

# IN SITU INFRARED SPECTROSCOPY AS A TOOL TO DECIPHER MONOMER AND POLYMER DEPOSITION OF SILICA SCALE

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## ABSTRACT

Silica scale deposition remains a challenging constraint to geothermal energy utilization. This is because silica deposition proceeds via several interconnected pathways, each with a complex dependence on variables in both the fluid composition, the nature of the solid surfaces and fluid flow conditions. In the solution phase silica polymerization produces nanometre sized colloidal  $\text{SiO}_2$  particles via many reactions and intermediates. Silica deposition on a metal surface can proceed via solution phase monomeric silicate ( $\text{H}_4\text{SiO}_4$ ) and/or colloidal silica ( $\text{SiO}_{2(\text{am})}$ ) binding to metal oxide layers that are present on metal surfaces. The progression of silica deposition depends on the interactions between the various reaction pathways and the chemical, electrostatic and fluid flow forces involved. In this paper we demonstrate the use of *in situ* Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy to differentiate between the various pathways in real time and as a function of the fluid and surface properties. In this technique an iron oxide that is representative of the oxide formed on a metal surface is deposited onto an infrared (IR) transparent crystal which is placed in a flow cell within an IR spectrophotometer. IR spectra can be collected while  $\text{H}_4\text{SiO}_4$  and  $\text{SiO}_{2(\text{am})}$  bearing solutions are flowed through the cell and the Si-O stretching region of the spectra ( $700\text{--}1300\text{ cm}^{-1}$ ) can yield both quantitative and structural information about the silicate species formed on the oxide surface. In this way the surface chemistry of  $\text{H}_4\text{SiO}_4/\text{SiO}_{2(\text{am})}$  can be studied *in situ* under the desired conditions of pH, Si concentration, ionic strength, and (with a heated flow cell) temperature.

## 1. INTRODUCTION

Energy extraction from geothermal fluids typically results in solutions that are supersaturated in silicic acid ( $\text{H}_4\text{SiO}_4$ ). The potential for  $\text{H}_4\text{SiO}_4$  polymerization then exists which can lead to deleterious silica scale formation, and avoiding silica scale can constrain geothermal energy utilization. Several processes can be involved in the formation of silica scale. Homogeneous nucleation refers to the initial step in the formation of  $\text{SiO}_2$  particles in a supersaturated solution by condensation reactions forming Si-O-Si (silanol) linkages between  $\text{H}_4\text{SiO}_4$  molecules. (McIntosh et al., 2011) This progresses randomly producing particles of amorphous  $\text{SiO}_2$  with little or no long range order. Homogeneous nucleation will only occur if the solution is supersaturated and typically involves an induction period, the length of which will depend on factors such as pH, degree of supersaturation, and the composition of the in solution.

Silicic acid can also undergo an analogous condensation reaction with hydroxide groups (-OH) present on a surface, such as the  $\equiv\text{FeOH}$  groups on the iron oxide that exists on iron metal surfaces. In this case Si-O-Fe linkages are formed and this can occur at  $\text{H}_4\text{SiO}_4$  concentrations that are undersaturated and without an induction period (Swedlund

et al., 2009). The  $\text{H}_4\text{SiO}_4$  on the iron oxide surface can then proceed to form Si-O-Si linkages with other  $\text{H}_4\text{SiO}_4$  molecules that are either in solution or also held on the surface. In this way the iron oxide surface can act as a template for the formation of a polymerized silicate phase. In addition to monomeric silicates sorbing and polymerizing on the oxide surface, the colloidal  $\text{SiO}_{2(\text{am})}$  particles can attach to the oxide surface. The aim of the current study is to use the *in situ* technique of Attenuated Total Reflectance Infrared (ATR-IR) spectroscopy to study the chemistry of  $\text{H}_4\text{SiO}_4$  and  $\text{SiO}_{2(\text{am})}$  at an iron oxide surface. This study involves the comparatively simple system of a pure iron oxide phase reacting with both undersaturated  $\text{H}_4\text{SiO}_4$  solutions and supersaturated  $\text{H}_4\text{SiO}_4$  suspensions containing colloidal particles of either 17 nm or 90 nm.

## 2. BACKGROUND

Attenuated Total Reflectance is a sampling technique that is conducive to the *in situ* infrared spectroscopic study of interfacial systems. An ATR crystal is used that is transparent to IR light over the desired wavelength range and is not soluble in the solvent being used. An IR beam enters the ATR crystal at an angle such that the light is totally reflected off the internal surface of the crystal (Figure 1). This reflection produces an evanescent wave that extends a few microns beyond the crystal surface (decaying exponentially with distance). Material placed on the crystal surface will therefore be sampled by the IR light. In our study an iron oxide film is dried onto the crystal which is then placed into a flow cell and IR spectra are collected as an  $\text{H}_4\text{SiO}_4$  solution is pumped through the cell. (Dol Hamid et al., 2011; Swedlund et al., 2010a; Swedlund et al., 2009; Swedlund et al., 2010b; Swedlund et al., 2011; Swedlund et al., 2012)

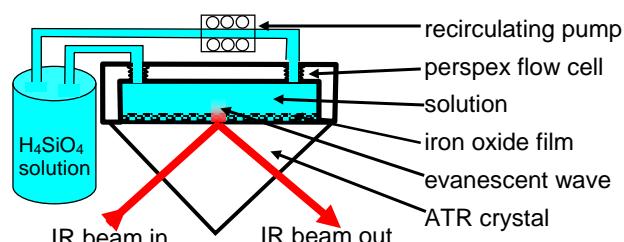
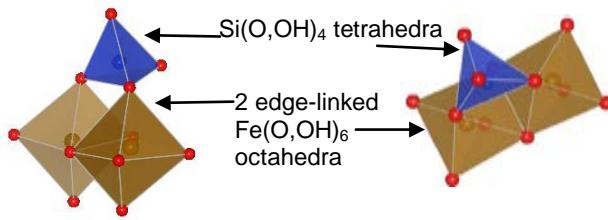


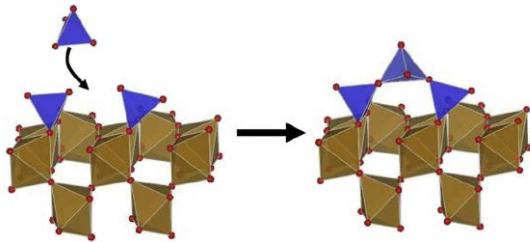
Figure 1: Schematic of the ATR-IR experimental set up. The crystal shown has a diameter of  $\approx 3\text{ mm}$ .

The type of complex that forms between  $\text{H}_4\text{SiO}_4$  (acting as a ligand) and ferric cations has been studied with Fe K-Edge Extended X-ray Adsorption Fine Structure (EXAFS) by Pokrovski et al (2003). When  $\text{Fe}^{\text{III}}$  was precipitated in the presence of  $\text{H}_4\text{SiO}_4$  the product had complexes with Si-Fe distances of 3.18 Å implying that  $\text{H}_4\text{SiO}_4$  shared two corners with the corners of two neighboring edge linked Fe octahedra (Figure 1). This is termed a <sup>2</sup>C complex and is bidentate (involves 2 of the silicate oxygens), binuclear (involves 2 Fe ions) and involves only a monomeric silicate species with no Si-O-Si bonds.



**Figure 2: Two views of the  $^{2\text{C}}$  Fe-Si complex formed during ferric hydrolysis in the presence of  $\text{H}_4\text{SiO}_4$  (Pokrovski et al., 2003).**

To understand the polymerization chemistry of  $\text{H}_4\text{SiO}_4$  on an iron oxide surface it is necessary to know the arrangement of corner sites on adjacent edge sharing iron octahedra (forming  $^{2\text{C}}$  bonding sites). This arrangement will depend upon the oxide's crystal structure and the nature of the crystal's enclosing faces. The observed ATR-IR spectra, the changes in the surface composition with time, and the arrangement of adsorption sites on the ferrihydrite surface are consistent with a model where the oligomer is formed when a solution  $\text{H}_4\text{SiO}_4$  forms a bridge between two monomers adsorbed on adjacent pairs of sites on the (021) face. This reaction is analogous to monomer adsorption in that the bridging  $\text{SiO}_4$  tetrahedra shares singly coordinated corner oxygens on two adjacent adsorbed  $\text{SiO}_4$  tetrahedra, whereas the monomer adsorption involves  $\text{H}_4\text{SiO}_4$  sharing the corners of two adjacent Fe octahedra. This model also explains why the spectra indicate a monomer forms when silicate initially adsorbs on ferrihydrite and then an oligomer that is larger than a dimer forms without a dimer as an observable intermediate.



**Figure 3: Interfacial oligomerization occurring by insertion of a solution  $\text{H}_4\text{SiO}_4$  between suitably orientated adjacent sorbed monomers**

### 3. METHODS

Detailed methods have been reported (Swedlund et al., 2009). A stock suspension of magnetite was prepared under a  $\text{N}_2$  atmosphere from a solution of  $\text{FeSO}_4$  (0.3 M) and  $\text{FeCl}_3$  (0.6 M). Magnetite formed immediately when the pH was raised from  $\approx 1$  to 10.5 by the addition of 28 % ammonium hydroxide. The magnetite suspension was diluted by  $\approx 200$  fold and 5  $\mu\text{L}$  of this suspension was deposited on a diamond crystal and allowed to dry under  $\text{N}_2$  producing a stable magnetite film adhered on the crystal surface. A flow cell was mounted over the magnetite film and an appropriate background solution pumped through the cell for approximately 1 hour after which time there was no change in the IR spectrum of the magnetite film over time. At this point a silicate solution or suspension was pumped through the flow cell and changes in the ATR-IR spectra were recorded as IR absorbance spectra over time.

Two silicate suspensions of different colloidal size (17 nm and 90 nm) were provided by Luke Sinclair from the University Canterbury University. These suspensions have

a Si concentration of  $\approx 28$  mM and were prepared from sodium silicate and sulfuric acid. The pH (8.75 and 9.25), particle size (17 and 90 nm), monomeric silicate concentration (2.2 and 2.3 mM) and  $\text{Na}_2\text{SO}_4$  concentration (both at 27 mM) were measured in our laboratory. Two solutions were prepared at Auckland that had the same ionic strength, pH and sulfate concentration as the provided suspensions. These were a silicate free background solution and a monomeric silicate solution (1.66 mM  $\text{H}_4\text{SiO}_4$ ).

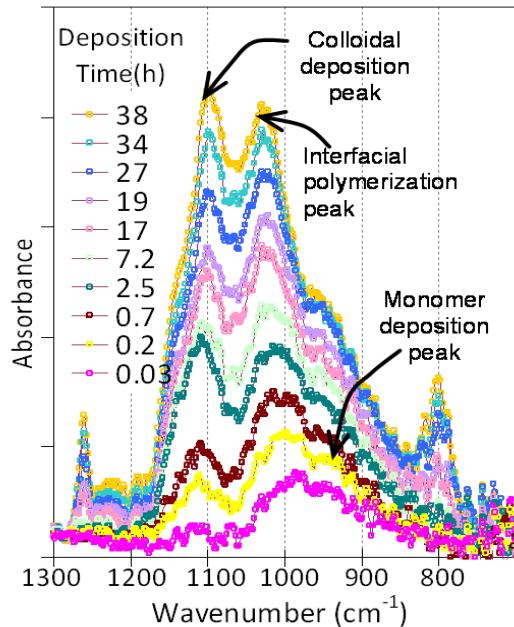
A Nicolet 8700 Spectrometer with DTGS detector and Omnic software was used to obtain ATR-IR spectra. The spectra were corrected for changes to the water signal, taking a horizontal baseline and ATR correction. Negative Savitsky-Golay 2nd derivatives were calculated to assist band identification. Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) was used to determine the IR spectra for the pure surface species and the amount of each surface species present using the constraints of non-negative concentration and non-negative spectra (Tauler et al., 1995).

### 4. RESULTS

A typical set of ATR-IR spectra collected over time as an iron oxide reacted with a solution containing  $\text{H}_4\text{SiO}_4$  and  $\text{SiO}_{2(\text{am})}$  colloids is shown in Figure 4. The spectra are in the Si-O stretching region of silicates. Over time the amount of Si on the ferrihydrite surface (termed  $\Gamma_{\text{Si}}$ ) increased and the area of the spectra increased linearly with  $\log(\text{time})$ . As  $\Gamma_{\text{Si}}$  increased the shape of the spectra changed representing a change in the Si surface species present as a function of  $\Gamma_{\text{Si}}$ . The IR spectra recorded when the iron oxide was first exposed to the  $\text{H}_4\text{SiO}_4/\text{SiO}_{2(\text{am})}$  solutions and  $\Gamma_{\text{Si}}$  was low have a main band at  $945\text{ cm}^{-1}$  which has a shoulder at  $880\text{ cm}^{-1}$ . When compared with the IR spectra of silicate minerals (where the silicate structure is known from XRD) it is apparent that a silicate species with bands at  $945$  and  $880\text{ cm}^{-1}$  is a monomeric species with no Si-O-Si linkages (Farmer, 1974). Furthermore the shape of the IR spectra indicates that this monomeric silicate is attached to the ferrihydrite surface via a bidentate linkage (Swedlund et al., 2009) consistent with the  $^{2\text{C}}$  complex proposed by Pokrovski et al. (2003) from EXAFS of ferric and  $\text{H}_4\text{SiO}_4$  coprecipitates.

The shape of the IR spectra changes as  $\Gamma_{\text{Si}}$  increased with proportionally more IR absorbance in the region between  $950$  and  $1150\text{ cm}^{-1}$ . The frequencies of the Si-O stretching vibrations in silicates are indicative of the degree of polymerization, with Si-O-Si bridging bonds having higher frequencies than non-bridging Si-O bonds. Therefore in silicate minerals the main Si-O stretching modes move to higher frequencies as the degree of polymerization increases. As increasing amounts of  $\text{H}_4\text{SiO}_4$  react at the ferrihydrite surface over time the position and relevant intensities of the bands associated with the band at  $1007\text{ cm}^{-1}$  do not change from when these bands first appear until they become the dominant feature of the spectra at the expense of the bands at  $945$  and  $880\text{ cm}^{-1}$ . This implies that the spectral feature associated with the  $1007\text{ cm}^{-1}$  band is due to a discrete silicate species rather than a growing polymer where the number of bands, and the position of the bands, would change as the degree of polymerization increased (Lazarev, 1972). By comparison with the IR spectra of silicate minerals it is apparent that the degree of polymerization in a silicate species with bands at  $918$ ,  $1007$ ,  $1070$ ,  $1108$  and  $1140\text{ cm}^{-1}$  is higher than that of a dimer but lower than that of a three dimensional  $\text{SiO}_2$  framework silicate. The bands and maximum absorbences of dimers and framework

silicates are respectively at lower and higher frequency than these values. In addition to the monomer and oligomer discussed above a feature is evident at  $\approx 1100 \text{ cm}^{-1}$  in the spectra at high  $\Gamma_{\text{Si}}$ . This indicates the deposition of polymeric silicate onto the oxide surface. The above analysis suggests the formation of three surface silicate species when iron oxides are exposed to  $\text{H}_4\text{SiO}_4 - \text{SiO}_{2(\text{am})}$  solutions; a monomer that dominates the surface at low  $\Gamma_{\text{Si}}$ , an oligomer that dominates the surface at intermediate  $\Gamma_{\text{Si}}$  and a polymeric  $\text{SiO}_2$ .



**Figure 4: Typical ATR-IR spectra recorded over time as an iron oxide reacts with a solution containing both  $\text{H}_4\text{SiO}_4$  and  $\text{SiO}_{2(\text{am})}$**

From the qualitative analysis of the data it was expected that all of the measured IR spectra should be able to be described by a linear combination of just three spectra representing the spectra for each of the three pure surface species. To test this hypothesis the entire 134 measured spectra (each with 209 data points) were analyzed by MCR-ALS. This technique decomposes the data matrix of measured spectra (a 134x209 matrix termed “**D**”) into the product of two matrices. The spectra matrix (termed “**S**”) has 3 rows and 209 columns, representing the spectra of each of the three pure surface species. The composition matrix (termed “**C**”) has 134 rows and 3 columns representing the contribution of each of the three surface species to each measured spectrum. MCR-ALS determines the **C** and **S** that minimizes the difference between the **D** and the product **CS** as indicated below.

$$\mathbf{D} = \begin{matrix} d_{1,1} & d_{1,2} & \dots & d_{1,209} \\ d_{2,1} & & & \vdots \\ \vdots & \ddots & & \vdots \\ & & \ddots & \vdots \\ d_{134,1} & \dots & \dots & d_{134,209} \end{matrix}$$

$$\mathbf{C} = \begin{matrix} c_{1,1} & c_{1,2} & c_{1,3} \\ c_{2,1} & \vdots & \vdots & s_{1,1} & s_{1,2} & \dots & s_{1,209} \\ \vdots & \vdots & \vdots & s_{2,1} & \dots & \dots & s_{2,209} \\ & & & s_{3,1} & \dots & \dots & s_{3,209} \\ c_{134,1} & c_{134,2} & c_{134,3} \end{matrix}$$

$$d_{m,n} \equiv c_{m,1} \times s_{1,n} + c_{m,2} \times s_{2,n} + c_{m,3} \times s_{3,n}$$

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