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Gas cell IR and ATR-IR spectroscopic studies for organic-inorganic interactions in adsorption of fulvic acid on the goethite surface generating CO_2

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ABSTRACT

Generation of CO_2 from Nordic fulvic acid (FA) solution in the presence of goethite (α-FeOOH) were observed in FA-goethite interaction experiments at 25–80 °C. CO_2 generation processes observed by gas cell infrared (IR) spectroscopy indicated two steps: the zeroth order slower CO_2 generation from FA solution commonly occurring in the heating experiments of the FA in the presence and absence of goethite (activation energy: 16–19 kJ mol^{-1}), and the first order faster CO_2 generation from FA solution with goethite (activation energy: 14 kJ mol^{-1}). This CO_2 generation from FA is possibly related to redox reactions between FA and goethite. In situ attenuated total reflection infrared (ATR-IR) spectroscopic measurements indicated rapid increases with time in IR bands due to COOH and COO^- of FA on the goethite surface. These are considered to be due to adsorption of FA on the goethite surface possibly driven by electrostatic attraction between the positively charged goethite surface and negatively charged deprotonated carboxylates (COO^-) in FA. Changes in concentration of the FA adsorbed on the goethite surface were well reproduced by the second order reaction model giving an activation energy around 13 kJ mol^{-1}. This process was faster than the CO_2 generation and was not its rate-determining step. The CO_2 generation from FA solution with goethite are faster than the

experimental thermal decoloration of stable structures of Nordic FA in our previous report possibly due to partial degradations of redox-sensitive labile structures in FA.

INTRODUCTION

"Humic Substance (HS)" is a general term of natural organic matter (NOM) composed of unspecified structures of complex organic polymers, which are considered to be originated from biomolecules.[1] Since it is a major constituent of NOM, it is influencing the circulation of organic substances, microbial nutrition and environmental pollution on the earth's surface.[2,3] HSs can be generated and decomposed by variable processes including biological activities and abiotic chemical pathways (e.g. the Maillard reaction, polymerization of phenol, etc.), and these processes can be catalyzed by inorganic materials.[2] HSs extracted from soils and natural waters by alkaline solutions and/or resins are classified into fulvic acid (water soluble in all pH range) and humic acid (precipitated under acidic condition), and they have been analyzed as representatives of HSs, in particular the standard fulvic and humic acids selected by the International Society for Humic Substances (IHSS).[4]

250–1900 years of mean residence times of HSs were reported by the ^{14}C dating method.[1] On the other hand, turnover time to CO_2 of soil organic carbon were reported to be in a range of 10 days to more than 300 years at 15 °C.[5] These time scales can be principally controlled by competitions between formation and degradation of HSs with complex multiple pathways including chemical and biological processes. However, there are few reports quantitatively studying time scales of HS formation and degradation based on kinetic evaluation of experimentally determined reaction rates.

Therefore, our research group has examined spectroscopic tracing and kinetic analyses of simulated formation and degradation of HSs. For tracing the simulated reactions, in situ spectroscopic methods were employed because in situ spectroscopy allowed continuous tracing of changes at fine time intervals. We estimated apparent reaction rate constants at several temperatures by fitting the spectroscopic changes with time by model reaction equations. Based on temperature dependence of the rate constants, we obtained activation energies of the changes. Activation energy is one of important parameters for estimating reactivities and time scales of chemical reactions in the real environments.

In our previous researches, we first focused on the simplest system simulating the formation process of HSs, which is the Maillard-type browning reactions from glycine and ribose. By in situ infrared (IR) and ultraviolet-visible (UV-Vis) spectroscopy, decrease rates of reactants and increase rates of products have been determined at 60–80 °C.[6,7] By using the activation energies (E_a) determined by these experiments ($E_a = 90$–100 kJ mol^{-1}), the formation time scales (half-saturation-times) of humic-like substances at the representative earth surface temperature of 15 °C have been estimated to be 30–100 years.[7,8] These time scales are somewhat smaller than the reported mean residence times of 250–1900 years by the ^{14}C dating method[1] suggesting that the degradation rates might be slower than the formation rates of HS.

We have then conducted degradation experiments of HSs by using standard IHSS humic and fulvic acids. As an example, decoloration rates of Nordic humic and fulvic acids have been determined at 80–180 °C by using ultraviolet absorbance at 254 nm (UV_{254}).[8] By using the activation energies (E_a) determined by these experiments (E_a = 88–101 kJ mol^{-1}), the degradation half-lives of humic and fulvic acids at 15 °C have been estimated to be 470–1980 years.[8] As expected, these degradation time scales are larger than the above formation time scales (30–100 years) and close to the mean residence times of 250–1900 years by Stevenson (1997)[1]. However, they are larger than turnover times of soil organic carbon (10 days to more than 300 years at 15 °C[5]). These differences might be originated from several factors such as difference of degradability between natural soils and the extracted HSs, the presence of minerals and microbial activities, and effects of concentrations of reactants, which could not be simulated by the simple experimental systems.

In order to compare these formation and degradation time scales estimated by simple experiments with a complex natural example, HSs at bottom sediments of Ago bay, Mie prefecture, Japan have been analyzed. Despite the small numbers of data points, these data indicate the formation time scales (half-saturation-times) of about 4–18 years at 15 °C for HSs.[8] These time scales are smaller than the formation time scales (30–100 years) estimated by our experiments in the simple system. Therefore, there may be effects of concentrations of reactants and presence of minerals and microbial activities in the real soils and sediments, which are different from the experimental systems.

On the other hand, soils and sediments include a variety of inorganic mineral constituents such as clay minerals, iron hydroxides, quartz and calcite.[9] HSs are reported to be adsorbed on some of these minerals.[1] Among them, goethite (α-FeOOH), one of thermodynamically stable iron hydroxides on the earth surface[10], adsorbs HSs[11,12]. Since the goethite surface is positively charged in near neutral pH conditions,[13] HS adsorption is considered to be occurring through anionic functional groups such as deprotonated carboxylic acids (carboxylates, COO^-).[14]

Moreover, goethite and organic materials in the natural environment interact through redox reactions.[15] For example, iron reduction by HSs were reported in some previous researches.[16–18] Krumina et al., (2017)[19] reported interactions between goethite and hydroquinones (one of microbial metabolites in the environment) resulting in reductive dissolution of iron, catalytic oxidation of hydroquinone, generation of hydroxyl radical (•OH) and degradation of the products. The radical •OH can also be generated by photodegradation of HSs without catalysts[20] and contributes to generation of CO_2 from HSs[21]. Since hydroquinone-like structures such as phenolic hydroxyl group can be in HSs general structure,[1] degradation of HSs can also be accelerated by goethite.

On the other hand, goethite was reported to enhance the formation of humic-like substances by the Maillard-type browning in our preliminary experiments.[22] In these catalytic enhancements of interactions of organic and inorganic materials, adsorption process is generally necessary to get their associations and may also have a role to increase local concentrations of reactants and to promote concentration-dependent reactions.

Soil organic matter (SOM) is one of the largest carbon storage sites, influencing significantly carbon cycles on the earth surface.[1] Soil organic carbon finally turnovers to CO_2 and its generation rates from soils have been studied by some experimental studies (e.g. Knorr et al., 2005[5]). The authors suggested that the CO_2 formation rates were affected by heterogeneities in the natures of soil organic carbons due to ease and difficulty of their decomposition.[5] Mineral oxides were reported to enhance CO_2 generation from organic materials.[23,24] However, few researches examined CO_2 generation from dissolved HS in the presence of minerals.

We have conducted preliminary experiments by a Fourier transform infrared (FT-IR) spectrometer with a multipath gas cell and a sample heating system to examine effects of goethite on CO_2 production rates from HS at 80 °C.[25] In this previous report, CO_2 generation from Nordic fulvic acid (FA) at 80 °C was found to be enhanced in the presence of goethite. Although this enhancement was possibly due to adsorption of FA on the surface of goethite, details including temperature dependence of the rates of FA-goethite interaction remained unknown.

Therefore, the present study aimed at performing more quantitative evaluation of interactions in the FA-goethite system at 25–80 °C by using two IR spectroscopic methods. First, CO_2 generation from FA at 25–80 °C has been measured by gas cell IR spectroscopy. Second, FA adsorption on the goethite surface has been investigated at 25–80 °C by in situ attenuated total reflection (ATR) IR spectroscopy.

MATERIALS AND METHODS

Preparation of sample materials

Goethite samples were prepared by the same method as our previous research[25], with reference to a method by Schwertmann and Cornell (2000)[26]. First, 180 mL of 5 mol L^{-1} KOH solution and 100 mL of 0.1 mol L^{-1} $Fe(NO_3)_3$ solution were mixed and iron hydroxide suspension was obtained. Second, it was diluted with 2 L of pure water (MilliQ: Electric resistivity > 18.2 MΩ cm) and heated at 70 °C for 60 hours. Finally, yellowish-brown precipitates were obtained by centrifugation and water-washing. X-ray diffraction and IR spectroscopy of the obtained precipitates indicated that they consisted mainly of goethite.[25,27] The surface area was 29.2 m^2 g^{-1} determined by a BET analysis.

Nordic fulvic acid powder was purchased from the International Humic Substances Society (IHSS). It was dissolved in pure water and 200 mg L^{-1} of fulvic acid stock solution was obtained.

Its pH was adjusted to pH = 4 by 0.01 mol L^{-1} HCl solution and 0.01 mol L^{-1} NaOH solution. By using pure water and the goethite powders, 100 mg L^{-1} fulvic acid aqueous solution without goethite (FAaq) and that containing 10 g L^{-1} of goethite (FAaq+g) were prepared. Total organic carbon content (TOC) of the FA was 52.3 %.

Gas cell IR spectroscopic measurements of CO_2 generated from the fulvic acid solutions

Hydrothermal experiments of FAaq and FAaq+g and IR spectroscopic measurements of generated CO_2 were conducted by using the same experimental setup as our previous researches[25,28], which consisted of the FT-IR spectrometer with a mercury cadmium telluride (MCT) detector (MB154, Bomem) and the multipath gas cell (10 m path length: 25 cm long cell with 40 times reflection by mirrors) equipped with a steel-lined PTFE (polytetrafluoroethylene) reaction vessel, a 20 mL plastic syringe used for introducing the sample solutions, a gas filter (SS-FCB, Swagelok) for removing water droplet, a vacuum pump and a N_2 gas bombe (99.9999% purity) to obtain non-oxidizing atmosphere throughout the whole system (Supplementary Fig. S1). Before the experiments, the sample solutions were purged with 99.9999% N_2 gas.

Most parts of generated gas from the sample solutions including dissolved ones were transported to the gas cell by bubbling the N_2 carrier gas in the sample solutions during the hydrothermal heating experiments (Purge-and-trap method). The hydrothermal experiments of 30 mL of FAaq were conducted at 25, 50 and 80 °C for 25 hours. Those of 30 mL of FAaq+g were conducted at 25, 50, 60, 70 and 80 °C for 24 hours. Gaseous products were introduced to the gas cell every few hours, and their IR spectra were measured. All the IR spectral measurements were accumulated for 128 scans with a wavenumber resolution of 1 cm^{-1}.

In situ measurements of adsorption of the fulvic acid on goethite by ATR-IR spectroscopy

In situ ATR-IR spectra of FAaq during its adsorption on goethite were measured by an FT-IR spectrometer with an MCT detector (VIR9500, Jasco), an ATR attachment (Specac horizontal ATR with a ZnSe crystal, about 5 times reflection) and a flow-through system for heating samples and the ATR attachment (Supplementary Fig. S2). Thin layers of goethite were made on the ATR crystal by a similar method to our previous research[22], which had been conducted with reference to methods by Hug (1996)[29] and Luengo et al. (2006)[30]. In the present study, 100 μL of a 10 g L^{-1} goethite suspension was dried on the ATR crystal at room temperature overnight, and the goethite layer was rinsed by pure water to remove excess goethite on the crystal surface. After drying the rinsed layer, the ATR crystal was rinsed again, and finally thin layers of goethite remained attached on the ATR crystal (Supplementary Fig. S3).

The ATR-IR spectral measurements were accumulated for 100 scans with a wavenumber resolution of 4 cm^{-1} in the 700–4000 cm^{-1} range. All spectra were recorded in absorbance mode against air background to obtain pATR spectra [$pATR = - \log_{10} I/I_0$ ($pATR$: intensity of pATR spectrum, I: reflection intensity, I_0: incident intensity, "*p*" means "- log")].[22,31] The I_0 was measured as background air spectrum measurements in the blank cell at room temperature. After the background measurements, pure water was injected into the ATR cell with a plastic syringe, and a pure water spectrum was measured. Then, after drying off water by 99.5% of nitrogen gas, the fulvic acid solution was injected with the syringe and plugs were tightly sealed. In situ adsorption experiments of FAaq on the goethite layers at pH 4.0 were conducted at 25, 50 and 80 °C. The fulvic acid solutions were heated at the target temperatures on a hot plate and circulated into the ATR cell (Fig. S2). In order to obtain spectral changes of the sample solution during the heating experiments, successive measurements were conducted by an interval-measurement program (Spectra Manager, Jasco) for 5 hours at an interval of every 120 seconds.

RESULTS

Gas cell IR spectroscopy of CO_2 generated from the fulvic acid solutions

Representative spectra of gaseous products during the hydrothermal experiments analyzed by gas cell IR spectroscopy (Fig. S1) are shown in Fig. 1. They indicate only CO_2 as a recognizable species. Absorptions around 2360 and 2340 cm^{-1} are P and R branches of the antisymmetric stretching band of CO_2.[32] CO_2 contents were estimated by a calibration line of band areas from 2200 to 2400 cm^{-1} by standard gas mixtures of 0.1–5 ppm CO_2 in N_2 (Supplementary Fig. s4).

In spite of some noisy spectra, cumulative amounts of CO_2 (C_{CO2}) formed from 30 mL of FAaq+g (goethite-containing FAaq) at 25, 50, 60, 70 and 80 °C could be traced quantitatively (Fig. 2a). They showed rapid increases at the initial stage, and then the CO_2 emission (C_{CO2}) continued linearly with time (t) (Fig. 2a). Assuming that CO_2 was formed by the independent first and zeroth order reactions, increases in CO_2 until 24 hours were fitted by:

$$C_{\mathrm{CO2}} = C_1\{1 - \exp(- {}^{1}k_{\mathrm{CO2}} \times t)\} + {}^{0}k_{\mathrm{CO2}} \times t$$

, where ${}^{1}k_{CO2}$ and ${}^{0}k_{CO2}$ are the apparent first and zeroth order reaction rate constants of the faster and slower reactions in the presence of goethite, respectively. The fitted curves are shown in Fig. 2a and obtained rate constants are listed in Table 1.

On the other hand, cumulative amounts of CO_2 (C_{CO2}) formed from 30 mL of FAaq without goethite linearly increased with time (Fig. 2b). These increases were fitted by the single zeroth order reaction:

$$C_{\mathrm{CO2}} = {}^{0}k_{\mathrm{CO2}} \times t$$

, where ${}^{0}k_{CO2}$ is the apparent zeroth order reaction rate constant in the experiment without goethite. The fitted lines are shown in Fig. 2b and obtained rate constants are listed in Table 1.

The obtained ${}^{0}k_{\mathrm{CO2}}$ with and without goethite were similar to each other (~ 10^{-11} mol s^{-1}).

In order to obtain better fittings for the data in Fig. 2a, increases in CO_2 in the experiments at 25, 50 and 80 °C with goethite for 24 hours were fitted again by:

$$C_{\mathrm{CO2}} = C_2\{1 - \exp(-\,{}^{1}k_{\mathrm{CO2}} \times t)\} + \;{}^{0}k_{\mathrm{CO2}} \times t$$

, with fitting parameters of C_2 and ${}^{1}k_{\mathrm{CO2}}$, using the fitted parameters of ${}^{0}k_{\mathrm{CO2}}$ for the experiments at 25, 50 and 80 °C "without" goethite already obtained by the fitting of the data in Fig. 2b. The fitted curves are shown in Fig. 2c and obtained rate constants are listed in Table 1. It should be noted that half-saturation-times $t_{1/2}$ (half-lives) of the first order reaction can be calculated by:

$$t_{1/2} = \frac{\ln 2}{{}^{1}k_{\mathrm{CO2}}}$$

In situ measurements of adsorption of the fulvic acid on goethite by ATR-IR spectroscopy

In situ observations of the fulvic acid adsorption on the goethite layers were conducted by using ATR-IR spectroscopy. By subtracting the pure water spectrum from the FAaq spectra, pATR spectra of Nordic fulvic acid on the goethite layer were successfully observed as shown in Fig. 3. A band at 1725 cm^{-1} is considered to be due to C=O stretch of COOH (carboxylic acid), and bands at 1585, 1400 and 1260 cm^{-1} are due to deprotonated forms of carboxylic acids, carboxylates (COO^{-}) of the FA.[33] They appeared to increase with time (Fig. 3).

FA concentration (C_{FA}) on the surface of goethite was quantified by a calibration line made by 1000–10000 mg L^{-1} FAaq at pH=4.0 (Supplementary Fig. S5) based on "peak heights" at 1725 cm^{-1} (baseline: 1675–1825 cm^{-1}). "Band areas" were not employed here because they include larger effects by fluctuations due to water vapor. The bands around 1585, 1400 and 1260 cm^{-1} due to COO^{-} were not used, because these bands by deprotonated COO^{-} can be affected by interactions with the positively charged goethite surface. Representative FA concentrations at 25, 50 and 80 °C during the experiments are shown in Fig. 4. The FA concentrations (C_{FA}) showed relatively fast increases in the first 1 hour, and then they became almost constant. It should be noted that the maximum FA concentrations (C_{FA}) around 5000–9000 mg L^{-1} are about 50–90 times of the initial FA concentrations (100 mg L^{-1}). This means that the FA are concentrated on the surface of goethite.

The increases in C_{FA} with time were fitted by the second order reaction in reference to previous works on kinetic analyses for adsorption of dissolved organic substances on inorganic minerals and activated carbon surfaces at the liquid/solid surfaces[34–38]:

$$\frac{t}{C_{\mathrm{FA}}} = \frac{1}{{}^{2}k_{\mathrm{FA}}\,(C_3)^2} + \frac{1}{C_3}t$$

, where ${}^{2}k_{\mathrm{FA}}$ is the apparent second order reaction rate constant and C_3 is the constant for concentration maximum at each temperature. It should be noted that half-saturation-times $t_{1/2}$ (half-lives) of the second order reaction can be calculated by:

$$t_{1/2} = \frac{1}{{}^{2}k_{\mathrm{FA}}\, C_3}$$

The fitted curves are shown in Fig. 4 and obtained rate constants ${}^{2}k_{\mathrm{FA}}$ are listed in Table 1.

The Arrhenius plots for the obtained apparent reaction rate constants

The obtained apparent zeroth order reaction rate constants at 25–80 °C for CO_2 generation with and without goethite (${}^{0}k_{\mathrm{CO2}}$) determined by fitting of the data in Figs. 2a and 2b are plotted in an Arrhenius diagram for the zeroth order rate constants (Fig. 5a).

Activation energy [E_a (kJ mol^{-1})] values were determined by fitting of experimental data by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_{\mathrm{a}}}{RT}$$

, where k is the reaction rate constant, A is the frequency factor (unit: the same as the rate constants), R is the gas constant (8.31×10^{-3} kJ mol^{-1} K^{-1}), T is the absolute temperature (K). The obtained E_a are listed in Table 1. The apparent zeroth order reaction rate constants for CO_2 generation with and without goethite (${}^{0}k_{\mathrm{CO2}}$) show similar values with activation energy values in the 16–19 kJ mol^{-1} range (Fig. 5a, Table 1).

The apparent first order reaction rate constants at 25–80 °C (${}^{1}k_{\mathrm{CO2}}$) determined by fitting of the data of CO_2 generation with goethite in Figs. 2a and 2c are plotted in an Arrhenius diagram for the first order rate constants (Fig. 5b). Although k^{1}_{CO2} values from Fig. 2a are scattered and not fitted by the Arrhenius equation, they are in the similar range to ${}^{1}k_{\mathrm{CO2}}$ from Fig. 2c showing an activation energy value around 14 kJ mol^{-1} (Fig. 5b, Table 1).

The apparent second order reaction rate constants ${}^{2}k_{\mathrm{FA}}$ at 25, 50 and 80 °C are also plotted in an Arrhenius diagram for the second order rate constants (Fig. 5c). They show a negative linear trend with an activation energy value around 13 kJ mol^{-1}.

DISCUSSION

CO_2 generation from FA independent of the presence of goethite

Without goethite, the FA solutions generated CO_2 and the apparent zeroth order reaction model well reproduced the increases in CO_2 amounts with time at 25–80 °C (Fig. 2b). The zeroth order CO_2 generation rate constants from FAaq+g (with goethite) have similar values to those from FAaq (without goethite) around 10^{-11} mol s^{-1} [Table 1 (${}^{0}k_{\mathrm{CO2}}$), Fig. 5a (${}^{0}k_{\mathrm{CO2}}$)]. Their activation energies (E_a) showed similar values around 16–19 kJ mol^{-1} (Fig. 5a). These processes are considered to correspond to generation of CO_2 by thermal decomposition of FA, which is independent of the presence of goethite.

These CO_2 molecules were considered to be generated from labile FA structures, which are rapidly decomposable. It should be noted that dissolved oxygen and light from outside were not severely prevented in the present experiments. Therefore, radicals might be generated by photodegradation of FA[20] and they might decompose easily-oxidizable structures in FA to generate CO_2. Although detailed mechanism for the CO_2 generation from FA needs further studies, we will concentrate next on interactions between FA and goethite.

Adsorption of FA on the goethite surface

The previous study in the same FA-goethite system suggested that the generation of CO_2 can be associated with the FA adsorption on goethite, based on the rapid decrease of FA in solution in the presence of goethite.[25] In the present study, by using the ATR-IR method, increases of carboxylic acids (COOH) and carboxylates (COO^-) of FA were observed on the goethite surfaces. The pH value of the FA-goethite system was 4.0, where the goethite surface is considered to be positively charged.[13] On the other hand, 62 % of carboxyl groups of FA can be in the deprotonated negative form (carboxylate, COO^-) and the other 48 % are protonated (carboxylic acid, COOH) at pH=4.0, based on a reported dissociation constant of carboxyl group in Nordic FA ($pK_a = 3.79$)[39] and the Henderson-Hasselbach equation:

$$\mathrm{pH} = \mathrm{pK}_a + \log{[\mathrm{ionized}]/[\mathrm{neutrized}]}$$

In fact, an IR absorption band due to COO^- were recognized in a spectrum for dried powder of FA before heating measured by a micro FT-IR spectrometer equipped with an MCT detector (Jasco, FTIR-620 and IRT-30) (Supplementary Fig. S6), supporting the presence of COO^- in FA. Therefore, it is considered that electrostatic attraction caused the adsorption of negative carboxylate anions COO^- of FA on positively charged goethite surface.

After the rapid adsorption of FA (0–1 hour), the concentration of FA (C_{FA}) was kept mostly constant around 5000–9000 mg L^{-1} (1–6 hours) (Fig. 4). This variation in saturation values might be due to changes in amounts of goethite in the observed region on the ATR crystal (Supplementary Fig. S3). However, by using the specific surface area of goethite (29.2 m^2 g^{-1}), adsorption amounts of FA per unit surface area of goethite was calculated as 0.25–0.45 mg m^{-2} (Supplementary materials B). This is close to reported ranges of 0.3–4.3 mg m^{-2} for adsorption of FA on goethite.[11,12] Therefore, the saturation value of FA on goethite can be limited by the adsorption capacities of goethite surfaces.

This adsorption process can increase local concentrations of the FA on the goethite surface. In fact, the maximum FA concentrations (C_{FA}) around 5000–9000 mg L^{-1} found on the goethite surface by the ATR-IR method (Fig. 4) are about 50–90 times of the initial FA concentrations (100 mg L^{-1}).

The increases with time in C_{FA} on the goethite surface (Fig. 4) can be well reproduced by the second order reaction model. Time scales of this adsorption were similar to those for the pseudo second order adsorption of phthalates on goethite[38] and of humic acids on a modified bentonite (one of clay minerals)[34]. Calculated half-saturation-times ($t_{1/2}$) for the present study ranged from 190 s to 270 s, which are on the same order as those calculated in adsorption of the humic acids on modified bentonite around ($t_{1/2}$ =) 650–1500 s.[34] However, these time scales are generally smaller than half-saturation times for adsorption of humic acids on activated carbons.[36,37] These differences might be due to differences in microscopic structures of the adsorbents.

The second order FA adsorption processes on goethite in the present study are generally faster than the initial first order CO_2 generation process (Figs. 2a, 2c and 4). Half-saturation-times for the FA adsorption were about 10 times smaller than those for the CO_2 generation. Therefore, the FA adsorption on goethite was not a rate-determining step for the CO_2 generation.

The activation energy for the FA adsorption on goethite [E_a = 13 kJ mol^{-1} (Fig. 5b, Table 1)] was similar to that for phthalate adsorption on aluminium hydroxide [E_a = 9.99 kJ mol^{-1} by Guan et al. (2006)[21]]. Such activation energies less than 21 kJ mol^{-1} might possibly suggest film-dissolution controlled adsorption.[21] However, as has been pointed out in the previous reports[36,37], the pseudo second order adsorption model does not have conclusive meaning on rate-determining adsorption mechanisms, and diffusion through porous layers should be considered. Although detailed mechanism for the FA adsorption needs further studies including well-controlled preparation of goethite layer and diffusion modeling of adsorption of FA on goethite, we will concentrate next on kinetic analyses on CO_2 generation from FA-goethite system, which can be rate-limited by slower reactions than the FA adsorption.

CO_2 generation from the FA-goethite system

Increases in CO_2 generated from the FA-goethite system following the FA adsorption on the goethite surface were well fitted by the first + zeroth order reaction model giving the activation energy around 14 kJ mol^{-1} for the first order processes (Table 1 and Fig. 5b). These CO_2 generation processes with goethite could also be fitted by the apparent second order reaction model (not shown). However, the obtained apparent second order CO_2 generation rate constants showed inappropriate positive trend in an Arrhenius plot giving negative activation energies (not shown). Therefore, CO_2 generation in the presence of goethite will be discussed in terms of the first order kinetics in the following section.

By the apparent first order rate constants of CO_2 generation in the presence of goethite around 10^{-4} s^{-1} [Table 1 (${}^{1}k_{CO2}$)] at 25 °C, 4 days of half-saturation-times can be estimated. On the other hand, at least 14 years are necessary for consumption of carbon (0.13 mmol) in the 30 ml of 100 mg L^{-1} FA solution by the apparent zeroth order CO_2 generation in the presence/absence of goethite at 25 °C [Table 1 (${}^{0}k_{CO2}$ and ${}^{0}k_{CO2}$ around 10^{-11} mol s^{-1})]. The carbon content is calculated by FAaq mass concentration (100 mg L^{-1}), volume of FAaq (30 mL), total organic carbon content of FA (52.3 %) and molar mass of carbon (12 g mol^{-1}):

$\{100\ (\mathrm{mg\ L^{-1}}) \times 0.030\ (\mathrm{L}) \times 0.523\} / 12\ (\mathrm{g\ mol^{-1}}) = 0.13\ (\mathrm{mmol})$

These time scales (4 days – 14 years) were included in the reported range of time scales of CO_2 generation from soil organic carbon (< 300 years)[5]. Since CO_2 emission from the more labile component was suggested to be the less temperature-dependent and have the smaller activation energy than the stable structures,[5] the CO_2 generation processes with the activation energies around 14–19 kJ mol^{-1} might correspond to degradation of labile parts of FA. Since amounts of generated CO_2 from FA were on the order of μmol in the present experiments and these are only about 1% of carbon contents in FA (0.13 mmol), such labile structures are possibly partial and limited.

On the other hand, our recent study[8] reported the apparent first order decoloration rates of Nordic FA solution with an activation energy of 87.6 kJ mol^{-1}. The time scales of decomposition of FA determined by decoloration of FA solution (480 years at 15 °C)[8] were much larger than those of CO_2 generation estimated in the present study. This is possibly because the decoloration of FA solution in the previous study might reflect decompositions of general structures including stable parts in the FA molecules while the CO_2 generation in the present study may reflect more easily decomposable labile structures in the FA, which are minor.

While the in situ spectroscopic measurements and kinetic analyses provided quantitative estimation of the time scales of apparent increases in CO_2 generated from the FA-goethite system, elementary processes of redox reactions, in particular rate-determining steps in the system, could not be clarified. One of possible redox-active structures in FA can be hydroquinone-like structures such as phenolic hydroxyl groups.[1] In the interactions between hydroquinone solution and ferrihydrite/goethite, Krumina et al. (2017)[19] proposed several possible chemical reactions including (1) reductive dissolution of Fe^{2+} from goethite, (2) a rapid process of surface-catalyzed oxidation of hydroquinone (H_2Q) producing quinones (Q) and hydrogen peroxides (H_2O_2), and (3) quinone decomposition by hydroxyl radicals (•OH) which can be possibly formed by Fenton-like processes. Fenton's reaction is a rapid reaction of Fe^{2+} and H_2O_2 generating •OH, which can occur in the natural water environment[40] and produce CO_2[21]. In fact, IR spectra of products precipitated in batch heating experiments of Nordic FA with goethite (Supplementary Fig. S6) indicated an appearance of C=O bonds around 1660 cm^{-1}. This band might correspond to unsaturated ketones[32], which can be derived from oxidized quinone-like structures. This suggests that oxidation of hydroquinone-like structures to quinone-like structures in the presence of goethite (organic-inorganic interaction) might have occurred in the heating experiments of FA-goethite system.

Although overlaps of multiple adsorption of the reactants/products on the goethite surfaces and bulk reactions including decomposition and polymerization of FA[8] can be expected, further detailed analyses are needed in the FA-goethite interactions. Longer-term experiments including monitoring of dissolved Fe^{2+} from goethite ($Fe^{3+}OOH$) are also needed because Fe^{3+} reduction by HS was reported to occur in a few days.[16–18] It is also necessary to use simplified organic molecules representing FA such as phthalic acid (aromatic carboxylic acid) for avoiding the above overlaps of multiple reactions.

By these future studies, quantitative bases of fates and time scales of organic-inorganic interactions in the natural environment will be provided.

CONCLUSION

Interactions of Nordic fulvic acid (FA) solution and goethite (α-FeOOH) were experimentally studied at 25–80 °C by gas cell IR spectroscopy for CO_2 generation and in situ ATR-IR spectroscopy for analyzing FA adsorption on the goethite surface. Continuous IR spectral monitoring at fine time intervals at several temperatures enabled determination of reaction rate constants, activation energies and reaction time scales.

1) Slow linear increases with time of generated CO_2 measured by the gas cell IR measurements could be described by the zeroth order CO_2 generation independent of the presence of goethite (E_a = 16–19 kJ mol^{-1}). On the other hand, CO_2 generation in the presence of goethite can be fitted by the first + zeroth order reaction. This first order process (E_a = 14 kJ mol^{-1}) can possibly include complex redox interactions between FA and goethite (organic-inorganic interaction).
2) IR bands due to carboxylic acids (COOH) and carboxylates (COO^-) increased rapidly with time in the ATR-IR spectroscopic measurements in the FA-goethite system. This can be explained by rapid adsorption of FA to the goethite surface by electrostatic attraction between the positively charged goethite surface and the negatively charged carboxylate anions (COO^-) in FA. These results could be simulated by the pseudo second order reaction model with a low activation energy (E_a = 13 kJ mol^{-1}). This adsorption process was generally faster than the CO_2 generation, suggesting adsorption of FA to the goethite surface was not a rate-limiting step of their interactions generating CO_2.
3) These interactions between FA and goethite possibly including redox reactions forming CO_2 with the low activation energies are rather fast (in 4 days – 14 years at 25 °C) possibly relating to decomposition of labile redox-sensitive structures of FA. On the other hand, decoloration rates of FA in our previous experiments with much higher activation energies (87.6 kJ mol^{-1}) might correspond to decomposition of more stable structures in FA.

Although further experimental studies are needed by using simplified analogue materials such as phthalic acid, the present study by two IR spectroscopic methods provided experimental methods for examining quantitatively complex organic-inorganic interactions including redox reactions generating CO_2, which can affect the carbon cycle on the earth surface.

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SUPPLEMENTARY MATERIALS

The supplementary materials A (Figs. S1, S2, S3, S4, S5 and S6) and B [Estimation of adsorption amounts of FA (fluvic acid) per unit surface area of goethite] can be accessed at the journal web site.

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TABLE

Table 1. The kinetic parameters (rate constants k and fitting parameters C) obtained by the first ($^1k_{CO2}$) and zeroth ($^0k_{CO2}$) order reaction fittings for CO_2 generation in the heating experiments on Nordic fulvic acid (FA) solutions with/without goethite at 25–80 °C, and the second ($^2k_{FA}$) order reaction fitting of adsorption of FA on goethite. The activation energy E_a values obtained from the temperature dependences of the apparent reaction rate constants ($^0k_{CO2}$, $^1k_{CO2}$ and $^2k_{FA}$) are also listed.

	Temp. (°C)	80	70	60	50	25	E_a (kJ mol^{-1})
CO_2 from FA with goethite (overall)	C_1 (10^{-6} mol)	1.2	0.58	0.66	0.48	0.30	-
	$^1k_{CO2}$ (10^{-4} s^{-1})	3.0	6.6	3.9	7.8	4.9	not fitted
	$^0k_{CO2}$ (10^{-11} mol s^{-1})	2.6	2.8	1.8	1.3	1.1	16 ± 6.1
CO_2 from FA w/o goethite (slow only)	$^0k_{CO2}$ (10^{-11} mol s^{-1})	2.3	-	-	1.4	0.70	19 ± 0.2
CO_2 from FA with goethite (fast)	C_2 (10^{-6} mol)	1.3	-	-	0.46	0.49	-
	$^1k_{CO2}$(10^{-4} s^{-1})	2.3	-	-	9.3	0.96	14 ± 3.6
Adsorption	C_3 (mg L^{-1})	5700	-	-	6300	9600	-
	$^2k_{FA}$ (10^{-7} L mg^{-1} s^{-1})	9.0	-	-	7.3	3.8	13 ± 0.4

FIGURES

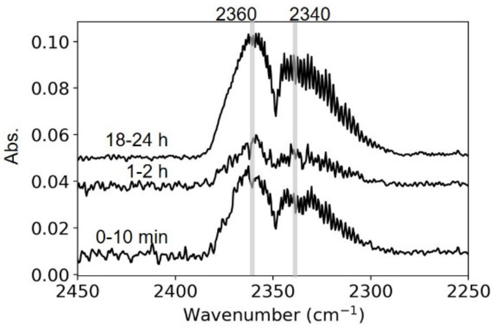

Fig. 1. Representative IR spectra in the 2250–2450 cm^{-1} range for the gaseous products from Nordic FA heated at 80 °C during the indicated periods (not "cumulative" ones) extracted from the reaction container. The spectra are vertically shifted for clarity. Adsorptions around 2360 and 2340 cm^{-1} are due to *P and R branches of the antisymmetric stretching band of CO_2.*

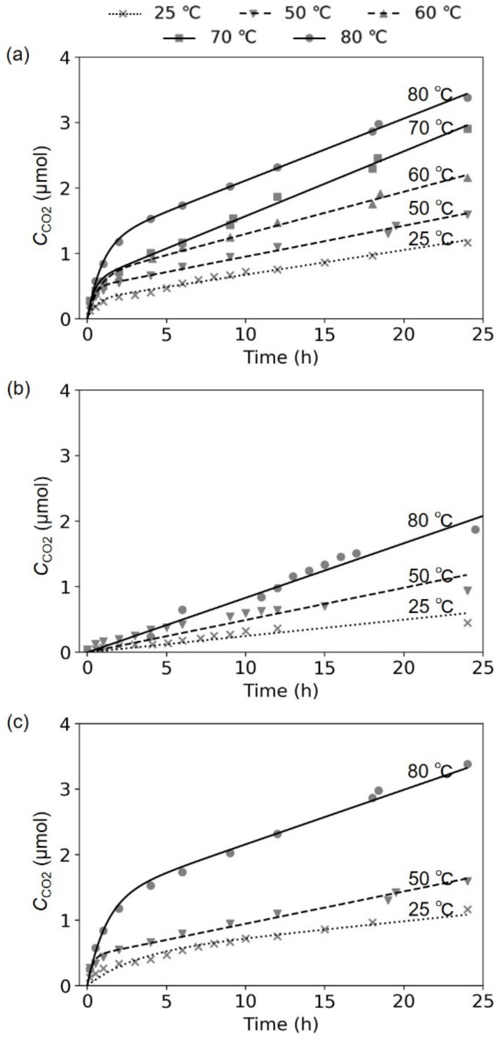

Fig. 2. Changes with time in C_{CO2} (μmol) during the heating experiments of (a) the FA-goethite system at 25, 50, 60, 70 and 80 °C, with fitting curves by the first + zeroth order reaction model, (b) the FA solution without goethite at 25, 50 and 80 °C with fitting lines by the zeroth order reaction model, and (c) the FA-goethite system at 25, 50 and 80 °C with fitting curves by the first + zeroth order reaction model using the values of the zeroth order rate constants determined in Fig. 2(b).

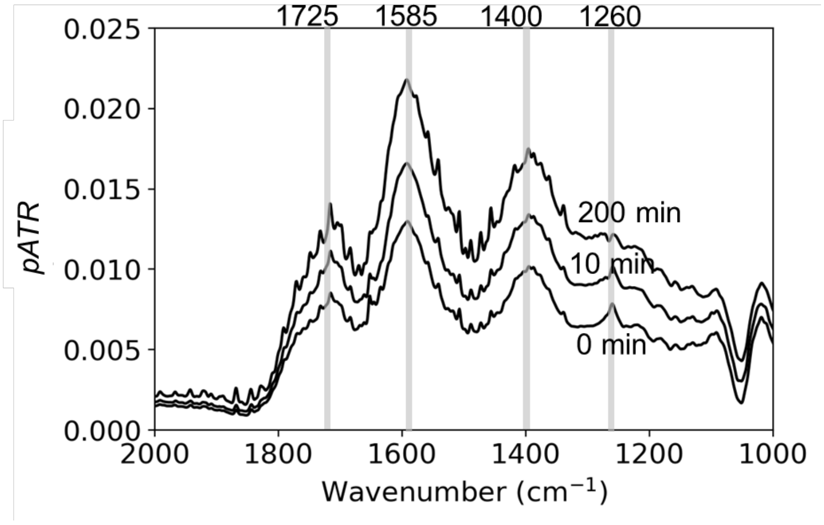

Fig. 3. Representative pATR (= - $\log_{10} I/I_0$) *spectra in the 1000–2000 cm*$^{-1}$ *range for Nordic FA on the goethite layer during the adsorption experiments at 50 °C for 0, 10 and 200 minutes.*

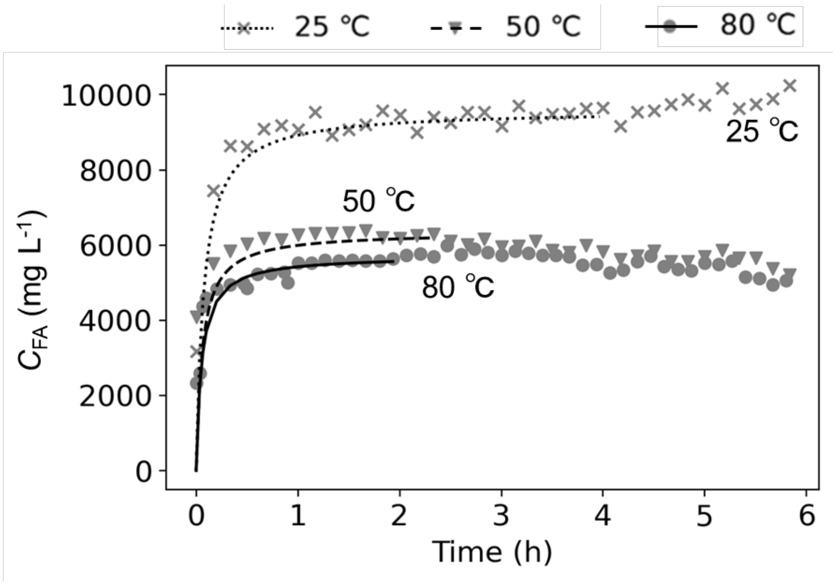

Fig. 4. Changes with time in the FA concentrations C_{FA} *(mg L*$^{-1}$*) during the adsorption experiments of FA on goethite at 25, 50 and 80 °C. Fitting curves by the second order reaction model until 2–4 hours.*

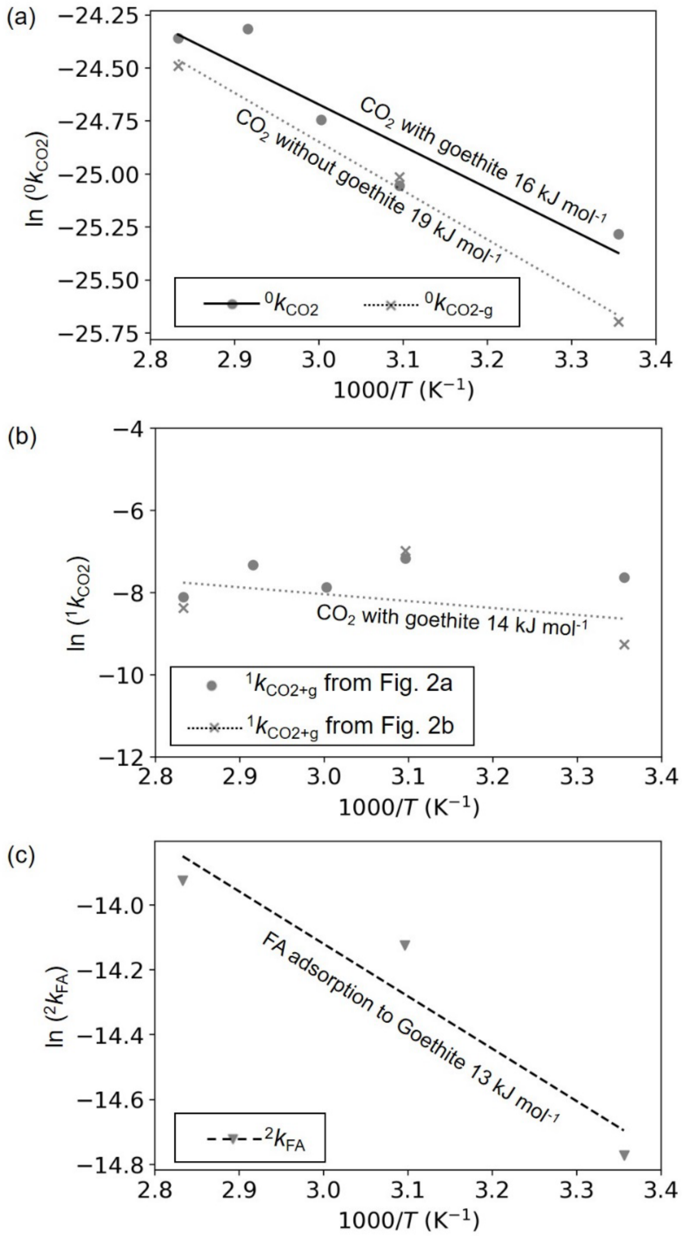

Fig. 5. Arrhenius plots of the rate constants obtained in the FA-goethite system. (a) The zeroth order rate constants of CO_2 generation with and without goethite ($^0k_{CO2}$) based on the data in Figs. 2a, b and c. (b) The first order rate constants of CO_2 generation with goethite ($^1k_{CO2}$) based on the data in Figs. 2a and c. (c) The second order rate constants of the adsorption of FA on goethite ($^2k_{FA}$) based on the data in Fig. 4. Fitting lines by the Arrhenius equation are shown with corresponding activation energy values.