The influence of surface structure on H_4SiO_4 sorption and oligomerization on goethite surfaces: An XPS study using goethites differing in morphology

Yantao Song [a], Peter J. Swedlund [a,*], Chongwen Zou [b], Rossuriati Dol Hamid [a,c]

[a] School of Chemical Sciences, University of Auckland, New Zealand
[b] National Synchrotron Radiation Laboratory, University of Science and Technology of China, China
[c] School of Chemistry and Environmental Studies, Faculty of Applied Sciences, Universiti Teknologi MARA, Malaysia

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ABSTRACT

Two important weathering products are solution phase silicic acid (H_4SiO_4) and the iron oxides. The chemistry of H_4SiO_4 on iron oxide surfaces is a complex mix of sorption and polymerization and this affects many iron oxide properties. For example the presence of H_4SiO_4 directs goethite growth to shorter and fatter needles which implies different H_4SiO_4 chemistry on different goethite faces and the purpose of this paper is to directly explore this and related phenomena. Isotherms and the Si 2s X-ray photoelectron spectra were measured for H_4SiO_4 on three goethite samples having different morphologies. Both the shape of the isotherms and the shifts in the Si 2s binding energies (BE) indicated different H_4SiO_4 chemistry on acicular crystalline goethite compared to previously reported behavior on ≈ 2 nm sized disordered particles of ferrihydrite. The H_4SiO_4 isotherm on acicular goethites had a plateau for silicic acid concentrations ($Si_{(sol)}$) between 0.01 and 0.3 mM but the isotherm increases steeply for $Si_{(sol)} > 0.3$ mM. The Si 2s BE for acicular goethites indicated monomeric sorption occurring at $Si_{(sol)} < 0.3$ mM but then the BE increases for $Si_{(sol)} > 0.3$ mM indicating the onset of H_4SiO_4 polymerization as also indicated by the increase in isotherm slope. The data are consistent with a model where monomers sorb on both the (110) and (021) faces (Pbnm space group) but at $Si_{(sol)}$ over ≈ 0.3 mM polymers form only on the (021) face. The arrangement of monomer sorption sites on the acicular goethite (021) face acts as a template for H_4SiO_4 polymerization. This would explain why the onset of polymerization occurs quite distinctly on the acicular goethite surface compared with that previously observed on ferrihydrite where there is a gradual increase in the significance of polymerization across the H_4SiO_4 isotherm.

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1. Introduction

Iron oxides are important phases produced from the weathering of primary minerals. Iron oxides have reactive surfaces that are chemically significant in natural aquatic systems and this reactivity is employed in many water treatment systems (Cornell and Schwertmann, 2003). Silicic acid (H_4SiO_4) is also a significant product from weathering and the adsorption and polymerization of H_4SiO_4 on iron oxide surfaces can have profound effects on the iron oxides' phase stability, morphology and surface chemistry. The presence of Si decreases the point zero of charge of ferrihydrite (Schwertmann and Fechter, 1982; Anderson and Benjamin, 1985), stabilizes ferrihydrite against transformation to goethite (Cornell et al., 1987; Quin et al., 1988) and alters the morphology of goethite that forms from ferrihydrite (Cornell and Giovanoli, 1987). Preferential silicate adsorption on specific crystallographic planes of goethite during crystal growth is considered to be the main factor influencing goethite morphology in siliceous systems (Cornell and Giovanoli, 1987; Quin et al., 1988). In addition H_4SiO_4 can compete for

adsorption sites on goethite and ferrihydrite and make their surface less accessible to other solution anions such as arsenate, chromate and phosphate (Swedlund and Webster, 1999; Luxton et al., 2008). In this way H_4SiO_4 chemistry on iron oxide surfaces influences the distribution of many elements in aquatic systems and is of fundamental importance to geochemistry.

Silicate can sorb as monomers on iron oxide surfaces via $Fe–O–Si$ bonds and can also form oligomeric or polymeric silicates with $Si–O–Si$ linkages. Sorbed monomers are believed to have a bidentate and binuclear linkage (Pokrovski et al., 2003; Hiemstra et al., 2007; Swedlund et al., 2010b) in which SiO_4 tetrahedra share two corners with singly coordinated oxygen ions (termed $\equiv Fe_1OH$) on the corners of adjacent edge sharing FeO_6 octahedra. Therefore each SiO_4 monomer has two terminal non-bonding OH groups and the proposed silicate oligomerization model involves insertion of a solution H_4SiO_4 between suitably orientated adjacent monomers forming in the first instance a linear trimeric silicate. For this reason it is expected that the arrangement of sorption sites on an oxide surface will have a pronounced effect on the propensity of silicates to undergo oligomerization on an oxide surface. For example the arrangement of TiO_6 octahedra on the rutile (110) face means that sorbed H_4SiO_4 monomers are oriented so as to

* Corresponding author. Tel.: +64 9 923 4296.
E-mail address: p.swedlund@auckland.ac.nz (P.J. Swedlund).

favor linear oligomer formation (Song et al., 2012). In addition, the rutile surface promotes the formation of silicates with a higher degree of polymerization such as 3-dimensional polymeric silica (Song et al., 2012). In comparison the disordered surfaces of nanometer sized particles of amorphous TiO_2 and ferrihydrite are less favorable to linear oligomer formation than rutile and the high surface curvature inherent to a ≈ 2 nm sized particle inhibits the formation of more highly polymerized silicates on these surfaces (Swedlund et al., 2012).

Little is known about the relationship between interfacial silicate polymerization and iron oxide mineralogy and morphology and in this paper we compare H_4SiO_4 sorption and polymerization on three goethite phases with different morphology. In the *Pbnm* space group acicular goethite has (110) and (021) major faces (Cornell and Schwertmann, 2003). The (110) faces have rows of singly coordinate oxygen ions on FeO_6 corners that alternate with rows of doubly coordinate oxygen ions on FeO_6 edges. In contrast the (021) faces terminate the ends of the needles and consist entirely of rows of pairs of singly coordinate oxygen ions along [100] direction that alternate in orientation. Singly coordinated oxygen ions from two adjacent FeO_6 octahedra are spaced at 3.02 Å and 2.96 Å on the (110) and (021) faces respectively. The (110) and (021) faces terminate the sides and ends of the needles respectively and more rapid crystal growth on (021) than (110) accounts for the acicular morphology. The edges of SiO_4 tetrahedra in silicate minerals range from 2.4 to 3.0 Å (Liebau, 1985) so that, with a little relaxation in the surface structure, both the (110) and (021) faces could provide sorption sites for monomeric silicate adsorption. Preferential sorption of silicates on the terminal (021) goethite faces has been considered to cause the observed decrease in aspect ratio of goethites grown in the presence of silicates (Cornell and Giovanoli, 1987). Silicate sorption and oligomerization on goethites with different proportions of (110) and (021) faces are explored in this paper.

There have been several studies of H_4SiO_4 sorption on goethite including batch H_4SiO_4 sorption experiments, modeling and spectroscopic studies (Hiemstra et al., 2007; Luxton et al., 2008; Eick et al., 2009). Hiemstra et al. (2007) measured H_4SiO_4 sorption on goethite in batch systems as a function of pH and $[H_4SiO_4]$ and modeled results with a multi-site surface complexation (MUSIC) model. When the solution Si concentration $(Si_{(sol)})$ was <0.1 mM adsorption could be described with a bidentate binuclear monomeric Si surface species. At higher $Si_{(sol)}$ the removal of Si from solution exceeded the maximum possible sorption density of these monomeric Si species and an oligomeric surface species was required to fit data with $Si_{(sol)} > 10^{-4}$ M which the authors noted is H_4SiO_4 saturation with respect to quartz. Luxton et al. (2008) measured *ex situ* IR spectra of goethites reacted with either 0.1 or 1 mM H_4SiO_4 over periods of 6 and 48 h. Samples with 0.1 mM H_4SiO_4 had a dominant feature Si–O stretching mode $(\nu(Si-O))$ in the IR spectra at 950–1000 cm^{-1} attributed to monomeric Fe–O–Si linkages. Samples with 1 mM H_4SiO_4 also had a dominant $\nu(Si-O)$ feature in the IR spectra at 1100–1200 cm^{-1} attributed to three dimensional polymeric silicate with Si–O–Si linkages. This shift in spectral position with Si adsorption density (Γ_{Si}) is quite distinct from that which was observed for H_4SiO_4 on ferrihydrite where the main feature in the IR spectra shifts from ≈ 950 to 1020 cm^{-1} as Γ_{Si} increases. The band at 1020 cm^{-1} indicated the dominance of a linear oligomeric silicate on the ferrihydrite surface and bands in the 1100–1200 cm^{-1} region, indicative of 3 dimensional silica, were not significant even at >1 mM H_4SiO_4.

In situ ATR-IR has been proved to be a very useful technique to investigate interfacial silicate polymerization (Swedlund et al., 2009, 2010b). However goethite has strong Fe–O–H bending modes at ~800 and ~900 cm^{-1} and these interfere with the Si–O stretching region of the sorbed silicate ATR-IR spectra. For this reason X-ray photoelectron spectroscopy (XPS) is used in this work to access the degree of Si polymerization (Seyama and Soma, 1985; Vempati et al., 1990; Soma et al., 1996; Swedlund et al., 2009). The positions of the Si 2s (Seyama and Soma, 1985; Swedlund et al., 2011) and the Si 2p (Vempati et al., 1990)

photoelectron peaks shift to higher binding energy as the degree of Si polymerization increases. For example the Si 2s binding energy (BE) increases from ≈ 152.8 eV for minerals with isolated SiO_4 tetrahedra to 154.4 eV for quartz with fully polymerized SiO_4 tetrahedra (Seyama and Soma, 1985). Similarly the Si 2s BE has been used to assess the degree of silicate polymerization in natural and synthetic ferrihydrites (Soma et al., 1996). The Si 2s BE increased from 153.1 to 153.9 eV for ferrihydrite adsorbed H_4SiO_4 with the surface H_4SiO_4 species changed from being almost exclusively monomeric to trimeric (Swedlund et al., 2011). This shift correlated to the increase in the wavenumber position of the asymmetric Si–O stretching modes of the same samples. The Si 2p BE has also been used to assess Si polymerization on ferrihydrite (Vempati et al., 1990), however an overlap between Si 2p and a shoulder on the Fe 3s XPS peak has been noted to interfere with the Si 2p BE peak (Glasauer et al., 2000; Swedlund et al., 2011). The current paper measured the sorption isotherms and Si 2s BE with XPS for three different goethites with sorbed silicate over a range of Γ_{Si}. The three goethites differed in morphology and were investigated to test our hypothesis of how goethite morphology influences Si polymerization.

2. Methods

2.1. Preparation and characterization of goethite

All solutions were made from analytical grade reagents and 18 MΩ cm resistivity deionized water which had been distilled, acidified with HCl to pH ≈ 3 and sparged with N_2 for 3–5 h to remove CO_2. Isothermally distilled HCl and low-carbonate NaOH solutions were used to adjust the pH. Three goethites were labeled G41, G82 and G250 based on their specific surface area and were prepared with different methods. G41 was prepared by rapid hydrolysis of ferric nitrate with KOH in a system with an OH^-:Fe^{3+} mole ratio of 4 (Boily et al., 2001). The mixture was kept at 60 °C for 2 days to allow goethite formation. G82 was formed in a two step process (Atkinson et al., 1968); nucleation from ferric nitrate with NaOH (with OH^-:Fe^{3+} mole ratio of 0.76) at room temperature for 50 h followed by crystal growth at pH 12 and 60 °C for 4 days. G250 was synthesized from the oxidation of ferrous sulfate at pH 3. The pH of a filtered (0.20 μm) ferrous sulfate solution (0.1 M, pH 2) was raised to 3 with 1 M NaOH solution. The solution was stirred and sparged with air at room temperature for 60 days and the pH kept at 3.0 using an autotitrator. Sulfate was removed from G250 by raising the pH to 10 for 30 min and then replacing the supernatant twice by centrifugation, decanting and resuspension in 0.1 mol kg^{-1} $NaNO_3$ at pH 10. Ion chromatography of the solutions showed that, within experimental error, all the SO_4^{-2} had desorbed after 30 min at pH 10. All goethite samples were rinsed with 3 cycles of centrifugation, decanting and re-suspension in water and were then freeze dried. Powders were characterized by XRD, BET N_2 adsorption isotherms after outgassing at for 12 h at 70 °C and ≈ 1 kPa and transmission electron microscopy (TEM).

Acid–base titrations were performed to assess the goethite surface site densities. Suspensions were equilibrated at I = 0.004 mol kg^{-1} and pH ≈ 9 for 24 h and then divided into three vessels and $NaNO_3$ added to raise the ionic strength of two suspensions to 0.020 and 0.10 mol kg^{-1}. After 24 h titrations were conducted with a Metrohm model 716 DMS Titrino using 0.1 mol L^{-1} NaOH or HNO_3 under an Ar atmosphere with the signal drift set to the lowest possible value of 0.5 mV min^{-1}. Initial titrations were in the vicinity of pH 9 to determine the PZC and then HNO_3 was added and the suspensions titrated from pH 4 to 11.

2.2. The isotherm and XPS of silicic acid adsorption on goethite

A 1.66 mM silicate stock solution was prepared as described in detail previously (Swedlund et al., 2009) by dissolving amorphous