{Si}.

193   *The Si 2p region*

194   For the Si peaks we first examine the Fe 3s and Si 2p XPS data to resolve one of the discrepancies

195 between the data of Vempati et al. (1990) and Soma et al. (1996).   The Fe 3s region of a pure

196 ferrihydrite (Figure 5a) has two components centered at 94.4 and 100.9 eV. The two components arise

197   from multiplet splitting because the spin of the remaining 3s electron may either be the same or opposite

198   to the spin of the 5 unpaired d electrons of Fe^{3+} (McIntyre and Zetaruk, 1977). The Si 2p BE's of quartz

199   and almandine are at 103.6 and 102.2 eV respectively (Figure 5b) while the low energy component of

200   the almandine Fe 3s peak is detected at $\approx$ 93.8 eV which is lower than that observed for ferrihydrite

201   because the Fe is divalent in almandine and trivalent in ferrihydrite. The Si 2p peaks of almandine and

202   quartz clearly would overlap with the broad 100.9 eV Fe 3s component from ferrihydrite. This Fe 3s

203   peak is the dominant feature in the Si 2p region of the ferrihydrite Si_{ads} at low Γ_{Si} (Figure 6a), and the

204   true Si 2p peak of adsorbed silicate at 101.9 eV becomes increasingly apparent above the broad 100.9

205   eV Fe 3s peak as Γ_{Si} increases up to 0.09. The position of this Si 2p peak is 0.3 eV lower than the Si 2p

206   almandine peak and does not shift as Γ_{Si} increases from 0.02 to 0.09. As Γ_{Si} increases above 0.09 the

207   maximum of the Si 2p peak shifts from 101.9 to 102.9 eV (Figure 6b).

208   Several conclusions can be drawn from these XPS spectra. The peak at 100.8-100.9 eV for

209   ferrihydrite with low Γ_{Si} that Vempati et al. (1990) attributed to a Si 2p transition may have a significant

210   contribution from the high BE component of the Fe 3s transition. This is supported by the data from this

211   work, the absence of a corresponding Si 2s peak (i.e. 51 eV higher than the Vempati et al (1990) Si 2p

212   attributed peak) in the spectra of Soma et al. (1996) and the large range (3.3 eV) in Si 2p BE values of

213   Vempati et al. (1990) from 100.8 to 104.1 eV is inconsistent with other studies of silicate systems. The

214   overlap between the Si 2p and Fe 3s XPS peaks has been noted by other authors (Galakhov et al., ;

215   Glasauer et al., 2000; Khare et al., 2008).

216   The Si 2p at low Γ_{Si} in the present study occurs at 101.9 eV which falls within the range of values

217   reported for orthosilicates and is 0.3 eV below the almandine value. When Γ_{Si} > 0.09 the Si 2p peak

218   increases in energy up to 102.9 eV which lies between the almandine and quartz Si 2p BE's of 102.1 and

219   103.6 eV respectively. These shifts are consistent with the model of silicate surface oligomerization

220   proposed by Swedlund et al (2010b) which will be further explored using the Si 2s peaks.

221   *The Si 2s region*

222   The Si 2s peaks for ferrihydrite-adsorbed silicate show the same trends as those observed in the Si 2p

223   region but without the confounding factor of the Fe 3s peak (Figure 7). The ferrihydrite-adsorbed

224   silicate, almandine and quartz Si 2s peaks can each be described with a single GL(80) shaped peak with

225   a Shirley background. The fitted peak maximum varied less than 0.05 eV with the choice of baseline

226   start and finish points. The full width at half maximum (FWHM) were 2.4 eV for almandine, 2.8 eV for

227   quartz and 2.2-2.3 eV for ferrihydrite-adsorbed silicate. The almandine and quartz peaks were centered

228   at 153.3 and 154.6 eV respectively. At the two lowest Γ_{Si} where the Si_{ads} is >95 % monomeric the Si 2s

229   BE peak is centered at 153.1 eV which is 0.2 eV lower than the almandine value. As Γ_{Si} increases from

230   0.03 to 0.22 the Si_{ads} goes from being 95 % monomeric to being 89 % oligomeric based on the DLM

231   calculations and the Si 2s BE increases steadily from 153.1 to 153.8 eV as this occurs. For Γ_{Si} > 0.22

232   the Si 2s BE plateaus at 153.9 eV (Fig 8) which is approximately half way between the almandine and

233   quartz Si 2s values. Figure 8 also shows that the change in the Si 2s BE is correlated with the ν(Si-O) in

234   the IR spectra as both signals are responding to the degree of silicate polymerization. The slight

235   difference in the shape of the response of ν(Si-O) and Si 2s BE to changing Γ_{Si} is due to the difference

236   in peak resolution (peak separation/peak width) for these measurements. Paradoxically the greater the

237   overlap between the two peaks (i.e. the poorer the peak resolution) the more indicative the position of

238   the maximum is of the proportions of the two peaks. This is illustrated for two theoretical Gaussian

239   peaks in Fig SI 3.

240   To assess the degree of silicate polymerization for the ferrihydrite-adsorbed Si the positions of the Si

241   2s peaks are compared to the data of Seyama and Soma (1985) for minerals with a known silicate anion

242   structures. The Si 2s BE for quartz (154.6 eV) and almandine (153.3 eV) in this study were both 0.4 eV

243   higher than the values of Seyama and Soma (1985) even though both studies used the adventitious

244   hydrocarbon C 1s of 285 eV as the energy reference. Similarly the Fe 2p BE in this study ($\approx$ 711.7 eV)

245   was $\approx$ 0.4 eV higher than the Soma et al. (1996) values of 711.3 and 711.4 eV. A difference of this

246   magnitude is not unprecedented, for example the tectosilicate Si 2p BE of Vempati et al. (1990)

247   corresponds to an Si 2s of 155.1 eV and this difference explains the high BE discrepancy between their

248   data and Soma et al. (1996). Reported Si 2s BE's for SiO_2 range from 154.0 (Anpo et al., 1986) to

249   155.3 (Clarke and Rizkalla, 1976) and demonstrate the importance of using reference materials to

250   calibrate the photoelectron energy scale. For the purpose of comparison with Seyama and Soma (1985)

251   0.4 eV was subtracted from the ferrihydrite adsorbed Si 2s BE's of the current study. At the lowest Γ_{Si}

252   the ferrihydrite sorbed Si adjusted BE of 152.7 eV was the same as one olivine sample and slightly less

253   than the 2nd olivine and almandine from Seyama and Soma (1985). This is consistent with the

254   monomeric species proposed from the IR spectra (Swedlund et al., 2010b). As Γ_{Si} increased the

255   adjusted Si 2s BE shifts to a value of 153.5 eV which is 0.1 eV above the Seyama and Soma (1985)

256   value for the orthopyroxene. The proposed surface one dimensional oligomer has Si bound to Fe^{3+}

257   cations so that the Si 2s BE is expected to be higher than the value for orthopyroxene which has Mg^{2+}

258   and Fe^{2+} cations for the same reason that the kaolinite Si 2s BE is higher than that of talc (Figure 2).

259   Thus both the XPS Si 2s BE's and the v(Si-O) frequencies in the IR spectra (Swedlund et al., 2010b) of

260   the surface ferrihydrite oligomer are similar to those of pyroxenes and the XPS data are consistent with

261   the proposed one dimensional oligomer model.

262   The small ferrihydrite primary particle size of 2-3 nm (Parfitt et al., 1992) limits the possible oligomer

263   length and short linear silicate oligomers contain Si with 2 different degrees of polymerization: the two

264   terminal SiO_4 units have one Si-O-Si linkage, like a $Si_2O_7^{6-}$ pyrosilicate, and the internal SiO_4 units have

265   two Si-O-Si linkages like a pyroxene. Seyama and Soma (1985) do not report XPS spectra of

266   pyrosilicates but the Si 2s would presumably lie between those of the orthosilicates and the pyroxenes.

267   If the Si 2s peaks could be resolved at such detail then the average oligomer length could be determined,

268   but the separations between the peak positions for a monomer, pyrosilicate and pyroxene are too small

269   (≈ 0.4 eV) compared to the peak width (≈ 2.2 eV) to allow for resolution of such detail. A feature of the

270   ferrihydrite-adsorbed silicate system is that all ATR-IR spectra of Swedlund et al. (2010b) could be

271   described by a linear combination of two main spectra; the spectra of a monomeric and an oligomeric

272   species, with a small amount (< 10 %) of a three dimensional polymeric silicate phase at high Γ_{Si}.

273   Similarly the Si_{ads} 2s peaks This could be reasonably described by a linear combination of the end

274   members i.e. a monomeric peak at 153.1 eV and an oligomeric peak at 153.9 eV. The small amount of

275   polymeric silicate was not evident in the XPS data. Examples of this fitting are shown in Figure SI 4

276   and the proportion of the monomeric peak to the total peak area as a function of Γ_{Si} (Fig. SI 5) agrees

277   reasonably with the modeled values determined from parameters for a paste that had not been dried.

278   Therefore freeze drying the ferrihydrite pastes did not appear to promote silicate oligomerization. The

279   relationship between Si 2s BE, ν(Si-O) and the percentage of the Si 2s peak that is attributable to the

280   oligomeric species centred at 153.9 eV is shown in Figure 9.

281   *Comparison to Previous Studies*

282   The data from the current study are compared to previously published data for natural and synthetic

283   samples in Figure 10. The synthetic samples from Soma et al. (1996) and Vempati et al. (1990) are not

284   shown because of the use of over saturated H_4SiO_4 solutions and the precipitation of an SiO_2 phase. The

285   included synthetic samples are from Carlson and Schwertmann (1981) who only reported the ν(Si-O).

286   These sample were prepared by a co-precipitation method that avoided the use of oversaturated H_4SiO_4

287   solutions by adding 2 mM Si solutions to 0.1 M $Fe(NO_3)_3$ and precipitating at pH 8 to yield products

288   with Γ_{Si} up to 0.18. These conditions are similar to those used for the preparation of the samples in the

289   current study apart from the fact that the H_4SiO_4 was present during precipitation of the ferirhydrite.

290   The precipitates of Carlson and Schwertmann (1981) were rinsed and freeze dried directly after

291   precipitation, and all ν(Si-O) were 925 - 935 cm^{-1} for Γ_{Si} from 0.02 to 0.18, in contrast with the samples

292   from this work where ν(Si-O) increased from 945 to 1007 cm^{-1} as Γ_{Si} increased from 0.09 to 0.17.

293   However Carlson and Schwertmann (1981) reported that ν(Si-O) shifted from 935 to 965 cm^{-1} when one

294   co-precipitated sample was aged in water for 242 days. The natural samples were generally precipitated

295   following Fe^{2+} oxidation, and form a cluster in Figure 10 with Γ_{Si} of 0.1-0.25, ν(Si-O) of 950-980 cm^{-1}

296   and Si 2s BE of 152.7-152.8 eV. The natural samples of Parfitt et al. (1992) had comparatively high

297 ν(Si-O) and one sample (PC863) had ν(Si-O) measured at 997 and 970 cm^{-1} by Parfitt et al. (1992) and

298 Childs et al. (1986) respectively. Both spectra were measured in KBr discs and the cause for this

299 difference was not discussed. In general the Si 2s BE and ν(Si-O) from the current study formed an

300 upper limit for the natural and synthetic co-precipitated ferrihydrites in Figure 10.

301 Parfitt et al. (1992) proposed a model in which the nanometer-sized primary ferrihydrite particles are

302 composed of between 20 and 60 domains which means the majority of the surface of the domains is on

303 internal surfaces (within the particle). In natural co-precipitated samples most of the silicate present was

304 not exchangeable with phosphate and was therefore was considered to be predominantly present on

305 internal surfaces between and possibly bridging the domains. A similar distribution was proposed for

306 silicate when co-precipitated with goethite based on rates of dissolution in HCl (Glasauer et al., 1999)

307 where some of the Si was immediately released to solution and this fraction was considered to exist on

308 the mineral surface. However, the majority ($\approx$ 60 %) of the goethite-adsorbed Si dissolved congruently

309 over time with the Fe and this fraction was considered to be located between the individual crystal

310 domains (Glasauer et al., 1999).

311 The lower values of Si 2s BE and ν(Si-O) for the synthetic and natural co-precipitated systems is

312 consistent with this model because SiO_4 tetrahedra that are bridging between the internal surfaces of two

313 domains will not have the opportunity to form oligomers. Ferric precipitation involves rapid

314 condensation of the $Fe(OH)_{3(aq)}$ species and then a slower growth and aggregation of these incipient

315 ferrihydrite particles or domains (Pham et al., 2006). Adsorption of H_4SiO_4 (and PO_4^{3-} or organic

316 anions) during co-precipitation is known to inhibit this growth and aggregation (Carlson and

317 Schwertmann, 1981) and will result in a large proportion of the adsorbed H_4SiO_4 being present on

318 internal surfaces. The increase in ν(Si-O) when the fresh synthetic co-precipitated sample (Carlson and

319 Schwertmann, 1981) was aged in water suggests a slow migration of SiO_4 from internal to external

320 surfaces followed by oligomerization. This implies that SiO_4 is present on internal surfaces for kinetic

321 reasons and that thermodynamic factors generally favors the formation of Fe-O-Fe linkages between

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322   domains and the expulsion of SiO_4. The similarity between the ν(Si-O) of the natural and the aged co-

323   precipitated samples is consistent with both the estimated age of the natural samples (where reported)

324   and also presumably a slower ferric precipitation process due to lower concentrations of Fe^{3+}.

325   **4.0 CONCLUSIONS**

326   In this study we have systematically examined silicate adsorption and polymerization on the surface of

327   a preformed ferrihydrite. We have measured the Si 2s and Si 2p BE's in the XPS spectra of silicate

328   adsorbed onto ferrihydrite for systems where the extent of silicate polymrization has been quantified by

329   ATR-IR. The position of both the Si 2s and Si 2p peaks are indicative of the degree of polymerization

330   of adsorbed silicate but the Si 2p peaks overlap with the Fe 3p multiplet splitting peak. The position of

331   the Si 2s peaks shifts from 153.1 to 153.9 eV as the silicate surface concentration increases. These Si 2s

332   peak positions correlate with the ν(Si-O) bands in the FTIR spectra and are consistent with a model in

333   which monomeric silicate species are present at low silicate surface concentration and one dimensional

334   oligomers are formed at higher surface concentration. The Si 2s and ν(Si-O) for synthetic and natural

335   ferrihydrites co-precipitated with silicates are substantially lower than those for silicate adsorbed onto

336   preformed ferrihydrite, clearly indicating a lower degree of silicate polymerization for silicate adsorbed

337   onto the internal surfaces between ferrihydrite domains. The Si 2s and ν(Si-O) for co-precipitated

338   ferrihydrites appear to be indicative of the age of the ferrihydrite and the rate of ferric precipitation.

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Figure 1 Model for the formation of surface oligomeric silicate species on ferrihydrite (reproduced from Swedlund et al. 2010a).

Figure 2 The Si 2s BE data from Seyama and Soma (1985) shown as a function of a) the degree of silicate polymerization b) the average charge density of the next nearest neighbors of the SiO_4^{4-} unit.   O1 and O2 are olivine $(Mg,Fe)SiO_4$, A is almandine $Fe_3Al_2Si_3O_{12}$, OP is orthopyroxene $(Mg,Fe)SiO_3$, W is wollastonite $CaSiO_3$, T is talc $Mg_3Si_4O_{10}(OH)_2$, K is kaolinite $Al_2Si_2O_5(OH)_4$ and Q is quartz SiO_2. Ionic radii for Ca^{2+}, Mg^{2+}, Fe^{2+}, Al^{3+} and Si^{4+} used were 1.12, 0.72, 0.78, 0.39 and 0.26 Å respectively.

Figure 3 a) Measured (■) and modeled (—) H_4SiO_4 adsorption isotherm at pH 8.5, 0.01 M NaCl, [Fe] = 1 to 2.5 mM and at ambient temperature. The modeled proportion of the adsorbed Si that is monomeric (- - -) is also shown and the isotherm points are labeled with these values.

Figure 4 a) Infrared spectra of H_4SiO_4 adsorbed on ferrihydrite for Γ_{Si} between 0.02 and 0.22 mol Si_{ads} (mol Fe)$^{-1}$ as indicated. b) Infrared spectra of quartz and almandine for comparison.

Figure 5. XPS spectra of the Si 2p and Fe 3s region for a) pure (Si free) ferrihydrite and b) quartz and almandine.

Figure 6. The Si 2p region of the XPS spectra for Si adsorbed onto ferrihydrites with Γ_{Si} in mol Si_{ads} (mol Fe)$^{-1}$ as indicated on the figure. a) Γ_{Si} 0 to 0.03 b)) Γ_{Si} 0.09 to 0.22. The quartz Si 2p BE at 103.6 is also shown.

Figure 7. XPS spectra in the Si 2s region for a) quartz and almandine and b) ferrihydrites with Γ_{Si} in mol Si_{ads} (mol Fe)$^{-1}$ as indicated. All peaks are fitted with a single GL(80) curve.

Figure 8. The Si 2s XPS BE and ν(Si-O) in the FTIR for ferrihydrite-adsorbed Si as a function of Γ_{Si} in mol Si (mol Fe)$^{-1}$. The dotted line is the sigmoidal fit to the XPS data.

Figure 9. The relationship between the Si 2s BE and ν(Si-O) to the percentage of the Si 2s XPS peak attributed to the oligomeric species with a peak at 153.9 eV.

Figure 10. The Si 2s BE (▲ and ▼) and ν(Si-O) (all other symbols) for ferrihydrite-adsorbed Si as a function of Γ_{Si} in mol Si (mol Fe)$^{-1}$. The dashed line is the sigmoidal fit to the XPS data from this work. Dotted line connects points for the same sample measured by different groups. The Si 2s BE from this study have had 0.4 eV subtracted for comparison with Soma et al. (1996) as described in the text.

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475 **Table 1**. The reactions used to model the formation of H_4SiO_4 monomers and trimers on the ferrihydrite surface.
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Species	H+	≡FeOH	H_4SiO_4	$e^{nF\Psi/RT}$ [a]	logK
≡FeOH	0	1	0	0	0
≡FeOH$_2^+$	1	1	0	1	7.29[b]
≡FeO$^-$	-1	1	0	-1	-8.93[b]
≡FeH$_3$SiO$_4^0$	0	1	1	0	3.56[c]
≡FeH$_2$SiO$_4^{-1}$	-1	1	1	-1	-3.12[c]
≡Fe$_2$H$_6$Si$_3$O$_{10}^0$	0	2	3	0	15.33[c]
≡Fe$_2$H$_4$Si$_3$O$_{10}^{-2}$	-2	2	3	-2	2.02[c]

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479 [a] values in this column are for n
480 [b] Dzombak and Morel (1990)
481 [c] Swedlund et al (2010)