

SURFACE CHARACTERIZATION OF GOETHITE-HUMATE CHELATIONS COMPLEXATED WITH QUARTZ

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Abstract

Metal oxide minerals ubiquitously exist with organic matter in sedimentary rocks. Therefore, the chelation of organic matter on mineral surfaces is expected to affect mineralization and the stability of detrital grains, such as quartz. Understanding the complexation of goethite-humate chelation with quartz is important because quartz is the fundamental material in reactions that affect the petrophysical properties and sorption capacity of sandstones. However, this complexation interaction has not been characterized. Hence, this study uses Field emission scanning electron microscopy (FESEM) and Transmission electron microscopy (TEM) as well as Fourier infrared transform and (FTIR) and X-ray photon (XPS) spectroscopic methods to characterize the chelation of humate on goethite, and the complexation of this chelation with quartz. The FESEM showed the adsorption and coating of the synthesized chelations on quartz substrates, forming secondary precipitates that occlude the quartz grains. The TEM images depict the chelations intruding the lattice spaces of quartz. The characteristic peaks for Fe-O, Si-O-Si, C-H and H-O-H bonds as well as that of XPS further confirmed the adsorption interactions between goethite-humate chelations and quartz. The study showed that the complexation reaction controls the binding of iron oxides to quartz thereby influencing the porosity of siliciclastics.

Keywords: Quartz; Surface microtextures; Goethite-humate complex; quartz dissolution.

1. Introduction

In surficial sedimentary rocks, phyllosilicates and metal oxide minerals ubiquitously exist with organic matter, thus affecting mineralization, the reactivity and bioavailability of dissolved and adsorbed ions as well as the stability of detrital grains, particularly ubiquitous minerals like quartz [1]. Associations relating to humic acid have been shown to influence the adsorption of both organic and inorganic compounds to mineral surfaces [1]. Compounds of trivalent ions such as goethite and hematite are specifically significant because of their characteristic high affinity for heavy metals [2]. The aforementioned studies showed that the aggregation and induration of surficial rocks by soil organic matter appear to be preferred by the presence of metal ions, which links the anionic polymeric organic matter to the negative ligands of the charged silicate surfaces of [3]. Nonetheless, little attention has been given to main components of these interactions, usually quartz. Moreover, there is dearth of experimental investigations on the impact of the interactions between organic matter associations and metal ions on quartz.

Given the ubiquitous co-existence of inorganic and organic compounds in sedimentary rocks, their chelating interactions are expected to affect the stability of primary quartz mineral [4]. Although, etch pits on quartz surfaces were discovered in a peat bog [5], as well as in an aquifer tainted with leachates of crude oil [5], while lichen has been shown to corrode quartz [6], the fact that these organic complexes actually affect quartz has not been elucidated. Understanding quartz interactions is important because quartz is the most abundant mineral in the Earth's crust and a fundamental material in reactions that affect porosity, permeability, capillarity buffering, and sorption capacity of sandstones [7-11]. Thus, it is imperative to characterize the impact of goethite

humate complexation with quartz in order to determine if this interaction affects the morphology of quartz in terms mineral absorption/adsorption or chemisorption. This will augment information on porosity enhancement or inhibition via mineral growth in siliciclastics.

2. Methodology

This study involves the synthesis of goethite, and the chelation of humic acid on the synthesized goethite crystals. The synthesized goethite-humate chelation was subsequently complexed with quartz grains. Afterwards, morphological characterization and surface composition analysis of the chelated grains were performed using a high-resolution field emission scanning electron microscope (FESEM: Carl Zeiss Supra 55VP; operated at 5 to 20 kV). The imaging was carried out under variable pressure (VP) ranging from 2Pa to 133Pa and probe current between 1pA and 10nA. Given the use of variable pressure, there was no need for coating the samples to prevent the 'charging' effect. FESEM microscopy examined the size and geometrical shape of iron oxide particles. Transmission electron microscopy (TEM) (Zeiss Libra 200FE) was used to provide high resolution mineralogical and textural analysis by differentiating the quartz from the as-synthesized secondary phases. Infrared spectra of the samples were obtained using Fourier-transform infrared [FT-IR] analysis to identify the bonds in the synthesized material and possible Fe³⁺ interdiffusion or adsorption on the quartz surface. FT-IR spectra were recorded at room temperature using a Shimadzu FTIR 8400S. X-ray photoelectron spectroscopy (XPS) was used to determine the composition, chemical state of elements and depth profiling of the material. The amount of dissolved silica, variations in quartz surface morphology and composition were analyzed using molybdate spectrophotometry method (HACH D2800).

2.1. Goethite synthesis

Goethite synthesis involved the oxidation of dissolved FeCl₂·4H₂O for duration of 48 h [12]. The paste form of the mineral was reacted with 30% H₂O₂ at 85°C for 10 min to eliminate surface-bound organic residues. After washing with deionized water, the dispersed goethite was decanted and the fine floating fraction (<2mm) collected [13]. The stock suspension of the <2mm goethite fraction was stored at room temperature.

2.2. Chelation of humate on goethite

The samples were prepared in de-ionized water. The goethite sample dispersed in 0.1 NaCl solution contained in 40mL tubes and centrifuged at 9000 rpm for 20 min to get rid of excess water. The humic acid in 50-mL was dissolved in 0.1 M NaCl and adjusted to pH 11 with 0.1 M NaOH. The sample was agitated in a shaker for 1 h, with the pH was tested intermittently. Prior to the addition of the humate suspension, the goethite was re-suspended in 0.1 M NaCl, with 0.1 M NaOH added to attain a pH of 8 while each mineral suspension was stirred continuously, an appropriate amount of humate stock was slowly added. The goethite-humic acid suspensions were acidified to ≈ pH 6 with 0.1 M HCl. The samples were agitated for 18 h at 25°C in a shaker; then the pH was tested and attuned to pH 5.6 as needed with 0.1 M HCl. These procedures were modified after the study by Alcacio *et al.* [1].

Afterwards, 2g of pure quartz grains were added into the goethite-humic stock and aged for a duration of 20 days. The amount of dissolved silica in the stock was subsequently measured using silica molybdate method. The quartz grains were then dried for 2 days at a 60°C before being characterized.

3. Results and interpretation

3.1. FESEM analysis

FESEM micrographs were acquired to show possible sorption of goethite-humate chelations complexed with quartz substrates. The surface morphological analysis shows that the quartz surface is entirely coated by the complex (Fig. 1A). The goethite-humate (H) complex consists of agglomeration of round subhedral crystals dispersed and admixed over the quartz surface, as shown in Fig. 1B. The EDX spectra (Fig. 2) obtained for the coating show composition of Fe

from the goethite, Si from dissolved silica and Na denoting the alkali solvent. Laths of unreacted goethite crystals (G) are observed beneath the goethite-humate (H) coating (Fig. 1).

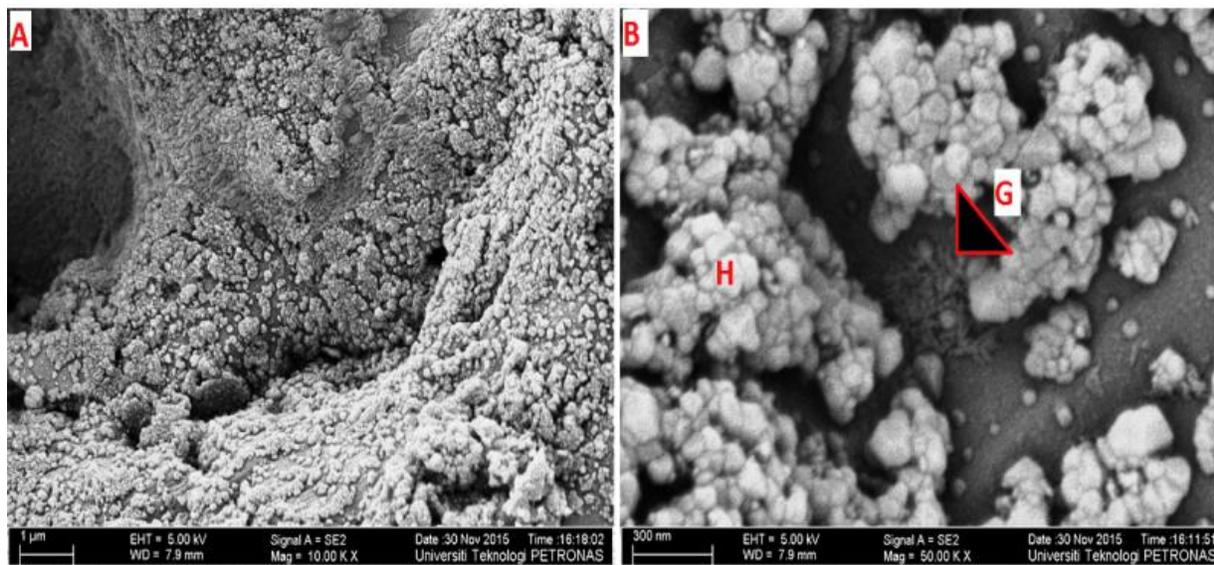


Fig. 1. FESEM micrographs showing goethite-humate complex chelated on quartz B] lath shaped goethite (G), and agglomeration of round subhedral humate compounds

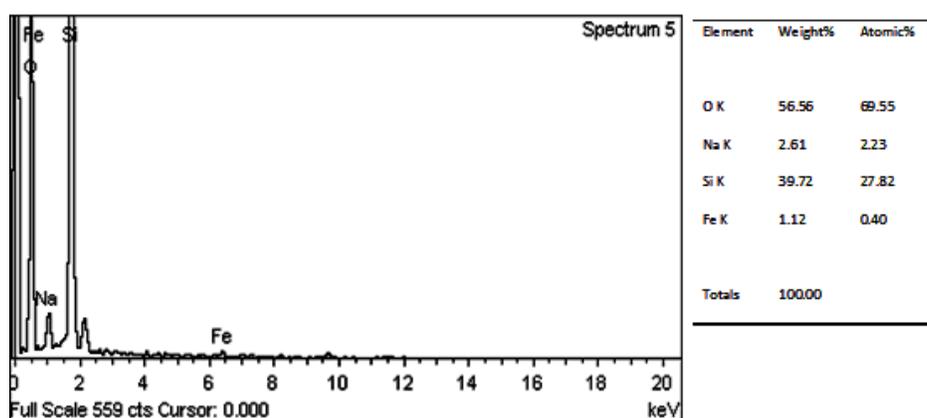


Fig.2. EDX of goethite-humate coating on quartz

3.2. TEM Analysis

To confirm the ionic interaction between quartz, goethite and humate compounds, high magnification images using TEM were acquired. The obtained TEM micrograph shows acicular lath shaped goethite needles chelated on the non-crystalline/amorphous humic material. This proves the successful synthesis of goethite and its subsequent sorption to humic material. The EELS spectra (Fig. 4) identified Fe^{2+} rather than Fe^{3+} . Once generated, the sparingly soluble Fe^{3+} oxides (goethite) cannot be re-dissolved by the reversal of hydrolysis (protonation), but complexation with organic ligands (biotic reduction) may bring about re-dissolution. The initially immobile Fe^{3+} in goethites is reduced to mobile Fe^{2+} ions by electrons from the oxidation of humate (represented by CH_2O). Eqn 1 provides a clear representation of the reaction. The sorption is further confirmed by the XPS data discussed below.



The reductive reaction goes on to prove the chelation of goethite on the humate compounds.

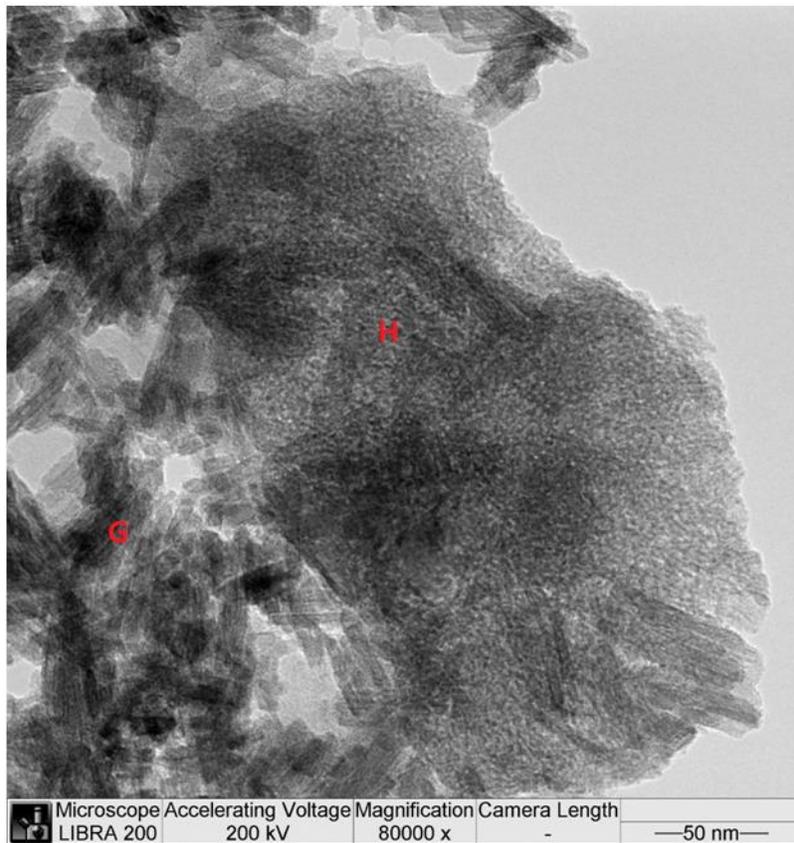


Fig.3. TEM micrograph of acicular goethite crystals (Fe) chelated on humate substrates (C)

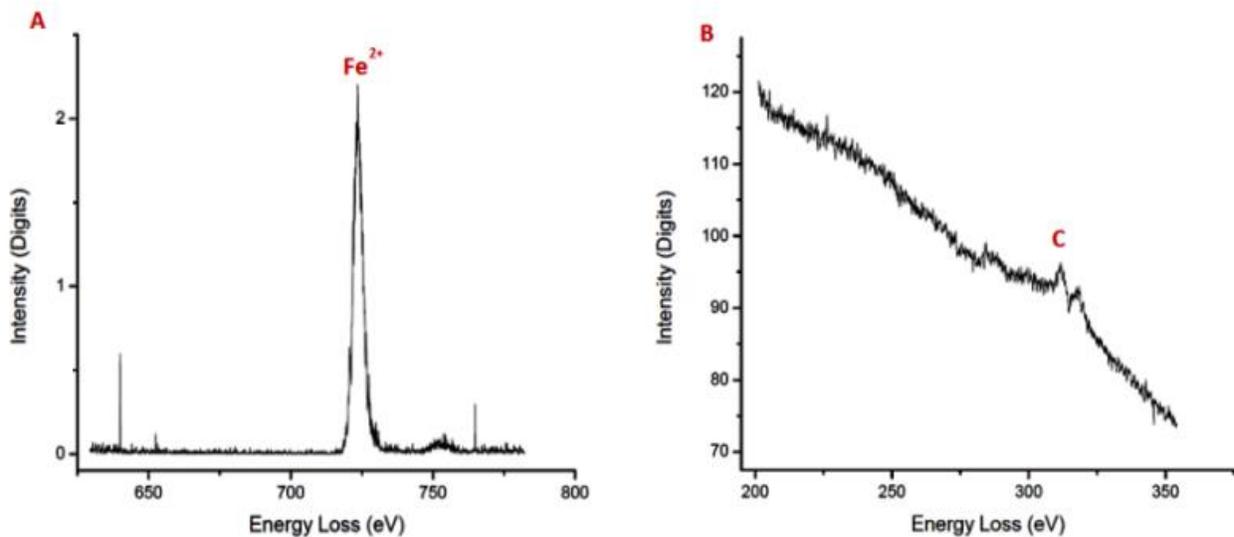


Fig.4. EELS spectra of the goethite-humate complex showing A) Fe^{2+} peak B) characteristic peak of carbon

Fig.5A shows that the randomly distributed agglomeration of goethite laths (Fe) amalgamated with humate compounds (C). This synthesized complex coats/occludes the quartz grains (Fig.5B). Fig.5B shows the chelations (G) intruding the lattice spaces quartz crystal structure (Q), confirming the complexation of the goethite-humate chelations with quartz.

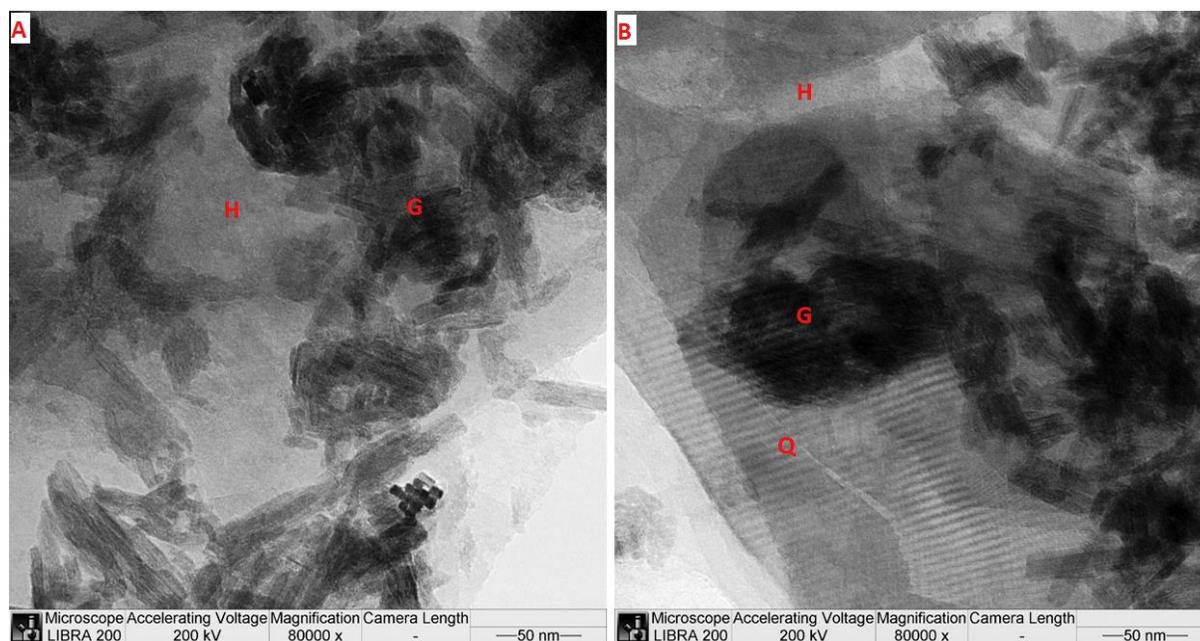


Fig. 5. TEM micrograph of randomly oriented goethite laths amalgamated with non-distinctive humate compounds (confirmed with EELS)

3.3. FT-IR

FTIR peaks identified at 534 denote Fe-O and Fe₂O₃, which indicate goethite mineralogy. The peak also indicates the possible presence of Si-O-Fe stretching bonds. The peak at 633 signifies Si-O-Si (siloxane) bond of quartz. Broad absorption bands between 4000 – 2500 cm⁻¹ are attributable to O – H stretching vibrations, with the broad asymmetric band at around 3400 cm⁻¹ due to hydrogen bonded molecular water [14-16]. The peak at ≈2911 suggest C-H bond signifying humate compound. The presence of all the identified peaks in one spectrum indicates successful chelation of humate on goethite and the complexation of this chelation with quartz.

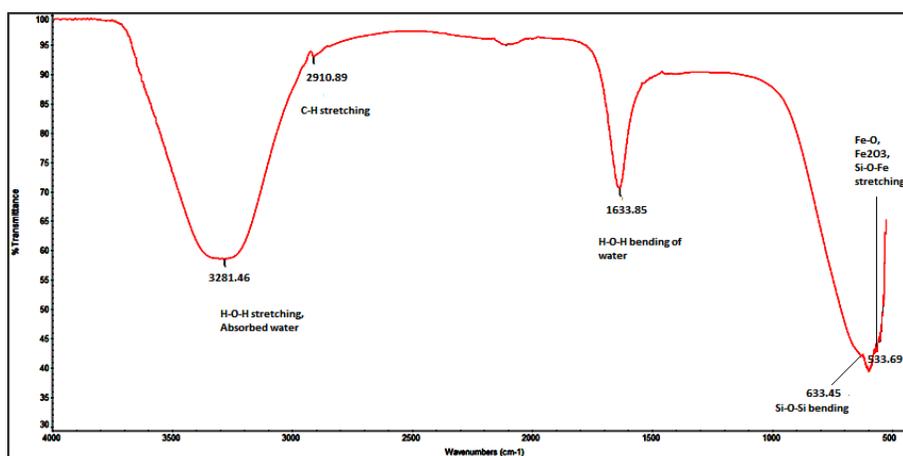


Fig. 5. FTIR spectra showing characteristic peaks for Fe-O, Si-O-Si, C-H and H-O-H bonds

3.4. XPS

The XPS spectra of the goethite-humate complex show carbon, Na (possibly from the NaOH solvent used), O, Fe (denoting goethite). Interestingly, SiO₂, Si, and SiC bonds were also identified, which further confirms the complexation of goethite-humate chelation with quartz. The strong intensity peak of C suggests organic/biogenic source or catalytic interaction of C and H-containing

compounds and the quartz surface, rather than from mere exposure to air. The C centered at 285eV denotes organic species with C-H, C-C and C-O bonds [17-18].

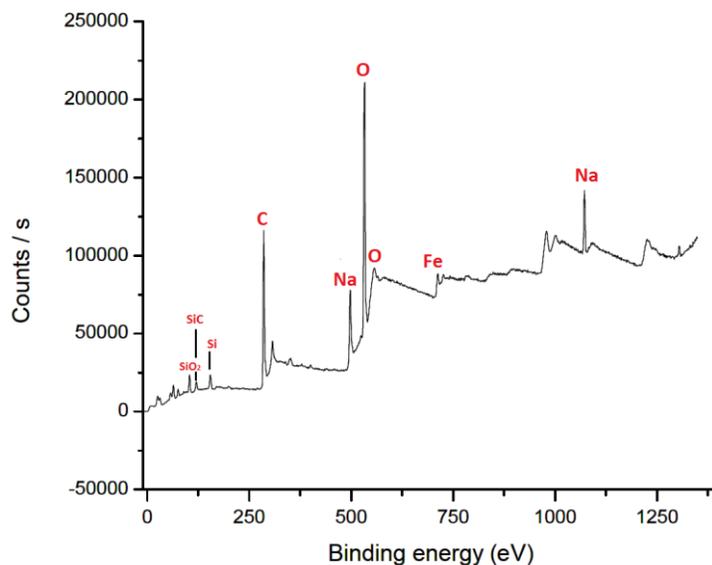


Fig. 6. XPS survey spectra of goethite-humate complex chelated on quartz showing characteristic peak for Si, C, O, Fe, and Na

3.5. Quartz dissolution

The effect of quartz interactions with Fe oxide (goethite), and goethite humate complex was also studied. The quartz substrates were subsequently aged in solutions of NaOH, goethite and goethite humate complex, separately, for a period of 20 days. The amount of dissolved silica varied from 36.5 mg/L in only NaOH solutions to 71.3 mg/L in solutions containing synthesized goethite to 92.4 mg/L in solutions comprising goethite humate complex.

4. Discussion

Chelation of organic molecules on Fe^{3+} may occur via the replacement of water molecules adjoining the inorganic ion by organic ligands to form a more complex coordination compound [19]. This chelation process is characterized by slow kinetics leading to the bonding between the metal and the organic molecule. The microscopic characterization showed the adherence of the synthesized chelation on quartz substrates, forming secondary precipitates that occlude the quartz grains. The relatively lower silica in the system comprising on goethite compared to the goethite-humate system suggests the organic compounds hinders quartz dissolution. The morphological implication of this study involves attachment of cations and anions, thin film growth and mineral growth (sorption). The possible consequence of the chelation includes rock or secondary mineral formation, reduction in porosity and permeability, and solute immobility. The complexation reaction induces mineral growth over quartz substrates, creating a thin film that occludes the sample and increases the surface area of the grains. The possible complexation of goethite-humate on quartz can reduce the width of pore spaces, thereby limiting porosity and inhibiting permeability and fluid flow.

5. Conclusion

This study confirms the chelation of humic compounds to goethite, and the complexation of this chelation with quartz substrates. The TEM micrographs showed the bonding of humic compounds with goethite laths as well as the intrusion of the synthesized goethite-humate chelations into the lattice spaces of the quartz crystal structure. The spectroscopic evidence for the structural changes induced by complexation of Fe(III) was the formation of SiC bonds,

as shown by the XPS spectra. Characteristic Fe-O, Si-O-Si, C-H and H-O-H bonds were also identified in one singular FTIR spectra. Given the abundant nature of iron bearing minerals and organic compounds, the complexation of goethite-humate chelation with quartz controls the binding effect of iron and dissolution of quartz in the environment.

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